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RESEARCH ARTICLE

Titanium dioxide incorporated thin film composite membrane for bisphenol A removal

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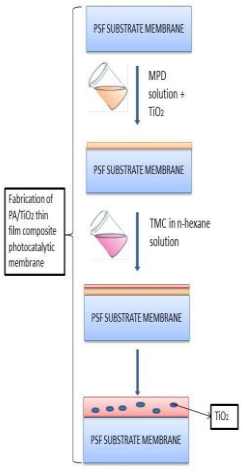
Graphical abstract



Abstract

The objective of this study was to evaluate the capability of Polyamide (PA) thin film composite (TFC) membrane immobilized with Titanium Dioxide (TiO_2) particles on the removal of Endocrine Disruptive Compounds (EDC). Since 1990`s, an increasing environmental pollution by EDC had been noticed, for instance in surface waters, agricultural areas, and atmosphere, especially since the analytical methods for EDC detection have been continuously improved. The estrogenic properties of bisphenol A (BPA), a ubiquitous synthetic monomer which categorized as an EDC that can leach into the food and water supply, have prompted considerable research into exposure-associated health risks in humans. In this study, PA/TiO_2 TFC membrane was fabricated via interfacial polymerization (IP), using Polysulfone (PSf) flat sheet as substrate membrane. Trimesoyl chloride (TMC) and m-phenylenediamine (MPD) have been used as monomer and aqueous solution, respectively. The performance of PA/TiO_2 TFC membrane and PSf substrate membrane on the removal of BPA has been compared and analysed. The membrane was analyzed for several characterizations using Field Emission Scanning Electron Microscopy (FESEM) and water contact angle analysis. Synthetic wastewater using 100ppm of BPA solution has been prepared for membranes performance. The existence of PA/TiO_2 TFC on top of PSf membrane has been confirmed by FESEM and EDX image. Meanwhile, the hydrophilicity of PSF membranes has been improved with the existence of TFC which is good for water treatment system since it improves membrane's pure water flux. The rejection of BPA has been done using ultrafiltration system and it was found that PA/TiO_2 TFC membrane could reject almost 99% of BPA from feed solution. From the data obtained in this study, the TFC membrane is found to be convincing for wastewater treatment that contains EDC.

Keywords: *Bisphenol A, endocrine disruptive compounds, thin film composite*

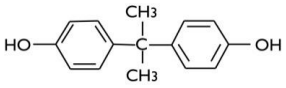
INTRODUCTION

As high quality drinking water becomes scarcer, unintentional indirect potable water reuse, where wastewater effluent is used as a part of a downstream drinking water source, has become a great concern throughout the world. Pharmaceuticals industries have shown fast development in these recent years due to the increase in human population and demand of pharmaceutical product (The Report: Argentina 2018). The worst thing about this pharmaceutical waste is it contains endocrine disruptive compound (EDC) and this compound has been discovered in wastewater all around the world. Researchers are confident that these compounds can produce detrimental effects on living things (Helland *et al.*, 2006). Besides, natural hormones in the endocrine system can be mimicked by EDC and it likely can cause some damages to living things, specifically to its endocrine system itself (Shane *et al.*, 2003 and Liu *et al.*, 2009). The term "endocrine disrupters" means synthetic chemicals and natural compounds that can influence the endocrine system (Helland *et al.*, 2006) and also means as exogenous medium which can disturb any activity of original hormones of living things that are in charge for the continuance of homeostasis, reproduction, growth, and function (Shane *et al.*, 2003).

One of EDCs that contributes to large abundance in wastewater is bisphenol A (BPA). This leads to the issues on the impact of daily BPA uses to human due to high volume production of this chemical. The estrogenic properties of BPA, an ubiquitous synthetic monomer that can leach into the food and water supply, have prompted considerable research into exposure-associated health risks in humans (Darcie *et al.*, 2016). This chemical is one of the EDCs that found in water and likely to perform as an endocrine disruptor even at environmentally appropriate amounts. BPA is one of the highest volume chemicals produced worldwide, with over 6 billion pounds produced and over 100 ton released into the atmosphere each year. Recent extensive literature has raised concerns about its possible implication in the etiology of some human chronic diseases such as diabetes, obesity, reproductive disorders, cardiovascular diseases, birth defects, chronic respiratory and kidney diseases and breast cancer (Raja *et al.*, 2014). BPA is a chemical known as important raw

material in the production of polycarbonate plastics and epoxy resins. BPA has been used in the production of many polycarbonate plastics, thermal paper and epoxy resins, thus it commonly appears in various products for everyday use including water-pipes, electronicequipment, paper or toys (Jaromir *et al.*, 2014 and Guergana *et al.*, 2014). It is also one of the most widely produced chemicals in the world today and found in most canned goods, plastics, and even household dust (Guergana *et al.*, 2014). Table 1 shows the important properties of BPA. BPA is one of the hazard compounds that belong to the non-biodegradable and highly resistant to chemical degradation. BPA is reasonably expected to be a human carcinogen specifically in the breast based on the definitions of "carcinogen" by the International Agency for Research on Cancer and the National Toxicology Program (Darcie *et al.*, 2016). Because of the wide range of BPA applications, researchers or scientists need to take an action in order to find the best solution to completely remove any sources of the BPA.

Table 1 Properties of BPA (Panigrahi *et al.*, 2013).

Molecular structure	4,4- (propane-2,2-diyl) diphenol (BPA) 
Molecular formula/ molecular weight	$C_{15}H_{16}O_2$/ 228.29 g/mol
Density (g/cc)	1.20
Water solubility (mg/L)	120-300
Melting Point/Boiling point (°C)	158/220

The greatest challenge for treatment of wastewater from pharmaceutical industry is no single approach or treatment method that can be applied to remove all compounds that presented in the waste. This means that one preferable treatment for one compound may not suitable for other compounds. This is the reason why treating pharmaceuticals waste is rather complicated compared to other industrial wastes.

Membrane filtration technology becomes the most promising technology in treating wastewater. Membrane processes is widely applied for wastewater treatment and it significantly can reduce color, impart sensation, and uneasy smell to water, as well as it can involve with some antitoxins to produce antitoxin byproducts and this process is widely applied in wastewater treatment especially in elimination of bacteria, microorganisms, particulates, and natural organic material. Polymers are the main materials in membrane technology with the advantages of good flexibility, toughness, and separation properties. Polymers like Polysulfone (PSf) are widely used in industry for membrane preparation (Mousavi *et al.*, 2012). PSf is a tough, rigid, high-strength and transparent thermoplastic, which maintains its characteristics over a wide range of temperatures, from −100 ◦C to over 160◦C. The chemical and physical properties of PSF including its good thermal and chemical stabilities, mechanical strength and excellent oxidative resistance, making it as the preferred material for use in a membrane substrate (Huang *et al.*, 2006). However, the effort to treat pharmaceutical waste that contains small particle size of pollutants such as BPA, has became quite challenging. The common ultrafiltration (UF) membrane is not efficient enough in removing small particles of pollutant since it has large pore size which in range of 0.1-0.001 micron.

Generally, since 1970s, a nanofiltration (NF) membrane that comes together with UF membrane has been created and called as thin film composite (TFC) membrane. TFC membrane is believed to be a great solution in removing small pollutants such as BPA from pharmaceutical wastewater since it comes with smaller pore size as compared to UF membrane. Today, TFC membranes prepared by coating a very thin layer of aromatic polyamide onto porous membrane are well accepted for water and wastewater treatment processes (Lau *et al.*, 2011). TFC membrane is consisted of UF membrane as support layer or called as substrate and another layer called as selective layer which made from several polymers such as polyamide (PA) and polyester amide (PEA) (Mollahosseini *et al.*, 2014). Thin layer on top of the porous support membrane carries out the main duty of NF process through control of solubilization and diffusion of solutes and water. In this study, the feasibility of polyamide (PA) thin film composite (TFC) membrane in pharmaceutical waste treatment has been studied. PA TFC membrane was fabricated through interfacial polymerization (IP) on top of PSF flat sheet membrane. Performance of these two types of membranes was compared to determine the efficiency in removing EDC. In this study, the TiO_2 incorporated in TFC membrane would act as photocatalyst since this type of membranes would be further studied as photocatalytic hybrid membrane.

EXPERIMENTAL

Materials

Commercial PSf membrane was purchased from Scientific Lab Trading to be used as substrate membrane. M-Phenylenediamine (MPD), N-hexane and 1, 3, 5-Benzenetricarboxylic acid chloride (TMC) were purchased from Sigma-Aldrich and used in preparation of PA TFC as selective layer. Titanium Dioxide (TiO_2) was also purchased from Sigma –Aldrich and used as additive in PA layer.

Methodology of polyamide thin film membrane's fabrication

The solution consisted of MPD/TiO_2/water and TMC/N-hexane was prepared before the fabrication. The solution was let to stir until MPD/TiO_2 and TMC were completely dissolved in water and N-hexane, respectively. In this study, 0.5g TiO_2 was added to MPD/water solution. Before PA TFC was fabricated, the PSf substrate membrane was soaked in water then let to be dried at atmosphere condition. Then, the PSf substrate was soaked in 2% (w/v, i.e., 2g MPD/100 mL water) MPD solution for 1 minutes. After removing MPD solution, the membrane was let to dry at atmosphere condition until no excess MPD solution was spotted which means the membrane surface was completely dried. After drying, 100 mL of 0.05% (w/v) TMC/N-hexane solution was gently poured onto substrate membrane surface. The TMC/N-hexane was let to react with the MPD for 1 minute to produce a polyamide selective layer, and continued by removing the overflow TMC/N-hexane solution from the membrane surface. The PSf flat sheet based TFC membrane was dried in 80°C oven for 3 minutes and kept in DI water for further use. Figure 1 illustrates the steps in the fabrication of PA TFC membrane through IP process.

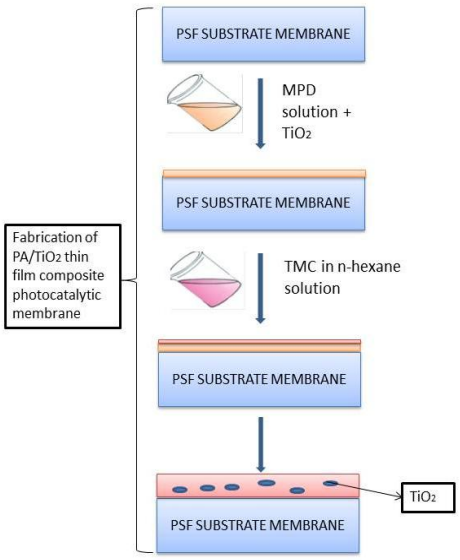


Figure 1 Interfacial polymerization process in fabricating PA TFC layer.

Characterization study of PSf substrate membrane and PSf PA/TiO_2 TFC membrane

Morphological analysis

The morphological structure of PSf substrate membrane and PA/TiO_2 TFC membrane was analyzed using Field Emission Scanning Electron Microscopy (FESEM). The membrane sample was broken in nitrogen liquid, and the fractured cross sections and the bottom surfaces of the membranes were observed. An energy dispersive X-ray analyzer (EDX, OXFORD INSTRUMENTS, USA) was used to quantify elemental analysis and dispersion of TiO_2 on top of the PSf PA TiO_2 thin film composite membrane. It is an accessory attached with the FESEM equipment.

Water contact angle analysis

The relative hydrophilicity of a membrane surface was determined by measuring the contact angle of a water drop (1µL) deposited onto the membrane surface. The contact angle was measured by static sessile drop method with goniometer. De-ionized water was used as the probe liquid in all measurements. To reduce evaporation effect, measurements were made as quickly as possible (less than 10 seconds) while 5 measurements taken for each sample and the average were calculated.

Preparation of synthetic pharmaceutical wastewater (BPA solution)

In this study, bisphenol A (BPA) was chosen as the organic compound to test the effectiveness of the fabricated membrane. Bisphenol A (BPA >99%) purchased from Sigma Aldrich (100mg/L) was prepared in a little amount of methanol since it is insoluble in water, freshly before being spiked into feed solution. In this study,100 ppm of BPA feed solution was prepared.

Performance study of PSf substrate membrane and PSf/PA TiO_2 TFC membrane

Pure water flux

The pure water flux (J) of the prepared sample was carried out using cross flow filtration system at 5 bar pressure at room temperature. The prepared membrane was pre-pressurized to minimize the compaction effect using deionized water for 30 min at the pressure of 5 bar before measurement. The pure water flux (J) was calculated using the following equation;

$$J = V / A.t$$

where J is the pure water flux (L/m^2·h), V is the permeated water volume (L), t is the permeation time (h), and A is the membrane area.

BPA rejection

The rejection of BPA was carried out through cross-flow filtration system. 1 liters of 100ppm BPA solution was used as the feed solution. The concentration of the feed and the permeate solution would be quantified using high performance liquid chromatography (HPLC, Agilent Technology 1200 Series) . The BPA rejection was expressed in term of percentage of rejection according to the following equation;

$$\text{Rejection of BPA} = \frac{C_f - C_p}{C_f} \times 100\%$$

Where C_f is concentration of feed solution and C_p is concentration of permeate solution.

RESULTS AND DISCUSSION

Morphological analysis by FESEM

Morphological structure for both surface and cross sectional image of PA/TiO_2 TFC membrane has been analyzed using FESEM. FESEM image was used to verify the existence of selective layer or PA layer on top of the PSf substrate membrane. As shown in Figure 2, PA thin layer has been spotted on top of PSf support membrane. This image clearly shows that TFC membrane was consisted of both porous layer and denser layer. Denser layer structure of membrane existed on top of the porous support was believed as polyamide thin film layer fabricated through interfacial polymerization, which providing a morphological evidence of potentiality to decline the permeability and enhancing the rejection capability. Since one of the disadvantages of dense layer membrane is the low water flux, therefore the dense layer need to be extremely thin in order to manage that issue. From FESEM image shown, the thickness of the PA/TiO_2 selective layer has been measured with thickness of about 155nm which was considerably as thin enough since normally thickness of PA film is around 200nm (Khorshidi *et al.*, 2015). The thickness formation might be due to the low concentration of TMC (0.05%), where the thickness of PA was directly proportional to the TMC concentration as stated by Khorshidi *et al.* (2015).

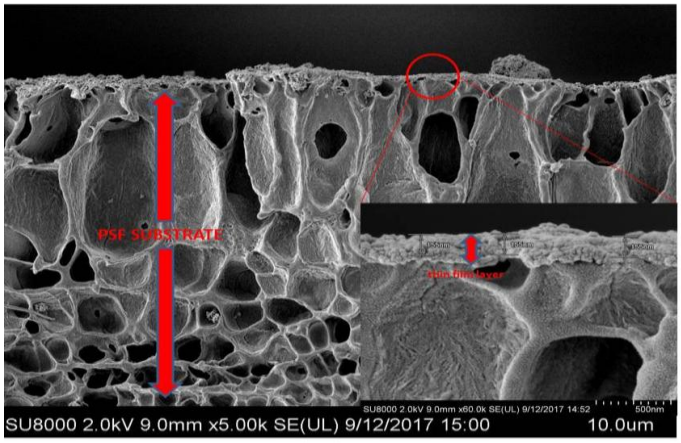
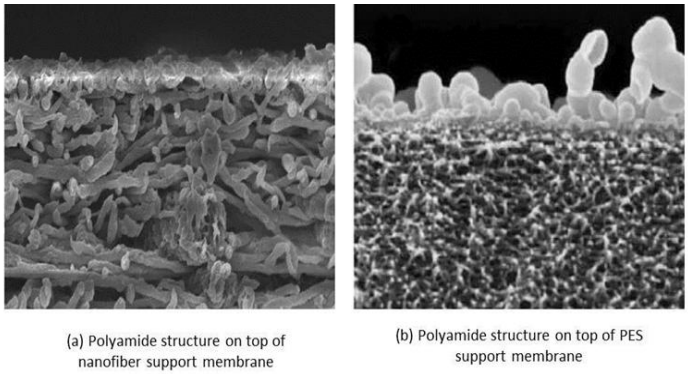


Figure 2 Cross section FESEM images of PA/TiO_2 TFC membrane.

In addition, the formation of "ridge and valley" structure is also an important indicator that proved the formation of PA layer on the PSf substrate (Tian *et al.*, 2013). Meanwhile, another study by Arash Mollahosseini and Ahmad Rahimpour also stated that typical ''ridge and valley'' structure was formed due to the interaction between MPD and TMC and also with the formation of polyamide on the surface of PSF support membranes. Figure 3(a) shows the example of "ridge and valley" structure of polyamide thin film on top of nanofiber substrate membrane and 3(b) on top of Polyethersulfone (PES) support membrane. Based on Figure 2, the "ridge and valley" structure could not be detected on top of the PSf substrate membrane. This might because of the TiO_2 particles that were immobilized in the polyamide layer and hence, affecting the structure. So, rather than just a distinct PA structural layer, a well dispersed TiO_2 particles can also be detected within PA layer. Since most nanomaterials exhibited strong interaction with polar solvents, the research on its immobilization in TFC has been focused on the dispersion of nanoparticles in MPD-aqueous solution. However, the nanoparticles cannot be integrated into the topmost of TFC layer, which has became the weakness of this approach (Khorshidi *et al.*, 2018). However, as shown from FESEM cross sectional image in Figure 2, the TiO_2 particles were embedded even on topmost of PA layer. This showed that even TiO_2 was dispersed into MPD-aqueous solution and integrated to top of PA layer.

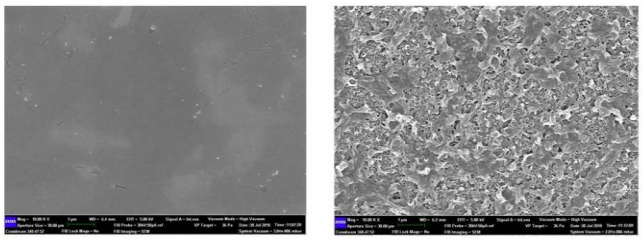
More than that, based on Figure 4(b), the iconic "ridge and valley" structure could also be observed through the membrane surface. A different surface image between Figure 4(a) and (b) illustrated a successful polymerization of PA TFC on top of PSF substrate. By referring to the Figure 4(b), where "ridge and valley" structure tended to form a rough surface structure whereas, PSf substrate has shown smooth and porous surface structure as shown in Figure 4(a). More than that, in order to confirm the existence of PA thin film layer on the PSf substrate, comparison of cross section SEM image between PSf support and PA/TiO_2 TFC has been done as shown in Figure 5.



(a) Polyamide structure on top of nanofiber support membrane

(b) Polyamide structure on top of PES support membrane

Figure 3 "Ridge and valley" structure of polyamide on top of substrate membrane.

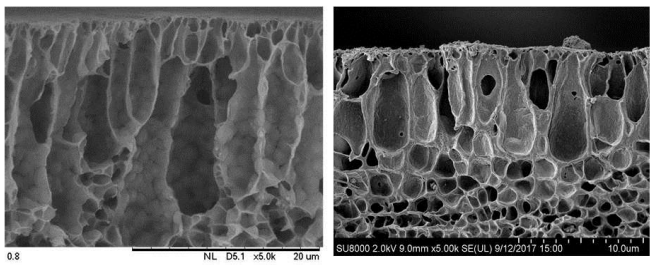


PSF SUBSTRATE

PA TFC

Figure 4 FESEM surface images of PSf substrate membrane and PA/TiO_2 TFC membrane.

Figure 5 shows the difference of cross section FESEM image between PSf substrate membrane with polyamide layer and without polyamide layer. As shown in Figure 5(a), there was a very thin layer detected on top of substrate membrane which was believed to be the PA layer which could not be seen in image (b). Figure 5(a) represents the image of PSf membrane after interfacial polymerization process while 5(b) shows the PSf membrane support before interfacial polymerization. Hence, both of these images (Figure 4 and 5) have proven that interfacial polymerization process has formed polyamide layer on top of PSf substrate membrane.



Cross section image of PSF substrate membrane

Cross section image of PA/TiO_2 TFC membrane

Figure 5 The cross section of FESEM images of (a) PA/TiO_2 TFC membrane and (b) PSf substrate membrane.

EDX analysis

The dispersion of TiO_2 particles on PA TFC membrane has been analysed using EDX image as shown in Figure 6. The image has proven the existence of particles on the membrane surface which might be the immobilized TiO_2. To verify the identity of the particles, EDX elemental mapping has be done. The elemental colour map obtained using EDX mapping analysis has verified the presence of TiO_2 phase since O and Ti elements were detected, which also showed the good distribution of TiO_2. This image has verified that immobilization of TiO_2 via IP process contributed to good distribution of nanoparticles with less agglomoration which could enhance membrane performance. This good distribution of TiO_2 might be due to the interaction between TiO_2 particles and PA structure since most nanomaterials exhibited strong interaction with polar solvents which in this study wasMPD-aqueous solution (Khorshidi *et al.*, 2018).

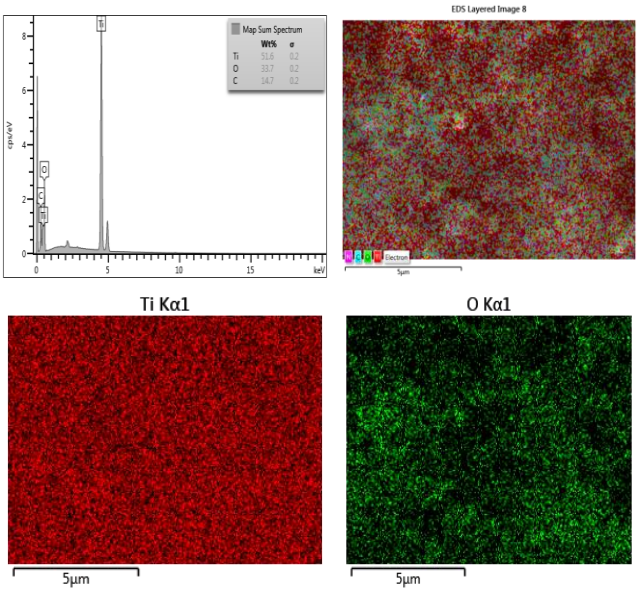


Figure 6 EDX images of PA/TiO_2 TFC membrane.

In addition, the EDX spectroscopy also showed a distinct peak of titanium at the membrane surface which also confirmed the effective addition via immobilization of the TiO_2 particles to the PA layer during the IP process (Khorshidi *et al.*, 2018).

Hydrophilicity test

The water contact angle is often used to evaluate the hydrophilicity of membranes; therefore the hydrophilicity property of PSf substrate membrane and PA/TiO_2 TFC was studied based on water contact angle (WCA) measurement. The WCA measurements shown in Figure 7 revealed that the hydrophilicity of the membrane surface was remarkably improved with the existence of PA/TiO_2 TFC layer.

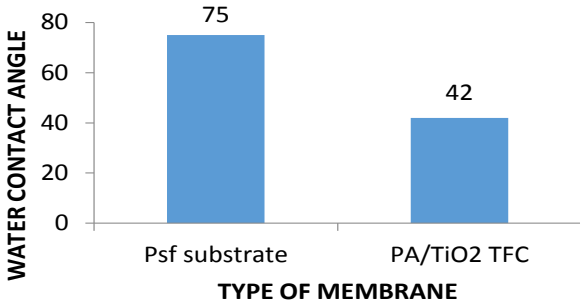


Figure 7 Water contact angle value for PSf substrate and PA/TiO_2 TFC membrane.

Based on Figure 7, the value of water contact angle of PA/TiO_2 TFC membrane was much lower compared to PSf substrate. The value of 75° has been reduced to 42° with the existence of PA/TiO_2 layer. Strong hydrophilic polar amides functional group which existed in PA layer structure was believed to be the factor that contributed to the low value of water contact angle compared to PSF susbtrate.

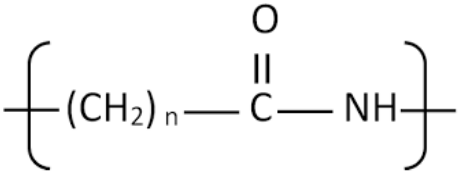


Figure 8 Polyamide structure.

Figure 8 shows the structure of polyamide which contained with amide group that contributed to the hydrophilicity properties of PA/TiO_2 TFC membrane. More than that, the addition of TiO_2 has been contributed the hydrophilicity of PA/TiO_2 TFC membrane due to the hydrophilic nature of TiO_2 particles. This supported by another study which stated that all TiO_2 incorporated thin film composites (TFC) showed higher hydrophilicity than the TFC membrane itself due to the hydrophilic nature of TiO_2 particles (Rajaeian *et al.*, 2013) which means the addition of TiO_2 particles has improved the hydrophilicity of PA TFC.

Performance test

Pure water flux

Figure 9 shows the difference of water flux value in L/m^2.h for both PSf substrate and PA/TiO_2 TFC membranes. As shown in Figure 9, the water flux value of PA/TiO_2 TFC membrane was much lower than PSf substrate. This result was relevant since NF membranes have much more lower water flux value compared to UF membranes. Generally, the morphological structure of each membranes would affect its performance such as water flux value. Based on morphological study as stated before, PSf substrate membrane has porous structure meanwhile PA/TiO_2 TFC has denser structure than PSf substrate. This denser structure might slow down the water flow through the membrane and significantly reduce the water flux value. The typical water flux value of TFC membranes is about 10 L/ m^2.h (W.J. Lau et al, 2015). As stated in Figure 9, the water flux value for PA/TiO_2 TFC membrane was lower than TFC typical water flux value. This might be due to the PSf substrate used has low water flux value compared to typical UF membrane's flux value which is in range from 100-2000 L/m^2.h (H. K. Shon et al, 2013).

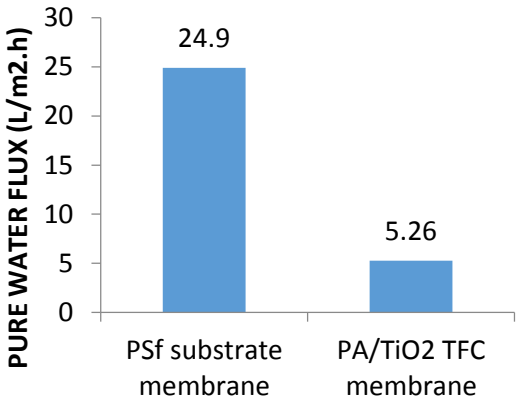


Figure 9 Pure water flux value for PSf substrate and PA/TiO_2 TFC membrane.

BPA removal

Figure 10 shows the rejection value of BPA by both PSf substrate and PA/TiO_2 TFC membranes. As shown in the figure, the PSf substrate was only rejected BPA from feed solution for about 19%. Meanwhile, PA/TiO_2 TFC membrane rejected BPA up to 99%. This result indicated that PA/TiO_2 TFC membrane fabricated via IP process could be applied to separate BPA from pharmaceutical wastewater. Practically, the PSf substrate is not efficient in removing BPA since it has larger pore size than BPA particle size. Particle size of BPA is around 6-7nm and since the PSf substrate is a membrane that categorized under UF membrane, it cannot be recommended for BPA removal. Since PA/TiO_2 TFC membrane rejects BPA almost 100%, its pore size must be much smaller than BPA itself. More than that, based on the morphological study, PSf substrate has been detected to exhibit porous structure, hence, explained the poor rejection of BPA since BPA is small in size and can easily pass through the membrane. Meanwhile, the denser layer of PA/TiO_2 on top of PSf substrate was believed to be the part that contributed to the high BPA separation. Based on the membrane performance result, NF membrane with PA layer showed a great BPA rejection ability compared to UF membrane.

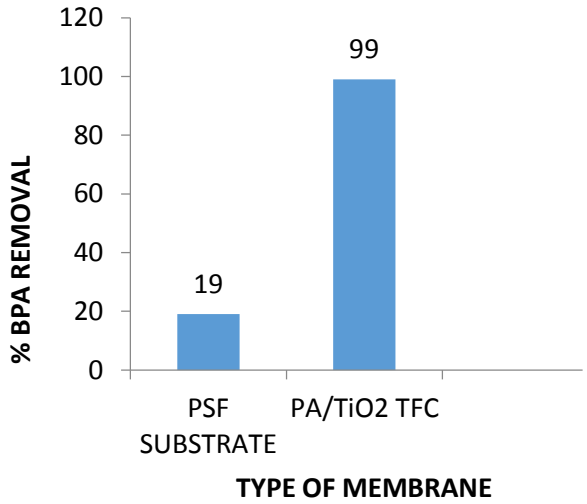


Figure 10 Percentage of BPA rejection by PSf substrate and PA/TiO_2 TFC membrane.

CONCLUSION

In this study, PA/TiO_2 TFC membrane was successfully fabricated through IP process with immobilization of TiO_2 particles on top of PSf substrate. From morphological characterization study through FESEM analysis, the existence of PA/TiO_2 layer has been spotted with good distribution of TiO_2 at the surface. Meanwhile, contact angle analysis data has proven that the hydrophilicity of PSF substrate membrane has been improved with existence of PA/TiO_2 layer. Based on the performance analysis of both PSf substrate and PA/TiO_2 TFC membrane, it could be stated that membrane that consisted of TFC layer was more promising to be applied in treating pharmaceutical wastewater which mostly contains small particles of pollutants. In other words, NF membrane is more practical and efficient than that of UF membrane in pharmaceutical wastewater application since NF membrane can reject almost 100% of pollutants.

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