Titanium Dioxide Incorporated Polyamide Thin Film Composite Photocatalytic Membrane for Bisphenol A Removal

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Abstract. Polyamide thin film composite immobilized with TiO2 is prepared using M-phenylene diamine and Trimesoyl chloride via interfacial polymerization. To determine the characteristics and performance of the membranes, effect of TiO2 loading is studied. 2 (w/v) % of MPD solution and 0.2 (w/v) % of TMC/n-hexane solution were used to prepare PA TFC membrane with different amount of TiO2 loading (0 wt. %, 0.1 wt. %, 0.2 wt. %, 0.3 wt. %, 0.4 wt. % and 0.5 wt. %). PA/TiO2 composite membranes are characterized by FESEM, EDX, FTIR and water contact angle. The properties of the membranes have improved upon TiO2 loading. With over 90% of BPA rejection exhibited by all the fabricated membranes, it is proved that the membranes especially PA/TiO2 TFC membrane with 0.4 wt. % TiO2 (with the highest rejection and degradation value of 99.9% and 14% respectively) are potentially employed as the hybrid photocatalytic membrane for BPA removal.

Keywords: polyamide, thin film composite, Bisphenol A, Titanium Dioxide, photocatalytic

1. Introduction

Worldwide development in the industrial sector has become one of the main factors of the global water crisis by means of destroyed clean water sources [1]. Thus, reuse of wastewater has become one of the solutions to augment freshwater resources. However, to win public confidence on the matter is a great challenge. Demonstration to the public about the reliability of the safe reusable water production technology is crucial [2]. This water crisis has induced researchers to explore and develop numerous water and wastewater treatment technologies to treat harmful pollutants and transform the water into reusable or even drinkable water. One of the pollutants found in wastewater that has become a great concern to researchers is endocrine-disrupting compounds (EDC). Generally, chemicals that can affect the endocrine system of animals including humans are called EDCs [3]. In a specific way, the word “endocrine disrupters” generally means the synthetic chemicals and natural plant compounds that may influence the endocrine system which is the communication system of glands, hormones, and cellular receptors in charge of the body’s internal functions. Many of these compounds have been related to developmental, reproductive, and other health issues in wildlife and laboratory animals [4].

One of the EDCs found in large abundance in wastewater is Bisphenol A (BPA). This leads to the issues of the impact of BPA exposures daily on humans due to its high-volume production. The estrogenic properties of BPA, a ubiquitous synthetic monomer that can leach into the food and water supply, have prompted considerable research into exposure-associated health risks in humans [5].
chemical is one of the EDCs found in water and likely to perform as an endocrine disruptor even at environmentally appropriate amounts.

Fortunately, research in membrane technology provides many great processes that can be used in water and wastewater treatment. Among them, there is one that has good separation and permeation characteristics [6] and has been reported to achieve high water flux in the membrane separation process [7] which is polyamide (PA) thin film membrane. Thin film that acts as an active layer is commonly produced via interfacial polymerization (IP) method that can provide good selectivity and high-water permeation rate. MPD and TMC are usually used in the fabrication of PA thin film by IP since these chemicals provide aromatic cross-linked PA layer and subsequently produce high water flux [8]. The dense structure of PA layer is the major aspect that contributes to the high separation performance meanwhile the porous support layer contributes to the high water flux. Other than that, PA layer acts as photocatalyst site where TiO$_2$ photocatalyst is embedded. TiO$_2$ is an excellent photocatalyst with applications in various fields. The main advantages of TiO$_2$ are its high chemical stability when exposed to acidic and basic compounds, its nontoxicity, its relatively low cost and its highly oxidizing power, which makes it a competitive candidate for many photocatalytic applications [9].

The main objective of this study is to investigate the effect of TiO$_2$ loading on the characteristics and performance of PA/TiO$_2$ TFC membrane. In this study, polysulfone (PSf) flat sheet membrane is used as the porous substrate of PA thin film meanwhile TiO$_2$ is immobilized into PA layer thus providing the dual effect as the photocatalytic membrane. PA/TiO$_2$ TFC photocatalytic hybrid membrane prepared in this study was believed to achieve better separation and photodegradation performance in eliminating BPA. The TiO$_2$ photocatalyst was exposed directly to light source since it was embedded on the top surface layer of membrane and this approach might enhance the light penetration towards the TiO$_2$ and consequently could improve the photocatalytic activity. The physicochemical properties and photocatalytic and membrane separation performances are determined as a function of TiO$_2$ loading to the PA TFC membranes.

2. Materials and methods

2.1 Fabrication of PA/TiO$_2$ thin film composites membranes by interfacial polymerization

The commercial PSf flat sheet membranes were used in this experiment as support or substrates membranes. These substrates membranes were soaked in 2% (w/v, i.e., 2g MPD/100 mL water) of MPD solution for 1 min. TiO$_2$ nanoparticles were immobilized in the MPD/water solution with different concentrations (0-0.5 wt.%). After removing the excess MPD solution on the substrate surface, 100 mL of 0.2% (w/v) TMC/n-hexane solution was gently poured onto the substrate surface. N-hexane was selected as the organic solvent. The TMC was allowed to react with the MPD for a fixed time (1 minute) to form a PA selective layer, followed by draining off the excess TMC solution from the membrane surface. Thermal treatment of MPD/TMC membranes involving placing fresh PA TFC membranes in ventilation oven at 80°C at ambient pressure for 5 min. The flat sheet based TFC membrane was stored in DI water for further use. The prepared membranes were recognized differently based on the amount of TiO$_2$ loading accordingly as PA/0.1 TiO$_2$, PA/0.2 TiO$_2$, PA/0.3 TiO$_2$, PA/0.4 TiO$_2$, PA/0.5 TiO$_2$ TFC membranes while PSf and PA substrate are control membranes.

2.2 Characterization of PA/TiO$_2$ thin film membranes

2.2.1 Morphological analysis by Field-Emission Scanning Electron Microscope (FESEM) and energy dispersive X-ray (EDX)

The morphological structure of PSf substrate membrane and PA/TiO$_2$ TFC membrane was analyzed using Field Emission Scanning Electron Microscopy (FESEM) image. The membranes sample was broken in liquid nitrogen, and the fractured cross sections and the bottom surface 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.

2.2.2 Fourier Transforms Infrared Spectroscopy (FTIR)
FT-IR spectra were carried out on a Perkin Elmer infrared spectrometer using attenuated total reflection (ATR) accessory to provide a non-destructive measurement method. All samples were directly put in contact with ATR diamond by clamping each sample onto the diamond surface, and then pressure was applied to ensure good optical contact between the sample and the diamond. All samples were scanned within the wave range of 650–4000 cm$^{-1}$ at room temperature.

2.2.3 Contact Angle Analysis
The relative hydrophilicity of the 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 a static sessile drop method with a goniometer. Deionized water was used as the probe liquid in all measurements. To reduce the evaporation effect, measurements were made as quickly as possible (less than 10 seconds) while 5 measurements were taken for each sample and the average calculated.

2.3 Preparation of Synthetic Pharmaceutical Wastewater (BPA solution)
In this study, BPA was chosen as the organic compound to evaluate the effectiveness of the fabricated PA/TiO$_2$ TFC membranes. The standard stock solution of the BPA >99% purchased from Sigma Aldrich was prepared in methanol, freshly before being spiked into the feed solution. The stock solution was diluted to the required concentration (100mg/L) for further use.

2.4 Performance Study of PSF/PA TiO$_2$ TFC Membrane
2.4.1 Pure Water Flux
The pure water flux ($J$) for the prepared membranes was carried out by using a cross flow filtration system at 5 bar pressure at room temperature. The prepared membranes were pre-pressurized to minimize the compaction effect by 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;

$$J = \frac{V}{A \cdot t}$$

where $J$ is the pure water flux (L•m$^{-2}$•h$^{-1}$), $V$ is the permeated water volume (L), $t$ is the permeation time (h), and $A$ is the membrane area.

2.4.2 BPA rejection
The rejection of BPA was carried out through the cross flow filtration system. 1 liter of 100ppm BPA solution was used as the feed solution. The concentration of the feed and the permeate solution was identified by using high performance liquid chromatography (HPLC) analyzer (Agilent Technology 1200 Series). The BPA rejection is expressed in terms 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 the feed concentration and $C_p$ is the permeate concentration.

2.4.3 BPA Degradation (Photocatalytic activity)
The photocatalytic activity of PA/TiO$_2$ fabricated membranes was run in a photocatalytic membrane reactor placed in the closed container made from stainless steel box with the dimension of (60 x 35 x 42) cm as shown in Figure 1. As the light source, UV lamp (Vilber lourmat, $\lambda$=312nm, 30 watt)
manufactured by Wuhan Co-shine Technology Co., Ltd, China was installed in the photocatalytic reactor. The prepared membrane was immersed in 1000 mL of 100 ppm BPA solution and was oxygenated in the dark for 120 minutes to achieve the adsorption/desorption equilibrium. The sample was collected every 30 minutes and was analyzed to determine the membranes adsorption. After 120 minutes has ended, the BPA solution along with the membrane was exposed to UV light for 5 hours and the sample was collected at regular time intervals (30 minutes) during irradiation within 5 hours. The degradation sample was quantified by using HPLC analyser (Agilent Technology 1200 Series) coupled with a programmable UV detector. The photocatalytic activity was expressed in the percentages of BPA degradation according to the following equation.

\[
\text{Degradation of BPA} = \frac{C_0 - C_t}{C_0} \times 100
\]

where \(C_0\) was the initial BPA concentration and \(C_t\) was the BPA concentration at time,\(t\).

3. Results and discussion

3.1 Morphological analysis by Field-Emission Scanning Electron Microscope (FESEM), Fourier Transforms Infrared Spectroscopy Analysis (FTIR) and energy dispersive X-ray (EDX)

3.1.1 Field-Emission Scanning Electron Microscope (FESEM) Analysis

The morphological structure of PSf substrate and PA/TiO\(_2\) TFC membranes has been analyzed using FESEM. FESEM image was used to verify the existence of the selective layer or PA layer. Figure 2 shows the comparison of surface morphological structure between PSf substrate and PA/TiO\(_2\) TFC membranes with different loadings of TiO\(_2\). Image for top of PSf substrate has shown smooth surface while PA TFC possessed a rough surface. The iconic “ridge and valley” structure that represents the PA structure tends to form this rough surface and it can be observed through the PA TFC membrane surface. The formation of the “ridge and valley” structure is an important indicator that proved the formation of PA layer on the PSf substrate [7]. Meanwhile, another study by Arash Mollahosseini and Ahmad Rahimpour [10] also stated that typical “ridge and valley” structure was formed due to the interaction between MPD and TMC and also with the formation of PA on the surface of PSf support membrane. IP process of MPD and TMC is believed to involve an incipient fast stage that forms a dense core barrier layer followed by a slow-growth stage that is MPD diffusion-limited. The first fast reaction generates the dense core layer that is significantly thinner than the extended loose layer formed later as monomer diffuses through the dense core layer. In addition, the PA contains a crosslinked portion (X) and a more hydrophilic linear moiety (Y) containing free carboxylic acid groups [11]. Figure 3 has shown the PA structure formed from an IP reaction between MPD and TMC which has a crosslinked portion (X-fraction) and linear moiety (Y-fraction), which has an unreacted acid chloride group that subsequently, hydrolyzes to a carboxylic acid group.
Figure 2: FESEM image of PSF substrate and PA/TiO$_2$ TFC membrane with different loading of TiO$_2$ (0-0.5\%)

Figure 3: The polyamide structure formed from an IP reaction between MPD and TMC has a crosslinked portion (X-fraction) and linear moiety (Y-fraction), which has an unreacted acid chloride group that subsequently, hydrolyzes to a carboxylic acid group

As shown in Figure 2, compared to PA TFC image with clear “ridge and valley” structure, the structure in PA/TiO$_2$ TFC membrane gets less visible since TiO$_2$ particles have covered it. This might happen due to the immobilization of TiO$_2$ in PA layer has affected the PA layer image structure. More than that, the addition of nanoparticles during IP process will affects PA integrity and reduces its crosslinking degree that significantly affect the ridge and valley structure formed [12]. Meanwhile, same pattern of FESEM results image has been recorded which has been studied by Thu and co-researchers [13]. In addition, white dots have been detected on all PA/TiO$_2$ TFC membranes which are strongly believed are TiO$_2$ particles. The white spot observed around the features was attributed to TiO$_2$ nanoparticles because of their more “spherical shape” [14]. As shown in this figure, TiO$_2$ particles have been distributed well on all PA/TiO$_2$ TFC membranes. This is supported by EDX mapping image in Figure 6 which has shown the distribution of TiO$_2$ in PA layer.
Figure 4: Cross-sectional FESEM image of PSF substrate and PA/TiO$_2$ TFC membrane with different loading of TiO$_2$ (0 wt.% - 0.5 wt.%)

Figure 4 shows the comparison of cross-sectional FESEM image between PSf substrate membrane and PA/TiO$_2$ TFC membrane with different loading of TiO$_2$. As can be seen in Figure 4, the PSf substrate membrane had a smooth surface with finger pore like structure at the bottom. Meanwhile, image that represents the PA TFC membrane, the surface of PSf substrate membrane has been covered with another rough layer which is believed as PA layer. According to the image of PA/TiO$_2$ TFC membrane, the formation of a dense selective layer of PA in TFC membrane has been detected which is absent in PSF substrate image. The same features were displayed by TFN membranes prepared by Wang and co-researchers when they were fabricating thin film nanocomposites membranes [15]. Through observation based on these two images, it can be stated that the fabrication of PA layer is a success on top of PSf substrate. As seen from this FESEM image, the cross-sectional image was not clear due to the error during the preparation of sample. However, the image has shown the rough surface and dense structure of PA layer which exists on top of PSf substrate membrane compared to the smooth surface of PSF substrate membrane. This image has proven that PA layer exists as the top layer in all PA/TiO$_2$ TFC membranes even when the “ridge and valley” structure of PA in Figure 2 has been covered by immobilization of TiO$_2$.

3.1.2 Fourier Transforms Infrared Spectroscopy Analysis
Figure 5: FTIR peak frequencies for PSf substrate membrane and PA TFC membrane and PA/TiO₂ TFC membrane.

Figure 5 displays the comparison of FTIR analysis data between PSf substrate, PA TFC and PA/TiO₂ TFC membranes. The results clearly show the existence of amides functional group at the frequency of 1660 cm⁻¹ attributed to the stretching vibration of C=O for PA TFC membranes which this corresponding peak was found absent in PSf substrate membrane. Besides that peak, there is one more peak that represents the amide functional group in PA TFC membranes which is at 1576 cm⁻¹ representing the N-H bending in PA bonding. All these bands are categorized in amide group produced by the polymerization process in PA structure formation, as stated by Li and co-researcher [16]. This functional group of amides that existed has verified the formation of PA layer on top of PSf substrate membrane which supported the morphological structure studied. The FTIR spectra of PA/TiO₂ TFC membrane are almost identical to PA TFC membrane, indicating the in-situ polymerization has occurred in the existence of TiO₂ photocatalyst. As seen from the image, the intensity of peaks for 0.4 PA/TiO₂ TFC and 0.5 PA/TiO₂ TFC membranes were found lower as compared to others membrane. This might be due to the higher content of TiO₂ in the membrane that have created more interaction with the PA.

3.1.3 EDX Analysis

Figure 6: EDX mapping image of PA/TiO₂ TFC membrane with various loading (0.1-0.5wt.%)

0.1 PA/TiO₂ TFC
0.2 PA/TiO₂ TFC
0.3 PA/TiO₂ TFC
0.4 PA/TiO₂ TFC
0.5 PA/TiO₂ TFC
### Table 1. The EDX data of PA/TiO₂ TFC membrane with various loading (0.1-0.5wt.%)

| Type of membrane | C (wt%) | O (wt%) | Ti (wt%) |
|------------------|---------|---------|----------|
| PA/0.1 TiO₂      | 73.2    | 25.0    | 1.8      |
| PA/0.2 TiO₂      | 74.4    | 22.6    | 3.0      |
| PA/0.3 TiO₂      | 74.1    | 21.9    | 4.0      |
| PA/0.4 TiO₂      | 44.9    | 27.7    | 27.4     |
| PA/0.5 TiO₂      | 66.8    | 27.8    | 5.4      |

To investigate the dispersion quality of TiO₂ nanoparticles, the EDX mapping analysis was also carried out throughout the hybrid polyamide thin films. Figure 6 shows the percentage of Ti detected which represents the quantity of TiO₂ distributed in PA/TiO₂ TFC membranes along with the mapping image. As shown in Figure 6, the amount of TiO₂ has been increased from 1.8% (PA/0.1 TiO₂ TFC membrane) up to 27.4% (PA/0.4 TiO₂ TFC membrane) then dropped to 5.4% (PA/0.5 TiO₂ TFC membrane). The dramatic drop might be due to the leaching of TiO₂ particles from PA layer when over amount of TiO₂ particles were added to the PA/TFC membrane. As can be see through Figure 6, the amount of colored dots that represent TiO₂ particles has become more obvious and clear from 0.1wt.% to 0.4wt.% TiO₂ loading but in 0.5wt.% TiO₂ loading, the dots have been reducing. The lowest density dispersion of TiO₂ nanoparticles has been obtained in the case of PA/0.1 TiO₂ TFC membrane. However, more concentrated dispersion of TiO₂ has been observed from PA/0.2 TiO₂ TFC membrane until PA/0.4 TiO₂ TFC membrane. Figure 6 has clearly shown that the maximum amount of TiO₂ identified in PA/TFC membranes is 27.4% which is in 0.4wt.% TiO₂ PA/TFC membrane. These results show that 0.4wt.% TiO₂ loading has become the optimum loading since the loading higher than that value has initiated the leaching problem. The thin film layer of aromatic polyamide TFC membranes is composed of the crosslinked form of three amide linkages and the linear form with pendant free carboxylic acid and two amide linkages. The behavior of TiO₂ on the polymer with COOH group is in two different adsorption ways. One way is that TiO₂ was bound with two oxygen atoms of carboxylate group via bidentate coordination to Ti⁴⁺ cations. The other way was to form a H-bond between carboxyl group and the surface hydroxyl group of TiO₂ [17].

### 3.2 Contact Angle Analysis

![Figure 7: Water contact angle data](image-url)
The water contact angle (WCA) is commonly applied to study the hydrophilicity of membranes; thus, the hydrophilicity features of PSf substrate, PA TFC membrane and PA/TiO2 TFC membranes were investigated and presented in Figure 7. Figure 7 shows that the hydrophilicity of the membrane surface has become much better with the presence of PA layer. As shown in the figure, the WCA value for PA TFC membrane is much lower than PSf substrate. The value of WCA was decreased from 85° to 70° for PSf substrate and PA TFC membranes respectively. The improved hydrophilicity properties make PA TFC membrane desirable for wastewater treatment application. Good hydrophilic polar amides functional group that exists in PA layer structure is the part that makes the value of WCA in PA TFC layer lower compared to PSf substrate. More than that, membrane with lower WCA value can pull more water molecules onto its surface and improve the transport of water across the membrane [18]. Based on other study, the value of WCA of their PSF membrane is around 75° [19]. The hydrophilicity of PSF membrane might vary depending on the method and parameters used during the membrane fabrication. Meanwhile, the hydrophilicity of PA TFC membranes studied by Rajaeian and co-researcher was 79° compared to its substrate which is 87.3°. Their finding in wetting properties of these two types of membrane is almost identical to this study.

Figure 7 also shows the WCA values for PA TFC membrane and PA/TiO2 TFC membranes at different loading of TiO2 immobilized. As shown in the graph, the value of WCA of PA TFC membrane without TiO2 particles is much higher compared to PA/TiO2 TFC membranes. The value of 70° has been gradually reduced with the existence of PA/TiO2 TFC layer. This proves that TiO2 has further improved the hydrophilicity of PA TFC membranes. The addition of TiO2 has contributed to the hydrophilicity of PA/TiO2 TFC membrane due to the hydrophilic nature of TiO2 particles. This was believed to be due to the presence of the rich hydroxyl group in the TiO2 photocatalyst that has high ability to attract water molecules onto the PA/TiO2 TFC membrane surface, which causes an increase in the degree of hydrophilicity [20]. As expected, the WCA value for PA/0.5 TiO2 TFC is higher than PA/0.4 TiO2 TFC which means that the hydrophilicity of the membrane has been decreased. This belief was correlated to the leaching of TiO2 particles from PA layer due to the overwhelming of TiO2 immobilization since the amount and dispersion of TiO2 particles is less in PA/0.5 TiO2 TFC membrane as shown in EDX mapping image in Figure 6.

3.3 Performance Study of PA TiO2 TFC Membrane

3.3.1 Pure Water Flux

Figure 8 shows the difference of water flux value in L/m2.h for PSf substrate, PA TFC and PA/TiO2 TFC membranes. As shown in Figure 8, the water flux value of PA TFC membrane is much lower than PSf substrate. This result is relevant since NF membranes have much lower water flux value compared to UF membranes. Generally, the morphological structure of each membrane is affecting its performance such as water flux value. Based on the morphological study as stated before, PSf substrate membrane has porous structure while PA TFC has denser structure than PSf substrate. This denser structure has slowed down the water flow through the membrane and significantly reduced the water flux value. The typical water flux value of TFC membranes is about 10 L/m2.h [21]. As stated in Figure 8, the water flux value for PA TFC membrane is lower than TFC typical water flux value. This may be due to the fact that PSf substrate used already has low water flux value compared to the typical UF membrane’s flux value which is in the range of 100-2000 L/m2.h [22].
Figure 8: Pure water flux data in L/m²·h at 5 bar

As shown in the figure, the lowest value is for PA TFC membrane without TiO₂ particles. Meanwhile, PA/0.4 TiO₂ TFC membrane exhibited the highest pure water flux value. Generally, all PA/TiO₂ TFC membranes in this study generated low water flux value due to the dense PA layer structure. However, the addition of TiO₂ particles also affects the pure water flux value since it is related to the hydrophilicity of the membrane. Since improving membrane hydrophilicity can increase the membrane flux, the highest water flux at 0.4% TiO₂ loading might be due to the high hydrophilicity properties of that membrane. The improvement in hydrophilicity properties might also be due to the higher proportion of oxygen-containing functional groups on the PA surface from the nucleophile neutralization of acyl chloride molecule during interfacial polymerization [23]. As expected, the WCA value for 0.5 PA/TiO2 TFC is higher than 0.4 PA/TiO2 TFC which means that the hydrophilicity of the membrane has been decrease. This believed was correlated to the leaching of TiO₂ particles from PA layer due to overwhelming of TiO₂ immobilization since the amount and dispersion of TiO₂ particles is less in 0.5 PA/TiO₂ TFC membrane as shown in EDX mapping image.

3.3.2 BPA rejection

Figure 9 shows the comparison of BPA removal efficiency between PSf substrate, PA TFC and PA/TiO₂ TFC membranes. Through the BPA rejection test, PSf substrate membrane can only remove about 19% of BPA from its initial feed value, 100ppm. This might happen due to the large pore size of PSf substrate membrane and the majority of BPA particles can pass through the membrane. This proves that UF substrate membrane is not practical for BPA removal. Meanwhile, PA TFC membrane has rejected about 98.5% BPA which is much more efficient compared to PSf substrate membrane. Based on the morphological study, PSf substrate has been detected to have porous structure, which explained the poor rejection of BPA since BPA is small in size and can easily pass through the membrane. Meanwhile, the dense layer of PA layer on top of PSf substrate is believed to be the part that contributes to the high BPA rejection.
As shown in the figure, the lowest rejection performed is by PA/TiO₂ TFC membrane with 0.1% TiO₂ loading which is 91.7%. Meanwhile, the highest rejection achieved is by PA/0.4 TiO₂ TFC membrane with 99.9% BPA rejection. All fabricated membranes have high BPA rejection which is 90% and above due to the structure of PA layer formed. The dense structure of PA layer contributes to high rejection of BPA. The solution-diffusion process is the most common mechanism for mass transport through nonporous membrane like PA TFC membrane which consists of five fundamental processes. The BPA molecules must first be transported or diffused through the liquid film. Then the BPA solution is in the upstream surface of the membrane and followed by diffusion through the membrane matrix. Then, desorption of solute molecules in the downstream side (permeated side) of the membrane and lastly the diffusion through the boundary layer of the permeate phase [24]. The variation in BPA removal is concluded associated to the physical characteristics of the membrane and also the physicochemical characteristics of the BPA [25,26]. The illustrations of possible BPA rejection mechanism through PSF and its nanocomposite membranes are shown as in Figure 10.
Figure 10: Illustration of possible BPA rejection mechanism through PSF and its nanocomposite membranes

3.3.3 Adsorption and Photocatalytic performance of PA/TiO$_2$ TFC membranes

The removal efficiency of the BPA by the prepared PA/TiO$_2$ TFC membranes were measured based on adsorption and photocatalytic degradation of BPA solution with an initial concentration of 100 ppm. The kinetic adsorption of the membrane is displayed in Figure 11. Figure 11 shows that most BPA adsorptions occur on the membrane surface in 90 minutes. Hence, the membrane is kept in the dark for 120 minutes ahead of UV irradiation. It is to confirm that the photodegradation under UV irradiation started after adsorption reach the equilibrium state [27]. After 120 minutes of BPA adsorption, 0.1 PA and 0.4 PA TiO$_2$ TFC membranes showed the maximum BPA adsorption, which is around 13%. The adsorption of 0.2 PA, 0.3 PA and 0.5 PA TiO$_2$ TFC membranes has adsorption value of 4%, 8% and 4% respectively. Similar study on adsorption of TiO$_2$ photocatalytic membrane towards BPA has reported that the adsorption value of BPA by their membrane is 15% which is quite identical to this study [28].
Figure 12 shows the photodegradation percentage performed by PA/TiO$_2$ TFC photocatalytic membranes with different loading of TiO$_2$. Based on the data obtained, the highest percentage of photodegradation of BPA achieved by this type of membrane is 14% which is performed by 0.4 PA/TiO$_2$ TFC photocatalytic membrane. Meanwhile, the lowest photodegradation is performed by 0.1 PA/TiO$_2$ TFC photocatalytic membrane which is 4.5%. 0.4 PA/TiO$_2$ TFC membrane achieved the highest photodegradation percentage value and this might be due to high TiO$_2$ particles embedded in this membrane compared to other PA/TiO$_2$ TFC membranes as shown in FESEM and EDX image before.

Figure 13: Photodegradation of BPA under UV irradiation

Meanwhile, based on Figure 13, it can be seen that degradation is still proceeding even after 300 minutes of irradiation time except for 0.2 PA/TiO$_2$ TFC membrane. Even after 300 minutes exposure to the UV light source, the degradation of BPA is low. Meanwhile, for 0.2 PA/TiO$_2$ TFC membrane, the degradation has stopped after 240 minutes of irradiation time. This can happen when there is no longer active site available for reaction to take place. However, for others membrane, based
on the data, the degradation of BPA might continue if the irradiation time is longer and the percentage of BPA degradation might be higher. It is proposed that the incorporation of the TiO$_2$ photocatalyst to the whole PA layer has produced a wide surface area of TiO$_2$ exposed to UV light and high porosity against the direct interaction with the BPA pollutants, hence promoting excellent BPA degradation process to take place [29]. Moreover, the existence of a uniform dispersion TiO$_2$ catalyst in the PA layer is believed to give the high degradation of the BPA particles. The low degradation of BPA in this study is highly caused by the insufficient amount of TiO$_2$ and the setup of the experiment. The large volume and high concentration of BPA without any movement to get a fast transportation to and from the catalyst other than diffusion during the photocatalytic process hinders a fast degradation of BPA, then results in low degradation of BPA.

Several studies on the degradation of BPA have been done using different types of photocatalytic membranes which resulted in higher degradation of BPA. It was well known that there were a number of variables and parameters that affect the photocatalytic performance which include intensity of the light source, type of catalyst and loading of catalyst. However, since the main variable considered in this study is the TiO$_2$ loading, it is worth comparing the photocatalytic performance of the hybrid membrane by only taking into account the TiO$_2$ content in the membrane. A study by Kamaluddin and team [30] has found that about 86.7% of BPA can be degraded by their dual layer hollow fiber (DHLF) membrane comprised of 7.5 wt% of TiO$_2$ photocatalyst. The TiO$_2$ has been incorporated into DHLF using co-extrusion phase inversion method in the outer layer of the membrane. The high loading of TiO$_2$ used (7.5 wt%) might also be the main contributor to the high BPA degradation. In another study, up to 88% of BPA can be degraded by the ceramic hollow fiber photocatalytic membrane comprised of 1.0 wt% of Ag/TiO$_2$ photocatalyst [31].

Based on these studies, the low degradation of BPA by PA/TiO$_2$ TFC membrane might be caused by the low content of TiO$_2$ available for photocatalysis to take place. However, though at lower loading of TiO$_2$ (0.4 wt.%), PA/TiO$_2$ TFC membrane manages to degrade up to 14% of BPA and hence it is anticipated that higher loading of TiO$_2$, could degrade more BPA. On top of that, the method of immobilizing TiO$_2$ in the membrane is an interesting subject that should be further studied in providing higher effective surface area of TiO$_2$ for photocatalysis activities.

4. 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. Through FESEM and EDX analysis, the TiO$_2$ particles spotted on PA TFC membrane increase as the TiO$_2$ loading increase but as it reaches 0.5wt.% TiO$_2$ loading, the TiO$_2$ particles have decreased due to the leaching issue. From the FTIR analysis, C=H stretching and N-H bending are present in PA TFC peaks which represents the amides group present in polyamide structure. From contact angle analysis, the hydrophilicity of the membranes improves as the TiO$_2$ loading increase but WCA becomes increased at 0.5wt.% TiO$_2$ loading since loss of TiO$_2$ particles happened. Based on results obtained through the porosimeter test, average pore diameter of PA/TiO$_2$ TFC is not much different for all loading but the average pore diameter of PA TFC membrane is much smaller than PSf substrate. In addition, from the performance study of these membranes, the water flux of PA/0.4 TiO$_2$ TFC membrane is the highest among other loadings while the lowest is at PA TFC membrane without TiO$_2$. From the rejection test, the percentage of removal by these membranes is not much different but the highest percentage of BPA removal is performed by PA/0.4 TiO$_2$ TFC membrane. Meanwhile, PA TFC membranes are much more applicable for BPA removal since PSf substrate only removes about 19% BPA. It is worth mentioning that more TiO$_2$ loading in the PA/TiO$_2$ TFC membranes could contribute to higher photocatalytic activities without compromising the uniformity of TiO$_2$ distribution in the membrane dense skin layer.
5. References

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