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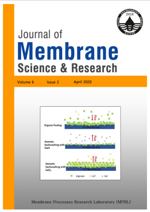

Research Paper

# Efficient Immobilised $TiO_2$ in Polyvinylidene fluoride (PVDF) Membrane for Photocatalytic Degradation of Methylene Blue

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## Article info

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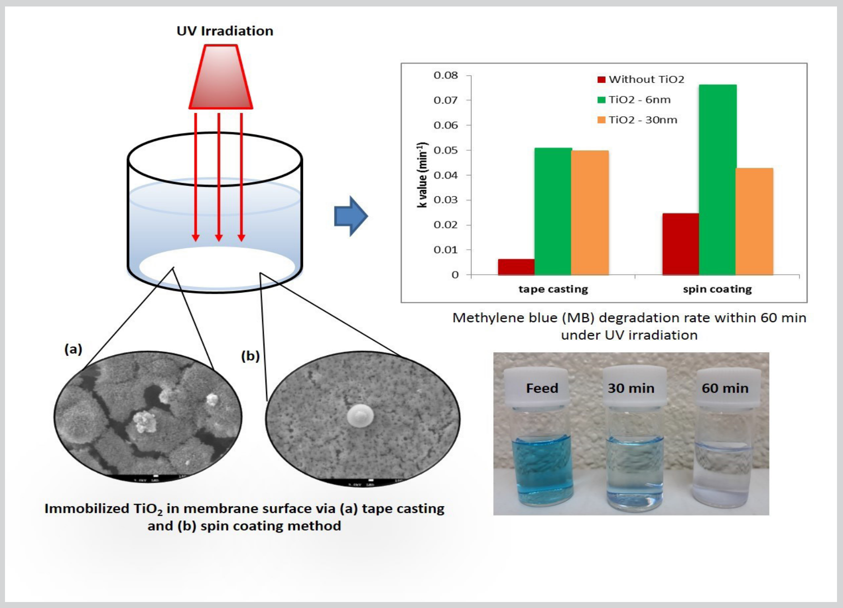
## Highlights

- The effect of different $TiO_2$ particle sizes immobilized in membrane structure was studied
- Photocatalytic membranes were prepared via tape casting and spin coating method
- The good distribution and uniformity of $TiO_2$ nanoparticles achieved via spin coating method
- Less aggregation of immobilized $TiO_2$ enhanced the MB photocatalytic degradation rate
- UV penetration up to 55.64µm of membrane thickness shows the optimum MB degradation rate

## Graphical abstract



## Abstract

Immobilised titanium dioxide ($TiO_2$) in membrane structures has recently become attractive. This is due to the elimination of the separation step after the process of photocatalytic degradation. The efficiency of the $TiO_2$ surface area exposed to UV light as the main important parameter needs to be considered. The immobilisation of $TiO_2$ nanoparticles in the polyvinylidene fluoride (PVDF) membrane structure with different particle sizes (6 nm and 30 nm) was prepared via various techniques including the tape casting and spin coating methods to study the distribution of $TiO_2$ nanoparticles in the membrane structure. Besides, the effects of the spinning speed in spin coating methods on the membrane structure and photocatalytic performance were investigated. The morphological and physical characteristics were also explored by field emission scanning electron microscope (FESEM) energy dispersion of X-ray (EDX), scanning electron microscopy (SEM) and atomic force microscopy (AFM) analysis. The prepared membranes were tested in a photocatalytic system using methylene blue (MB) as a model pollutant. The results showed that the immobilisation of $TiO_2$ nanoparticles in membrane structure could enhance the rate of MB degradation. The aggregation of the 6 nm and 30 nm $TiO_2$ particle sizes prepared by tape casting method shows similar performance in MB degradation rate but contradict the result of the spin coating method. The good distribution and uniformity of the 6 nm $TiO_2$ particle size exhibit a higher MB degradation rate. The thickness of the membrane can be tailored using the spin coating method and UV penetration towards the photocatalytic membrane up to 55.64 µm of thickness, which could enhance the MB photocatalytic degradation rate.

## 1. Introduction

Nowadays, synthetic dyes are widely used in the textile industry. Some of the chemicals found in synthetic dyes are sulphur, nitrates, acetic acid, soaps, heavy metals such as copper, arsenic, lead, cadmium and other chemicals [1]. These chemicals are highly toxic and may have a high impact on wastewater quality. As for the activities to treat wastewater, the most widely accepted approach for achieving environmental safety is by effluent treatment plants [2]. Typically, dye wastewater is treated by conventional methods such as biological process, ozonation, adsorption, coagulation and oxidation. Among

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these methods, advanced oxidation processes (AOPs) are considered efficient methods. This is due to the generation of highly active hydroxyl radicals, which can oxidise a considerable variety of organic contaminants [3].

Among the AOP methods, heterogeneous photocatalysis has been developed successfully using $TiO_2$. The method, which commonly utilises a photocatalyst, is non-toxic in nature, low cost and environmentally friendly [4]. Most researchers have modified the photocatalyst to get a smaller band gap that can be activated under visible light by integration with various potential materials such as graphene oxide, ferric oxide and zinc oxide [5, 6]. Besides, ZnO–$SnO_2$ nanocomposites also show the highest efficiency in MB photocatalytic degradation compared to pure ZnO [7]. However, in order to separate the catalyst from the treated water after the degradation is required as the additional step.

Therefore, the primary aim of immobilising $TiO_2$ onto/within solid supports such as polymeric membrane is to avoid the post-separation challenges associated with the powdered $TiO_2$ catalyst. The most recognised method for the fabrication of a flat sheet membrane is via the casting method. This approach uses a knife-like tool to control the thickness of the nascent membrane and disperse the polymer solution [8, 9]. In contrast, the spin coating method is more efficient at applying thin and uniform films by depositing a viscous fluid on a horizontal rotating disc [10]. In this work, an attempt has been made to prepare immobilised $TiO_2$ on PVDF membrane through the spin coating method and the tape casting as a comparative method. Furthermore, the effects of spinning speed on the mass transfer kinetics of the spin coating method along with the membrane structure and photocatalytic performance, were also investigated. The different particle sizes of $TiO_2$ nanoparticles were used to investigate the distribution within/outside the membrane surface using both methods.

## 2. Experimental

### 2.1. Materials

In this study, polyvinylidene fluoride (PVDF 18734, powder, Polysciences Inc.) and N-N, dimethylacetamide (DMAc, FUJIFILM Wako Pure Chemical Industries Ltd.) were used as the polymer base and solvent, respectively without purification. The $TiO_2$ nanoparticles with 6 nm and 30 nm particle sizes and specific surface area 280 $m^2/g$ and 52 $m^2/g$, respectively were supplied by Tayca Corporation, Japan. The $TiO_2$ nanoparticles were used as the photocatalyst in the photocatalytic degradation of methylene blue (Cl-52015, Nacalai tesque) experiments. Ethanol (99.5%, FUJIFILM Wako Pure Chemical Industries, Ltd) was used for the post-treatment process.

### 2.2. Preparation of casting solution

The 3 wt.% $TiO_2$ nanoparticles and 82 wt.% DMAc were mixed and stirred inside a Scott bottle at 400 rpm for 24 hours. 15 wt.% of PVDF powder was gradually added after the $TiO_2$ mixture was adequately dispersed in the solution. This casting solution was prepared for both the 6 nm and 30 nm $TiO_2$ particles. Similarly, a separate casting solution was prepared without $TiO_2$ nanoparticles as a control sample. This was a mixture of 18 wt.% and 82 wt.% of PVDF and DMAc, respectively.

### 2.3. Fabrication of photocatalytic membrane

#### 2.3.1. Traditional tape casting method

The prepared casting solution was poured onto a clean and smooth glass plate of 20 cm × 20 cm at room temperature using a casting knife. The thickness of the photocatalytic membranes was controlled using an adhesive tape that was stuck on the glass plate. In order to remove any residual solvent, the cast film was then immediately immersed into a water bath for 1 day. Prior to air drying, 50:50 wt.% of ethanol:water were used for post-treated of the photocatalytic membranes in 1 hour and followed by 100% ethanol in 1 hour for the wettability and pore collapse improvement. Lastly, the photocatalytic membranes were dried for 1 day at room temperature. The photocatalytic membranes prepared via tape casting were labelled; M1, M2 and M3 for PVDF, PVDF/$TiO_2$ 6 nm and PVDF/$TiO_2$ 30 nm of $TiO_2$ nanoparticles, respectively.

#### 2.3.2. Spin coating method

The membranes were prepared through the spin coating method by coagulating them into the non-solvent bath. Next, 2 mL of homogeneous casting solution with 6 nm $TiO_2$ particle size was dropped on a Petri dish with a spin coater (Aiden) at different spinning speeds; 500, 700, 900, 1100 and 1300 rpm with a 30-second duration for samples M4, M5, M6, M7 and M8, respectively. After coating, the nascent membranes were immediately immersed into a water bath, and the post-treatment was similar to the tape casting method. The membranes were subsequently cut into 5 cm diameter before subjecting to photocatalytic experiment. The photocatalytic membranes were prepared via the spin coating method at 700 rpm spinning speed (optimised conditions) for duration of 30 seconds to create M9 and M10 for PVDF and PVDF/$TiO_2$ 30 nm of $TiO_2$ nanoparticles, respectively.

### 2.4. Characterisation methods

The dry samples were immersed into liquid nitrogen and carefully fractured to give a clean break in order to observe the cross-sectional structures of the membranes. Then, all the specimens were fixed on metal support and sputtered a layer of palladium-platinum under vacuum for 2 minutes. After that, scanning electron microscope (SEM, Model: JEOL JSM-5600) was used to examine the membrane structures. The distribution of the $TiO_2$ nanoparticles in photocatalytic membranes was determined by energy dispersive x-ray (EDX, Model S250, EDAX) analysis. The EDX line scan was randomly drawn across the sample surfaces to profile the distribution of $TiO_2$ nanoparticles. Consequently, the sizes of the $TiO_2$ nanoparticles distributed on the photocatalytic membrane surfaces were measured from the field emission scanning electron microscope (FESEM, Model: Jeol JSM-7800F) images at 30.00 kx magnification. Lastly, the surface roughness was measured using atomic force microscopy (AFM, Model: JOEL, JSPM-5200 Scanning Probe Microscope).

### 2.5. Photocatalytic performance

In order to evaluate the methylene blue (MB) degradation efficiency of the membranes, the photocatalytic degradation tests were conducted. The prepared membrane (diameter: 5 cm; membrane area: 78.54 $cm^2$) was then placed in the batch photoreactor system using a high-pressure mercury lamp as a light source. The feed solution was 300 mL of 10 ppm MB solution. The equilibrium was reached before the photocatalytic degradation process by stirring mixture at 298 K in the dark conditions. In order to prevent MB deposition at the bottom of the reactor, the reaction solution was moderately stirred using the magnetic stirrer. The distance of UV light sources and the membrane was fixed at 10cm. The activation of immobilised $TiO_2$ in the flat sheet membrane was started by turning on a high pressure mercury lamp. Next, aluminium foils was used to cover the glass container in order to prevent the escape of harmful UV light. It should be noted that the membranes were not subjected to filtration during the photocatalytic reaction.

### 2.6. Analytical determinations and kinetics measurement

In every 10 minutes, 5 mL of aliquots were taken from the photocatalytic reactor within the hour. The decreasing of MB concentration was measured in order to evaluate the kinetic reaction. Consequently, the MB concentration was monitored using the UV-Vis Spectrophotometer (Model: Shimadzu UV Mini 1240) at a wavelength of 664 nm. The concentration of MB in the feed solution during the photocatalysis process was calculated based on the calibration curve obtained from the absorbance value of the MB solution where the linear correlation is $y = 0.8308x$. By obtaining the concentration of MB, percentage of MB degradation was calculated and the photocatalytic degradation kinetics of MB solution was described using the pseudo-first-order kinetics model [11].

## 3. Results and discussion

### 3.1. MB Photocatalytic Degradation Performance

#### 3.1.1. Effect of $TiO_2$ nanoparticle sizes

Surface area is a significant property of a photocatalyst. Therefore, the reduction in nanoparticle size increases not only the surface area but also the photocatalytic activity. This statement is typically associated with photocatalysts working in suspension experiments. This is because the photocatalyst is directly exposed to UV irradiation and the contact surface of photocatalyst with a polluted solution. However, once the photocatalyst is embedded within the membrane, it shows different results due to the dispersion of photocatalyst at the membrane surface.

The experiment was done at different nanoparticle sizes of $TiO_2$, where the 3 wt.% loadings were embedded within the photocatalytic membrane via the tape casting method. Figure 1(a) shows the particle size effects of the $TiO_2$ nanoparticles on photocatalytic degradation of MB under UV irradiation for

60 min. The addition of $TiO_2$ nanoparticles to membrane structure (M2 and M3) could enhance the MB photocatalytic degradation compared to the neat membrane (M1) as shown in Figure 1(a). The immobilisation of the different $TiO_2$ particle sizes, 6 nm and 30 nm in flat sheet membrane, shows 95% MB degradation at 0.0507 and 0.0497 $min^{-1}$ of MB degradation rate, respectively. It is due to the occurrence of the aggregation phenomena during the fabrication of the flat sheet membrane. As mentioned in section *2.1*, the specific surface area of the 6 nm $TiO_2$ nanoparticles is 5 times higher than the 30 nm particle size. The small particle size of $TiO_2$ leads to an increase in the surface area, which can be translated as an increase in the available surface-active sites. However, in this study, the different surface areas of immobilised $TiO_2$ nanoparticles in membrane structure via the tape casting method did not show any significant effect on the MB photocatalytic degradation. It is interesting to note that the fabrication method of the membrane also influenced the photocatalytic activity. This statement is further discussed in section *3.1.3*, where the comparative method for photocatalytic membrane preparation towards the MB degradation rate is explained.

Generally, the active site and photoabsorption of the catalyst were influenced the degradation rate of the pollutant. Therefore, the distribution of immobilised $TiO_2$ nanoparticles at the outer surface is the most critical surface under consideration. From the FESEM images shown in Figures 2 (a1) and (b1), the existence of $TiO_2$ nanoparticles at the outer membrane surfaces is evident. The distribution of the elements (Figures 2 (a2) and (b2)) on the membrane surfaces was determined using the elemental mapping was performed by SEM-EDX analysis. For close observation of the images using FESEM, the 10k zoom in magnification was applied to measure the particle size of the immobilised $TiO_2$ at the outer membrane surfaces (Figures 2 (a3) and (b3)). It proved that the aggregation particle sizes of 6 nm and 30 nm occurred during membrane preparation via the tape casting method and the estimated sizes became 385 nm and 568 nm, respectively. Normally, the major factors that influence the photocatalytic degradation performance is aggregation. This is due to the increase in the $TiO_2$ particle size and reduction of surface area, which consequently affects the photocatalytic activity. The aggregation is formed by the high surface tension between the solvent and $TiO_2$ nanoparticles during dope solution preparation [12]. However, based on the observation during the photocatalytic experiment, the visible colour of the MB solution changed from dark blue to colourless, which proves MB photocatalytic degradation, as shown in Figure 1(b).

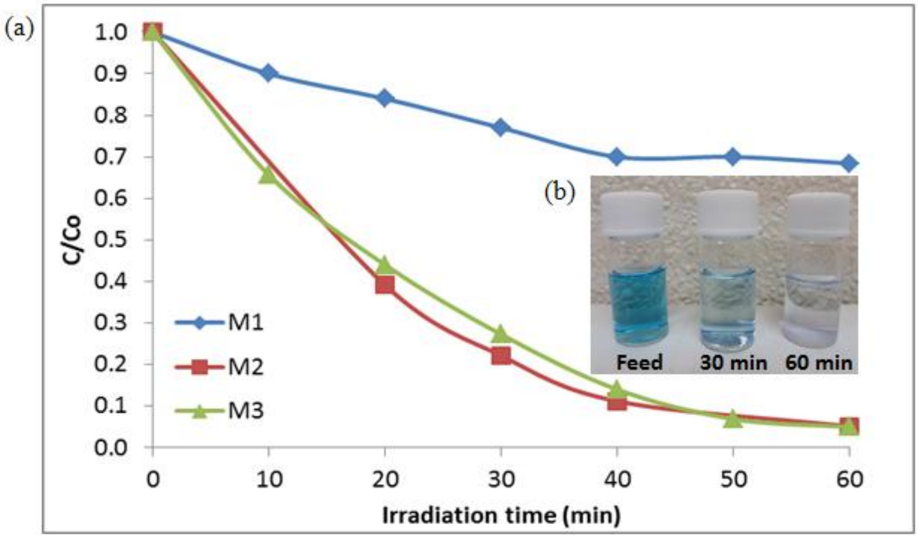

**Fig. 1.** (a) Effect of different $TiO_2$ particle sizes immobilised in the membrane structure of the MB photodegradation with UV irradiation, (b) Visible colour change of MB within 60 min of UV irradiation.

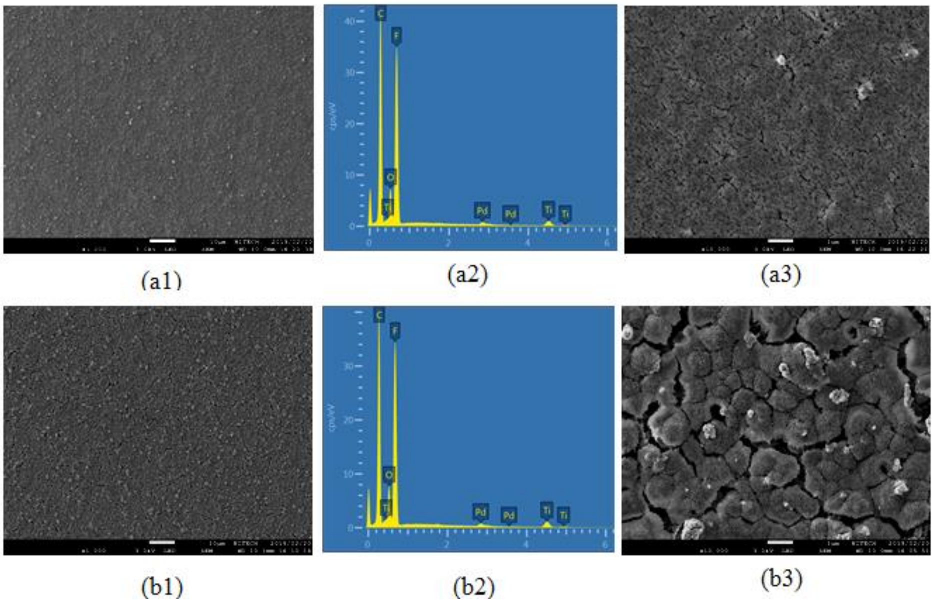

**Fig. 2.** FESEM images of (a) M2 and (b) M3 outer membrane surface at (1) 1k and (2) EDX images of element distribution at 1k magnification and (3) 10k of magnification.

### *3.1.2. Effect of different spinning speed on the spin coating method*

Cross-sectional structures and the outer surface of the photocatalytic membranes prepared via the spin coating method at different spinning speeds are shown in Figure 3. As observed in Figure 3, the change in spinning speeds influenced the thickness of the photocatalytic membrane, which is due to the spinning effect of the process and solvent evaporation. The solvent was evaporated from the deposited layer due to the increase in spinning speed. Typically, the more the solvent evaporated, the higher the viscosity of the layer, which slows down the rate of subsequent solvent evaporation. As a result, the thickness of the remaining liquid film decreases. In summary, it can be surmised that the film thickness is quantitatively correlated with the relative rate of solvent evaporation.

The spin coating method allows $TiO_2$ nanoparticles to be evenly dispersed in the membrane structure through the centrifugal force produced by the spinning effect. Besides spreading $TiO_2$ uniformly, the centrifugal force disperses the excess casting solution during spinning. In this study, the spinning speeds above 1300 rpm enhanced more significant loss of the casting solution volume. As shown in Figure 3 (a2 - e2), by increasing the spinning speed, the uniform distribution of $TiO_2$ nanoparticles at the outer surface membrane was improved. It can be surmised that the membrane thickness and $TiO_2$ nanoparticles uniformity depends on the spin speed. 30 µm of flat sheet membrane thickness was successfully prepared using a spin coating method, as observed in Figure 3 (e1).

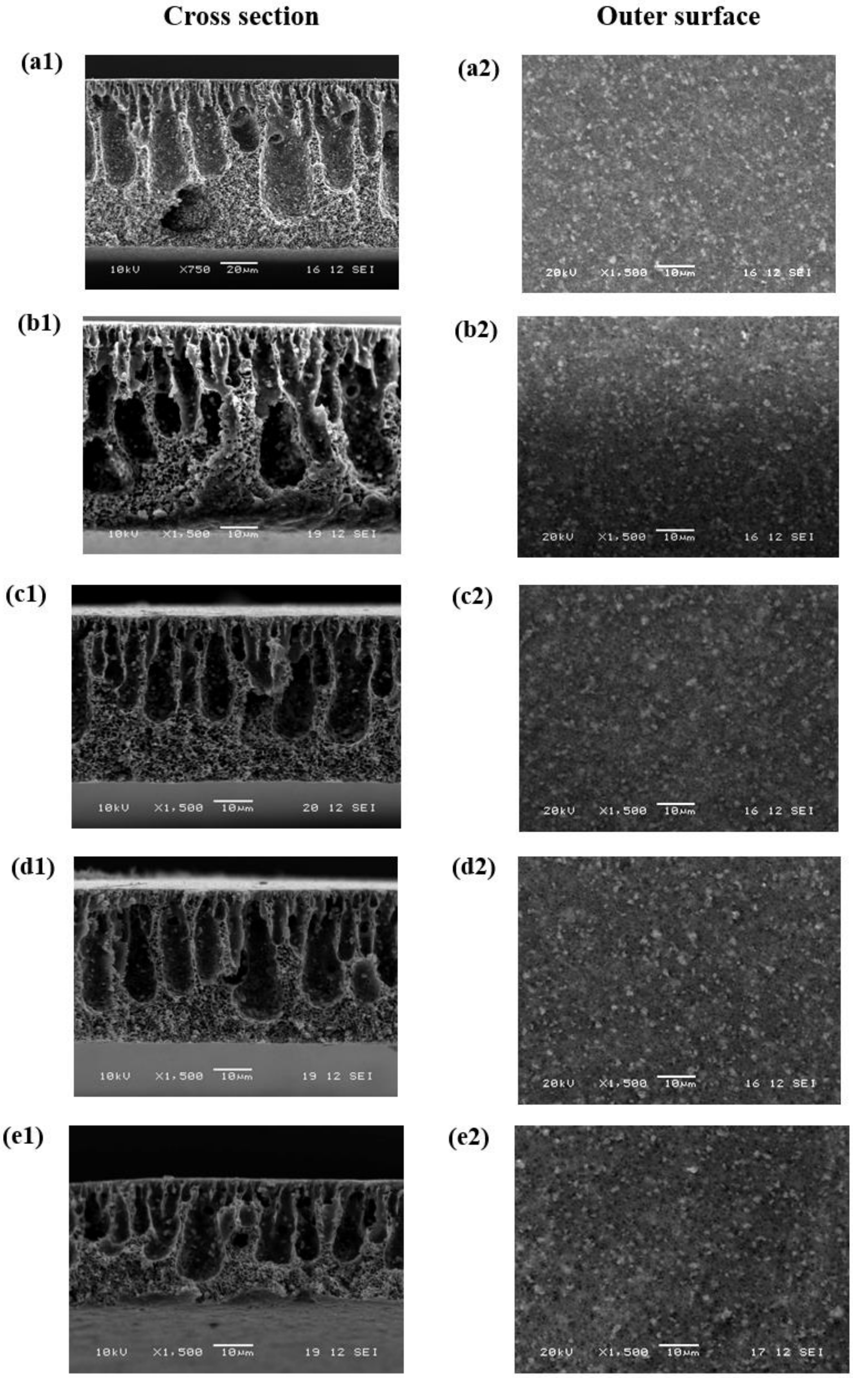

**Figure 3**: SEM images of the cross-section and membrane outer surface of the photocatalytic membrane prepared via the spin coating method at different spinning speeds (a) 500, (b) 700, (c) 900, (d) 1100 and (e) 1300 rpm.

Figure 4 shows the effect of membrane thickness on the MB photocatalytic degradation rate. As observed, the thickness of the photocatalytic membrane affects the MB degradation rate due to the distribution of $TiO_2$ nanoparticles inside the membrane. The penetration of UV irradiation towards the thickness of the photocatalytic membrane is only dominant when the spinning speed is below 1300 rpm until 700 rpm, where the MB degradation rate decreased at the spinning speed of 500 rpm. Hence, it can be assumed that the membrane thickness exceeded its critical level (threshold) when the spinning speed reached 500 rpm, and as a result, the MB degradation rate decreased. As illustrated in Figure 5, the UV penetrated the photocatalytic membrane up to a thickness of 55.64 µm (700 rpm), which can activate the $TiO_2$ nanoparticles and OH radical formed on the photocatalyst to increase the MB photocatalytic degradation rate.

### 3.1.3 Comparison of photocatalytic membrane preparation methods

The morphological structures of the photocatalytic membrane, which consists of finger-like and sponge-like structures, prepared via the spin coating method, are similar to the tape casting method. However, the thickness of the membranes prepared via the spin coating method was thinner than the tape casting method, as shown in Figure 6. This is due to the shear force applied during the spin coating and the fast solvent evaporation. Thus, the membrane's cross sections were more compacted compared to the membranes prepared from tape casting.

Figure 7 shows the MB degradation rate of the membrane prepared using tape casting and spin coating. The membrane prepared via the spin coating method exhibited the highest MB degradation rate compared to tape casting method of 6 nm $TiO_2$ particle size. This observation is due to the good distribution and low aggregation of 6 nm $TiO_2$ nanoparticles at the membrane surface. As illustrated in the UV-Vis absorption spectrum in Figure 8, the MB degradation achieved during the photocatalytic reaction under UV light irradiation was 100% during the 60 min process.

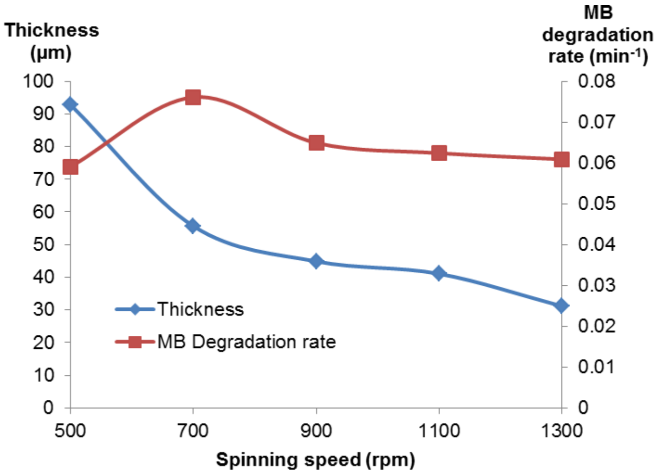

**Fig. 4.** MB photocatalytic degradation rate and different thickness of membrane formed during the spin coating method at different spinning speeds.

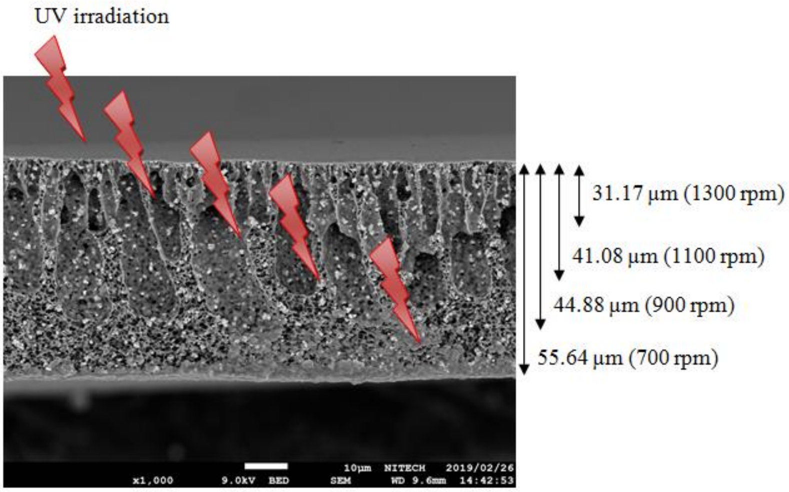

**Fig. 5.** Illustration of UV penetration towards the photocatalytic membrane with different thickness (Backscattered FESEM images of M5 membrane).

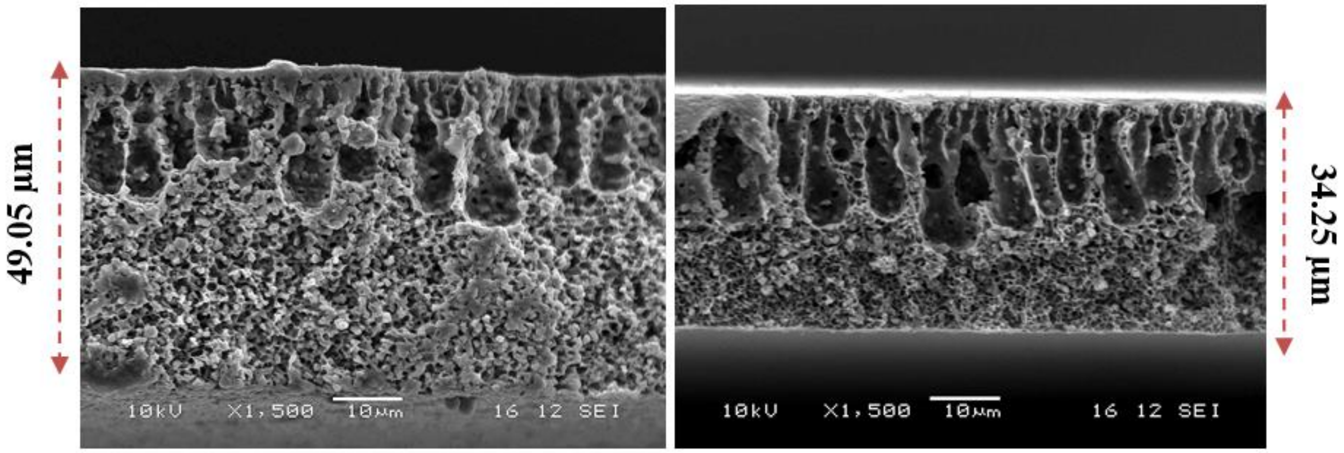

**Figure 6:** SEM images of the cross sections of M2 and M5 photocatalytic membrane prepared via (a) tape casting and (b) spin coating method.

Surprisingly, the MB degradation rate of the 30 nm $TiO_2$ particle size shows a similar value for the membrane prepared via both methods. These results are due to the aggregation factor of $TiO_2$ nanoparticles, which create a larger particle with the lower surface area for photocatalytic degradation to occur. As shown by the enlarged FESEM images of the outer surface membrane, the aggregation particle size of 30 nm $TiO_2$ nanoparticles is 564 nm using spin coating method, which is similar in size to tape casting method (Figure 9d). It is interesting to note that the aggregation factor during membrane preparation method affects the MB photocatalytic degradation of the 30nm $TiO_2$ particle size. Contrary to the 6 nm $TiO_2$ particle size, the spherical shape of $TiO_2$ nanoparticles was formed using a spin coating method. This resulted in good dispersion without interfacial gaps between the $TiO_2$ nanoparticles and the polymer, as shown in Figure 9(c). Even though aggregation also occurred via this method, the particle size formed was smaller than the tape casting method. Hence, this characterisation provides better insights into the MB photocatalytic performance and thus showed the highest MB degradation rate.

As shown in Figures 9(c) and (d), the outer membrane surface prepared via spin casting is smoother than the tape casting method. As mentioned by Burmann et al. (2014), the interplay of the centrifugal driving force and the viscous resisting force of the fluid affected spreading, membrane formation, and the final membrane properties [13]. The AFM images proved that the smoother membrane surface was created via spin coating rather than tape casting, as shown in Figure 10. The spreading of the membrane precursor on the dish and the evaporation of the solvent is directly influenced by the velocity of the rotating Petri dish. In general, the $TiO_2$ nanoparticles were well distributed and homogeneously axial in the PVDF membrane.

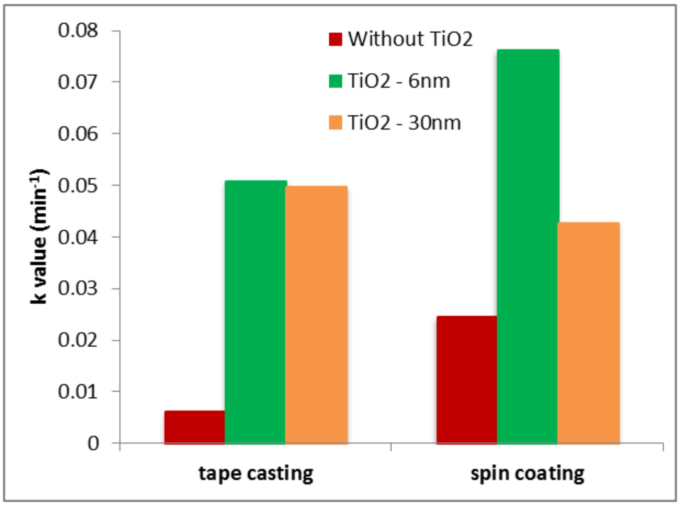

**Fig. 7.** Comparison of the MB degradation rate by embedded 6 nm and 30 nm of $TiO_2$ nanoparticles in photocatalytic membranes prepared by different methods.

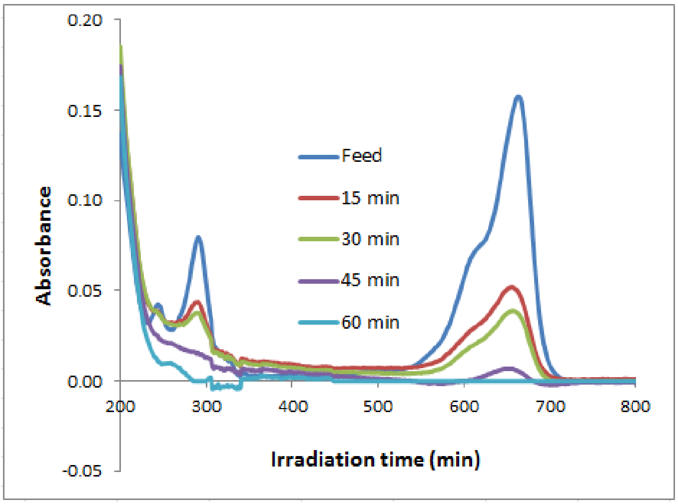

**Fig. 8.** UV-Vis absorption spectra of the MB solution during the decomposition reaction under UV irradiation by using M5 membrane.

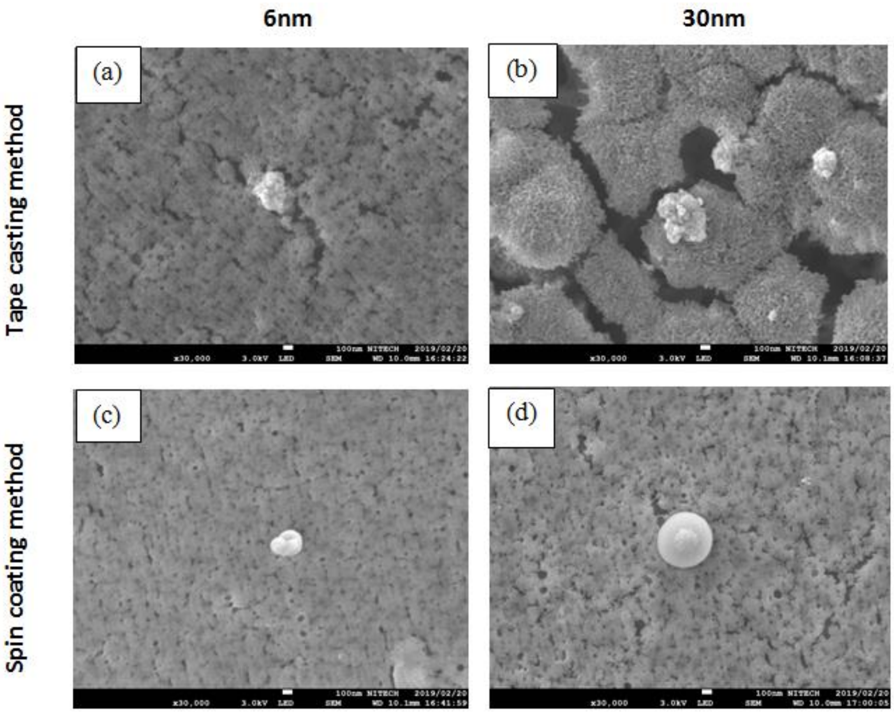

**Fig. 9.** FESEM images with a 30k magnification for (a) M2, (b) M3, (c) M5 and (d) M10.

### *3.2. Comparison result with similar studies*

Table 1 shows some of the earlier works reported on the MB degradation by immobilised photocatalysts with various techniques, as comparison with present work. As observed, the degradation results that were presented in this work are comparable to other works carried out on the immobilised support and using $TiO_2$ as a photocatalyst [14, 15]. The small difference in the data between these studies may be due to the types of the light source and initial concentration of MB solution. From Table 1, it shows that most of the previous studies on MB photocatalytic degradation mainly focused on the type of photocatalyst such as zinc oxide (ZnO) [16], enhancement of MB degradation by adding argentum nanoparticles [14] and graphene (GO) as dispersant [17]. Therefore, to the best of our knowledge, the present work could be considered as the first report based on comparison of immobilised $TiO_2$ nanoparticles in membrane structure via the tape casting and spin coating methods for MB degradation. Furthermore, this research is significant because the distribution of $TiO_2$ nanoparticles is the most important parameter for determination of photocatalytic degradation efficiency.

## 4. Conclusions

The photocatalytic performance of MB degradation was extensively studied by immobilised $TiO_2$ nanoparticles on the membrane surface with different particle sizes and fabricated via the tape casting and spin coating methods. The different particle sizes of $TiO_2$ nanoparticles via the tape casting method did not show any significant effect on the MB photocatalytic degradation. The aggregation of $TiO_2$ nanoparticles was observed on the membrane structure, and thus influenced the MB degradation rate. Compared to the spin coating method, the immobilised $TiO_2$ nanoparticle in the membrane surface was uniformly distributed and experienced less aggregation compared to tape casting method. The evident performance of MB photocatalytic degradation was observed via the spin coating method for the different particle sizes of the $TiO_2$ nanoparticles. In conclusion, the effects of spinning speed on membrane thickness were investigated and shown to have a significant effect on the MB photocatalytic degradation.

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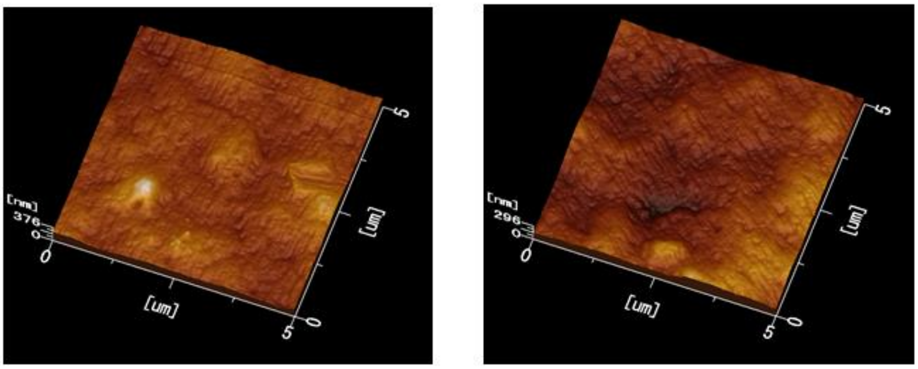

**Fig. 10.** AFM images of surface roughness measurement for (a) M2 and (b) M5 of outer surface membrane.

**Table 1**
Comparison of different methods of immobilised photocatalysts on the membrane structure for MB degradation with literature.

| Photocatalyst membrane | Initial concentration | Light source | Immobilised method | Time (min) | Degradation (%) | Ref. |
|---|---|---|---|---|---|---|
| $TiO_2$-ENR-PVC | 20 mg/L | Fluorescent lamp (45W) | Dip coating | 480 | 93 | [15] |
| CAB-ZnO nanocomposites | 0.01 mM | Tungsten lamp (100W) | Electrospinning and chemical deposition | 1200 | 95 | [16] |
| PVDF/Ag/$TiO_2$ | 10 mg/L | Fluorescent lamp (20W) | Blending/photoreduction combined method | 100 | 51 | [14] |
| P(VDF-TrFE)/ZnO | 17.6 μM | UV A lamp (8W) | Solvent casting | 300 | 85 | [18] |
| PVDF/GO/ZnO | 10 mg/L | Xenon lamp (300W) | Immersion-precipitation phase transformation | 100 | 86.84 | [17] |
| PVDF/ $TiO_2$ | 0.67 μM | High pressure mercury lamp | Tape casting<br>Spin coating | 60 | 95<br>100 | This work |

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