

Research Article

Effect of Polymer Concentration on the Photocatalytic Membrane Performance of PAN/TiO₂/CNT Nanofiber for Methylene Blue Removal through Cross-Flow Membrane Reactor

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Abstract

A photocatalytic membrane combining photocatalyst and membrane technology based on polyacrylonitrile (PAN) and TiO₂/CNT has been developed. Such combination is to overcome fouling formation on the membrane, thus prolonging the membrane lifetime and enhancing the efficiency on the waste treatment. PAN nanofiber was prepared by electrospinning method. The precursor solution was dissolved PAN and dispersed TiO₂/CNT in N,N-Dimethylformamide (DMF). PAN concentration in the precursor solution was varied at 4.5, 5.5, 6.5, 7.5, and 8.5%. The effect of PAN concentration on the fiber morphology and pore size was discussed. The performance of the resulted membrane on methylene blue (MB) removal was also investigated on a cross-flow system. SEM images of the resulted membrane identified that PAN nanofiber was successfully fabricated with random orientation. The PAN 6.5% showed the highest diffraction intensity of the anatase crystalline phase of TiO₂. The additions of CNT and TiO₂ lead to the formation of a cluster of beads as confirmed by TEM. Increasing the concentration of PAN increased the fiber diameter from 206 to 506 nm, slightly decreased the surface area and pore size, respectively, from 32.739 to 21.077 m².g⁻¹ and from 6.38 to 4.75 nm. The PAN/TiO₂/CNT nanofibers show type IV of the adsorption-desorption N₂ isotherms with the H1 hysteresis loops. Membrane PAN/TiO₂/CNT at PAN concentration of 6.5% shows the optimum performance on the MB color removal by maintaining the percentage of rejection (%R) at 90% for 240 min and permeability of 750 LMH.

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1. Introduction

Widespread discharge of industrial wastewater containing organic dyes onto land

and aquatic bodies has resulted in severe contamination. Toxic metabolites can be produced by weathering organic dyes through oxidation, hydrolysis, or other chemical reactions in the wastewater phase [1]. The most viable strategy to address these concerns could be efficient wastewater treatment and long-term use of re-

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newable energy sources. Membrane technology is a fascinating technique in this regard because of its tunable and varied features [2].

Membrane separation technologies for water and wastewater treatment are rapidly evolving due to their significant role in water purification. Membranes operate as a physical barrier for substances, depending on the molecule and pore size. Membrane technology is thus a promising and trustworthy area of research for the treatment of water and wastewater [3]. However, the development of membrane technology has lagged considerably behind expectations, and one of the biggest roadblocks to their more comprehensive implementation is that filtration performance invariably diminishes with filtration duration. Membrane fouling is a phrase that refers to the blocking of membrane pores during filtration as a result of a combination of sieving and adsorption of particles and chemicals onto the membrane surface or within the membrane pores [4]. Pore obstruction lowers the rate of permeate generation and complicates the membrane filtration process. It is the most challenging problem to solve in membrane development and applications [5].

Modifying membrane with photocatalyst has become a novel and promising strategy to prevent fouling in the membrane. Photocatalytic membranes (PMs) have recently attracted attention because they combine membrane separation with photocatalysis in a single unit and allow for the management of products and by-products [6]. The reactive oxygen species (ROSs) generated by photocatalysts under light irradiation can degrade organic pollutants on the membrane surface. Thus, preventing the formation of a cake layer on the membrane surface, reducing pore blocking, and inhibiting membrane fouling to some extent. Meanwhile, the membrane substrate serves as both a selective barrier for the species to be removed and a support for photocatalysts to skip the separation phase; thus, no additional time or space is required [7].

TiO₂ with a relatively large band-gap energy (3.2 eV), has been the most commonly used material for making PMs, due to its high quantum yield, chemical and thermal stability, low toxicity, and low cost [6,8]. However, the large band-gap of the TiO₂ becomes one of the drawbacks in the photocatalytic reaction. The low availability of UV light in nature inhibits the application of TiO₂ on a large scale. Thus, modifying TiO₂ with doping metal, non-metal, or surface modification becomes an effective way to introduce a new energy level in the band-gap of TiO₂, leading to the absorption of visible

light [9]. One of the non-metal doping is carbon and carbon nanotubes (CNT) became popular to be used because of their unique mechanical, physical, chemical, electroconductive, and field emission properties [10]. The CNT has unique charge transfer and electron-conducting properties. In particular, Olowoyo *et al.* [11] has reported that the doping of 5% CNT in the composite of CNT-TiO₂ shifted the band-gap energy from 3.2 eV to 2.9 eV. Thus, the composite creates electron-hole pairs when excited by visible light. The formation of Ti-O-C bond confirmed the formation of new energy level in the band-gap energy of TiO₂.

In PMs, ultra- to nanofiber structure is widely used and preferred. There are many processes for producing ultrafine fibers such as self-assembly [12], template synthesis [13], electrohydrodynamic direct writing [14], centrifugal jet spinning [15], plasma-induced synthesis [16], and solvothermal synthesis [17]. But one known as electrospinning, has proven to be successful. Because the procedure is easy and inexpensive, it becomes the preferred method for nanofiber manufacturing. Electrospinning is the process of applying a high voltage to a confined polymer solution to create electrically charged jets of solution that are driven via a spinneret toward a grounded target that serves as a collector [18]. These jets dry, as they approach the target, are creating beads or nanofibers. With electrospinning, highly functional nanofiber mats with a high surface area to volume ratio, high porosity, and homogeneous shape may be easily created [19].

Electrospinning can be done with a variety of polymers [20]. Polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP) [21], cellulose acetate (CA) [22], and polyacrylonitrile (PAN) [23] are examples of synthetic polymers that have succeeded in generating nanofiber. Because of the low density, high polymer strength, elasticity, superior solvent resistance, and capacity to maintain shape during the pyrolysis process of PAN polymer [24], PAN nanofiber is widely used in membrane air filters, water filters, and carbon fiber [25].

The applied voltage, the distance between the tip and the collector, the feed rates of solutions, the collector's rotating speed, and the kind of collector are all controllable process factors that must be optimized for electrospinning. Surface tension, viscosity, concentration, conductivity, dielectric constants of the solvent and polymer, polymer molecular weight and polydispersity, polymer chemical structure, and presence of interactions are some intrinsic parameters of polymeric solutions that affect

the characteristics of the final material. However, it should be noted that, among others, polymer concentration and electrical potential are the two key characteristics that have a significant impact on the electrospinning process [26]. The size of the fibers is greatly influenced by the concentration of the solution; for example, the diameter of the electrospun nanofibers grows with the concentration of the solution according to a power-law ratio. Controlling these variables would allow for creating an ideal nanofiber mat [20]. Tarus *et al.* [18] investigated the effect of polymer concentration on the morphology and mechanical characteristic of CA fiber mats. The result indicates that polymer concentration alters the fiber diameter and mechanical strength of the fiber mats. The fiber diameter and the uniformity were found to increase with the increase of CA concentration (optimum concentration of CA was 16%).

Extensive researches have been done on the fabrication of nanofiber through the electrospinning technique [19,24,27]. However, the understanding of this method and the correlation to the membrane characteristic and performance are still very limited, especially on the photocatalytic membrane. Low polymer concentration has resulted in a bead-on-string structure, while at high polymer concentration, the jet is subjected to uniform tensile tension under the surface charge and electric field forces [28]. The optimum polymer concentration also affects the distribution of the photocatalyst in the fiber thereby minimizing agglomeration [29]. In this study, we investigate the effect of polymer concentration on the performance of photocatalytic membrane of PAN/TiO₂/CNT through a cross-flow PM reactor. The optimum polymer concentration is supposed to produce a smooth and uniform size fiber without lumps/beads that is suitable for the filtration process. To the best of our knowledge, there is no information available regarding the effect of PAN concentration on the PAN/TiO₂/CNT photocatalytic membrane performance for MB color removal through a cross-flow membrane reactor. The PAN concentration was varied from 4.5 to 8.5% due to the preferred viscosity range for electrospinning using our instrumentation. Characterization of the resulted membrane was performed using XRD, SEM, TEM, N₂ adsorption-desorption analysis. The performance of the PAN/TiO₂/CNT photocatalytic membrane was evaluated for MB color removal by using a cross-flow membrane reactor for 240 min at 5 mg.L⁻¹.

2. Materials and Methods

2.1 Materials

Titanium dioxide (TiO₂) powder (anatase 100%), hydrogen chloride (HCl), and ethanol (pro-analysis) were obtained from Merck. Carbon Nanotubes (CNT) were from SAT Nano Technology Material Co., Ltd with the specification of a multi-walled nanotube (MWNT). Polyacrylonitrile (PAN, MW = 150.000), N, N-Dimethylformamide 99.8% (DMF), and methylene blue (MB) were purchased from Sigma-Aldrich. Cellulose Acetate (CA) membrane (diameter 47 mm, thickness 0.1 µm) was from Axiva.

2.2 Photocatalytic Membrane Preparation and Characterization

Precursor solution for electrospinning was prepared by dissolving PAN in the DMF solvent at concentration of 4.5, 5.5, 6.5, 7.5, and 8.5 wt% at room temperature. Then, CNT and TiO₂ powder (CNT:TiO₂ = 1:50) mixture was separately dispersed in a DMF solution (5 mL). The PAN solution was added to the TiO₂/CNT suspension and stirred until obtaining a homogenous PAN/TiO₂/CNT suspension. The resulted mixtures were used as the precursor for membrane fabrication by electrospinning. The electrospinning equipment was set at 7 kV with the distance between needle-tip and collector of 10 cm. The process was run for 5 h to get the same membrane thickness (~0.60–0.70 mm). The diameter of the membrane was 47 mm, following the size of the reactor. All the prepared membranes were characterized and evaluated through the PM reactor of a cross-flow system.

The crystalline structure of all the prepared membranes was investigated by X-ray diffraction (XRD, Shimadzu 6000; Cu-Kα (0.15406 nm) at a scan rate of 2°.min⁻¹ in the range of 10–80°). The morphology was characterized using a scanning electron microscope (SEM, JEOL JSM6510LA) at 15 kV with 5000x magnification and Transmission Electron Microscope (TEM, JEOL JEM-1400) at 120 kV. The specific surface area, pore size and pore size distribution were evaluated by N₂ gas adsorption-desorption isotherm obtained through NOVA Quantachrome gas sorption analyzer. The degassing condition was performed under vacuum condition at 200 °C for 3 h.

2.3 Performance Testing of the Photocatalytic Membrane in a Membrane Reactor

The PM performance for MB removal was assessed using a cross-flow membrane reactor cell (diameter of membrane holder was 47 mm and round shape) under the specific flow rate of $0.21 \text{ L} \cdot \text{min}^{-1}$ (LPM) for 180 min. The photocatalytic membrane reactor is shown in Figure 1. The feed tank capacity is 1.5 L. The volume of the feed solution in the feed tank was maintained to be constant to maintain the pressure and flow rate of the pollutant solution (Figure 1(a)). The MB with concentrations of 5 ppm was placed in the feed tank. The membrane was irradiated using a visible LED lamp (Phillips, 14.5 W) at room temperature and the system pH of 5. The LED lamps emit visible light at 425–660 nm (tested with Spectrograph SA-100W-HPCB1024/C at Laser and Optoelec-

tronic Laboratory, Department of Physic, Universitas Diponegoro, Indonesia) and has no UV emission, as confirmed by a UV-meter (Hagner EC-1 UV A). The membrane reactor is also equipped with a coolant layer to avoid overheating due to light irradiation. The distance between pollutant and lamp is 15 cm. The reactor is equipped with a lid that is connected to the lamp. During operating, the reactor is closed to avoid the possibility of outside light entering the reactor (Figure 1(b)). The membrane flux (J) ($\text{L}/\text{m}^2 \cdot \text{h}$ (LMH)) was calculated by Equation (1).

$$J = \frac{\Delta V}{A_m \Delta t} \quad (1)$$

where, ΔV is volume permeated (L), Δt is the time operation (h) and A_m is the membrane area. The rejection (% R) of dyes was investigated

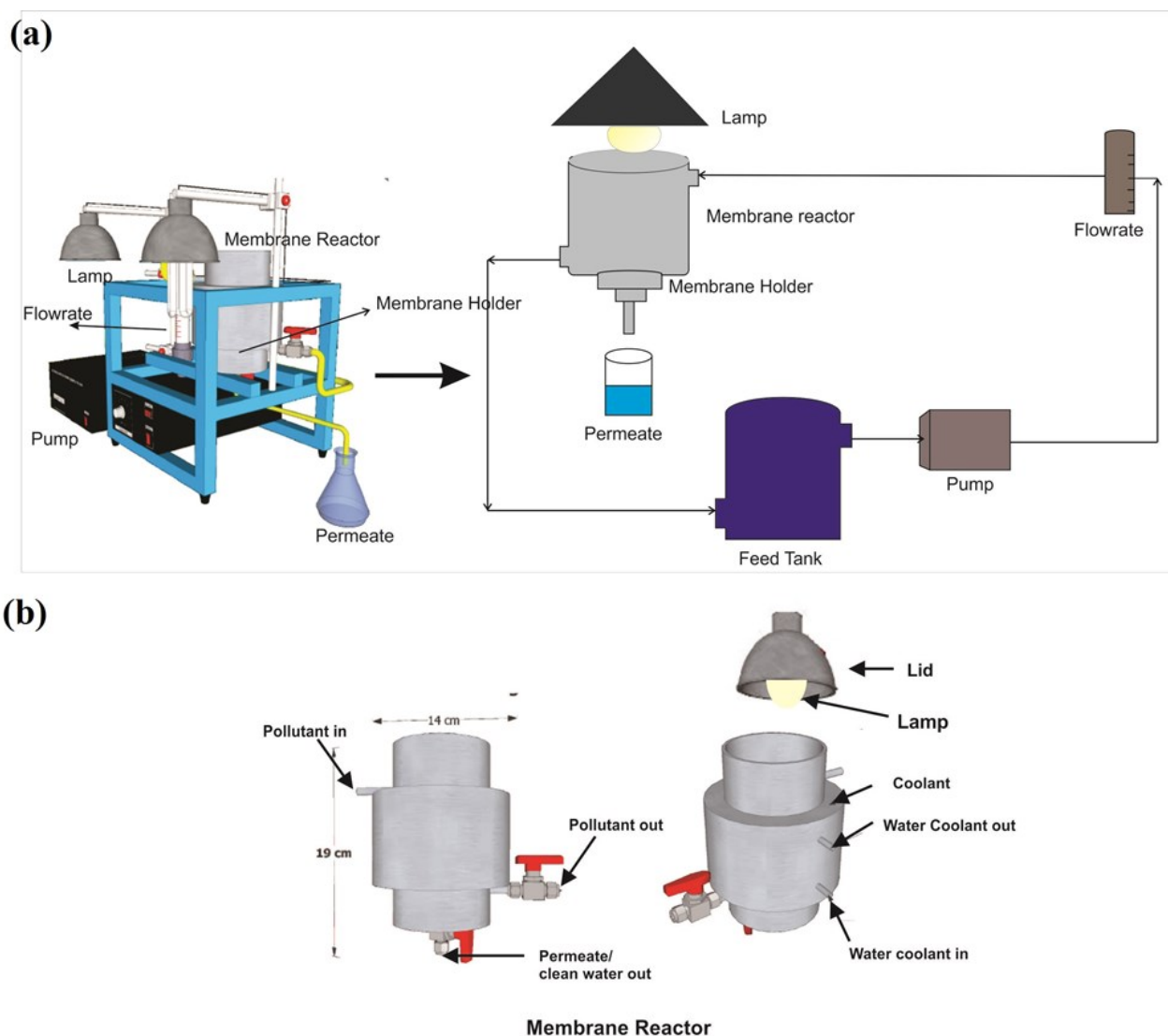


Figure 1. Setting of the photocatalytic membrane reactor with a cross-flow system (a); membrane reactor detail with lid and coolant system (b).

using Equation (2).

$$\%R = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (2)$$

where, C_t and C_0 are the concentration of dyes in permeate and feed solutions, respectively. The concentration was measured with a UV-Vis spectrophotometer (Genesys 10S) at a maximum wavelength (λ_{max}) of 664 nm.

3. Results and Discussion

Crystallinity is an important factor for photocatalytic performance. The diffraction patterns of the PAN/TiO₂/CNT at various concentrations of PAN are shown in Figure 2. All membrane showed anatase phase for TiO₂ with the peak characteristic at $2\theta = 25.2^\circ$, 37.76° , 48.02° , 54.05° , 55.03° , and 62.80° . Similar results were also reported by other researchers [11,27]. Meanwhile, PAN nanofiber is an amorphous organic polymer, thus does not show a distinct diffraction pattern in the XRD analysis result. PAN nanofiber has a very broad peak at $2\theta = 17^\circ$.

Based on the XRD analysis, the deposition of TiO₂/CNT in the PAN nanofiber by electrospinning does not change the crystallographic structure of the photocatalyst. The variation in PAN concentration also does not alter the diffraction pattern of the TiO₂/CNT. The optimum

intensity of the diffraction pattern was shown at 6.5 % of PAN. At higher and lower concentration polymer, the anatase crystallinity decreased. PAN seems to affect the crystal growth of anatase, so it has an optimum concentration to result in high intensity peaks of anatase phase. The role of polymer to the anatase nanofiber crystal growth is still unclear.

In photocatalytic membrane, both photocatalyst and membrane play their own function for MB color removal. It is known that the filtration and adsorption performance of the membrane depend on the morphology of the membrane. In this study, we analyze the membrane surface morphology at various PAN concentration through the SEM analyses shown in Figure 3. Based on the SEM result, it is observed that not all of the nanofiber is successfully produced at the low concentration of PAN (4.5%). Figure 3(a) shows that there are lumps of polymer between the fibers, indicating that not all polymers that reach the collector have succeeded in forming nanofibers. At low concentration of polymer (Figures 3(a) and (c)), the nanofiber is discontinuous. While, at a high concentration of the polymer (Figure 3(g) and (i)), the diameter of the membrane gets higher. The diameter uniformity of the fiber decreased as the concentration of the polymer increased.

The formation of lumps at low concentration polymer and increasing diameter of nanofiber at high polymer concentration could be attributed to the viscosity. During the electrospinning process, the low concentration solution results in a low viscoelastic force. It leads to the partially breaking up jet because the viscoelastic force does not match with the electrostatic and Coulombic repulsion that stretches the electrospinning jet. The high number of solvents in the solution leads to the formation of lumps because of the surface tension [22]. Meanwhile, with the increase in the polymer concentration, the viscosity also increases, thus causing the improvement of the viscoelastic force, leading to the partially jet break up prevention. Another reason for the increasing nanofiber diameter with the increasing concentration is the increased viscoelastic force that limits the stretching effect of the electrostatic and Coulombic repulsion force [28]. Less solvent molecules also produce low surface tension that plays an important role in creating smooth fiber. Even though the nanofiber produced at more concentrated polymer is more well-organized, operating electrospinning at a concentration higher than 6.5 wt% is getting more difficult. Viscous colloidal precursor solution preventing the formation of a continuous jet

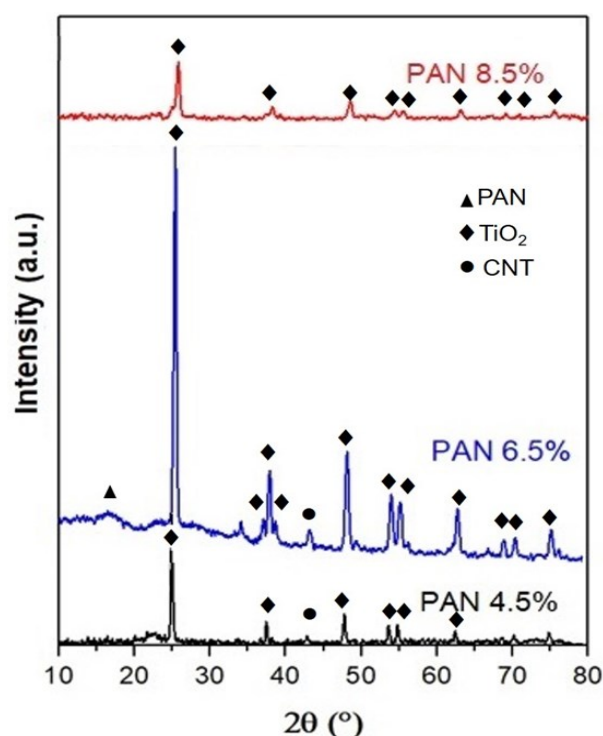


Figure 2. Diffraction patterns of PAN/TiO₂/CNT membrane at various PAN concentrations.

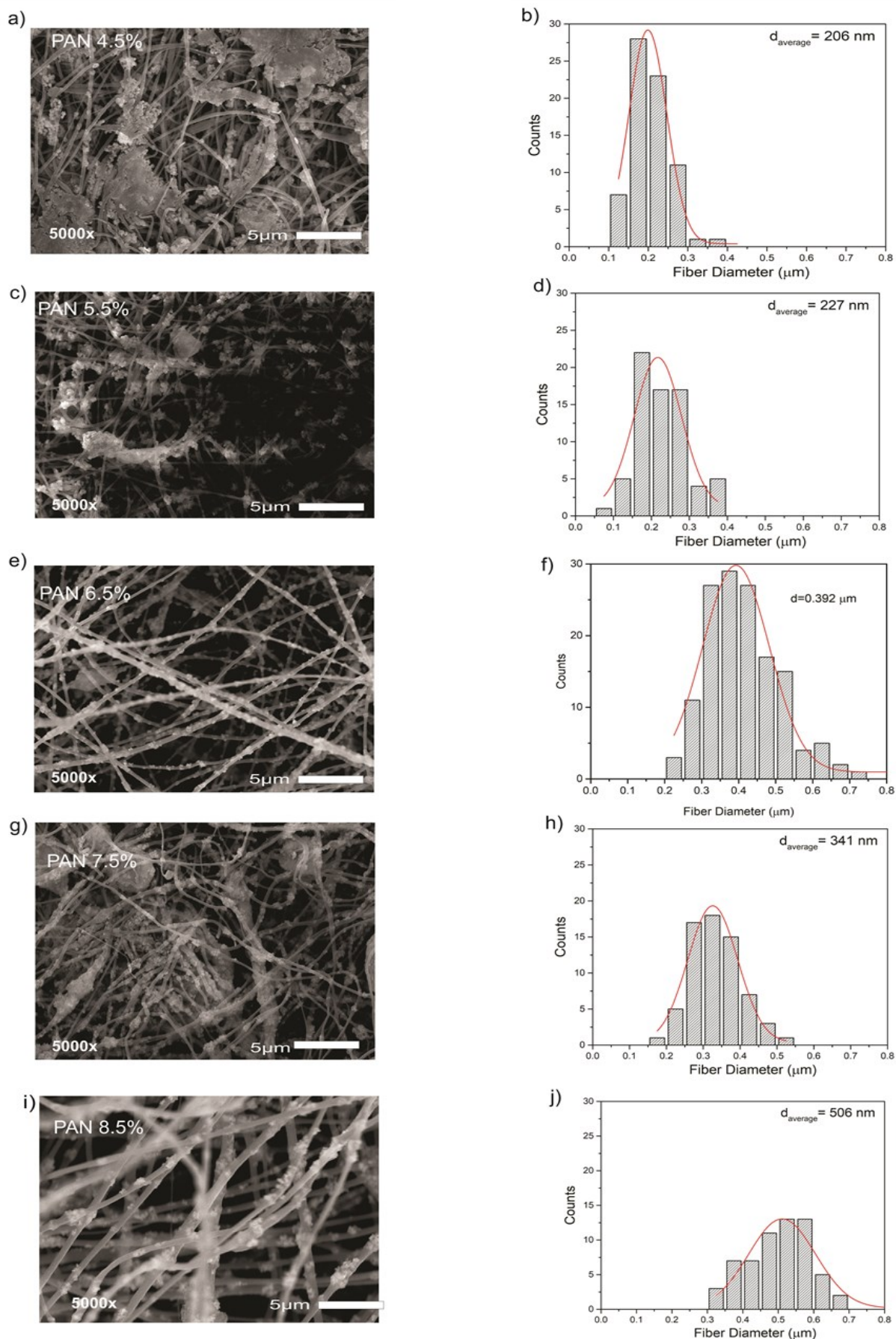


Figure 3. SEM micrographs and the corresponding fiber size distribution of PAN 4.5% (a, b); PAN 5.5% (c, d); PAN 6.5% (e, f); PAN 7.5% (g, h); and PAN 8.5% (i, j).

because of the fast-drying precursor. This makes the needle tip become easily clogged.

Figures 3(b), (d), (f), (h), and (j) show the fiber size distribution calculated based on the SEM image. Figure 3(b) shows a relatively narrow fiber size distribution of PAN 4.5%. Meanwhile, at higher concentrations (Figures 3(d) and (f)), the fiber size distribution is wider when compared to PAN 4.5%. This is possible because of the increase in concentration which causes a change in the viscosity of the precursor. Besides, the presence of CNT and TiO_2 also provides different surface tension and net charge density, thus affecting the size of the resulting fiber. Meanwhile, at higher concentrations (Figures 3(h) and (j)), the fiber size distribution was slightly narrower when compared to the PAN 6.5%. This phenomenon is possible because, at higher concentrations, the interactions between polymer molecules may be more dominant than the effect given by the presence of CNT and TiO_2 so that the fiber size distribution is slightly narrower.

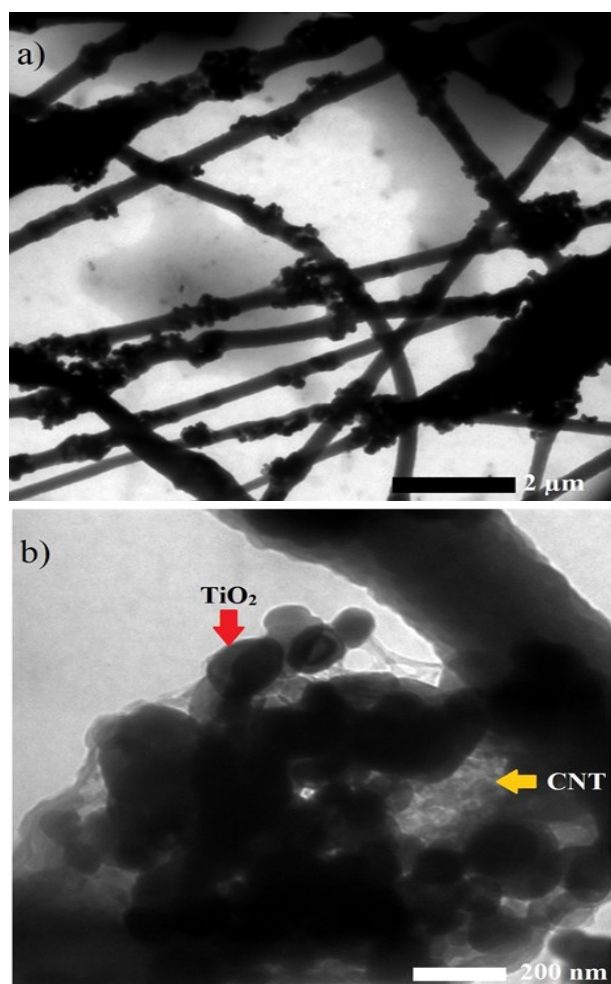


Figure 4. TEM images of PAN/ TiO_2 /CNT with 6.5% PAN at different magnification.

As seen in Figure 3, the beads decorated the fibers. The beads are predicted as TiO_2 and CNT. Similar results have also been observed by Yar *et al.* [29] as TiO_2 added. Closer observation was performed by TEM in Figure 4. Based on the SEM (Figure 3(e)) and XRD results, it is expected that composite membrane PAN/ TiO_2 /CNT nanofiber with the concentration of PAN 6.5 wt% is the optimum concentration and expected to have optimum performance in the MB color removal through the cross-flow membrane reactor.

Figure 4 shows the TEM image of the composite membrane of PAN/ TiO_2 /CNT nanofiber at 6.5 wt% of PAN. The TEM image provides closer observation of the composite structure. It can be seen that the beads containing TiO_2 and CNT are incorporated in the PAN nanofiber not just attached to the surface of the PAN nanofiber. This structure may minimize the potential of the photocatalyst leaching from the membrane. It is also observed that TiO_2 and CNT in the PAN nanofiber strand tend to agglomerate. This could be due to the van der Waals interaction [28].

The effect of PAN concentration on the textural properties of the resulting membrane composite is evaluated by performing N_2 gas sorption test. Figure 5 shows the N_2 adsorption-desorption isotherms of the resulting membranes at various PAN concentrations with type IV isotherms indicating porous composite nanofibers. The wide hysteresis loops indicate mesoporosity with pore condensation at high pressure. Hysteresis loops are commonly related to filling and emptying mesopores in the multilayer range of physisorption isotherms. The effect of capillary condensation in

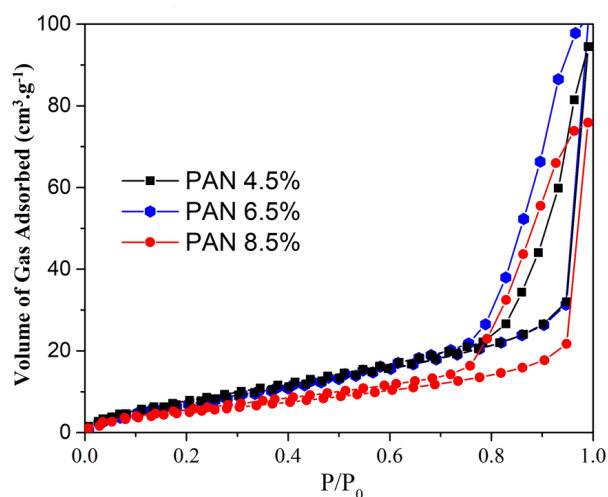


Figure 5. N_2 adsorption / desorption of PAN/ TiO_2 /CNT at various PAN concentrations.

the mesopores was attributed to an H3-type hysteresis loop of the IUPAC classification, in the relative pressure range of 0.75–0.99. Based on the results, the hysteresis loops of all PAN concentrations have the same profile (or shape), but slightly different in the width of the hysteresis loops. The BET surface area was determined using the monolayer of nitrogen gas adsorbed calculated for PAN 4.5% was 32.739 m².g⁻¹. In comparison, the increased concentration of PAN decreases the surface area to 32.238 for PAN 6.5% and 21.077 m².g⁻¹ PAN 8.5%, respectively (Table 1). The decrease in surface area is probably attributed to the increase of the fiber diameter.

The effect of PAN concentration on the pore size distribution was shown in Figure 6. The pore size distribution was calculated by Barret-Joyner-Halenda (BJH). The summary of the porosity was stated in Table 1. The increase in the concentration of PAN in the precursor decreases the pore size. The decrease in the pore size was attributed to the increase in the fiber diameter. The larger fiber makes the space between the fiber strand smaller, thus decreasing the pore size of the photocatalytic membrane. Based on the pore size distribution, the higher concentration of PAN shows a wider distribution of pore size. This is in accordance with the hysteresis loop pattern in Figure 5 which gets wider with the increasing PAN concentration.

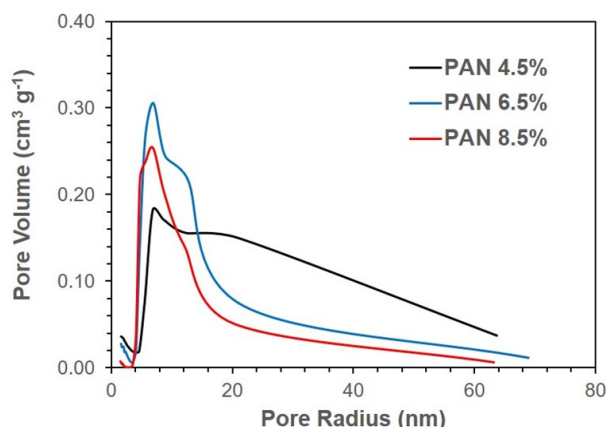


Figure 6. Pore size distribution of PAN/TiO₂/CNT at various PAN concentrations based on BJH model.

Based on our previous study, the addition of CNT in the photocatalytic membrane PAN/TiO₂/CNT nanofiber shifted the band-gap of TiO₂ from 3.19 eV to 2.77 eV [30]. This result implies in performance of composite membrane PAN/TiO₂/CNT nanofiber to be more active under the irradiation of visible light. Moreover, based on our previous result, the incorporation of CNT has proven to have a good performance for MB color removal under LED visible light irradiation in the batch system (more than 95% MB successfully removed in 135 min) [30]. CA membrane was used at the bottom of the membrane nanofiber to increase the mechanical strength of the membrane thus, the membrane is stable under water pressure. Membrane CA does not have any capabilities to filter the MB based on the experimental result.

The next step in this study was to examine the impact of PAN concentration on membrane performance for MB color removal through a cross-flow membrane reactor. The result of membrane performance was shown in Figure 7. Membrane performance is expressed in terms of the percentage of rejection. Rejection could be defined as the number of pollutants that have been removed from the feedwater. The test was carried out for 240 min by analyzing the concentration of MB remaining in the permeate. Based on the result, at the first 30 min, PAN 8.5% showed the lowest %rejection

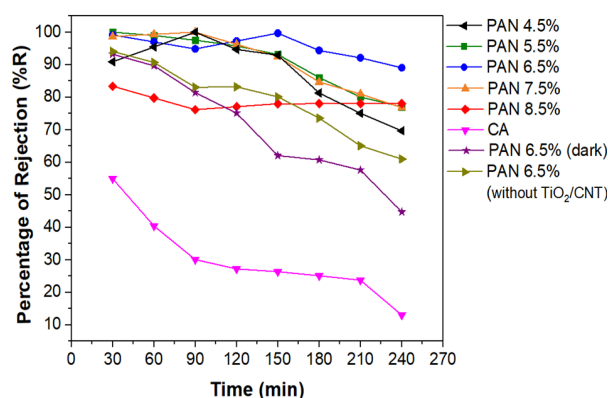


Figure 7. The membrane performance at various membranes with different PAN concentrations. Cellulose acetate (CA) membrane was used as a comparison.

Table 1. Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}), pore volume and pore size of composite membrane PAN/TiO₂/CNT with variation concentrations of PAN.

Sample	S_{BET} (m ² .g ⁻¹)	Pore Volume (BJH) (cm ³ .g ⁻¹)	Pore Size (BJH) (nm)
PAN 4.5%	32.739	0.1446	6.38
PAN 6.5%	32.238	0.1624	5.59
PAN 8.5%	21.077	0.1220	4.75

toward MB compared with other PAN concentrations. This is possible due to the pore character of the 8.5% PAN membrane.

The membrane composite PAN/TiO₂/CNT with a PAN concentration of 6.5% shows the best performance in the MB color removal. After 120 min, the performance of PAN 4.5; 5.5 and 7.5% start showing a decrease, while PAN 6.5% membrane performance shows relatively constant. The result is in accordance with the membrane properties. As PAN 6.5% shows the highest crystallinity anatase phase of TiO₂, it implies in its performance to remove the MB dyes. It seems that the photocatalyst TiO₂/CNT to degrade the pollutant accumulation on the membrane surface, then the fouling of the membrane could be minimized, thus extending the membrane performance up to 240 min. Since the concentration of photocatalyst inserted into the membrane is the same, the properties and characteristics of the fiber have a role in the photocatalytic reaction. As shown in SEM micrograph, in the PAN 4.5% and 5.5%, the lumps observed might affect the photocatalytic performance of the photocatalytic membrane. This could be due to the difference in the surface area. The presence of lumps in the fiber strands causes the photocatalytic agglomeration to increase and reduce the surface area thus affecting the photocatalytic reaction efficiency. The membrane performance in the MB color removal decreases because of inhibition in the photocatalytic reaction.

At high PAN concentration (7.5%), the fiber tends to be thicker, so that the photocatalyst in the fiber strands may encounter difficulty to access the pollutants. This probably caused the efficiency of photocatalytic reaction to decrease. PAN 8.5% shows constants performance in the rejection of MB until 240 min, but at low rejection. The phenomenon is slightly different compared to the other concentrations. It indicates

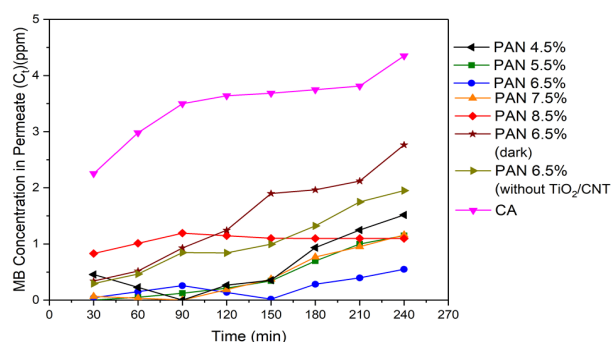


Figure 8. The remaining concentration of MB in the permeate for various membranes as a function of time.

that pore of the membrane may contribute dominantly to the performance of PAN 8.5%. The pore size of PAN 8.5% shows smallest among the other concentrations. With the small pore size, the capability of membrane to filter MB is better. However, as the crystallinity of PAN 8.5% is low, the photocatalytic function in the photocatalytic membrane system seems not to have significant role to enhance the color removal. However, it may contribute to the constant rejection over time to 240 min. Those discussed behavior of PAN photocatalytic membranes at various PAN concentrations suggest the role of the photocatalytic sites not only to synergistically enhance the color removal but also to prolong the membrane lifetime by minimizing fouling. The photocatalyst may degrade the pollutant buildup on the membrane surface.

The role of photocatalysts in photocatalytic membranes for the MB color removal through cross-flow reactors is supported by the decrease in the membrane performance when operating in dark conditions, as shown in Figure 7. PAN 6.5% decreased in performance with increasing operating time in the dark conditions. The performance of the membrane was not as good as the PAN 6.5% under light conditions. This indicates that the photocatalyst act to degrade the accumulated pollutants on the membrane surface at the same time degrading the MB permeate under light condition. Significant decrease of the rejection was also observed for PAN membrane without photocatalyst. Figure 8 shows the remaining concentration of MB in the permeate solution, which has passed through the membrane as a function of time. The results shown in Figure 8 strongly support

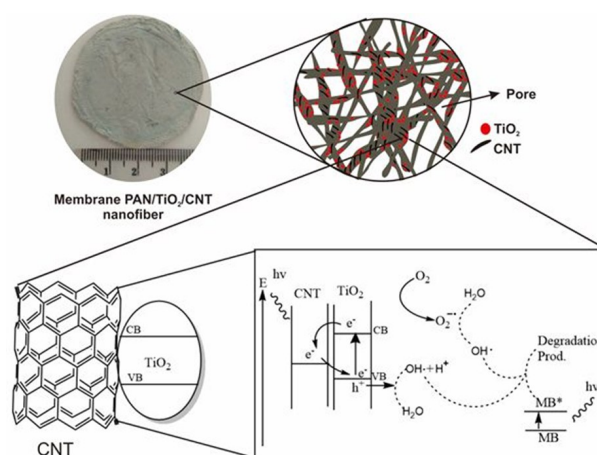


Figure 9. Proposed photocatalytic mechanism of the photocatalytic membrane of PAN/TiO₂/CNT.

the photocatalytic action of the membranes. The MB concentration steadily increases as a function of time for the membrane without photocatalyst (membranes of CA and the PAN 6.5% without TiO₂ and CNT) or at a condition without light (membrane 6.5% (dark)).

The addition of CNT in the composite of PAN/TiO₂/CNT increases the photocatalytic activity under the irradiation of visible-light. Based on our previous study [30], the addition of CNT shifted the band-gap energy of the TiO₂ from 3.19 eV to 2.77 eV. CNT also acts as electron acceptor that hinder the recombination time of photocatalyst. Olowoyo *et al.* also reported the formation of Ti–O–C bond as confirmed by X-ray Photoelectron Spectroscopy (XPS) analysis which is the possible reason why the band-gap energy shifted by the addition of CNT [11]. As the new carbonaceous bond formed, CNT might create a new energy level within the chemical state of the TiO₂ [31]. The possible interaction between CNT and TiO₂ is explained by Figure 9.

The coupling of CNT and TiO₂ can form a heterojunction which prolong the recombination time of electron-hole pair and act as defect site which increase the ability of visible light absorption [32]. CNT has the ability called ballistic transport which can transport the electron since it can be freely moving through the structure, thus can form O₂^{•-} and •OH. The radical hydroxyl plays a role in the degradation of MB. As TiO₂/CNT incorporated in the fiber strands, the PAN nanofiber acts as a membrane substrate but the photocatalytic activity is conducted by TiO₂/CNT. The following reaction equations explain the mechanism of degradation by the composite nanofiber [32]:

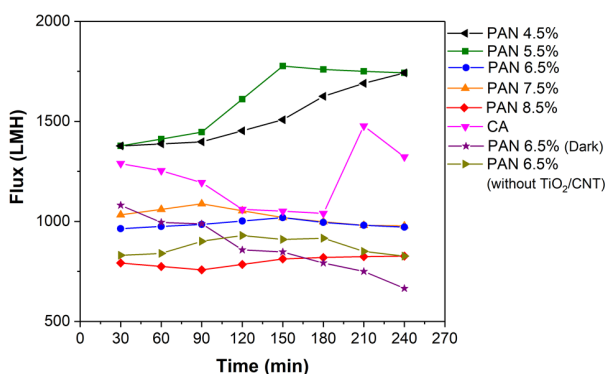


Figure 10. The effect of PAN concentration on the membrane permeability.

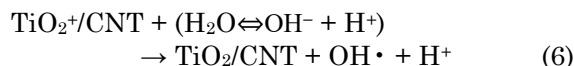


Figure 10 displays the relatively high membrane permeability of PAN/TiO₂/CNT membranes at various PAN concentrations. Composite membrane with PAN 4.5 and 5.5% shows the highest flux of more than 1000 LMH. It is probably related to the fiber diameter as shown by the SEM micrograph for the corresponding membranes. The low PAN concentration in the composite's attributes to the decrease in the fiber diameter. As the concentration of PAN gets higher, the pore size gets smaller, thus decreasing the permeability. PAN 8.5% shows the lowest permeability compared to membranes at other concentrations. The permeability of the membrane is very dependent on the fiber strands which are arranged to form the fiber mat. PAN 6.5% in the dark condition shows a decreasing trend with the increasing operating time. This is in accordance with the percentage of rejections shown in Figure 7. As the fouling happens, the permeability of the membrane tends to decrease. Overall, the permeability of the membranes with different concentrations of PAN is relatively stable for 240 min of operation time.

Lombardi *et al.* [33] has reported membrane polyamide-6 containing TiO₂ for MB degradation, the addition of TiO₂ content increases the fiber diameter, with degradation performance of 80% after 180 min in a batch system. Another research has also been reported by Cossich *et al.* [34]. The membrane of TiO₂-Polyamide-12 nanofiber shows an optimum ratio concentration of polyamide:TiO₂ 5:1 in degrading MB for 120 min (~100%). However, both studies were performed in a batch system, which has less advantages for industrial scale. The effect of polymer concentration on the membrane performance also has not been studied. We have shown that under a cross-flow reactor, the photocatalytic membrane of PAN/ TiO₂/CNT at 6.5% PAN demonstrates high percentage of rejection (90–100%) even after running for 240 min. Application to the industrial scale could be recommended.

4. Conclusions

This work exhibited the potential for the photocatalytic membrane of PAN/TiO₂/CNT with high and steady rejection performance for 240 min for dyes color removal by altering the polymer concentration. The membrane crystallinity, morphology and the pore size distribu-

tion of the PAN/TiO₂/CNT membrane have been affected by the concentration of PAN in the precursor solution for electrospinning. Increasing the concentration of polymer increases the fiber diameter from 206 nm to 506 nm resulting in low membrane permeability. However, steady high flux has been achieved even after 240 min of running the photocatalytic membrane on a cross-flow reactor. The photocatalytic center of TiO₂/CNT in the PAN/TiO₂/CNT membrane has played a significant role as inferred by steady value of the percentage of rejection and high flux. The optimum performance on the MB color removal through a cross-flow membrane reactor was shown by PAN 6.5% by maintaining the rejection of 90% for 240 min. Industrial application is then envisaged. Further study to reveal the role of the polymer affecting the anatase crystal growth is suggested so that optimal condition to achieve highly crystalline anatase phase of TiO₂ can be designed. It is also important to justify the anti-fouling mechanism into more detail by observing separately the photocatalytic action in the surface of the membrane.

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