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Mitigation of membrane fouling in dye wastewater using a ternary WO_3/CNT/ZnO composite photocatalytic membrane

Wei Tze Chong[1], and *Yit Thai* Ong[1,2*]

[1]Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia
[2]Centre for Environment and Green Technology, Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia

Abstract. The membrane filtration has been widely utilized in the water reclamation due to its simplicity in operation and outstanding separation performance. Nevertheless, the membrane filtration always suffers from the fouling issue which deteriorate the permeability of membrane. This study targeted to diminish the membrane fouling using a photocatalytic membrane. A ternary tungsten trioxide/carbon nanotube/zinc oxide (WO_3/CNT/ZnO) composite photocatalyst was applied to form a ternary WO_3/CNT/ZnO composite photocatalytic membrane via a wet processing technique. The highest efficiency to photodegrade methylene blue (MB) were obtained using the M5 ternary composite photocatalytic membrane. The presence of CNT and WO_3 intensifies the photocatalysis in the ternary photocatalytic membrane to degrade MB. The ternary composite photocatalyst in membrane form displayed a competitive effectiveness in degrading MB when compared to particle form. The ternary composite photocatalytic membrane demonstrated a decreased permeation flux, accompanied by an increased rejection toward the MB when increasing the loading of ternary composite photocatalyst in the photocatalytic membrane. The analysis on the antifouling behaviour of the ternary composite photocatalytic membrane showed that approximately 95% of flux recovery ratio (R_{fr}) and 5% of irreversible fouling ratio (R_{if}) were obtained.

1 Introduction

The water pollution has intensified over the years due to the consistent release of wastewater that produced from industrial and anthropogenic activities [1]. There are over 1000 of textile factories have been operated in Malaysia with the process involves weaving, dyeing, and finishing. The textile industries heavily rely on the use of dyes with more than 10000 types of dyes and an annual production reaching 700000 tonnes [2]. The level of water consumption in the textile industry is around 200 L of water is required to treat 1 kg of textile product. Over the year, it has been one of the main categories of wastewater which account approximately 22% of total industrial wastewater generated in Malaysia [3]. The discharge

*Corresponding author: ongyt@utar.edu.my

of textile wastewater which mainly consists of dye into the water system would trigger a serious environmental hazard to the ecosystem considering that the majority of the dyes are not biodegradable and possess toxicity that leads to rashes on the skin and allergies [4].

The water reclamation from the wastewater can be considered a viable solution to diminish the effluent that is released into the environment. Among the wastewater treatment processes, membrane filtration is one of the frequently employed tertiary treatment processes to obtain high-quality of reclaimed water with its outstanding performance in rejection capability [5]. Membrane filtration applies a thin, semi-permeable porous film layer that made of polymer, ceramic or metallic to serve as a selective barrier and gatekeeper to selectively monitor the mass transfer. Global water scarcity and governmental regulation on the management of wastewater provide an opportunity for the growth of the application of membranes [6]. Membrane filtration showed promising performance in dye removal. An ultrafiltration membrane that composed of bentonite deposited on a ceramic perlite support attained 80% of rhodamine B (RhB) rejection with a 100 mg/L of RhB as a feed solution [7]. However, the feasibility of membrane filtration faces a major obstacle in fouling issue which is brought from the deposition and adhesion of foulant on the membrane. The foulant that adheres on the membrane increases the permeation resistance because of the increased overall thickness for permeation, then decreases the permeation flux of the membrane [8].

The incorporation of photocatalysts into the membrane matrix to form a photocatalytic membrane has arisen as a progressive technology to alleviate membrane fouling. The formation of a photocatalytic membrane enables the simultaneous occurrence of photocatalytic degradation and selective barrier separation [9]. In our previous study [10], a ternary composite photocatalyst consisting of WO_3, CNT and ZnO was developed and exhibited excellent performance in degrading MB. Hence, as a continuation to the previous work, the objective of the study is to form a free-standing ternary WO_3/CNT/ZnO composite photocatalytic membrane by using the ternary composite photocatalyst. The permeation characteristics as well as the antifouling properties of the ternary composite photocatalytic membrane were assessed using a MB solution.

2 Methodology

2.1 Materials

Zinc nitrate hexahydrate was procured from Systerm while WO_3 was obtained from Alfa Aesar. Ammonium hydroxide and CNT were purchased from Synerlab and NovaScientific, respectively. MB and Acetic acid were bought from HmbG Chemicals while ethanol and chitosan were got from Gene Chemicals and Aldrich, respectively.

2.2 Formation of photocatalytic

The ternary WO_3/CNT/ZnO composite photocatalyst was synthesized using sol-gel and deposition methods as reported elsewhere [10]. It was then dispersed in ethanol and vacuum filtered through a polyvinylidene difluoride (PVDF) membrane filter, followed by infiltration with chitosan solution. The as-formed ternary WO_3/CNT/ZnO composite photocatalytic membrane was then peeled off from the membrane filter. The ternary composite photocatalytic membrane was prepared in five different loadings of photocatalyst: 0.08 g (M1), 0.10 g (M2), 0.12 g (M3), 0.14 g (M4) and 0.16 g (M5).

2.3 Characterization of the photocatalytic membrane

The morphology of the ternary composite photocatalytic membrane was inspected by the field emission scanning electron microscopy (FESEM). This sample was coated with silver prior to the analysis.

2.4 Photocatalytic activities of the photocatalytic membrane

The photocatalytic performance of the ternary composite photocatalytic membrane were evaluate based on the MB degradation. The photocatalytic membrane was immersed in 40 mg/L of MB solution for half an hour in dark condition to attain adsorption equilibrium, followed by illumination under sunlight for 2 hours. The concentration of MB was measured using UV-vis spectrophotometer in 662 nm wavelength. The degradation performance was evaluated by the Equation 1 [10].

$$D_e = (C_0 - C) / C_0 \times 100\% \quad (1)$$

where D_e is the degradation efficiency, C_0 and C are the initial and residual concentration.

The permeation of ternary composite photocatalytic membrane was conducted in a dead end membrane filtration system with 40 mg/L MB and determined using the Equation 2:

$$J = V / (A \times t) \quad (2)$$

where J is the permeation flux, V is the total volume of permeate collected, A is the surface area and t is the permeation time.

The concentration of MB solution was measured by UV-vis spectrophotometer while the rejection property of ternary photocatalytic membrane was identified using Equation 3:

$$R = (1 - C_p / C_f) \times 100\% \quad (3)$$

where R is the rejection, C_p and C_f represent the concentration of permeate and feed solutions.

The antifouling performance of ternary composite photocatalytic membrane were measured using MB. Firstly, the permeation flux of the photocatalytic membrane in distilled water (J_{w1}) was recorded. Then, photocatalytic membrane was filtered with the MB (40 mg/L) solution. After the filtration, the fouled photocatalytic membrane was irradiated with sunlight for 30 minutes to activate the photocatalysis to degrade the accumulated foulant. Next, the photocatalytic membrane was again permeated with distilled water and the permeation flux (J_{w2}) was recorded. The fouling process was analyzed using the equations as follows [11]:

$$R_{fr} = J_{w2} / J_{w1} \times 100\% \quad (4)$$
$$R_{if} = (1 - J_{w2} / J_{w1}) \times 100\% \quad (5)$$

R_{fr} is a dominant parameter to determine the antifouling property of membrane through the fraction of permeation flux can be recovered after the filtration processes. R_{if} denotes the fraction of irreversible foulant that is adhered to the membrane [12].

3 Discussion

3.1 FESEM analysis of photocatalytic membrane

The structure of the ternary composite photocatalytic membrane is illustrated in Figure 1.

The entanglement of the CNT thread is responsible for assembling the photocatalyst into the membrane.

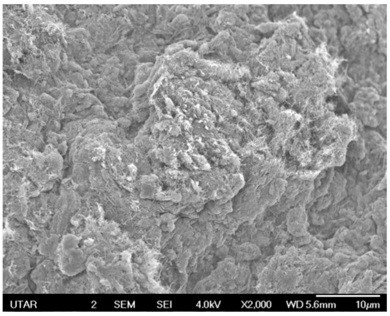

Fig. 1. FESEM images of surface morphology for the ternary photocatalytic membrane.

3.2 Degradation of MB by photocatalytic membrane and photocatalyst

The ability of ternary composite photocatalytic membranes to degrade the foulant via photocatalysis was assessed based on the degradation of MB under sunlight illumination. Figure 2. demonstrates the results illustrating the photocatalytic activity of the ternary composite photocatalytic membranes to degrade the MB.

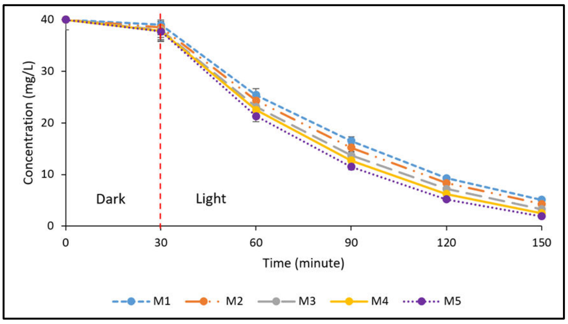

Fig. 2. Photocatalysis studies using ternary photocatalytic membrane on MB (40 mg/L).

The degradation of MB followed an ascending order: 87.3% (M1), 89.3% (M2), 91.8% (M3), 93.8% (M4), and 95.3% (M5), highlighting an improved photocatalytic activity toward MB degradation with higher loading of photocatalyst in the photocatalytic membrane. Besides that, the existence of CNT and WO_3 improves the photodegradation of photocatalytic membrane toward MB which can be attributed to the charge movement supplied in CNT while WO_3 enhances the capability of the photocatalytic membrane to absorb more light energy from the sun thereby promotes the excitation of electron for photocatalysis [10]. The efficiency of the ternary composite photocatalyst and photocatalytic membrane forms were compared and the outcome is displayed in Figure 3. The ternary composite photocatalyst achieved a 100% of MB degradation. Meanwhile the ternary composite photocatalytic membrane achieved 95.3% degradation in MB solution. This showed that the performance of ternary composite photocatalyst was marginally decreased after assembled into membrane form yet remained relatively competitive in terms of effectiveness in degrading MB.

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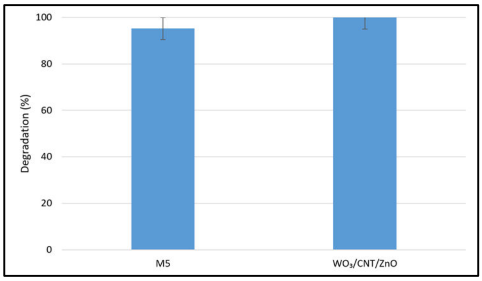

Fig. 3. Degradation of MB by M5 photocatalytic membrane and ternary composite photocatalyst.

3.3 Permeability and rejection analysis of photocatalytic membrane

The effect of photocatalyst's loading on the photocatalytic membranes was assessed by measuring the permeation flux and rejection toward MB solution, as displayed in Figure 4.

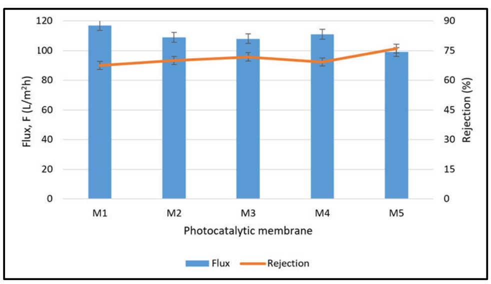

Fig. 4. Permeation and rejection of ternary composite photocatalytic membrane on MB filtration.

In overall, the permeation flux of the ternary composite photocatalytic membrane exhibited a decrease trend from 117 L/m^2h to 99 L/m^2h when the loading of ternary composite photocatalyst in the photocatalytic membrane was increased from 0.08 g (M1) to 0.16 g (M5). The permeation flux of photocatalytic membrane is mainly depended on the average pore size of membrane [13]. In general, a higher loading of photocatalyst tends to create a denser structure, which results in the formation of smaller pore sizes in the photocatalytic membrane, eventually generate a lower permeation flux. Besides that, the chitosan infiltrated may reduce the pore size of the ternary composite photocatalytic membrane as well [14]. In the rejection property of the ternary composite photocatalytic membranes, the rejection toward MB was enhanced from 67.5% to 76% when the loading of ternary composite photocatalyst was increased. The outcome showed a general trade-off between the rejection property and permeation flux in membrane separation process. The ability of the photocatalytic membrane to reject the MB could potentially result in membrane fouling issue.

3.4 Antifouling analysis of photocatalytic membrane

The antifouling properties of the ternary composite photocatalytic membrane was measured based on R_{fr} and R_{if} with MB as displayed in Figure 5. There was around 95% of R_{fr} obtained for all the ternary composite photocatalytic membranes in Figure. 5(a). The insignificant change of R_{fr} can be due to the loading of ternary composite photocatalyst in the photocatalytic membrane was sufficient to achieve the maximum degradation property. The R_{if} of all ternary composite photocatalytic membranes in MB solution was approximately 5%. The R_{if} remained low which indicated that there was a less portion of foulant attached on membrane. The outcome of the ternary composite photocatalytic membrane in MB without the photocatalytic treatment, which was conducted as controlled samples, is shown in Figure 5(b). The R_{fr} of all ternary composite photocatalytic membranes from M1 to M5 was around 90% while the R_{if} of all ternary composite photocatalytic membranes was approximately 10%. The difference in the R_{fr} and R_{if} of ternary photocatalytic membrane that subjected to photocatalytic treatment and without photocatalytic treatment would indicate the presence of photodegradation action by the ternary composite photocatalyst in the photocatalytic membrane to mitigate the irreversible membrane fouling.

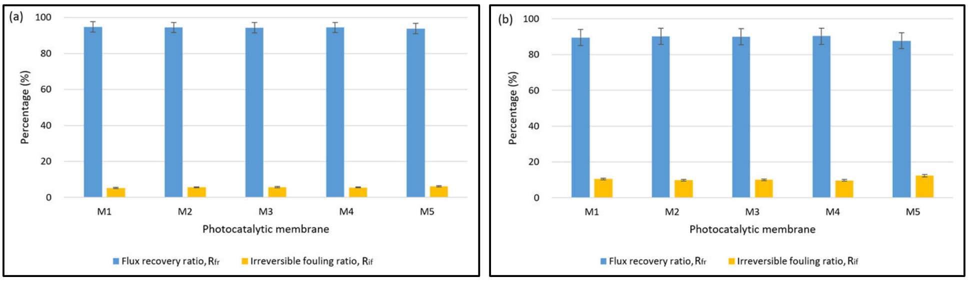

Fig. 5. Antifouling property of ternary composite photocatalytic membrane in MB solution (a) with and (b) without photocatalytic treatment.

4 Conclusion

The ternary WO_3/CNT/ZnO composite photocatalytic membrane was formed via a wet processing technique with five different loading of ternary composite photocatalyst ranging from 0.08 g (M1) to 0.16 g (M5). The morphology study using FESEM revealed that the formation of the ternary composite photocatalytic membrane can be associated with the entanglement of CNT. The ternary composite photocatalytic membrane showed increased MB degradation with increasing loading of ternary composite photocatalyst wherein the highest MB degradation (95.3%) was achieved using M5 photocatalytic membrane. This could be ascribed to the effective charge transfer supplied CNT while WO_3 assisted the ternary photocatalytic membrane to harvest more sunlight energy for photodegradation. In the permeation characteristic, the rejection of ternary photocatalytic membrane toward MB solution was increased with higher loading of ternary composite photocatalyst. However, as the inherent trade-off relationship, the permeation flux of ternary photocatalytic membrane was decreased. This could be ascribed to the decreasing pore size in photocatalytic membrane with higher loading of ternary composite photocatalyst. Meanwhile, the ternary composite photocatalytic membrane exhibited a reasonable antifouling property. The antifouling study using MB as model foulant obtained approximately 95% of R_{fr} and 5% of R_{if}. The ternary photocatalytic membrane comprised of competitive performance in permeation, rejection and antifouling which can be applied in the water reclamation.

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