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Preparation of PVDF–TiO₂ mixed-matrix membrane and its evaluation on dye adsorption and UV-cleaning properties

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HIGHLIGHTS
- The hydrophilicity of the mixed-matrix membrane was greatly enhanced.
- Both standard blocking and cake filtration mechanisms took part in the filtration.
- The mixed-matrix membrane has significant self-cleaning properties.
- The mixed-matrix membrane could provide 100% flux recovery ratios.

ABSTRACT
In this study, the polyvinylidene fluoride (PVDF)–Titanium dioxide (TiO₂) mixed-matrix membranes were prepared via phase inversion technique. The properties of PVDF–TiO₂ mixed-matrix membranes were characterized based on pore size distribution, membrane porosity, field emission scanning electron microscope (FESEM) and photocatalytic behavior. The hydrophilicity of the mixed-matrix membrane was enhanced and resulted in the improved pure water permeability (392.81 ± 10.93 l/m² h bar) compared to that 76.99 ± 4.87 l/m² h bar of the neat membrane. The neat and mixed-matrix membranes were further investigated in terms of filtration, adsorption and UV-cleaning properties based on methylene blue (MB) solution. Mixed-matrix membranes showed excellent removal efficiency (~99%) when sodium dodecyl sulfate (SDS) was introduced into the MB feed solution. The produced mixed-matrix membrane shows some slight photocatalytic properties improvement as FTIR results reviewed that the cleavage of -C=N bonding due to MB adsorption reduced more significantly with the presence of TiO₂ NPs and ultraviolet (UV) light irradiation. The UV-cleaning properties of the mixed-matrix membrane were further proved by the 100% flux recovery ratios (FRRs) for mixed-matrix membrane, suggesting that the embedded TiO₂ NPs was photocatalytically active and able to degrade the adsorbed MB in the membrane.

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1. Introduction
Membrane technology has emerged as an advanced separation technology in various industrial applications over the past few decades. In recent year, ultrafiltration (UF) is considered as a promising method which can be operated with minimal chemical additives, very low energy usage, easy automation, and optimal quality of treated water [1]. Micellar enhanced ultrafiltration (MEUF) is one of the energy efficient membrane separation process useful in wastewater treatment. The process involves the addition of sodium dodecyl sulfate (SDS) surfactant at a concentration higher than its critical micelle concentration (CMC) to form the large amphiphilic aggregate micelles. The micelles are formed through ionic binding between the solutes with the oppositely charged micelle surface which...
facilitated the removal of metal ions and trace organic pollutants using lower pressure method [2]. Micelles containing solubilized organic compounds (having larger size than the membrane pore) are retained by the membrane and a permeate stream passing through the membrane is nearly free from impurities [1,3]. However, one of the main barriers to extensive use of such UF process is membrane fouling. Decline in permeate flux due to adsorption of organic compounds on the membrane surface causes serious issues related to membrane fouling [4–8]. Besides, MB also caused serious irreversible fouling on membrane matrix which attract great attention on membrane fouling analysis.

The semi crystalline polyvinylidene fluoride (PVDF) is one of the most attractive polymer materials in microporous membrane industry because of its thermal stabilization and high mechanical strength [9,10]. However, the PVDF UF membrane exhibits hydrophobic nature, leading to severe membrane fouling and decline in membrane permeability, which have become a barrier for wastewater treatment due to its high surface energy between water and membrane surface [11]. Various methods have been applied to improve the hydrophilicity and performance of PVDF membrane. Membrane fouling can be reduced by addition of hydrophilicity materials to the membrane casting solution [12–14]. The preparation of novel organic-inorganic composite membranes with control properties has been widely used recently. Titanium dioxide nanoparticles (TiO2 NPs) have received most attention over other NPs due to its stability, commercial availability, excellent photocatalytic, antibacterial and UV-cleaning properties [12,14–16]. Recent studies indicate that photocatalytic oxidation is an emerging alternative technology for wastewater treatment involving reactive dyes such as methylene blue (MB). It has been demonstrated that organic contaminants can be oxidized to carbon dioxide, water and simple mineral acids at low temperatures on TiO2 photocatalysts in the presence of UV or near-UV illumination [17]. Lakshmi et al. [18], Tayade et al. [19], as well as Yu and Chuang [20] studied the photocatalytic oxidation of MB in aqueous TiO2 suspension. The use of TiO2 in suspension is a promising method for MB photodegradation due to its large surface area of TiO2 available for the reaction. However, the TiO2 NPs must be removed in the post-treatment process which requires a solid–liquid separation stage, leading to higher overall operating cost in the process. Alternatively, TiO2 NPs incorporation onto PVDF membrane matrix was carried out in this study to eliminate the need of post-treatment.

Many research works had been carried out on the passive anti-fouling properties of mixed-matrix membrane by determining its fouling rate based on protein adsorption. However, in the present work, not only we observed the adsorption and sieving phenomenon of dye or micellar enhanced dye of the mixed-matrix membrane but for the first time, we provide a direct investigation on the membrane UV-cleaning properties based on the photodegradation of dye adsorbed on the membrane surface. The performance of mixed-matrix membranes was compared with that of neat membranes under similar operating conditions in order to evaluate its flux recovery ratio (FRR) under ultraviolet (UV) light irradiation.

### 2. Materials and methods

#### 2.1. Materials

Polyvinylidene fluoride (Solef® PVDF) was supplied by Solvay Solexis, France. N,N-dimethylacetamide (DMAc), sodium dodecyl sulfate (SDS) and methylene blue (MB) were purchased from Merck, Germany. Anatase TiO2 NPs, PC-20 (20 nm) was purchased from TitanPE Technologies, Inc., Shanghai. PVDF and TiO2 NPs were dried in an oven at 70 °C for overnight prior to use, while other organic chemicals were obtained in reagent grade purities and used as received. Distilled water was used for all the experiments.

#### 2.2. Membrane preparation

TiO2 NPs (1.5 wt.%) was dispersed in the DMAc solvent under sonication for 15 min. The PVDF powder was then dissolved into the TiO2 solution and stirred at 60–70 °C for 4 h to ensure a complete dissolution. The solution was left to stir overnight at 40 °C to form a homogenous solution. The final solution was subjected to further sonication for 30 min and allowed to cool down to room temperature. Solvent loss by evaporation was negligible due to the high boiling points of DMAc (164–166 °C). The details of the membrane synthesis parameters on MEUF process are summarized in Table 1.

The solution was then cast on the tightly woven polyester sheet using automatic film applicator (Elcometer 4340, EU). Subsequently, it was immediately immersed into the water bath of distilled water to allow the phase inversion to occur for 24 h to remove the residual solvent. The PVDF membrane was kept in the distilled water prior to use.

#### 2.3. Membrane characterization

##### 2.3.1. Pore size distribution

The pore size distribution of the membrane was determined using the Capillary Flow Porometer, Porolux 1000 (Benelux Scientific, Belgium). The membrane samples with diameter of 20 mm were immersed in perfluoroethers (wetting liquid) prior to test and characterized using a liquid extrusion technique in which the differential gas pressure and flow rates through wet and dry samples were measured. The pore size distributions were then analyzed using the LabView software.

##### 2.3.2. Membrane porosity

The asymmetric porous membrane porosity, $A_\text{b}$, was defined as the volume of the pores divided by the total volume of the membrane. To prepare the wet and dry membranes, three pieces of square flat sheet membranes with the size of 2.5 cm × 2.5 cm were dried in an oven at 60 °C until constant weight was observed and the weight of dry membrane was recorded. The membrane samples were then immersed into 2-butanol (Merck, Germany), and degassed for 30 s to avoid air trap in the membrane pores, and left at room temperature for 2 h. Lastly, the membrane surface was dried using filter paper and weighted immediately to avoid evaporation of 2-butanol from membranes pores. The membrane porosity was calculated using the following equation:

$$A_\text{b} = \frac{(w_1 - w_2) \rho_2}{w_1 \rho_2 + w_2 \rho_b} \times 100\%$$  \hspace{1cm} (1)

where $A_\text{b}$ is the porosity of the membrane (%), $w_1$ and $w_2$ are the weights of the wet and dry membrane (g), respectively, $\rho_2$ and $\rho_b$ are the specific gravities of the PVDF polymer (1.78 g/cm³) and 2-butanol (0.81 g/cm³) (assuming that all materials kept their specific gravity constant in the wetted condition, and there was no air trap in the membrane pores), respectively. 2-Butanol a non-solvent for PVDF

<table>
<thead>
<tr>
<th>Membrane</th>
<th>PVDF (wt%)</th>
<th>DMAc (wt%)</th>
<th>TiO2 (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat membrane</td>
<td>18</td>
<td>82</td>
<td>0</td>
</tr>
<tr>
<td>Mixed-matrix membrane</td>
<td>18</td>
<td>80.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 1

The detail of the membrane synthesis parameter on MEUF process.

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PVDF [21] was chosen as a wetting liquid because it did not swell the PVDF membrane and wetted well the hydrophobic PVDF membrane to ensure complete pores filling by capillarity [22].

2.3.3. Field emission scanning electron microscope
The cross-sectional morphologies of the neat and mixed-matrix membranes were observed under field emission scanning electron microscope (FESEM CARL ZEISS SUPRA 35VP, Germany). The membranes were initially dried with a filter paper to remove the remaining distilled water on the membrane surface, and air dried for FESEM observation. The membranes were immersed in liquid nitrogen and fractured carefully to have a clean brittle fracture for FESEM images. Membrane surface was coated with a thin layer of gold under vacuum before being tested using K 550 sputter coater to provide electrical conductivity. The samples were examined under the FESEM at potentials of 10.0 kV at 1000× image magnifications.

2.3.4. Adsorption study
The adsorption studies were carried out using a dead-end stirred cell (Amicon 8200, Millipore Co., USA) with a capacity of 200 ml, where the disc membrane has a diameter of 6 cm with a geometric area of 28.27 cm² (excluding the area cover by the O-ring). The synthesized flat sheet membrane was cut into the disc shape and laid on top of the membrane holder in a circular stirred cell unit, thus covered and tightened with a rubber O-ring. The stirring speed was maintained at 200 rpm using the controllable magnetic hot plate stirrer (Heidolph MR Hei-Standard, Germany). The desired MB concentration in the feed solution was achieved by diluting the appropriate volume from a stock MB solution of 100 mg/l to a final volume of 1000 ml. The predetermined amount of SDS was added as binding agent to the feed solution before UF process. In each experimental run, the feed solution was stirred at 300 rpm for 30 min and introduced to the feed tank of the dead-end UF unit. The permeate flux and filtration efficiency were measured for every 10 ml of permeate collected. The permeate flux (J) was calculated by the following equation:

\[
J = \frac{V}{AM} \tag{2}
\]

where \(V \text{(m}^3\text{)}\) is the volume of permeated water, \(A \text{(m}^2\text{)}\) is the membrane area, and \(t \text{(h)}\) is the UF operating time. The concentrations of MB with and without SDS surfactant in the feed and permeate were measured using a UV spectrophotometer (UV Mini-1240, Shimadzu) on the basis of measurement of color intensity at the maximum absorbance of 662 nm.

2.3.5. Photodegradation experiment
The neat and mixed-matrix membrane after MB UF process were cut into several small square coupons and mounted onto glass slides using double-sided tape to ensure a flat membrane surface. The glass slides were immersed in a petri dish which was filled with ~50 ml of distilled water to ensure the same water level throughout the whole photodegradation experiment. The photodegradation ability of neat and mixed-matrix membrane were carried out using Ultra Violet A (UVA) light chamber with Tubular low-pressure mercury vapor fluorescent lamps, UVA lamp (Actinic BL TL-K 40W/10-R1S, Philip) at light intensity of 2.5 ± 0.2 mW/m² measured using sensor monitor (Model 5.0 classic version, sglux).

The acquired Fourier transform infrared spectroscopy (FTIR) spectra were obtained from the neat and mixed-matrix membrane surfaces using an FTIR spectroscopy (Thermo Scientific, Nicolet iS10, USA) to determine the extent of MB degradation. The FTIR spectroscopy was equipped with an OMNI-Sample Attenuated Total Reflection (ATR) smart accessory with diamond crystal operated at 45°. The membranes were scans at a resolution of 4 cm⁻¹ within wave number of 4000–525 cm⁻¹. The changes of absorbance over different reaction time were determined based on the wave number of 1599 cm⁻¹ which indicated the C=O bonding. To minimize experimental error, the FTIR spectra measurements were repeated 10 times for each sample at different point locations of membrane and the results were then averaged.

2.4. Dead-end UF experiment
The UF experiments were performed in a dead-end stirred cell (Amicon 8200, Millipore Co., USA) with a capacity of 200 ml, where the disc membrane had a diameter of 60 mm with a geometric area of 28.27 cm² (excluding the area cover by the O-ring). The applied pressure of the UF system was controlled by N₂ gas and the operating temperature was 27 ± 2°C. The stirring speed was maintained at 200 rpm using a controllable magnetic hot plate stirrer (Heidolph MR Hei-Standard, Germany). The desired MB concentration in the feed solution was achieved by diluting the appropriate volume from a stock MB solution of 100 mg/l to a final volume of 1000 ml. The predetermined amount of SDS was added as binding agent to the feed solution before UF process. In each experimental run, the feed solution was stirred at 300 rpm for 30 min and introduced to the feed tank of the dead-end UF unit. The permeate flux and filtration efficiency were measured for every 10 ml of permeate collected. The permeate flux (J) was calculated by the following equation:

\[
J = \frac{V}{AM} \tag{2}
\]

where \(V \text{(m}^3\text{)}\) is the volume of permeated water, \(A \text{(m}^2\text{)}\) is the membrane area, and \(t \text{(h)}\) is the UF operating time. The concentrations of MB with and without SDS surfactant in the feed and permeate were measured using a UV spectrophotometer (UV Mini-1240, Shimadzu) on the basis of measurement of color intensity at the maximum absorbance of 662 and 665 nm. Two calibration curves using different standard solutions containing different concentrations of
MB and MB with SDS were determined. The UF efficiency of the dye removal from the feed solution was calculated using the following equation:

\[ R(\%) = \left[ 1 - \frac{C_p}{C_0} \right] \times 100\% \]  

(3)

where \( C_p \) is the dye concentration in the permeate and \( C_0 \) is the initial concentration of the dye in the feed.

The schematic diagram of dead-end UF unit is shown in Fig. 1.

2.5. Cross-flow UF experiment

The UV-cleaning experiments were carried out in a cross-flow UF unit, where the disc membrane had a diameter of 4 cm with a geometric area of 12.57 cm² (excluding the area covered by the O-ring). The applied pressure of the filtration system was controlled by a needle valve to a constant pressure of 0.5 bar. The operating temperature was 27 ± 2°C.

The desired MB concentration in the feed solution was achieved by diluting the appropriate volume from a stock solution of 100 mg/l MB to a final volume of 1000 ml of 10 mg/l MB and introduced to the feed tank of the cross-flow UF unit. Feed pressure was continually monitored to ensure that constant pressure was applied throughout the experiments. The pure water and MB solution were charged into a 2-L feed tank and recirculated at a constant flow rate of 60 ml/min using a peristaltic pump (Materflex L/S Digital Economy Drive, Model: 77800-60, Cole Parmer Instrument Company). Permeate flow rate were continually recorded using an electronic balance which was connected to a data acquisition system (AND Super Hybrid Sensor, Model: Fx-3000i, A&D Company, Limited). The permeate flux (J) was calculated using Eq. (2).

All the results presented were average data obtained from three membrane samples. The schematic diagram of cross-flow UF unit is shown in Fig. 2.

3. Results and discussion

3.1. Effect of operating pressure on membrane flux and rejection

The feed solutions consist of MB and SDS was subjected to the UF process at the operating pressures of 0.2, 0.4, 0.6, 0.8 and 1.0 bar. The effects of operating pressure on neat and mixed-matrix membrane are presented in Fig. 3. It is evident that both the water and MB–SDS permeate flux increased linearly with operating pressure. Operating pressure is the effective driving force for UF process, suggesting that increasing the operation pressure will increase the effective driving force for the solvent transport and resulting in high permeate flux [23–25].

Mixed-matrix membrane showed higher permeability as compared to neat membrane in both pure water and MB–SDS UF processes. The pure water permeabilities were 392.81 ± 10.93 and 76.99 ± 4.87 l/m² h bar, whereas the MB–SDS permeabilities were 138.43 ± 4.25 and 31.72 ± 3.12 l/m² h bar for mixed-matrix and neat membranes, respectively. The higher pure water permeabilities of mixed-matrix membrane over the neat membrane permeabilities could be attributed to the changes of membrane pore size.

Fig. 4 shows that mixed-matrix membrane had larger maximum pore radius (45 nm) compared to the neat membrane (25 nm). It could be further proved from the FESEM cross-sectional images (Fig. 5) which revealed that larger inner pore size for mixed-matrix membrane was observed as compared to that for neat membrane. The membranes have the physical properties as listed in Table 2.

According to Hagen Poiseuille Equation, membrane flux could be predicted using the following equation:
by considering the pore size distribution, the total flux could be expressed as

\[ J = \frac{\sum N Q_p}{\sum N \pi d_p^4/4} \]

where \( Q_p \) is the volumetric flow rate of single pore (L/h), \( \Delta P \) is the operating pressure (bars), \( d_p \) is the pore diameter (nm), \( \Delta x \) is the membrane thickness (\( \mu \text{m} \)) and \( \mu \) is the solution viscosity (Pa s).

By considering the pore size distribution, the total flux could be expressed as

\[ J = \frac{\sum N \Delta P d_p^4/(128 \mu \Delta x)}{\sum N \pi d_p^4/4} \]

where \( J \) is the volumetric flux (L/h m\(^2\)), \( A_m \) is the membrane porosity, \( N \) is the number of pores having diameter of \( d_p \), \( f_i \) is the fraction of the number of pores with diameter \( d_p \), and \( N \) is the total number of pores.

The theoretical flux ratio between mixed matrix membrane and neat membrane could be expressed as

\[ J_{MM}/J_{NE} = \frac{\sum f_i d_p^4}{\sum f_i^4 d_p^4} \]

The theoretical flux ratio (\( J_{MM}/J_{NE} \)) calculated based on the membrane properties was 3.0, whereas the experimental value of the flux ratio was 5.1, indicating that the flux enhancement of mixed-matrix membrane was not solely caused by the changes of physical properties, but to certain extent by the pore hydrophilization due to the incorporation of TiO\(_2\) NPs. TiO\(_2\) NPs could form surface hydroxyl group that attracted water molecules to pass through the membrane, leading to the permeate flux increment.

Bae and Tak\(^{[26]}\) observed similar phenomenon that TiO\(_2\) composite membrane could be more hydrophilic than neat polymeric membrane due to the higher affinity of TiO\(_2\) towards water.

Fig. 6 shows the effect of operating pressure on the MB–SDS rejection for neat and mixed-matrix membranes. It can be seen that neat membrane had better rejection performance at higher operating pressure compared to the mixed-matrix membrane. The subscript MM represents mixed-matrix membrane whereas the subscript NE represents neat membrane.

The physical properties of the neat and mixed-matrix membranes are listed in Table 2.

<table>
<thead>
<tr>
<th>Physical properties of the neat and mixed-matrix membranes.</th>
<th>Neat membrane</th>
<th>Mixed-matrix membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum pore radius (( r_p ), nm)</td>
<td>25</td>
<td>45</td>
</tr>
<tr>
<td>Pure water permeability (( J_v/\Delta P ), L/(m(^2) h bar))</td>
<td>76.99 ± 4.87</td>
<td>392.81 ± 10.93</td>
</tr>
<tr>
<td>Porosity (( A_p ), %)</td>
<td>64.53 ± 0.07</td>
<td>65.13 ± 0.05</td>
</tr>
<tr>
<td>Thickness (( \Delta x ), ( \mu \text{m} ))</td>
<td>117 ± 0.85</td>
<td>110 ± 0.33</td>
</tr>
</tbody>
</table>

Table 2

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For mixed-matrix membrane, MB–SDS rejection decreased slightly
with the increase of operating pressure, ranging from 99.71% at
0.2 bar to 96.09% at 1.0 bar, respectively. These data provided us
the important information regarding the maximum operating
pressure that can be used for such systems. It can also be observed
in Fig. 6 that the optimum operating pressure for such systems was
found to be 0.5 bar and the corresponding rejections for neat and
mixed-matrix membrane exceeded 99%.

It is not surprising that the rejection capability of mixed-matrix
membrane decreased compared to that of the neat membrane at
higher pressure as mixed-matrix membrane had larger pore size.
At higher operating pressure, the higher pore to solute ratio of
mixed-matrix membrane allowed the convective transport of sol-
utes through the membrane [27]. Moreover, higher operating pres-
sure also resulted in micelles compaction that enabled the micelle
to squeeze through the membrane pores [6]. Ahmad and Puasa
[23] also observed the same phenomenon as the operating pres-
sure increased, the micellar enhanced dye rejection would de-
crease accordingly. Besides, a compacted micelle would reduce
the dye solubility which led to less amount of dye removed.

3.2. Effect of SDS concentration on MB flux and rejection

In this experiment, the MB concentration in the feed solution
was fixed at 10 mg/l and an operating pressure of 0.5 bar was ap-
plied, while the feed SDS concentrations were adjusted to 0, 0.25,
0.5, 1.0 and 2.5 CMC where CMC is critical micelle concentration
(1 CMC = 8 mM of SDS) [28].

Fig. 7 shows the effect of SDS concentration on the flux of neat
and mixed-matrix membrane. It was found that the permeate
fluxes for both neat and mixed-matrix membrane decreased as
the SDS concentration increased. Zaghibani et al. [29] reported
the phenomenon of flux reduction at higher SDS concentration is
generally attributed to the effects of membrane fouling and con-
centration polarization. Concentration polarization which was
caused by deposition of SDS micelles on the membrane surface
led to the increased solution mass transfer resistance. Beyond the
solubility limit, the micelles deposited on membrane surface
would build up gel type layer and caused pores blockage. Besides,
higher SDS concentration formed small and compact micelles as
reported by Fang et al. whereby the small and compact micelles
might plug the membrane pores easily as compared to large and
incompact micelles which only deposited on membrane surface
[30].

Fig. 7 shows that permeate fluxes decreased as much as 53.72%
and 56.94% with the increasing SDS concentration in the feed solu-
tion from 0 to 2.5 CMC, for neat and mixed-matrix membranes,
structure which make the PVDF sites more accessible to the dye adsorption through diffusion.

Fig. 8 reviews that the rejections for both membranes were sharply increased to nearly 100% when SDS was added into the feed solution, a phenomenon also observed by Huang et al. [8] and Zaghbani et al. [29]. The reasons of this phenomenon might be due to (i) concentration polarization effect and cake layer formation, (ii) precipitation of MB with small amount of SDS surfactant, and (iii) direct adsorption of MB on membrane surface and pores as discussed earlier. Theoretically, there was almost negligible micelle formed at the SDS concentration below 1.0 CMC, however, as concentration polarization occurred on the membrane surface, the concentration of SDS might exceed 1 CMC and resulted in micelle formation. For reason (ii), as reported by Misra et al. [31], for MB feed solution with SDS below 1.0 CMC, MB could be rejected by precipitation with a small amount of SDS molecules. Lastly, the direct adsorption of MB onto the TiO2 surface could be enhanced as SDS could reduce the surface tension between the solution and constricted pore size which created more accessible adsorption sites. As a result, the rejections of both membranes were improved drastically.

3.3. Effect of methylene blue concentration

The SDS concentration in the feed solution was fixed at 20 mM [29] and an operating pressure of 0.5 bar was applied to observe the effect of MB concentration on the permeate flux and rejection. The experiments were carried out by varying the MB concentration at 10, 50 and 100 mg/l. Fig. 10 shows the effect of MB concentration on permeate fluxes of neat and mixed-matrix membranes. The permeate fluxes decreased as the MB concentration increased, where increasing 10 times in MB concentration had reduced the flux as much as 20.3% and 7.5% for neat and mixed-matrix membranes, respectively. However, compared to the effect of SDS, membrane fouling contributed by the amphiphilic SDS concentration is more significant. The reduction in permeate flux was at higher MB concentration is due to the buildup of free MB adsorption onto the membrane surface which formed the deposit layer near the membrane surface, and eventually building up additional resistance for permeate to pass through the membrane. Huang et al. [8] also found that the permeate flux decreased as the feed MB concentration increased. The higher fouling rate of neat membrane compared to that of the mixed-matrix membrane was mainly caused by the previously postulated reason in which MB is more favorable to adsorbed on the PVDF matrix than TiO2.

Fig. 11 shows the effect of MB concentration in the feed solution on MB–SDS rejection. The rejection decreased for both neat and mixed-matrix membranes when the MB concentrations increased. This result could be due to the complete coverage of adsorption site onto membrane surface at higher MB concentrations, leading to the decreasing of MB–SDS rejection. The rejection for neat and mixed-matrix membranes were reduced as much as 20% and 13.6%, respectively when the MB concentrations were increased from 10 to 100 mg/l. At high MB concentrations, mixed-matrix membrane showed better rejection compared to neat membrane, suggesting that mixed-matrix membrane provided more accessible adsorption sites compared to the neat membrane as illustrated in Fig. 12.

3.4. UV-cleaning properties of neat and mixed-matrix membranes

The UV-cleaning properties of neat and mixed-matrix membranes were studied using cross-flow UF process containing 10 mg/l MB solution without SDS. Its performance was based on the flux recovery of pure water performed over a period of time. Figs. 13 and 14 show the time-dependent permeate flux of the neat and mixed-matrix membranes, respectively. The pure water flux recoveries were observed for three consecutive ultraviolet (UV) light irradiation cycles. In order to study the UV-cleaning proper-

![Image of Fig. 10](image1.jpg)

**Fig. 10.** Effect of the MB concentration on the MB–SDS flux for neat and mixed-matrix membranes. The SDS concentration and operating pressure were 20 mM and 0.5 bar, respectively at room temperature.

![Image of Fig. 11](image2.jpg)

**Fig. 11.** Effect of the MB concentration on the MB–SDS rejection for neat and mixed-matrix membranes. The SDS concentration and operating pressure were 20 mM and 0.5 bar at room temperature.

![Image of Fig. 12](image3.jpg)

**Fig. 12.** Schematic diagram of dye adsorption on (a) neat membrane and (b) mixed-matrix membrane.

![Image of Fig. 13](image4.jpg)

**Fig. 13.** The time-dependent permeation flux of the neat membrane during five cycles of cross-flow UF process.
ties, both membranes were subjected to pure MB fouling through cross-flow filtration. It was observed that the rate of permeation flux decline for MB filtration was higher during the initial 20 min and then became slower and approached plateau after 1 h. Fouling normally occurred at different stages as discussed earlier. Initially, the MB started to be adsorbed and accumulate on membrane pores and surface, leading to the reduction of membrane permeability due to the pore constriction. It was then forming a definite thickness of cake layer after certain period of filtration time which gradually decelerated the permeation flux and reached a constant flux.

After the flux reaching the constant, the membranes were rinsed by circulating pure water to remove loosely bound MB with and without UV light irradiation. The flux profiles were recorded and presented in Figs. 13 and 14. The flux recovery ratios (FRRs) were determined based on the following equation:

$$\text{FRR} = \frac{J_{\text{pw},t}}{J_{\text{pw},i}} \times 100\%$$

where $J_{\text{pw},t}$ is the pure water flux at any predetermined time and cleaning condition, $J_{\text{pw},i}$ is the initial pure water flux.

It was observed that the flux could be recovered through surface scoring by recirculating the pure water across the surface at 60 ml/min. The FRR value for neat membrane (94.19%) was slightly higher than that for mixed-matrix membrane (91.35%), indicating that the pore constriction is more serious for the bigger pores. The photosponse of the membranes was further tested under UV light irradiation. After subsequent cleaning by rinsing with pure water and UV light irradiation, further flux increment was observed for mixed-matrix membrane but not for the neat membrane. As shown in Figs. 13 and 14, the FRRs for neat membrane was maintained at 94.19% but for mixed-matrix membrane, a cascading increased of FRR to about 100% was achieved within 1 h of irradiation. This observation indicates that the embedded TiO$_2$ was photocatalytically active and able to degrade the adsorbed MB more effectively in the membrane.

In order to prove the better photodegradation ability of the mixed-matrix membrane, the time-dependent MB degradation by UV light irradiation on neat and mixed-matrix membranes were carried out through FTIR bonding cleavage observation. As illustrated in Fig. 15, it could be clearly seen that the (C=N) bonding (1599 cm$^{-1}$) on membrane could be scissor from aromatic ring in the MB structure by UV light irradiation. The disappearance of the C=N bonds in the MB adsorbed on the membrane as shown in Fig. 16 was used as an indicator for the degree of degradation. Fig. 17 shows the relative C=N absorbance value for the MB adsorbed on the membrane. If could be observed that rapid bonding cleavage occurred within 1 h of UV light irradiation with the higher rate of degradation for mixed-matrix membrane compared to that for the neat membrane. Being the primary oxidizing species in the photocatalytic oxidation process, a group of active oxidant reagents such as hydroxyl radical (OH$^-$) and superoxide radical anion (H$^-$) from TiO$_2$ NPs photocatalysed degradation process appeared on the surface of mixed-matrix membrane after UV light irradiation. The electron in the conduction band could be absorbed by the dye molecules, leading to the formation of a dye radical anion [32]. The subsequent reaction of the radical anion could lead to...
degradation and removal of the membrane foulant effectively as compared to neat membrane. On the other hand, the photocatalytic behavior of neat membrane was not a surprising phenomenon as the MB was light sensitive which also photosensitizer [33].

4. Conclusions

PVDF-TiO2 mixed-matrix UF membrane was prepared via phase inversion by dispersing TiO2 NPs into the PVDF matrix. Although the mixed-matrix membrane had some physical properties changes, the membranes hydrophilicity and subsequently permeation flux were greatly improved. The addition of TiO2, NPs also improved the permeability of membrane. The pure water permeabilities were 392.81 ± 3.12 and 31.72 ± 4.87 l/m² h bar for mixed-matrix and neat membrane, respectively. The produced mixed-matrix membrane with its adsorptive properties could be operated under pressure as low as 0.5 bar with the corresponding rejection exceeded 99% with the presence of SDS even below its CMC value. Performance of mixed-matrix membrane surpassed the neat membrane at higher MB concentration as NPs could provide extra adsorption sites for MB. It was proven that the mixed matrix membrane was photocatalytically active as it shows better MB degradation compared to the neat membrane with ~100% pure water flux recovery under 1 h of UV light irradiation.

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