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# Preparation of PVDF-TiO<sub>2</sub> mixed-matrix membrane and its evaluation on dye adsorption and UV-cleaning properties

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# HIGHLIGHTS

- The hydrophilicity of the mixedmatrix membrane was greatly
- 14 enhanced.
  15 Both standard blocking and cake
  16 filtration mechanisms took part in
- 17 the filtration.18 ► The mixed-matrix membrane has
- 19 significant self-cleaning properties.
- The mixed-matrix membrane could
   provide 100% flux recovery ratios.

#### G R A P H I C A L A B S T R A C T



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# In this study, th

ABSTRACT

In this study, the polyvinylidene fluoride (PVDF)-Titanium dioxide (TiO<sub>2</sub>) mixed-matrix membranes were prepared via phase inversion technique. The properties of PVDF-TiO<sub>2</sub> 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/m<sup>2</sup> h bar) compared to that 76.99 ± 4.87 l/m<sup>2</sup> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> NPs was photocatalytically active and able to degrade the adsorbed MB in the membrane. © 2012 Published by Elsevier B.V.

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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

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1385-8947/\$ - see front matter @ 2012 Published by Elsevier B.V. http://dx.doi.org/10.1016/j.cej.2012.05.050 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

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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 (TiO<sub>2</sub> 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 101 102 emerging alternative technology for wastewater treatment involv-103 ing reactive dyes such as methylene blue (MB). It has been demon-104 strated that organic contaminants can be oxidized to carbon 105 dioxide, water and simple mineral acids at low temperatures on 106 TiO<sub>2</sub> photocatalysts in the presence of UV or near-UV illumination 107 [17]. Lakshmi et al. [18], Tayade et al. [19], as well as Yu and Chu-108 ang [20] studied the photocatalytic oxidation of MB in aqueous 109  $TiO_2$  suspension. The use of  $TiO_2$  in suspension is a promising 110 method for MB photodegradation due to its large surface area of 111 TiO<sub>2</sub> available for the reaction. However, the TiO<sub>2</sub> NPs must be re-112 moved in the post-treatment process which requires a solid-liquid 113 separation stage, leading to higher overall operating cost in the process. Alternatively, TiO<sub>2</sub> NPs incorporation onto PVDF mem-114 brane matrix was carried out in this study to eliminate the need 115 116 of post-treatment.

Many research works had been carried out on the passive anti-117 118 fouling properties of mixed-matrix membrane by determining its 119 fouling rate based on protein adsorption. However, in the present 120 work, not only we observed the adsorption and sieving phenome-121 non of dye or micellar enhanced dye of the mixed-matrix mem-122 brane but for the first time, we provide a direct investigation on 123 the membrane UV-cleaning properties based on the photodegradation of dye adsorbed on the membrane surface. The performance of 124 mixed-matrix membranes was compared with that of neat mem-125 branes under similar operating conditions in order to evaluate its 126 127 flux recovery ratio (FRR) under ultraviolet (UV) light irradiation.

#### 128 **2. Materials and methods**

#### 129 2.1. Materials

Polyvinylidene fluoride (Solef<sup>®</sup> 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 TiO<sub>2</sub> NPs, PC-20 (20 nm) was purchased
from TitanPE Technologies, Inc., Shanghai. PVDF and TiO<sub>2</sub> 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

TiO<sub>2</sub> NPs (1.5 wt.%) was dispersed in the DMAc solvent under sonication for 15 min. The PVDF powder was then dissolved into the TiO<sub>2</sub> 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 then 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, <u>FU</u>). Subsequently, it was immediately immersed into the water bath of distilled water to allow the phase inversion to occur for 24 <u>h</u> 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,  $A_k$ , 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:

$$A_{k} = \frac{\frac{(w_{1}-w_{2})}{\rho_{b}}}{\frac{(w_{1}-w_{2})}{\rho_{b}} + \frac{w_{2}}{\rho_{a}}} \times 100\%$$
(1)

where  $A_k$  is the porosity of the membrane (%),  $w_1$  and  $w_2$  are the weights of the wet and dry membrane (g), respectively,  $\rho_p$  and  $\rho_b$  are the specific gravities of the PVDF polymer (1.78 g/cm<sup>3</sup>) and 2-butanol (0.81 g/cm<sup>3</sup>) (assuming that all materials kept their specify gravity constant in the wetted condition, and there was no air trap in the membrane pores), respectively. 2-Butanol a non-solvent for

Table 1	
The detail	of th

The detail	of the	membrane	synthesis	parameter	on	MEUF	process
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Membrane	PVDF (wt%)	DMA <sub>C</sub> (wt%)	TiO <sub>2</sub> (wt%)
Neat membrane	18	82	0
Mixed-matrix membrane	18	80.5	1.5

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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].

#### 190 2.3.3. Field emission scanning electron microscope

191 The cross-sectional morphologies of the neat and mixed-matrix membranes were observed under field emission scanning electron 192 193 microscope (FESEM CARL ZEISS SUPRA 35VP, Germany). The membranes were initially dried with a filter paper to remove the 194 195 remaining distilled water on the membrane surface, and air dried for FESEM observation. The membranes were immersed in liquid 196 197 nitrogen and fractured carefully to have a clean brittle fracture 198 for FESEM images. Membrane surface was coated with a thin layer 199 of gold under vacuum before being tested using K 550 sputter coat-200 er to provide electrical conductivity. The samples were examined under the FESEM at potentials of 10.0 kV at  $1000 \times$  image 201 202 magnifications.

#### 203 2.3.4. Adsorption study

204 The adsorption studies were carried out using a dead-end stirred cell (Amicon 8200, Millipore Co., USA) with a capacity of 205 200 ml, where the disc membrane has a diameter of 6 cm with a 206 207 geometric area of 28.27 cm<sup>2</sup> (excluding the area cover by the O-208 ring). The synthesized flat sheet membrane was cut into the disc 209 shape and laid on top of the membrane holder in a circular stirred 210 cell unit, thus covered and tightened with a rubber O-ring. The stir-211 ring speed was maintained at 200 rpm using the controllable magnetic hot plate stirrer and the operating temperature was  $27 \pm 2$  °C. 212 The adsorption efficiency was monitored continuous for 24 h by 213 collecting 2 ml of samples at every predetermined time. The de-214 sired concentration of MB-SDS in the feed solution and MB-SDS 215 samples concentration analysis were measured using a UV spectro-216 217 photometer (UV Mini-1240, Shimadzu) on the basis of measurement of color intensity at the maximum absorbance of 662 nm. 218

#### 219 2.3.5. Photodegradation experiment

The neat and mixed-matrix membrane after MB UF process 220 221 were cut into several small square coupons and mounted onto 222 glass slides using double-sided tape to ensure a flat membrane surface. The glass slides were immersed in a petri dish which was 223 224 filled with  $\sim$ 50 ml of distilled water to ensure the same water level 225 throughout the whole photodegradation experiment. The photodegradation ability of neat and mixed-matrix membrane were car-226 ried out using Ultra Violet A (UVA) light chamber with Tubular 227 228 low-pressure mercury vapor fluorescent lamps, UVA lamp (Actinic

BL TL-K 40W/10-R1SL, Philip) at light intensity of 2.5 ± 0.2 mW/m<sup>2</sup> measured using sensor monitor (Model 5.0 classic version, sglux).

The acquired fourier transform infrared spectroscopy (FTIR) 231 spectra were obtained from the neat and mixed-matrix membrane 232 233 surfaces using an FTIR spectroscopy (Thermo Scientific, Nicolet iS10, USA) to determine the extent of MB degradation. The FTIR 234 spectroscopy was equipped with an OMNI-Sample Attenuated To-235 tal Reflection (ATR) smart accessory with diamond crystal operated 236 at 45°. The membranes were scans at a resolution of  $4 \text{ cm}^{-1}_{\perp}$  within 237 wave number of  $\frac{4000-525}{100}$  cm<sup>-1</sup>. The changes of absorbance over 238 different reaction time were determined based on the wave num-239 ber of 1599 cm<sup>-1</sup> which indicated the C=N bonding. To minimize 240 experimental error, the FTIR spectra measurements were repeated 241 10 times for each sample at different point locations of membrane 242 and the results were then averaged. 243

#### 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 cm<sup>2</sup> (excluding the area covered by the O-ring). The applied pressure of the UF system was controlled by N<sub>2</sub> gas and the operating temperature was 27 ± 2 °C. The stirring speed was maintained at 200 rpm using a controllable magnetic hot plate stirrer (Heidoph 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:

$$I = \frac{V}{A\Delta t} \tag{2}$$

where  $V(m^3)$  is the volume of permeated water,  $A(m^2)$  is the membrane area, and  $\Delta t$  (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





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Fig. 2. Schematic diagram of cross-flow UF unit.

272 MB and MB with SDS were determined. The UF efficiency of the dye 273 removal from the feed solution was calculated using the following 274 275 equation:

$$R(\%) = \left[1 - \frac{C_p}{C_o}\right] \times 100\% \tag{3}$$

278 where  $C_p$  is the dye concentration in the permeate and  $C_0$  is the ini-279 tial 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 281

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The UV-cleaning experiments were carried out in a cross-flow 282 UF unit, where the disc membrane had a diameter of 4 cm with a 283 geometric area of 12.57 cm<sup>2</sup> (excluding the area covered by the 284 285 O-ring). The applied pressure of the filtration system was con-286 trolled by a needle valve to a constant pressure of 0.5 bar. The 287 operating temperature was  $27 \pm 2$  °C.

The desired MB concentration in the feed solution was achieved 288 289 by diluting the appropriate volume from a stock solution of 290 100 mg/l MB to a final volume of 1000 ml of 10 mg/l MB and intro-291 duced to the feed tank of the cross-flow UF unit. Feed pressure was 292 continually monitored to ensure that constant pressure was ap-293 plied throughout the experiments. The pure water and MB solution 294 were charged into a 2-L feed tank and re-circulated at a constant flow rate of 60 ml/min using a peristaltic pump (Materflex L/S Dig-295 ital Economy Drive, Model: 77800-60, Cole Parmer Instrument 296 297 Company). Permeate flow rate were continually recorded using 298 an electronic balance which was connected to a data acquisition 299 system (AND Super Hybrid Sensor, Model: Fx-3000i, A&D Com-300 pany, Limited). The permeate flux (1) was calculated using Eq. (2). 301 All the results presented were average data obtained from three 302 membrane samples. The schematic diagram of cross-flow UF unit 303 is shown in Fig. 2.

#### 3. Results and discussion 304

#### 3.1. Effect of operating pressure on membrane flux and rejection 305

306 The feed solutions consist of MB and SDS was subjected to the 307 UF process at the operating pressures of 0.2, 0.4, 0.6, 0.8 and 308 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 309 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  $76.99 \pm 4.87 \text{ l/m}^2 \text{ h bar,}$  whereas the MB-SDS permeabilities were 318  $138.43 \pm 4.25$  and  $31.72 \pm 3.12 \text{ l/m}^2$  h bar for mixed-matrix and 319 neat membranes, respectively. The higher pure water permeabi-320 lites of mixed-matrix membrane over the neat membrane perme-321 abilities could be attributed to the changes of membrane pore size. 322 Fig. 4 shows that mixed-matrix membrane had larger maximum 323 pore radius (45 nm) compared to the neat membrane (25 nm). It 324 could be further proved from the FESEM cross-sectional images 325 (Fig. 5) which revealed that larger inner pore size for mixed-matrix 326 membrane was observed as compared to that for neat membrane. 327 The membranes have the physical properties as listed in Table 2. 328

According to Hagen Poiseuille Equation, membrane flux could be predicted using the following equation:



Fig. 3. Effect of the operating pressure on membrane permeability for neat and mixed-matrix membranes for MB and SDS concentrations at 10 and 20 mM, respectively under room temperature

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Fig. 4. Pore size distributions of neat and mixed-matrix membranes.

$$Q_p = \frac{\Delta P \pi d_p^4}{128 \mu \Delta x}$$
(4)

334 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 335 336 membrane thickness (um) and u is the solution viscosity (Pa s).

337 By considering the pore size distribution, the total flux could be expressed as 338

$$J = \frac{\sum N_i Q_p}{\sum N_i \pi d_p^2 / 4} \tag{5}$$

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$$J = \frac{\sum N_i \Delta P \pi d_p^4 / (128\mu\Delta x)}{\sum N_i \pi d_p^2 / 4} = \frac{A_k \Delta P}{32\mu\Delta x} \frac{\sum N_i d_p^4}{\sum N_i d_p^2}$$

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$$J = \frac{A_k \Delta P}{32\mu \Delta x} \frac{\sum N_i d_p^4}{\sum N_i d_p^2} = \frac{A_k \Delta P}{32\mu \Delta x} \frac{\sum f_i N d_p^4}{\sum f_i N d_p^2} = \frac{A_k \Delta P}{32\mu \Delta x} \frac{\sum f_i d_p^4}{\sum f_i d_p^2}$$

where J is the volumetric flux ( $1/h m^2$ ),  $A_k$  is the membrane porosity, 348  $\overline{N}_i$  is the number of pores having diameter of  $d_{p,i}$ ,  $f_i$  is the fraction of 349 350 the number of pores with diameter  $d_{p,i}$  and N is the total number of 351 pores.

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

$$\frac{J_{MM}}{J_{NE}} = \frac{(A_k)_{MM}}{(A_k)_{NE}} \frac{(\Delta x)_{NE}}{(\Delta x)_{MM}} \frac{(\sum f_i d_p^4)_{MM}}{(\sum f_i d_p^4)_{NE}} \frac{(\sum f_i d_p^2)_{NE}}{(\sum f_i d_p^2)_{MM}}$$
(8)

Table 2

Physical properties of the neat and mixed-matrix membranes.

Membrane characteristics	Neat membrane	Mixed-matrix membrane
Maximum pore radius $(r_p)$ , nm Pure water permeability $(J_v/\Delta P)$ , l/ m <sup>2</sup> h bar	25 76.99 ± 4.87	45 392.81 ± 10.93
Porosity ( $A_k$ ), % Thickness ( $\Delta x$ ), $\mu$ m	64.53 ± 0.07 117 ± 0.85	65.13 ± 0.05 110 ± 0.33

The subscript *MM* represents mixed-matrix membrane whereas the subscript NE represents neat membrane.

The theoretical flux ratio  $(I_{V,MM}/I_{V,NE})$  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<sub>2</sub> NPs. TiO<sub>2</sub> 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<sub>2</sub> composite membrane could be more hydrophilic than neat polymeric membrane due to the higher affinity of TiO<sub>2</sub> 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.



Fig. 6. Effect of the operating pressure on the MB-SDS rejection for neat and mixedmatrix membranes.



(6)

7)

Fig. 5. Cross-section of: (a) neat, (b) mixed-matrix UF membranes.

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374 For mixed-matrix membrane, MB-SDS rejection decreased slightly 375 with the increase of operating pressure, ranging from 99.71% at 376 0.2 bar to 96.09% at 1.0 bar, respectively. These data provided us 377 the important information regarding the maximum operating pressure that can be used for such systems. It can also be observed 378 in Fig. 6 that the optimum operating pressure for such systems was 379 380 found to be 0.5 bar and the corresponding rejections for neat and 381 mixed-matrix membrane exceeded 99%.

It is not surprising that the rejection capability of mixed-matrix 382 membrane decreased compared to that of the neat membrane at 383 higher pressure as mixed matrix-membrane had larger pore size. 384 At higher operating pressure, the higher pore to solute ratio of 385 mixed-matrix membrane allowed the convective transport of sol-386 utes through the membrane [27]. Moreover, higher operating pres-387 388 sure also resulted in micelles compaction that enabled the micelle 389 to squeeze through the membrane pores [6]. Ahmad and Puasa 390 [23] also observed the same phenomenon as the operating pressure increased, the micellar enhanced dye rejection would de-391 crease accordingly. Besides, a compacted micelle would reduce 392 the dye solubility which led to less amount of dye removed. 393

#### 394 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 applied, 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].

400 Fig. 7 shows the effect of SDS concentration on the flux of neat and mixed-matrix membrane. It was found that the permeate 401 fluxes for both neat and mixed-matrix membrane decreased as 402 403 the SDS concentration increased. Zaghbani et al. [29] reported 404 the phenomenon of flux reduction at higher SDS concentration is 405 generally attributed to the effects of membrane fouling and concentration polarization. Concentration polarization which was 406 caused by deposition of SDS micelles on the membrane surface 407 led to the increased solution mass transfer resistance. Beyond the 408 solubility limit, the micelles deposited on membrane surface 409 410 would build up gel type layer and caused pores blockage. Besides, higher SDS concentration formed small and compact micelles as 411 412 reported by Fang et al. whereby the small and compact micelles 413 might plug the membrane pores easily as compared to large and 414 incompact micelles which only deposited on membrane surface 415 [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,

□ Neat Membrane ■Mixed-matrix Membrane

**Fig. 7.** Effect of the SDS concentration on MB–SDS flux for neat membrane and mixed-matrix membranes. MB concentration and operating pressure were 10 mg/L and 0.5 bar, respectively at room temperature.



**Fig. 8.** Effect of the SDS concentration on MB–SDS rejection for neat and mixedmatrix membranes. The MB concentration and operating pressure were 10 mg/L and 0.5 bar, respectively at room temperature.

respectively. Beyond 1.0 CMC (8 mM), a higher reduction in flux was observed for mixed-matrix membrane, indicating that micelles formation greatly provided higher resistance to permeate flow through cake layer formation. However, its effect on the neat membrane was slightly lesser due to the larger micelle to pore ratio (0.04) compared to that (0.02) for the mixed matrix membrane. 424

Fig. 8 shows the effect of SDS concentration in the feed solution 425 on membrane rejection. Without the SDS, there were about 45% 426 and 22% of MB rejections for neat membrane and mixed-matrix 427 membrane, respectively. Under SDS free condition, it was unlikely 428 that the better rejection of neat membrane could be attributed to 429 its smaller pore size as both had relatively very small solute to pore 430 size ratio. Adsorption is the most possible mechanism for dye re-431 moval as it could be noticed from the rapid presence of blue stain 432 on the membrane surface which was difficult to be cleaned. In or-433 der to prove that, dye adsorption study was carried out using the 434 same stirred cell without applying pressure. The adsorption profile 435 of MB-SDS in similar conditions (membranes with 0.06 m diame-436 ter immersed in 200 ml of MB-SDS solution of 10 mg/l MB and 437 20 mM SDS at room temperature) were measured for both neat 438 and mixed-matrix membrane. Fig. 9 shows that complete adsorp-439 tion could be achieved within 30 h for both membranes. Mixed-440 matrix membranes had higher rate of adsorption compared to 441 the neat membrane, mainly due to the highly connected pore 442



Fig. 9. Rate of adsorption of MB-SDS for neat and mixed-matrix membranes.

Please cite this article in press as: H.P. Ngang et al., Preparation of PVDF-TiO<sub>2</sub> mixed-matrix membrane and its evaluation on dye adsorption and UV-cleaning properties, Chem. Eng. J. (2012), http://dx.doi.org/10.1016/j.cej.2012.05.050 structure which make the PVDF sites more accessible to the dyeadsorption though diffusion.

445 Fig. 8 reviews that the rejections for both membranes were 446 sharply increased to nearly 100% when SDS was added into the feed solution, a phenomenon also observed by Huang et al. [8] 447 and Zaghbani et al. [29]. The reasons of this phenomenon might 448 be due to (i) concentration polarization effect and cake layer for-449 mation, (ii) precipitation of MB with small amount of SDS surfac-450 tant, and (iii) direct adsorption of MB on membrane surface and 451 pores as discussed earlier. Theoretically, there was almost negligi-452 ble micelle formed at the SDS concentration below 1.0 CMC, how-453 ever, as concentration polarization occurred on the membrane 454 surface, the concentration of SDS might exceed 1 CMC and resulted 455 in micelle formation. For reason (ii), as reported by Misra et al. [31], 456 457 for MB feed solution with SDS below 1.0 CMC, MB could be rejected 458 by precipitation with a small amount of SDS molecules. Lastly, the direct adsorption of MB onto the TiO<sub>2</sub> surface could be enhanced as 459 SDS could reduce the surface tension between the solution and 460 constricted pore size which created more accessible adsorption 461 sites. As a result, the rejections of both membranes were improved 462 463 drastically.

#### 464 3.3. Effect of methylene blue concentration

The SDS concentration in the feed solution was fixed at 20 mM 465 [29] and an operating pressure of 0.5 bar was applied to observe 466 the effect of MB concentration on the permeate flux and rejection. 467 The experiments were carried out by varying the MB concentration 468 at 10, 50 and 100 mg/l. Fig. 10 shows the effect of MB concentra-469 470 tion on permeate fluxes of neat and mixed-matrix membranes. 471 The permeate fluxes decreased as the MB concentration increased, where increasing 10 times in MB concentration had reduced the 472 473 flux as much as 20.3% and 7.5% for neat and mixed-matrix mem-474 branes, respectively. However, compared to the effect of SDS, 475 membrane fouling contributed by the amphiphilic SDS concentration is more significant. The reduction in permeate flux was at 476 higher MB concentration is due to the buildup of free MB adsorp-477 tion onto the membrane surface which formed the deposit layer 478 479 near the membrane surface, and eventually building up additional 480 resistance for permeate to pass through the membrane. Huang 481 et al. [8] also found that the permeate flux decreased as the feed 482 MB concentration increased. The higher fouling rate of neat mem-483 brane compared to that of the mixed-matrix membrane was 484 mainly caused by the previously postulated reason in which MB 485 is more favorable to adsorbed on the PVDF matrix than TiO<sub>2</sub>.

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.



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



□Neat Membrane ■Mixed-matrix Membrane

**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.



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

This result could be due to the complete coverage of adsorption 489 site onto membrane surface at higher MB concentrations, leading 490 to the decreasing of MB-SDS rejection. The rejection for neat and 491 mixed-matrix membranes were reduced as much as 20% and 492 13.6%, respectively when the MB concentrations were increased 493 from 10 to 100 mg/l. At high MB concentrations, mixed-matrix 494 membrane showed better rejection compared to neat membrane, 495 suggesting that mixed-matrix membrane provided more accessible 496 adsorption sites compared to the neat membrane as illustrated in 497 Fig. 12. 498

#### 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-





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Fig. 14. The time-dependent permeation flux of the mixed-matrix membrane during five cycles of cross-flow UF process.

508 ties, both membranes were subjected to pure MB fouling through 509 cross-flow filtration. It were observed that the rate of permeation 510 flux decline for MB filtration was higher during the initial 20 min 511 and then became slower and approached plateau after 1 h. Fouling normally occurred at different stages as discussed earlier. Initially, 512 the MB started to be adsorbed and accumulate on membrane pores 513 and surface, leading to the reduction of membrane permeability 514 due to the pore constriction. It was then forming a definite thick-515 ness of cake layer after certain period of filtration time which grad-516 ually decelerated the permeation flux and reached a constant flux. 517

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:

525 
$$FRR = \frac{J_{w,t}}{J_{w,i}} \times 100\%$$

526 where  $J_{w,t}$  is the pure water flux at any predetermined time and cleaning condition,  $I_{wi}$  is the initial pure water flux. 527

It was observed that the flux could be recovered through sur-528 529 face scoring by recirculating the pure water across the surface at 60 ml/min. The FRR value for neat membrane (94.19%) was slightly 530 higher than that for mixed-matrix membrane (91.35%), indicating 531 that the pore constriction is more serious for the bigger pores. 532 533 The photoresponse of the membranes was further tested under UV light irradiation. After subsequent cleaning by rinsing with 534 535 pure water and UV light irradiation, further flux increment was ob-536 served for mixed-matrix membrane but not for the neat membrane. As shown in Figs. 13 and 14, the FRRs for neat membrane 537 was maintained at 94.19% but for mixed-matrix membrane, a cas-538 539 cading increased of FRR to about 100% was achieved within 1 h of 540 irradiation. This observation indicates that the embedded  $TiO_2$  was photocatalytically active and able to degrade the adsorbed MB 541 more effectively in the membrane. 542

In order to prove the better photodegradation ability of the 543 mixed-matrix membrane, the time-dependent MB degradation 544 by UV light irradiation on neat and mixed-matrix membranes were 545 546 carried out through FTIR bonding cleavage observation. As illustrated in Fig. 15, it could be clearly seen that the (C=N) bonding 547 (1599 cm<sup>-1</sup>) on membrane could be scissor from aromatic ring in 548 the MB structure by UV light irradiation. The disappearance of 549 the C=N bonds in the MB adsorbed on the membrane as shown 550 in Fig. 16 was used as an indicator for the degree of degradation. 551 Fig. 17 shows the relative C=N absorbance value for the MB ad-552 553 sorbed on the membrane. If could be observed that rapid bonding 554 cleavage occurred within 1 h of UV light irradiation with the higher 555 rate of degradation for mixed-matrix membrane compared to that



Fig. 15. Photocatalytic degradation pathway of the MB [34].



Fig. 16. Effect of UV light irradiation time interval during C=N bond scission for MB molecules degradation



Fig. 17. The time-dependent MB degradation by UV light treatment for neat and mixed-matrix membranes.

for the neat membrane. Being the primary oxidizing species in the 556 photocatalytic oxidation process, a group of active oxidant reagents such as hydroxyl radical (OH<sup>•</sup>) and superoxide radical anion  $(H^{+})$  from TiO<sub>2</sub> 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 563

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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].

#### 568 4. Conclusions

569 PVDF-TiO<sub>2</sub> mixed-matrix UF membrane was prepared via phase inversion by dispersing TiO<sub>2</sub> NPs into the PVDF matrix. Although 570 the mixed-matrix membrane had some physical properties 571 changes, the membranes hydrophilicity and subsequently perme-572 573 ation flux were greatly improved. The addition of TiO<sub>2</sub> NPs also im-574 proved the permeability of membrane. The pure water permeabilities were  $392.81 \pm 10.93$  and  $76.99 \pm 4.87 \text{ l/m}^2 \text{ h bar}$ , 575 whereas the MB-SDS permeabilities were  $138.43 \pm 4.25$  and 576  $31.72 \pm 3.12 \, l/m^2 \, h$  bar for mixed-matrix and neat membrane, 577 578 respectively. The produced mixed-matrix membrane with its 579 adsorptive properties could be operated under pressure as low as 580 0.5 bar with the corresponding rejection exceeded 99% with the presence of SDS even below its CMC value. Performance of 581 582 mixed-matrix membrane surpassed the neat membrane at higher MB concentration as NPs could provide extra adsorption sites for 583 the MB. It was proven that the mixed matrix membrane is photo-584 catalytically active as it shows better MB degradation compared to 585 the neat membrane with  $\sim 100\%$  pure water flux recovery under 586 587 1 h of UV light irradiation.

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