

# Mixed-Matrix Membrane for Humic Acid Removal: Influence of Different Types of TiO<sub>2</sub> on Membrane Morphology and Performance

Y. H. Teow, B. S. Ooi, A. L. Ahmad, and J. K. Lim

**Abstract**—Different types of titanium dioxide (TiO<sub>2</sub>) nanoparticles (NPs) (PC-20, P25 and X500), with various particle sizes in coagulation bath were incorporated as an nanofiller into membrane matrix. The NPs were added to the polyvinylidene (PVDF) ultrafiltration (UF) membranes via phase inversion and colloidal precipitation method. A series of test, such as surface field emission scanning electron microscopy (FESEM) images, energy-dispersive X-ray spectroscopy (EDX) mapping and pore size measurement were performed to characterize the modified mixed-matrix membranes. FESEM was applied to observe the distribution pattern of TiO<sub>2</sub> NPs in the membrane matrix and its distribution was examined using (EDX). The size and distribution of TiO<sub>2</sub> NPs on the membrane surface was affected to a very great extent by the size of TiO<sub>2</sub> prepared in the coagulation bath. Conversely, the presence of TiO<sub>2</sub> on membrane surface does not provide any significant changes on the membrane pore size distribution, suggesting that in situ precipitation method is suitable to prepare mixed-matrix membrane without scarifying the membrane rejection ability. The performance of the UF membranes fabricated from the nano-sized TiO<sub>2</sub> particles were evaluated by measuring the membrane permeates flux and humic acid (HA) rejection. The experiment demonstrated that the flux improvements of the membranes were improved due to the pore enlargement (defect) as well as increasing membrane hydrophilicity. The flux of the mixed-matrix membrane prepared by adding X500 nanofiller was the greatest (44.06 L/m<sup>2</sup> h), which was determine as the optimum TiO<sub>2</sub> type without scarified the membrane rejection (98.44%) compared to PC-20 and P25. This is due to the relatively small size of X500 which provides better dispersibility in the membrane matrix whereby flux was enhanced due to improve of hydrophilicity without the expense of poor humic acid rejection.

**Index Terms**—Hydrophilicity, colloidal precipitation method, mixed-matrix membrane, ultrafiltration

## I. INTRODUCTION

Attributed to its unique large surface-to-volume ratio and strong reactivity properties, nano-sized colloidal particles have extended their advance applications into membrane technologies for two major purposes. One of the purposes is to produce membrane with desirable structure due to the

particles interaction with polymer chains and/or solvent during membrane preparation [1]. The other aim is to improve the synergetic effects on water and wastewater treatment due to improved hydrophilic properties [2], [3]. These structural modifications have been proven and reported by many researcher such as Li *et al.* (2007), Kim *et al.* (2003), Kim and Bruggen (2010) and Razjou *et al.* (2011) that favor a higher selectivity and permeability in water separation and satisfactory performance in ultrafiltration (UF) and nanofiltration (NF) membranes [4]-[7].

Among metal oxide nanoparticles (NPs), titanium dioxide (TiO<sub>2</sub>) with photocatalytic and desirable hydrophilic properties emerges as a highly promising candidate to be incorporated into polymeric matrix [8], [9]. In recent years, TiO<sub>2</sub> nano-inorganic mixed matrix membranes have attracted great research interests to provide a solution to the trade-off problem faced by the polymeric membranes in water separation [10]-[12] and to improve the membrane performance by increasing hydrophilicity [4], [5], [13], [14]. Two common technical innovations in mixed matrix membranes production have been carried out: assembling NPs on the surface of the porous membranes [5], [13], [15], [16] or blending NPs into the polymeric casting solution [5], [16]-[19]. However, the high surface energy of TiO<sub>2</sub> NPs added in the casting solution often results in poor NPs distribution in the membrane matrix through entrapment of TiO<sub>2</sub> NPs in a polymer matrix of membrane. The poor distribution is due to the poor mixing or shearing of the polymer solution as well as low stability of the colloid; leading to low functional surface area, which is a conspicuous drawback for application. Therefore, for feasible application, the preparation of size-controlled, monodispersed NPs is of primary importance.

In the present work, mixed-matrix polyvinylidene fluoride (PVDF/TiO<sub>2</sub>) membrane was prepared via in situ colloidal precipitation method. Mechanical and chemical approaches were applied for TiO<sub>2</sub> modification to increase homogeneity in dispersion, reduce agglomeration, improve stability of TiO<sub>2</sub> NPs and enhance the nanofiller-polymer interaction. The aim of the current work is to investigate the effect of sizes and types of TiO<sub>2</sub> NPs on the membrane hydrophilicity enhancement and structure of the TiO<sub>2</sub> embedded PVDF UF membrane prepared by in situ colloidal precipitation method. Three different sizes (from 8 nm to 21 nm) and types (PC-20, P25 and X500) of TiO<sub>2</sub> NPs were used. The influence of dispersing TiO<sub>2</sub> NPs on membrane properties was examined based on surface morphology, membrane permeability and humic acid (HA) rejection.

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The authors are with the School of Chemical Engineering, Universiti Sains Malaysia, Penang, Malaysia (e-mail: yeithaan@hotmail.com, chobs@eng.usm.my, chlatif@eng.usm.my, chjtkangl@eng.usm.my).

## II. MATERIALS AND METHODS

### A. Materials

Polyvinylidene fluoride (PVDF) (TA6010/1001, Solvay Plastics, Inc., USA) ultrafiltration flat sheet membranes were fabricated by casting the PVDF in N-N-dimethylacetamide, DMAc (Merck, Germany) (Assay (GC, area %)  $\geq$  99%) solution at 200  $\mu\text{m}$  thickness. Three different types of commercial titanium dioxide,  $\text{TiO}_2$  nanopowder were purchased from TitanPE Technologies, Inc., China (trade name: PC-20 and X500) and Sigma-Aldrich, St. Louis, MO, USA (trade name: P25). The characteristics of these nanoparticles (NPs) are presented in Table 1. Synthetic HA with molecular weight mainly ranging from 20,000 to 50,000 was obtained from Sigma-Aldrich and used as the organic foulant during the experiment without further purification. Sodium hydroxide, NaOH solution was used to improve the dissolution of HA in water. For permeation test, feed solutions were prepared by dissolving a pre-weighed 20 mg of HA powder in 1L of distilled water under vigorous stirring and the solution pH was adjusted to pH 10 by addition of a small quantity of 0.1 M NaOH.

TABLE I: CHARACTERISTICS OF THE USED  $\text{TiO}_2$  NANOPOWDER

$\text{TiO}_2$ Samples	Crystalline phase	Average crystalline size (nm)	Average size in suspension (nm)
PC-20	75% Anatase 25% Rutile	20	461.3
P25	80% Anatase 20% Rutile	~21	200
X500	Anatase	< 8	38

### B. Preparation of Stable $\text{TiO}_2$ Suspension

Chemical and mechanical methods were carried out to enhance the  $\text{TiO}_2$  colloidal stability in the coagulation bath as described below.

*Chemical method.* Firstly, in order to increase the stability of the  $\text{TiO}_2$  NPs in distilled water, the chemical modification of the original  $\text{TiO}_2$  nanopowder was carried out by adjusting the pH value of the  $\text{TiO}_2$  suspension. Hydrochloride acid solution (HCl) was added drop-wise and mechanically stirred until it reaches an equilibrium of pH 4.0 to achieve electrostatic stability (zeta potential  $> +30\text{mV}$ ). The pH value of the  $\text{TiO}_2$  suspensions was measured using a pH meter (Eutech Instruments).

*Mechanical method.* The  $\text{TiO}_2$  cluster was further broken down by subjecting the  $\text{TiO}_2$  solution to 15 min ultrasonic irradiation using Telsonic ultrasonic horn (SG-24-500P, Telsonic Ultrasonics). Frequency of the ultrasound was kept constant at 18.4 kHz.

### C. Membrane Formation and in Situ Particle Embedment

The membrane casting solutions were prepared by dissolving pre-dried PVDF (24 h of oven drying at  $70^\circ\text{C}$ ) using the polymer solvents; DMAc in a 200 mL beaker. Composition of the PVDF/DMAc was kept constant at 18:82 in weight percentage.

In order to obtain complete dissolution and optimal dispersion of the polymer solution, the mixture was subjected to an initial constant stirring of 250 rpm at  $65^\circ\text{C}$  for 4 hours to form a homogenous solution. The homogenous membrane

polymer solution was then left overnight under stirring at  $40^\circ\text{C}$ . The trapped air bubbles were removed by standing the solution overnight. Solvent loss by evaporation was negligible due to the high boiling point of DMAc (164-166  $^\circ\text{C}$ ).

The polymer solution was cast using a thin film applicator (Elcometer 4340, Elcometer (Asia) Pte. Ltd.) on a flat glass plate wrapped with non-woven polyester fabric (Holleytex 3329, Ahlstrom) to form a solution layer at nominal thickness of 200  $\mu\text{m}$ . The polyester fabric acts as membrane support layer, providing mechanical strength to the membrane for pressure resistance. The nascent membrane on the glass plate was then solidified by immediate immersion into a coagulation bath at room temperature ( $26^\circ\text{C}$ ) to avoid excessive surface evaporation. The immersion was left for a day to ensure complete solidification and removal of residual solvent from the membranes. The fabricated membrane was then recovered from the coagulation bath after detaching it from the glass plate and subsequently rinsed with and soaked in a bath of fresh distilled water. Drying was sequentially done after dipping the membrane in ethanol to avoid microbial growth.

In order to introduce  $\text{TiO}_2$  NPs onto the membrane surface, PVDF solution layers were immersed into the coagulation bath with 0.1 g/L of  $\text{TiO}_2$  colloidal suspension as prepared by using the method stated in Section II B. Since the membrane surface solidification and NPs embedment occur simultaneously, this NPs incorporation method is an in situ approach to embed NPs onto the membrane surface.

### D. Membrane Characterization

In order to probe the top surfaces morphology and examine the composition of the PVDF/ $\text{TiO}_2$  mixed-matrix membranes, field emission scanning electron microscope (FESEM) and energy dispersive X-ray (EDX) were performed using a SUPRA 35 VP, Carl Zesis Inc. The membrane samples were cut into an appropriate size and mounted on the sample holders. K 550 sputter coater was used to coat the outer surface of the membrane sample with a thin layer of gold under vacuum to provide electrical conductivity. After gold sputtering, the samples were examined under the electron microscope at a 10.0 kV potentials.

The membranes pore size was determined using gas flow/liquid displacement method via Capillary Flow Porometer Porolux 1000 (Benelux Scientific, Germany). Membrane samples with a 10mm diameter were characterized using the "dry up-wet up" method. In this method, gas flow was measured as a function of transmembrane pressure, initially through wetting of membrane with 1, 1, 2, 3, 3, 3-haxafluoropropene followed by dry flow of gas through the membrane. The pore size distribution was estimated using PMI software (Benelux Scientific, Germany).

### E. Permeation Flux and Rejection of Membranes

A laboratory bench scale cross-flow recirculation unit was used to study permeation flux and rejection of the mixed-matrix membrane using 20 mg/L HA as model solution at ambient temperature ( $25^\circ\text{C}$ ). The produced flat sheet membrane was cut into the disc shape and laid on top of

the membrane holder in a designed stainless steel circular membrane test cell with a diameter of 5.1 cm (effective membrane filtration area of 20.43 cm<sup>2</sup>) and sealed with a rubber O-ring. Synthetic HA solution was charged into a 5L feed tank and re-circulated at a constant cross-flow rate of 0.04 L/min using the peristaltic pump (Hydra-Cell, Wanner International). Filtration pressure was controlled by a needle valve to 0.5 bar. Absorbance of the collected permeates was measured using UV spectrophotometer (UV mini-1240, Shimadzu) at wavelength of 254 nm.

Pure water flux was determined by direct measurement of the permeate volume over time,

$$F = \frac{V}{At} \quad (1)$$

where  $F$  is the pure water flux (L/m<sup>2</sup> h),  $V$  is the permeate volume (L),  $A$  is the membrane effective surface area (m<sup>2</sup>), and  $t$  is the permeation time (h).

Experimental rejection of solute ( $R$ ) was calculated from the feed solution (HA solution) and permeate solution using the following equation:

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

where  $R$  is the rejection ultrafiltration process (%),  $C_p$  is the concentration of the permeate solution and  $C_f$  is the concentration of the feed solution.

### III. RESULTS AND DISCUSSIONS

#### A. Morphologies of PVDF/TiO<sub>2</sub> Mixed-Matrix Membrane

Fig. 1(a) shows the SEM top surface images of PVDF/TiO<sub>2</sub> mixed-matrix membranes immersed in colloidal suspension of different TiO<sub>2</sub> type at concentration of 0.1 g/L. As could be seen from the Fig. 1(a) with 5.00 k $\times$  of magnification, connected pores appeared on the surface of all PVDF membrane using DMAc as solvent.

The presence of TiO<sub>2</sub> Nps in the membrane structure was further confirmed by energy-dispersive X-ray spectrometer (EDX) mapping. Sizes of TiO<sub>2</sub> NPs distributed on the PVDF/TiO<sub>2</sub> mixed-matrix membrane were observed and the results are presented in Fig. 1(b). It could be clearly seen that membrane using X500 (which is the smallest size TiO<sub>2</sub>) as hydrophilic filler was able to disperse uniformly into the membrane matrix compared to the membrane prepared by PC-20 and P25. The lesser degree of TiO<sub>2</sub> clustering for membrane prepared using X500 is probably due to the higher thermodynamic stability of X500 in coagulation bath system when it was brought into contact with the solvent and polymer which agrees well with the theory proposed by Mackay et al. [20]. Mackay et al. found that the dispersion of NPs into a polymeric liquid is thermodynamically stable for systems where the radius of gyration ( $R_g$ ) of the linear polymer is greater than the radius of the NPs ( $R_p$ ) [20]. In this case, different TiO<sub>2</sub> most likely affect the thermodynamic stability of the system. The relation between the root-mean

square radius of gyration of the chain in DMAc and the molecular weight obtained by Ali and Raina [21] using the theory of Inagaki et al. [22], was  $\langle S^2 \rangle = 2.95 \times 10^{-1} M_w^{0.55}$ ,  $R_g/R_p$  ratio for PC-20, P25 and X500 are 1:14, 1:6 and 1:1 respectively. X500 which contributes to greater  $R_g/R_p$  ratio compared to PC-20 and P25 has better thermodynamic stability. This result is consistent with Bagchi [23] who found that when particles exhibit robust stabilization, such as repelling each other sterically and providing thermodynamic stability, the particles do not cluster. So, it is not surprising to observe that PC-20 and P25 with much bigger average particle sizes (5-12 times bigger than X500) in water suspension induced an aggregate of TiO<sub>2</sub> particles adsorbing or embedding on the surface of PVDF/TiO<sub>2</sub> mixed-matrix membranes during the phase inversion. For mixed-matrix membranes prepared from PC-20 and P25, the tendency to promote the particle clustering gave a relative poor particle size distribution whereby the TiO<sub>2</sub> particles deposited on the surface exist in different sizes of snowflakes. TiO<sub>2</sub> cluster blocked the pores therefore decreasing the microporosity of the PVDF membranes. In general, the type of TiO<sub>2</sub> has a profound effect on the distributions of TiO<sub>2</sub> but it has very slight effect on the membrane structure.

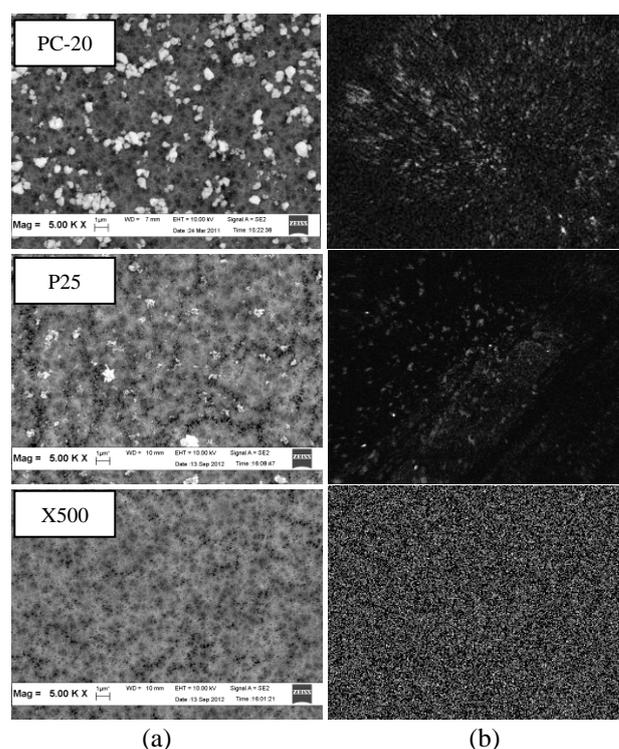


Fig. 1. The surface (a) FESEM micrographs and (b) EDX mapping of PVDF/TiO<sub>2</sub> mixed-matrix membrane.

#### B. Pore Size Distribution

Pore size distributions of the neat and PVDF/TiO<sub>2</sub> mixed-matrix membrane were shown in Fig. 2. As can be seen from Fig. 2, all the membranes prepared had quite similar pore size distributions. The maximum diameter of pore,  $d_{p,max}$  for the neat membrane was around 0.05  $\mu$ m while for membrane prepared using PC-20, P25 and X500 were around 0.042  $\mu$ m, 0.061  $\mu$ m and 0.028  $\mu$ m, respectively.

Result showed that the addition of P25 into the membrane polymeric matrix enlarged the pores slightly. The pore

enlargement is probably due to increase of the stress between polymer and TiO<sub>2</sub> Nps, resulted from the organic shrinkage that occurred during the precipitation process of wet-casting polymeric membranes. On the other hand, for membranes prepared using PC-20 and X500 as hydrophilic filler, it has a tendency to reduce its pore size. For X500, due to its smaller NPs size, it provides the seeding effect which induced the early vitrification of the polymer [24]. Followed by solidification, smaller pore size on the surface was observed. Nonetheless, it could not be denied that pore narrowing of mixed-matrix membrane prepared by X500 occurred too. Due to the relatively small particle size of X500, pore blocking is likely to happen. On the other hand, membrane prepared by PC-20 shows stringer evidence of pore blocking due to the precipitation of NPs on the pore wall which further reduced the pore size. These results were similar with what was observed by Damodar *et al.* who found that the number of small-sized pores increase with increasing TiO<sub>2</sub> content [25].

In overall, the changes of membrane pore size were not significant as compared to its particle size distribution using colloidal precipitation method. This indicated that colloidal precipitation method is an ideal method to prepare membrane with minimum changes to its physical properties.

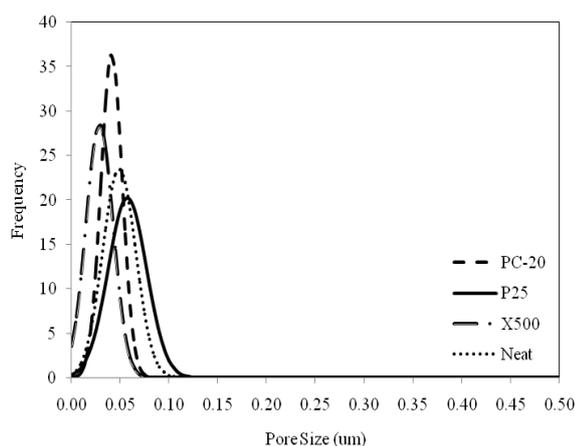


Fig. 2. Pore size distribution of the PVDF/TiO<sub>2</sub> mixed matrix membrane and neat membrane.

### C. Permeation Flux and Rejection of Membranes

The effect of different types of TiO<sub>2</sub> on mixed-matrix membrane permeability flux and rejection of HA were investigated through cross-flow membrane filtration experiments. The membrane performances were summarized in Table 2. All the presented membrane permeability and rejection of HA results were obtained using the average of three replications with the membrane tested which was randomly chosen from different independent sheets.

The effect of membrane morphology and hydrophilization on PVDF/TiO<sub>2</sub> mixed-matrix membranes can be evaluated by the performance of HA solution flux (F). Comparing HA permeation of the neat PVDF membrane and the PVDF/TiO<sub>2</sub> mixed-matrix membrane using PC-20, P25 and X500 as hydrophilic filler, which were labeled as M1, M2, M3 and M4 respectively, the PVDF/TiO<sub>2</sub> mixed-matrix membrane always have higher fluxes in comparison with the neat membrane. This result coincides with experimental results by

Luo *et al.*, (2005) which demonstrated that the flux and retention of the TiO<sub>2</sub> composite membrane increased greatly from 70.2 L/m<sup>2</sup> h to 102.9 L/m<sup>2</sup> h and from 21.9% to 34.5% respectively as compared to the neat UF poly(ether sulfone), PES membrane for polyethylene glycol-5000 separation [12]. Additionally, according to Bae *et al.* (2006), it was clear that the initial sharp drop of flux observed for PES polymeric membrane during MBR sludge filtration was alleviated by TiO<sub>2</sub> immobilization whereby the TiO<sub>2</sub> nanocomposite membrane maintained a higher stabilized relative flux (36% of the initial flux) than that of the PES membrane (20% of the initial flux) [26].

It was proposed that the enhanced permeability of mixed-matrix membranes was due to the increasing porosity of the membrane that was resulted from the reduced polymer chain packing by the nanofillers [27],[28]. Table 2 demonstrated that X500 with the best particle distribution contribute to the most excellent result in increasing membrane permeability compared to the other membrane. The flux increased dramatically from 34.97 L/m<sup>2</sup>·h to 45.36 L/m<sup>2</sup>·h with improved HA rejection. These improvements are due to the pore narrowing as well as improved hydrophilicity of the membrane as suggested previously. A homogeneous particle dispersion offers a larger surface area of NPs which leads to adsorption of more water molecules that are located on the surface of the membrane [29]. On the other hand, the permeability of PC-20 and P25 membranes increased with the compensation of decreasing rejection capability. This phenomenon can be explained by considering the aggregation of PC-20 and P25 in water suspension which blocks the membrane pores. However, this phenomenon deviates from work reported by Shawky *et al.* (2011) in which the incorporation of multi-wall carbon nanotube (MWCNT) into the 10% aromatic polyamide (PA) nanocomposite membrane had increased the HA removal by 54 to 90% with a small sacrifice in the permeate flux; mainly due to the structural compactness of the composite membranes resulted from the strong interaction between MWCNTs and PA matrix which suggests a network structure [30]. The poor thermodynamic stability between the NPs and the polymer enabled the removal of NPs from the surface and resulted in the defect of the membrane structure. This result was proven by the increased flux but reduced rejection capability phenomenon. Additionally, the membrane permeability for the membrane using PC-20 and P25 was slightly decreased compared to the membrane using X500. This phenomenon can be explained by the high aggregation tendency of PC-20 and P25 which reduces the effective surface of NPs and therefore, declines the hydroxyl groups on the surface of mixed-matrix membranes. These results are in good agreement with previous reported works [26],[31].

The observed flux increase (improved hydrophilicity) upon integration of TiO<sub>2</sub> NPs can be explained as such; the PVDF/TiO<sub>2</sub> mixed-matrix membrane is more hydrophilic than the neat PVDF membrane due to the higher affinity of TiO<sub>2</sub> towards water had reduced the hydrophobic adsorption between HA particle and PVDF/TiO<sub>2</sub> mixed-matrix membrane. Therefore, water molecules are attracted into the membrane matrix and promoted to pass through the membrane, thus enhancing the membrane flux. These results

are consistent with those by other researchers [32]-[34] who found that the modified membrane with addition of TiO<sub>2</sub> showed higher flux for sludge filtration than neat polymeric membrane. As a result, fouling-resistant property can also be improved by this method as the hydrophilic membrane will be covered with a layer of water.

TABLE II: THE EFFECT OF TiO<sub>2</sub> TYPE ON PERMEATE FLUX AND HUMIC ACID REJECTION

Membrane samples	Membrane number	Permeate flux (L/m <sup>2</sup> h)	Rejection (%)
Neat	M1	34.97±2.25	98.20±0.13
PC-20	M2	39.70±4.74	98.06±0.55
P25	M3	38.81±0.58	97.77±0.43
X500	M4	45.36±1.47	98.67±0.14

#### IV. CONCLUSION

Stable TiO<sub>2</sub> colloids in coagulation bath were successfully embedded to the membrane matrix through phase inversion and colloidal precipitation method. It was found that the membrane prepared with DMAc as solvent and immersed in coagulation bath with 0.1 g/L X500 has relatively well distributed, regular and smaller TiO<sub>2</sub> NPs on membrane surface. The particle size distribution is mainly contributed by the colloidal stability of X500 in the polymer matrix. Membrane prepared using PC-20 and P25 have slightly bigger particle size which provides poor binding force to the membrane matrix.

The PVDF/TiO<sub>2</sub> mixed-matrix membranes had similar structure to the neat PVDF membrane. However, permeation tests with HA solution proved that permeability of the mixed-matrix membrane was significantly improved due to its bigger pore size (defect) as well as enhanced hydrophilicity. By adding 0.1 g/L X500 into the coagulation bath, the membrane performance (flux and rejection) improved dramatically which could be attributed to the narrow pore size and increased hydrophilicity of the membrane. Membrane prepared using X500 is the best membrane which gives 45.36 L/m<sup>2</sup> hr of flux and rejection as high as 98.67% of HA. However, for membranes prepared using PC-20 and P25, the poor HA rejection was compensated by the flux increment due to the nonuniformity of the particle distribution which created defects on the membrane surface.

Although the membrane prepared using X500 as hydrophilic filler presented a good result on particle size distribution with flux enhancement, further research on long hours HA filtration test has to be carried out in the future to test on the chemical stability of TiO<sub>2</sub> dispersed in PVDF matrix and its antifouling (self-cleaning) properties under UV light irradiation.

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**Y. H. Teow** is currently a Ph. D scholar of School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia (USM), Penang, Malaysia. She obtained her Bachelor of Engineering (Hons) Chemical Engineering from Universiti Tunku Abdul Rahman (UTAR), Kuala Lumpur, Malaysia in 2010. She has authored three publications in *Desalination*, *Journal of Applied Polymer Science* and *Global Journal of Physical Chemistry*. Her research activities is principally dedicated in the fields of membrane technology in water purification, ultrafiltration mixed-matrix membrane and the combination of water pollution problem and nanotechnology.