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Membrane Processing of Refined Palm Oil Wastewater using TiO_2 EntrappedNanoporous PVDFMembrane

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Abstract. An explosive growth of interest has been developed in creating of alternative process of crude palm oil wastewater treatment. Membrane processing offers many advantages as it can be used in almost the stage of oily wastewater treatment. Aim of this study was to investigate nanoporous membrane morphology and performance for refined palm oil wastewater treatment. The comparison of performance and morphology was carried out between neat PVDF and PVDF nanoporous membranes with nanosized TiO_2 particles of different compositions. Results of permeability and instrumental analysis illustrated that nanometer size obviously affected the PVDF membranes performance and structure. Smaller nanoparticles could improve the antifouling property of PVDF membrane more remarkably. Cross-section of membranes were observed with a field electronic scanning electron microscope (FESEM). The TiO_2/PVDF membrane with smaller nanoparticles had smaller mean pore size on its surface and more apertures inside the membrane. X-ray diffraction (XRD) experiment was also suggested that the addition of 1.0 % TiO_2 nanoparticles had stronger effect on crystallization of PVDF molecules, poresize of 34.05 nm, contact angle of 53^o and flux of 88.50 L/m^2h of poresize. It can be concluded that nanoporous PVDF membrane with adding of TiO_2 has better performance for treating refined palm oil wastewater.

Introduction

Over the last few decades, the Indonesian palm oil industry has grown to become a very important agriculture-based industry, where the country is today the world's leading producer and exporter of palm oil [1]. Oil palm industry is the leading agriculture corp in Indonesia, specially in Sumatera, meanwhile is still occurring on Sumatra, with an additional 980,000 hectares being planted between 2007 and 2011, or nearly increase of 200,000 hectares per year [2]. It has been also reported that for every ton of crude palm oil produced, about 3.5 m^3 of wastewater is generated. The conventional wastewater treatment system has been improved by introduction of membrane technology. The comparison of the membrane materials performance and morphology affected the permeability and instrumental analysis of filtration.

Poly(vinylidene fluoride) (PVDF) is a common membrane material because of its excellent chemical resistance and thermal stability [3]. Though its hydrophobic nature is favor of promoting the selective absorption and transport of the organic component of an organic/water feed solution, the neat PVDF membrane is liable to be contaminated by proteins and some other impurities in water and oily wastewater treatment, which leads to a sharp drop of pure water flux of the membrane [4]. Chemical modification method could be employed to improve the hydrophilicity of the membrane, but the main chain of PVDF molecule would be changed and the advantages of the PVDF membrane might be depressed [5]. Usually, physical modification method such as mixture was used, and the mixture materials were macromolecules [5,6].

It is well known that nanoparticles have unique electronic, magnetic and optical properties to improve the capabilities of polymers in a certain extent because of their small sizes, large ratio surface areas and strong activities [7]. The presence of finely dispersed inorganic particles in the

polymer matrix has proven very useful in the improvement of membrane performance [8]. A typical nanoparticle containing atoms or molecules numbering from tens to tens of thousands has length between a few and a few tens of nanometers. The introduced nanoparticles to polymer membranes might be SiO_2 [9], Al_2O_3 [10], and TiO_2 [11-13]. Among different metal oxide nanoparticles, TiO_2 had received the most attention because of its stability, availability, and promise for applications such as painting, catalysis and photocatalysis, battery, cosmetic, etc. In order to accelerate the degradation of organic contaminants, TiO_2 are often used as a photocatalyst in water and wastewater treatment. When dispersed to PVDF membrane, TiO_2 nanoparticles can not only improve the hydrophility of PVDF membranes to enhance the flux but kill bacteria and mitigate the fouling problem of PVDF membrane and MBR system [14].

In this study, TiO_2/PVDF membranes were made using a phase inversion method and characterized by pure water flux. Three different compositions of TiO_2/PVDF were used as membrane material. The average pore size and hydrophilicity of the surface membranes were also measured. The morphologies of membrane surfaces and cross-sections were observed with a field emission scanning electron microscope (JEOL JSM-6700F) (FESEM). X-ray diffraction (XRD) was employed to analyze the crystalline change of PVDF molecules.

The aim of this study was to investigated the effect of entrapped TiO_2 on PVDF nanoporous membrane for treating refined palm oil wastewater. The more understanding of the membrane morphology and performance for refined palm oil wastewater treatment using membrane technology was described clearly.

Experimental

Materials. Membranes have been prepared using Kynar®740 PVDF polymer pellets which were purchased from Arkema Inc.,Philadelphia, USA. The solvent N,N-dimethylacetamide (DMAc,Aldrich Chemical) (Synthesis Grade, Merck, 99%) was used aspolymer solvent without further purification. Nanoparticles titanium dioxide (TiO_2) was used as inorganic additives that was purchased from Sigma-Aldrich. Glycerol was purchased from MERCK (Germany) and used as non-solvent for the post treatment of membrane. In all cases, tap water was used as the external coagulation bath medium in the spinning process.

Membrane preparation. Membranes were prepared from 16 wt.% PVDF in DMAc at different TiO_2 concentrations (0, 1.0, 2.0 wt.%) at room temperature by phase inversion process. The polymer solution was produced at 50°C for 48 h. The spinning dope was extruded from spinneret (spinneret dimension of 1.1 mm (outer diameter) and 0.55 mm (inner diameter)) and then spun with adjusted air gap length. The spun hollow fibers were immersed in the water bath for a period of 3 days, with daily change of the water, to remove the residual DMAc and the additives. The fibers were then post-treated using 10 wt.% glycerol aqueous solution as a non-solvent exchange for 1 day in order to minimize fiber shrinkage and pore collapse. After the fibers were dried for 3 days, they were ready for making hollow fiber test modules.

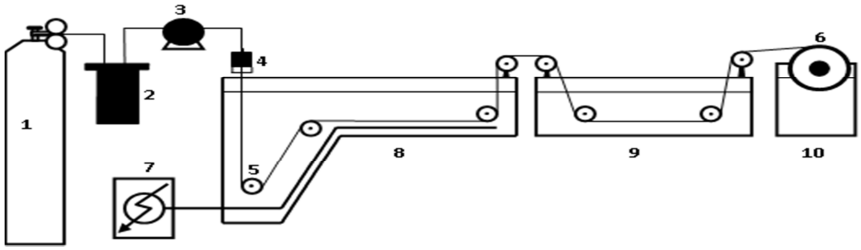

Fig 1. Schematic diagram of the spinning system: (1) high purity nitrogen, (2) storage reservoir, (3) gear pump, (4) spinneret, (5) roller, (6) wind-up drum, (7) refrigeration unit, (8) coagulation bath, (9) washing bath, (10) collecting drum.

Membrane performance. Membrane performance was tested with a membrane bundle having 11.23 dm^2 of membrane surface area. Pure water flux was measured at 100 kPa after the flux was steady, then calculated as

$$F = V/At \quad (1)$$

where F is the pure water flux (L/m^2h), V the permeate volume (l), A the membrane surface area (cm^2) and t is the time (h).

XRD analysis. X-Ray diffraction patterns were obtained with an X-Ray diffractometer (D/max-rB 12 kW Rigaku, Japan: 45 kV, 40 mA) operated at 50 mA and 50 kV from 10^o to 80^o.

Membrane average pore size and surface hydrophilicity analysis. Average pore radius, r_m, was determined by filtration velocity method, in which pure water flux of the wet membrane was measured by applying pressure (0.1 MP) for a limited period (20 h). It represents the average pore size along the membrane thickness (ℓ) that was the difference between external radius and internal radius of the hollow fiber membrane. According to Guerout-Elford-Ferry equation, r_m could be calculated by Yu *et al*., 2006 [15].

$$r_m = \sqrt{\frac{(2.9-1.75\varepsilon)\times 8\eta\ell Q}{\varepsilon\times A\times \Delta P}} \quad (2)$$

where η is water viscosity (8.9 x 10^{-4} Pa s), ℓ is the membrane thickness (m), ΔP is the operation pressure (0.1MPa), ε is the porosity of the membrane (%), Q is volume of permeate water per unit time ($m^3\ s^{-1}$), A is effective area of membrane (m^2).

The contact angle measurements were carried out with a contact angle meter to measure the surface hydrophilicity. The sample membranes were dipped into distilled water for 30 min, then dried with N_2 gas blowing before the experiments. The reported values were the averages of the contact angle of three droplets.

FESEM analysis. A field emission scanning electronic microscope (FESEM, Hitachi Model S-520 Japan) was employed to observe cross-section of the prepared PVDF membranes [16]. Prior to analysis, the membranes were cryogenically fractured in liquid nitrogen anf then sputtered with platinum. The FESEM micrographs were taken at certain magnifications.

Results and Discussion

Performance and surface hydrophilicity of membrane. The membranes were prepared via a phase inversion method. All the compositions in the dope solutions with 16 wt.% PVDF were optimized. The obtained membranes were typical ultrafiltration membranes. The flux reduction coefficients (m) decreased by % and %, respectively showed in Table 2. It suggested that the capabilities of the anti-fouling were improved remarkably.

Chiang *et al*. [17] modified the PVDF hollow fiber membrane by adding about 10 wt.% TiO_2 into the casting solution. They considered that the surface of TiO_2 was abundant with hydroxyl which could enhance the flux of PVDF membrane. Oh *et al*. [18] figured three hydrogen-bonds effect between the fourine atoms in PVDF and oxygen atoms in TiO_2. The association between PVDF and TiO_2 also changed the surface potential of PVDF. In this work, it found large amount of TiO_2 nanoparticles in dope solution were not acceptable because of the TiO_2 nanoparticles aggregate and sedimentation which would weaken the nanometer effect.

The contact angle of membrane with better hydrophilicity should decrease more rapidly in theory when the average pore size and morphology is similar. The initial contact angles of TiO_2/PVDF nanoporous membranes were smaller than that of the pure PVDF membrane, as shown in the Table 1.

Table 1 The performance, average pore size and contact angle of the PVDF nanoporous membrane

Wt.% TiO_2	Fluks	m(%)	Average pore size (nm)	Contact angle (^{o})
0	27.07	29.9	28.2	82
1	30.35	28.2	14.93	65
2	88.50	18.3	34.05	53

At the same time the drop diameters was almost constant with the drop age so it revealed that the decraese in contact angle was cause by the penetration of water into membrane. It can be observed that the contact angle of nanoporous membrane decreased more rapidly as the increase of TiO_2 content. It can be concluded that the introducing of the TiO_2 nanoparticles made the membrane more hydrophilic. But this difference was smaller than that the former reports on ultrafiltration membrane which reported by Oh *et al.* [18].

Crystallizations of membrane. XRD patterns for TiO_2, PVDF membrane and TiO_2/PVDF membranes were illustrated in Fig. 2 which proved the change in dominant crystal phases due to TiO_2 nanoparticles in the PVDF membranes. It can be observed that the pattern of TiO_2 crystal powders had one peak at2Θ of 36.2^o (Fig. 2.a) and three crystalline characteristics peaks of 20.2^o, 29.4^o, and 36.2^o, respectively as shown in Fig. 2 b,c. The pattern of TiO_2/PVDF nanoporous membranes also had three crystalline characteristic peaks in addition to the dispersions showed a little shift. It indicated that TiO_2 nanoparticles has distributed to the membrane matrix and had also existed interaction between TiO_2 and PVDF.

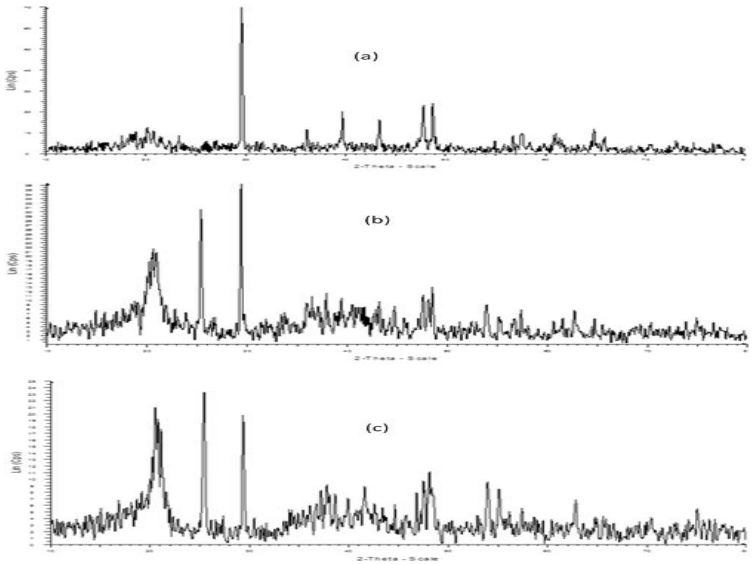

Figure 2. X-ray diffractograms of PVDF/TiO_2 blend membranes with various mass ratio (a)16:0 (b) 16:1 (c) 16:2

Membrane morphology. Fig.3 shows the FESEM micrographs of the nanoporous PVDF membranes. Improvement of membrane morphology is observed for addition of a small amount of TiO_2 nanoparticles. TiO_2 nanoparticles have high specific areas and hydrophilicity, which will affect the mass transfer during the spinning process. The cross-sectional images for all hollow fibers consist of finger-like macrovoids extending from both inner and outer wall of the hollow fiber, and an intermediate sponge-like layer. The thickness of the sponge-like layer decreases initially with an increase in TiO_2 concentration of 0 wt.%, 1.0 wt.%, and 2.0 wt.% (Figs.3a-3c). This phenomenon can be explained by the kinetic effect on the rate of solvent-nonsolvent exchange in the phase inversion process. At lower TiO_2 concentration, an increase in the amount of hydrophilic TiO_2 tends to draw more water into the polymer dope, resulting in an increase in the length of finger-like macrovoids and decrease in the thickness of the intermediate sponge-like layer. Whereas at higher concentrations of TiO_2, an increase in TiO_2 concentration increases the viscosity of the polymer dope, decreasing the rate of water intrusion into the polymer dope, which results in the shorter finger-like macrovoids and thicker intermediate sponge-like layer [12].

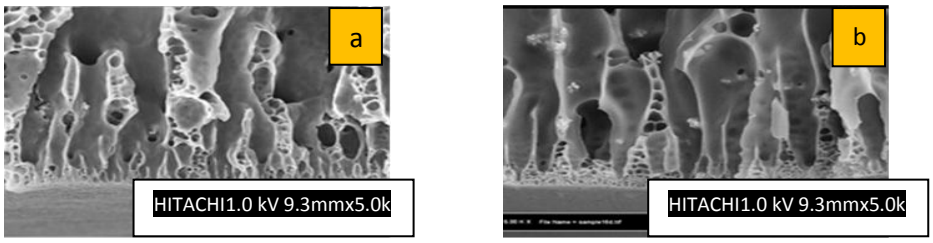

Figure 3. FESEM images of the a) 1 wt.% TiO_2/PVDF, (b) 2 wt.% TiO_2/PVDF nanoporous membranes.

Conclusions

TiO_2/PVDF nanoporous membranes were prepared via phase inversion by dispersing the TiO_2 nanoparticles in the PVDF dope solutions. XRD and DSC analysis showed there existed the interaction between TiO_2 and PVDF. Nanoporous membranes had better thermal stability than the pure PVDF membrane. Cross-section morphology of membranes were produced due to the effect of TiO_2 nanoparticles on the solution viscosity and the mass transfer in VIPS stage. TiO_2 nanoparticles distributed uniformly at low loading amount, while it would leach out at high loading amount for the unstable distribution in membrane matrix. The nanoporous membrane hydrophilicity enhanced with increasing of TiO_2 content. Membranes with maximum flux of 88.50 L/m^2h and pore size of 34.05 nm were calculated when the amount of TiO_2 was 0 - 2.0 wt.% and occured also the significant aggregation.

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