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Photocatalytic Degradation of Oil using Polyvinylidene Fluoride/Titanium Dioxide Composite Membrane for Oily Wastewater Treatment

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Abstract. Production of industrial wastewater is increasing as the oil and gas industry grows rapidly over the years. The constituents in the industrial wastewater such as organic and inorganic matters, dispersed and lubricant oil and metals which have high toxicity become the major concern to the environment and ecosystem. There are many technologies are being used for oil removal from industrial wastewater. However, there are still needs to find an effective technology to treat oily wastewater before in can be discharge safely to the environment. Membrane technology is an attractive separation technology to treat oily wastewater. The aim of this study is to fabricate polyvinylidene/titanium dioxide (PVDF/TiO_2) composite membrane with further treatment using hot pressed method to enhance the adhesion between TiO_2 with the membrane surfaces. In this study the structural and physical properties of fabricated membrane were conducted using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) respectively. The photocatalytic degradation of oil was measured using UV-Vis Spectroscopy. The FTIR results confirmed that, hot pressed PVDF/TiO_2 membrane TiO2 was successfully deposited onto PVDF membranes surface and XRD results shows that the XRD pattern of PVDF//TiO_2 found that the crystalline structure was remained unchanged after hot pressed. Clear water was obtained after synthetic oily wastewater was exposed to visible light for at least 6 hours. In conclusion, PVDF/TiO_2 composite membrane can be a potential candidate to degrade oil in oily wastewater and suggested to possess an excellent performance if perform simultaneously with membrane separation process.

1 Introduction

Oil and gas extraction operations produced wastewater which is constitutes the industry's most significant waste stream on the basis of volume. Annually, the oil and gas industry produces which is about 14 billion bbls of water (Siriverdin and Dallbauman, 2008). Wastewater contains many constituents such as organic and inorganic matters, dispersed oil, lubricant oil, chemicals and metals which may be toxic to environment. Discharging industrial wastewater without being treated can contaminate water and soil which will lead disturbances to the ecosystem. Membrane technology is an attractive separation technology (X. Zhang, Wang, & Diniz Da Costa, 2014).

The advantage of this technology is it has a high energy efficiency. Membrane system has a high area-to-volume ratio and it is easy to scale-up because of its modular design (Rajovic et al., 2015). The membrane properties, such as pore size distribution and porosity will also affect the membrane performance as an absorption and separation technology. Thus, good pore size and narrow pore size distribution of microporous membranes are required (X. Zhang et al., 2014) to ensure the high permeate flux and rejection in membrane separation process. Recently, the most popular and available membrane materials are polytetrafluoroethylene (PTFE), polypropylene (PP), polyethersulfone (PES) and polyvinylidene fluoride (PVDF). In membrane separation fields, porous membranes are commonly applied in membrane distillation, supported liquid membrane, osmotic distillation, membrane based gas absorption, membrane contact and others. Polyvinylidene fluoride (PVDF) is one of the most commonly used as polymer membrane due its excellent properties such as chemical resistance, thermal stability and good mechanical strength (Lee, Elam, & Darling, 2015). PVDF is a semi-crystalline polymer where the crystalline phase offers mechanical strength and impact resistance and the amorphous phase provides flexibility (Liu, 2011).

Porous PVDF membranes can be produced through a phase inversion method (Damodar, You, & Chou, 2009), where it is the common industrial processes in large scale membrane production. Furthermore, PVDF is soluble in high-boiling point and organic solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAC) and N,Ndimethylformamide (DMF), which make it easier to produce more permeable asymmetric membranes through the dry/wet phase inversion process. Besides, the high mechanical strength of PVDF (Yu, Shen, & Xu, 2009) makes PVDF membranes suitable in water application and wastewater treatment process (Ji et al., 2015).

Titanium dioxide (TiO_2) is a metal oxide semiconductor used in environment applications due to its non-toxic, strong ultraviolet (UV) absorption, good stability in photocatalyst reaction and commonly energy band gap of 3.2 eV (S. Zhang et al., 2013 and Suphankij et al., 2013). Photocatalysis with semiconductor materials has been widely explored among others advanced oxidation processes to treat toxic organic compounds in wastewater (Berry & Mueller, 1994). In specific, photocatalysis based on titanium dioxide (TiO_2) has involved a great deal of consideration due to its functional properties such as chemical and thermal stability and strong mechanical properties (Yu et al., 2009). In order to enhance the adhesion between the TiO_2 with membrane, and to further increase the efficiency of the membrane, pre-treatments such as hot press have been used (Kim et al., 2013). Recently, mechanical pressure was applied to break outer sheaths, thereby exposing the membrane accomplishing a high surface area (Liu, Chu, & Ding, 2004). As the oil and gas industry in which the refinery process or any petrochemical industries generate a big amount of wastewater, the wastewater treatment is significant in order to meet environmental standard set by government. A proper treatment of wastewater is a must as it will affect the environment. Thus, this paper presents a preliminary study on the performances of TiO_2 composite PVDF membrane with hot press treatment on photocatalytic degradation of oil in oily wastewater.

2 Methodology

2.1. Materials

The material used in this research were commercial polyvinylidene fluoride (PVDF) pellets (Kynar® 740) purchased from Arkema Inc. USA as the polymer for membrane formation, N-N-dimethylacetamide (DMAC) used as the solvent and distilled water used as coagulants during membrane fabrication. TiO_2 powder (Sigma-Aldrich) was used as additive in membrane dope.

2.2. Membrane Preparation

Dope solution was prepared by dissolving PVDF (13 wt%) pellet with DMAC (85 wt%) in a scott bottle and stirred at 60℃ and 600 rpm overnight in order to produce homogeneous solution. Then, TiO_2 (2 wt%) powder was added into dope solution and stirred for 2 hours. The prepared dope solution was sonicated for 1hour to remove micro bubbles. After that, prepared dope solution was casted on a glass plate with the thickness of 300 µm. After 30 second exposed to the air, the plate was immersed into deionized water coagulation bath and the membrane was slowly formed due to polymer precipitation. After 10 minutes or when the membrane was started to detached from the plate, the membrane was soaked into deionized water overnight to remove the excessive solvent before it can be dried and ready to be used. The prepared membrane was further treated using hot press method to enhance the adhesion between the TiO2 with the membrane. PVDF/TiO_2 membrane was hot pressed using hot press machine at temperature of 150 °C with pressure of 30 psi for 15 minutes to form a network of large pores.

2.3. Characterization

Characterizations of the prepared membranes were carried out using x-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR) to measure structural and physical properties of the membranes.

2.4. Photocatalytic Degradation Measurement

Synthetic oily wastewater was formulated using 90 ml of distilled water, 5 ml of lubricant oil and 5 ml of surfactant (SPAN 80) and mixed thoroughly in 200 ml beaker before sonicated for 1 hour. The membrane sample (15 cm^2) was immersed into synthetic oily wastewater under 18W fluorescent light for 4 hours. The suspensions of 3ml were collected at 60 minutes interval for analysis. UV-Vis spectroscopy was used to measure the concentration change of oil throughout experiment at 377 nm wavelength. The photocatalytic activity was measured in percentages of oil degradation using the following equation (Mohamed, 2015):

$$\text{Degradation of oil} = (C_o - C_t)/C_t \times 100 \quad (1)$$

Where C_o is and C_t are the initial concentration at time t=0 and the concentration at time (60, 120, 180, 240, 300 and 360 minutes), respectively.

3 Results and Discussion

3.1. Characterization

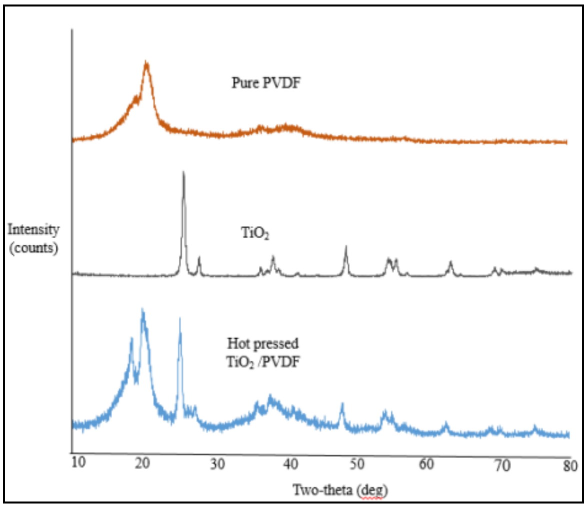

Figure 1: XRD pattern of pure PVDF and hot pressed PVDF/TiO_2 composite membrane.

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The XRD patterns of PVDF/TiO_2 (1 wt%) shown in Figure 1 illustrates that the peak positions of PVDF in hot pressed PVDF/TiO_2 composite membrane exist at 2θ = 18.74 which corresponding to (0 2 0) plane and 2θ = 20.463 corresponding to (1 1 0) plane of monoclinic structure. Meanwhile, the peak positions of TiO_2 were observed at 2θ = 25.14 (1 0 1), 27.13 (1 0 1), 27.416 (1 0 1), 35.821 (1 1 2), 37.696 (1 1 2), 337.859 (1 1 2), 47.957 (2 0 0), 54.898 (1 0 5), 56.528 (1 0 5), 62.535 (2 0 4), 70.104 (2 2 0) and 75.043 (2 1 5) which identified as anatase phase. Result for hot pressed PVDF/TiO_2 membrane confirmed that the TiO_2 was successfully deposited onto PVDF membranes surface. This result is in agreement with work done by Devikala et al., (2014) mentioned that pure PVDF with monoclinic structure and was found at peak positions of 2θ = 18.48(0 2 0) and 20.18 (1 1 0). The results proved that the structure of PVDF/TiO_2 membrane was preserved after hot pressed

Figure 2 shows the FTIR spectra of pure PVDF and hot pressed PVDF/TiO_2 composite membrane. The results show that the presence of PVDF was identified by the C–F stretching vibration peak centred at 1169.08 cm^{-1} in hot pressed PVDF/ TiO_2 membrane.

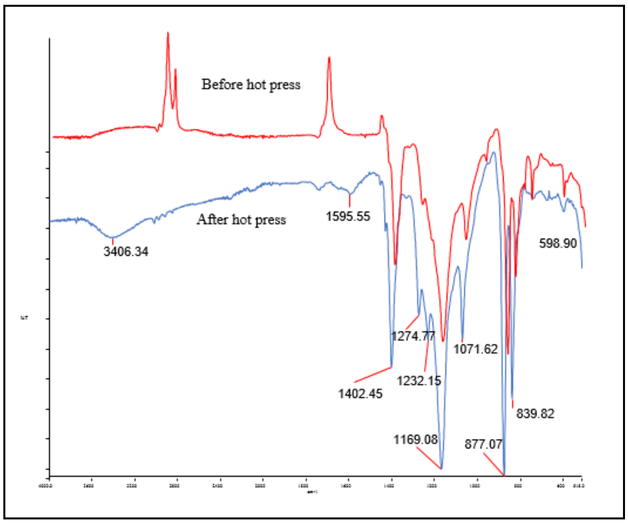

Figure 2: FTIR spectra of pure PVDF and hot pressed PVDF/ TiO_2 composite membrane

The observed vibrational band at 1402.45 cm^{-1} was related to deformation vibration of the CH_2 group and the band at 1071.62 cm^{-1} exists due to β crystalline phase of PVDF. The peaks observed at 877.07 and 839.82 cm^{-1} were rocking mode of vinylidene group of the polymer. The bands at 598.90 cm^{-1} was due to the shaking and bending vibration of CF_2. In the meantime, a band at 598.90 cm^{-1} appeared because of stretching vibration of Ti-O anatase in the composite. According to Devikala et al., (2014), the bands appeared between 800 to 1400 cm^{-1} were due to lattice vibrations of TiO_2 in the composite. The interaction between PVDF and TiO_2 make the intensity of crystalline phase of PVDF at 762 cm^{-1} peak decreased with the increase amounts of TiO_2 (Devikala et. al., 2014). The FTIR results concluded that hot press on PVDF/TiO_2 does not affect the bonding of TiO_2 on the PVDF surface as the important peak of TiO_2 remained presence at 598.90 cm^{-1}.

3.2. Photocatalytic Degradation Measurement

In photocatalytic degradation measurement oil concentrations were measured using UV-vis spectrophotometer with absorbance at 377 nm which the maximum absorption occured. During photocatalytic degradation, photo-induced electrons were produced and large amounts of OH radicals were generated because of dissociation of water molecules through oxygen vacancies. Table shows the absorbance reading for respective sampels.

Table 1: UV-Vis absorbance with respective oil concentration in photocatalytic degradation

Time	Absorbance		Oil Concentration (ppm)	
(hour)	Pure PVDF	TiO_2/PVDF	Pure PVDF	TiO_2/PVDF
0	1.377	1.377	1000	1000
1	1.252	1.184	889	839
2	1.247	1.109	885	781
3	1.271	1.122	904	791
4	1.227	0.9185	870	635
5	1.286	0.7636	915	515
6	1.263	0.5593	898	359

Figure 3 shows the effect of TiO_2 loading into PVDF membrane on oil degradation. Overall, oil concentration decreased with increased of time for both pure PVDF and PVDF/TiO_2. Oil particles were photodegraded within 6 hours of visible light from 18W fluorescent lamp source.

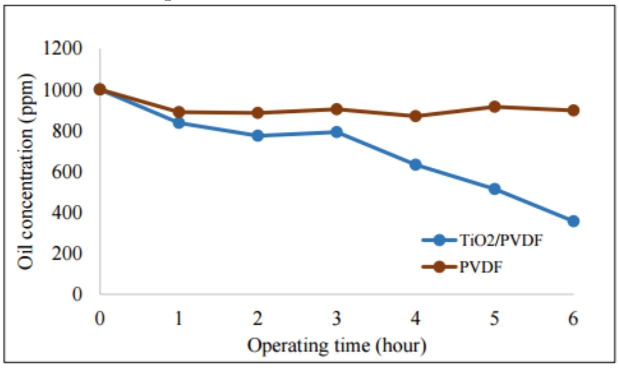

Figure 3: Effect of TiO_2 loading in PVDF membrane on oil degradation

Within 6 hours, the oil degradation using PVDF/TiO_2 composite membrane was more that 60% as compared to using soley PVDF membrane which only degraded the oil about less than 5%. This results is in agreement with result gain by Nor et al., (2016). Oil degradation using PVDF/TiO_2 composite membrane was higher as compared to pure PVDF membrane, confirmed the important role of TiO_2 catalyst in oil degradation. Owing to the photoinduced-hydrophilicity effect of TiO2 catalyst embedded within membrane matrix, the oil degradation was reported to be increased with increased of TiO_2 loading from 0 wt%, 1 wt% and 2 wt. %. Similar results have also been reported by Ong et al., 2014, where they found that membrane hydrophilicity was remarkably increased with increasing TiO_2 loading. Besides that, it was also observed that the oil degradation using pure PVDF and PVDF/TiO_2 composite membrane were increased with time. The important of oil degradation in the case of PVDF/TiO_2 composite membrane can be explained by the generation of strong oxidants from TiO_2 highest electrovalent band under visible light which oxidized most of organic compounds found in the feed solution (Ong et al., 2014). Figure 4 indicates the colour changes of oily water after 7hours exposed to visible light. From this visual observation, a clear water was obtained after at least 6hours period of time.

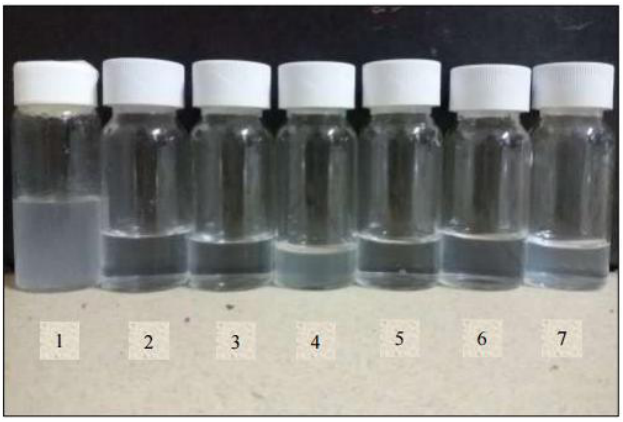

Figure 4: The colour changes of oily water after 7 hours exposed to visible light

4 Conclusions

The key to present research project was to develop a hot pressed TiO2/PVDF composite membrane and performance of degradation of oil in oily wastewater. The improvement in PVDF membrane has been achieved through the modification of the surface of PVDF membrane by incorporation with TiO2 particles membrane and further treatment using hot press method. Based on XRD diffraction peaks, the peak positions of TiO_2 after hot press appeared at 2θ = 25.14 (1 0 1), 27.13 (1 0 1), 27.416 (1 0 1), 35.821 (1 1 2), 37.696 (1 1 2), 337.859 (1 1 2), 47.957 (2 0 0), 54.898 (1 0 5), 56.528 (1 0 5), 62.535 (2 0 4), 70.104 (2 2 0) and 75.043 (2 1 5) which identified as anatase phase. Result for hot pressed PVDF/TiO_2 membrane confirmed that the TiO_2 was successfully deposited onto PVDF membranes surface. The FTIR results concluded that hot press on PVDF/TiO_2 does not affect the bonding of TiO_2 on the PVDF surface as the important peak of TiO_2 remained presence at 598.90 cm^{-1}. In photocatalytic degradation, the oil degradation using PVDF/TiO_2 composite membrane was extremely higher compared to pure PVDF membrane which suggested that the important role of TiO_2 catalyst in PVDF membrane for oil degradation. The oil degradation using PVDF/TiO_2 composite membrane was more that 60% as compared to using soley PVDF membrane which only degraded the oil about less than 5%. Clear water was obtained after synthetic oily wastewater was exposed to visible light for at least 6 hours. In conclusion, PVDF/TiO_2 composite membrane can be a potential candidates to degrade oil in oily wastewater and suggested to possess an excellent performance if perform simultaneously with membrane separation process.

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