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RESEARCH ARTICLE

PVDF/Fe_2O_3 mixed matrix membrane for oily wastewater treatment

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Abstract

Oily wastewater has been recognized as one of the most concerned environmental pollutions that come from a variety of sources. The increasing of these uncontrollable oily wastewater discharges consequently leads to environmental problems. The current barrier in this situation is when dealing with finely emulsified oily wastewater streams with small droplet size (< 20 μm in diameter). To tackle this issue, it is found that the utilization of the membrane technology is most effective due to its highly effective separation process and simplicity. Nevertheless, traditional filtration membranes are mostly afflicted with low flux and rejection rate as a consequence of easy fouling caused by the plugging of oil and surfactant. Thus, the wettability and antifouling properties of the membrane play an important role in dealing with this issue. The aim of this study was to evaluate the performance and operation of the membrane when treating oily wastewater. PVDF was chosen as the host polymer based on its outstanding properties and 0.2 wt% of Fe_2O_3 loading was utilized to enhance the hydrophilicity of the membrane. The effects of mixed matrix membrane (MMM) and neat poly (vinylidene fluoride) (PVDF) membrane relating to their differences in the SEM images, water flux and oil rejection were studied. The presence of additive in the polymeric composition has helped to achieve 40% higher flux increment with an oil removal efficacy of ~97 %, as compared to the unmodified PVDF membrane.

Keywords: PVDF, mixed matrix membrane, hydrophilic, oily wastewater

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INTRODUCTION

The discharge of domestic sewage and oily wastewater is constantly increasing, in line with the rapid development. Generally, the discharge contains high amount of hydrocarbon that leads to additional toxicity of the oily wastewater. This toxicity gives high risk of mutations and cancers to human beings, as well as it slows down growth in animals and plants. This matter needs to be overcomed in order to avoid the issue and at the same time, engage in a clean environment for all living things. Therefore, it is essential to carry out the oily wastewater treatment prior to release it into the surrounding. Otherwise, the surrounding and environment such as the coastal waters, estuaries, rivers, groundwater, seashore and soil will be severely polluted by its high mineral and organic content (Uan, 2013).

Yu *et al.* (2013) reported a review on the treatment methods that have been used for oily wastewater such as flotation, coagulation, biological treatment, electrochemical catalysis, and membrane separation technology, where each of them has its own specific scope, advantages and disadvantages. Membrane technology is one of the promising technologies utilized when dealing with the abovementioned phenomenon. Membrane technology is known for its high separation efficiency and relatively simple operational processes. Basically, membrane technology refers to the separation of certain particle sizes to pass through the membrane layer and block bigger size particles from exceeding the barrier. Even with the polymeric membrane's disadvantages, researchers are still urged to produce the same kind of membrane, but with higher performance level. Various membranes are produced by mixing the host polymer with the additive polymer (polymer-polymer blending) or an inorganic material (mixed matrix membrane).

Mixed matrix membrane (MMM) is a common membrane applied in oily wastewater treatment as it contributes to improve the hydrophilicity and performance of the membrane (Gohari *et al.*, 2014). Kusworo and Utomo (2017) studied the effect of nanoparticles in MMM by incorporating the nano-silicon dioxide (SiO_2) and nano-zinc oxide (ZnO) in PES membrane in terms of oil/water separation performance. The test performance was taken after 150 minutes of the operation. The permeability of PES-nano-SiO_2 had reduced from 30 L/m^2.h.bar to 11.8 L/m^2.h.bar, while that of the PES-nano-ZnO went from 19.5 L/ m^2.h.bar to 9.3 L/m^2.h.bar due to pore blockages. It was reported that the PES-nano-SiO_2 had a higher permeate flux than PES-nano-ZnO, owing to its greater number of oxygen molecules per mole of SiO_2. At the same time, the addition of nano-SiO_2 in the membrane had improved the hydrophilicity, as well as the permeability flux of the membrane.

Moreover, the use of iron oxide in MMM can also induce high hydrophilicity characteristic and water flux. A novel iron(II) phthalocyanine (FePc)/poly(vinylidene fluoride) (PVDF) composite membrane was prepared by Chen *et al.* (2018). It was found that there were enhancements in the porosity, mean pore size, surface hydrophilicity, and negative charge of the readily-prepared composite membranes through the adding of FePc in the MMM. Consequently, this improved the permeability and antifouling properties of the membrane. The use of 2.5 wt% of FePc in the membrane had produced a 92% efficiency level in the oil separation process and water flux permeation of 156 L/m^2.h. In addition, Ikhsan *et al.* (2018) synthesized the nanocomposites and ferric chloride hexahydrate ($FeCl \cdot 6H_2O$) that were used as some of the materials to synthesize the HNT-HFO nanocomposite. The presence of HNT-HFO in the PES membrane matrix has affected the wetting properties as the hydrophilicty of the membrane was increased. The MMM had obtained water permeability or water flux at 650 L/m^2.h.bar with 99.7% of oil rejection.

On the other hand, Song *et al.* (2017) utilized the ferric ions (Fe(III)) in a different way, where the performance of the membrane was studied by comparing the surface coating method of Fe(III) and tannic acid (TA) on the polypropylene (PP) membrane surface. PP membrane that was coated in the TA solution and then coated in the Fe(III) solution had attained a higher perfomance compared to PP membrane coated in TA and Fe(III) solutions. The PP membrane with two-step coating exhibited water permeability at 7092 L/m^{2}h.bar with 0° water contact angle, compared to the one-step coating water permeability and water contact angle of 1587.4 ± 288.5 L/m^{2}h.bar and 71.8 ± 9.1°, respectively. This was due to the membrane surface of the two-step coating had employed more O and Fe on its surface than that of the one-step coating. This showed that Fe played an important role in hydrophilicity and water flux or water permeability.

This work aimed to investigate the potential of a PVDF membrane incorporated with the iron oxide, Fe_2O_3. PVDF was chosen as the host polymer for its outstanding properties due to its anti-oxidation activity, high thermal stability, good organic selectivity, as well as its excellent chemical and mechanical resistances. The presence of Fe_2O_3 was not only improved the hydrophilicity and water flux of the membrane, but it also helped to reduce potential fouling problem (Muthukumar *et al.*, 2018). The Fe_2O_3 was mixed with PVDF and the MMM result was compared to the pristine PVDF in terms of the SEM images and the results were correlated with the membrane water flux and oil rejection.

EXPERIMENTAL

Materials

Poly (vinylidene fluoride) (PVDF) in pellet form was supplied by Arkema (Xiamen Agency, China) and dried at 80°C for 12 h before use. 1-methyl-2-pyrrolidinone (NMP, purity 99%) was purchased from Merck and utilized as solvent. Fe_2O_3 and sodium dodecyl sulfate (SDS) were supplied by NovaScientific and Sigma Aldrich, respectively. Both of the materials were dried in the oven for 12 h before use, while the oil utilized in this study was the cooking oil that bought from a grocery store.

Preparation of dope solution

The neat PVDF membrane was prepared by mixing 18 wt% of PVDF with NMP, while the MMM was prepared by adding 0.2 wt% of Fe_2O_3 in 18 wt% of PVDF in NMP. The additive was added gradually in the solution to avoid precipitation. Both of the solutions were stirred separately for 24 h untill a homogeneous solution was obtained. It was later sonicated for 4 h to eliminate bubbles that were formed during the stirring process.

Preparation of flat sheet membrane

To prepare a flat sheet membrane, 20 mL of dope solution was first poured onto a smooth and clean glass plate. The solution was then cast by a roller glass at a speed of 5 cm/s to form a membrane thickness in the range of 250–300 mm. The cast film, together with the glass plate, were then immersed into a tab water bath to allow phase inversion to take place. Once the membrane was peeled off naturally from the glass plate, it was transferred to another water bath and immersed for another 3 days to remove residual solvent. Finally, the membrane was dried in oven at a temperature of 40°C for 24 h. Three different samples were tested and three readings were taken for each of the samples.

Membrane characterization

Scanning electron microscopy (SEM) model JEOL JSM-5610LV was used to observe the morphological structure of the membrane.

Eq. (1) is the gravimetric method that was used to calculate the porosity of the membrane.

$$\varepsilon = \frac{\omega_1 - \omega_2}{A \times l \times d_w} \tag{1}$$

where ω_1 is the weight of the wet membrane, ω_2 is the weight of the dry membrane, A is the membrane effective area (m^2), d_w is the water density (0.998 g/cm^3) and l is the membrane thickness (m). Deionized water was used to immerse the membrane for 1 min and the wetted membrane was weighted and determined. Then, the membrane went through the drying process until the measuring of its weight stayed consistent.

Furthermore, the Guerout–Elford–Ferry equation below was employed, using the water permeability and porosity data to evaluate the mean pore radius (r_m) of the membrane.

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

where η is the water viscosity (8.9×10^{-4} Pa s), Q is the volume of the permeate pure water per unit time (m_3/s), and ΔP is the operation pressure (0.5 MPa). Using the method proposed by Xie *et al.* (2011), the vacuum drying of the membranes was done at 100 °C for 24 h, where they were then weighed and immersed in the deionized water for another 24 h at room temperature for the purpose of water uptake analysis of the membrane. Next, the wet membranes had to be wiped dry and immediately reweighed. The water uptake analysis of the membranes was illustrated in weight percent, as shown below:

$$Water\_uptake = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{3}$$

where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively.

Pure water flux

The cross-flow membrane system was adopted in the determination of pure water flux of the membranes. As such, all membranes were compacted at 101.32 kPa for 30 min until a steady-state condition was achieved before conducting the flux determination. Then, at 0.1 kPa, the equation below was used to calculate the pure water flux of the membrane (J_w, L/m^2.h).

$$Jw = Q/(A \times \Delta T) \tag{4}$$

where Q is the quantity of permeate (L), A is the effective membrane surface area (m^2) and ΔT is the sampling time (h).

Oil rejection

Gohari *et al.* (2014) proposed an approach of using a cross-flow study to determine the rate of oil rejection. The equation below is capable of evaluating the efficacy of oil molecules separation from the oil-in-water emulsion done by the membrane.

$$R = \left(1 - \frac{C_p}{C_f} \times 100\right) \tag{5}$$

where R is the rejection ultrafiltration process (%), C_p is the concentration of the permeate (%) and C_f is the concentration of the feed (%). The oil concentration in the feed and permeate samples could be determined using UV–vis spectrophotometer (DR5000, Hach) at wavelength of 305 nm. The cooking oil solutions (1000 ppm) were prepared according to the method used by Lai *et al.* (2017). Sodium dodecyl sulfate (SDS) was used as surfactant to produce a stable oil-in water emulsion. The ratio of cooking oil to SDS used in the oily solution preparation was fixed at 9:1 (w/w).

RESULTS AND DISCUSSION

Membrane morphology

Fig. 1 shows the surface and cross-sectional morphology of neat PVDF membrane and MMM (PVDF with 0.2 wt% of Fe_2O_3). The surface of pristine PVDF membrane showed that there were some parts of the surface that were more denser as compared to MMM, where the pores were not clearly seen. Meanwhile, the membrane cross-section showed that it consisted of small finger-like structures at the top part while large finger-like structures were observed at the middle and at the bottom of the membrane cross-section. These finger-like structures were obtained during the non-solvent induced phase separation (NIPS) process when immersing the flat sheet membrane in the water bath tub.

On the other hand, the MMM produced clearer and greater number of pores compared to the pristine PVDF membrane. The presence of Fe_2O_3 induced the generation of more pores in the MMM. Moreover, this inorganic nanoparticle improved the porosity of the membrane and its mean pore size (Chen *et al.*, 2018; Liu *et al.*, 2016). Said *et al.* (2017) reported that the addition of iron oxide nanoparticles in the host polymer would increase the porosity and surface hydrophilicity, by increasing the surface roughness of the membrane. Membrane with high hydrophilicity and surface roughness has a low tendency of fouling effect, where this will contribute to a long-term membrane stability and water flux. It is demonstrated that the surface roughness has a significant relevance to membrane fouling (Panda *et al.*, 2015).

The MMM cross-section showed a straight finger-like structure compared to the pristine PVDF membrane that obtained a longer and bent finger-like structure. Based on Fig. 1, this phenomenon was resulted during the NIPS process, where the solvent in the MMM was ejected faster from the membrane that was induced by Fe_2O_3. The pristine PVDF membrane obtained a longer and bent finger-like structure due to the delay of solvent that came out from the membrane.

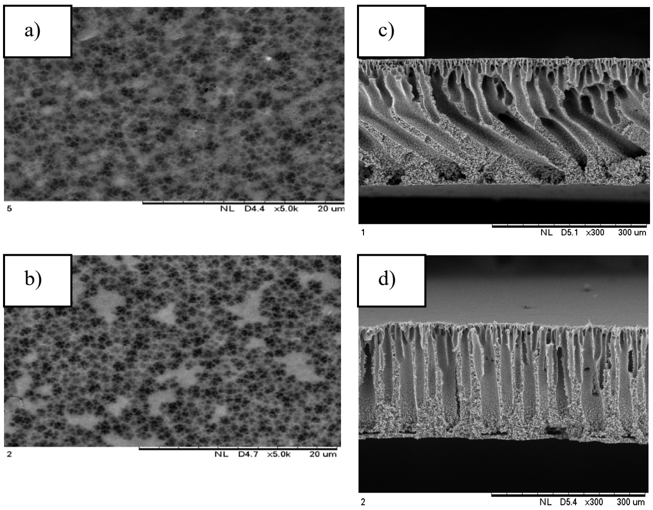

Fig. 1 The surface and cross section membrane of SEM images for neat PVDF (a and c) membrane and MMM (b and d).

Membrane performance

The pure water flux obtained by the neat PVDF and MMM was 33 L/m^2.h and 46 L/m^2.h, respectively. MMM with the addition of Fe_2O_3 had increased the performance of the membrane by 20% compared to that in the neat PVDF. The addition of additive loading in the polymeric solution improved the wetting properties, where the Fe_2O_3 increased the hydrophilicity of the membrane compared to what it did to the pristine PVDF membrane. This phenomenon was due to the growth of the membrane sublayer, thus improving the porosity of the membrane as compared to that of the neat PVDF membrane (Said *et al.*, 2017). The presence of Fe_2O_3 incorporated in the membrane helped to improve the surface hydrophilicity, which further promoted the interactions between the membrane surface and water.

The oil rejection of PVDF membrane and MMM obtained was higher than 90%, where both achieved oil rejection of 94% and 97%, respectively. Moreover, the addition of this inorganic material improved the underwater oleophobic characteristics of the membrane (Song *et al.*, 2017). The underwater oleophobic membrane is a good candidate to be applied in the oily wastewater treatment as it helps in reducing the fouling problem because the membrane tends to repel the oil droplet molecules (Li *et al.*, 2018). This situation can improve the membrane flux due to the oleophobic layer that acts as a resistance by avoiding oil from sticking or attaching on to the membrane surface.

Apart from that, the high water flux and oil rejection performances were contributed by the membrane morphological structure. As for the pristine PVDF membrane morphology, the dense surface of membrane resulted in the low attainability of water molecules to pass through the membrane. This was due to the PVDF hydrophobic nature that reduced the water affinity between water molecules and membrane surface (Liu *et al.*, 2017). On the other hand, the hydrophilic modified PVDF/ Fe_2O_3 changed the finger-like structure of the pristine PVDF as mentioned in membrane morphology part. The straight MMM finger-like structure driven the water molecules to transport faster without obstacles as in pristine PVDF membrane.

During the oily wastewater operation, the membrane fouling and flux decline issues are not new to oily wastewater treatment. The accumulation of emulsified oil droplets on the membrane surface is likely to occur, resulting to the formation of cake layer, clogged pore and coalescence of oil (Huang *et al.*, 2018). Hence, a material that can induce oleophobic characteristics is required to fulfil the requirement for oily wastewater treatment. The PVDF nanocomposite with the presence of Fe_2O_3 can induce the negative charge of the MMM as PVDF itself is a negative charge material when immersing in oil/water emulsion (Chen *et al.*, 2018). Thus, this will increase the repellence between the membrane surface and oil droplets as the oil droplet~~s~~ is also a negative charge – increase membrane oleophobicity. This repellence increases the MMM performance due to the enhancement in hydrophilicity and olephobicity which can reduce the fouling issue. Fig. 2 shows the results of pure water flux and oil rejection percentage for neat PVDF membrane and MMM.

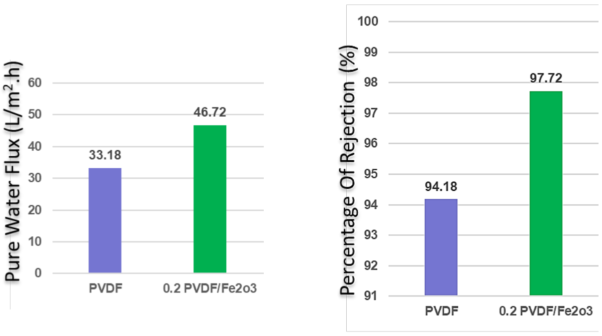

Fig. 2 Pure water flux and oil rejection percentage of neat PVDF membrane and MMM.

Comparison of membrane application for oily wastewater treatment

The result of the present work had been compared with the literature and summarized in Table 1. Lai *et al.* (2017) composed MMM by combining two nanofillers, which were the hydrous manganese oxide (HMO) and titanium dioxide (TiO_2) with PES as the main polymer. The incorporation of HMO contained higher amount of -OH functional groups compared to TiO_2. The optimum ratio of the material was studied in order to obtain membrane with high water flux and wetting properties. The HMO:TiO_2 ratio of 0.75:0.25 achieved water flux at 31.73% higher than the neat PES. The fabricated membrane managed to obtain water flux at 43.4 L/m^2.h and oil rejection of 99.5%.

Furthermore, inorganic material is also used as a coated layer by surface coating modification of polymeric membrane. Silica nanoparticles (SiNPs) was utilized by surface coating on the chitosan/perfluorooctanoate (PFO)-PVDF membrane. SiNPs was used to increase the surface roughness of the membrane, hence, improving its hydrophilicity. Chitosan/(PFO)-PVDF coated with SiNPs has a highly stable performance with good fouling resistance compared to the chitosan-PVDF due to the contribution of PFO that lowered the surface energy. Chitosan/(PFO)-PVDF + SiNPs exhibited water flux at 26.80 ± 0.68 L/ m^2.h and oil rejection of almost 100% with superhydrophilicity and underwater superoleophobicity characteristic.

As the main polymer itself may not fulfil the requirement of the membrane for oily wastewater treatment, thus one of the modifications that can be made is by adding additive polymer. Wang *et al.* (2017) chose PVDF as the main polymer blending with various weight percentages of polycarbonate (PC). Increasing the PC content might also increase the concentration of the polymer blending solution, thus inducing low-porosity and dense spongy membrane morphology structure. The highest permeate flux of 28.59 L/m^2.h and oil rejection of 97.8% were achieved when 20 wt% of PC was blended with PVDF.

Apart from the polymeric membrane, ceramic membrane is a reliable process for the oily wastewater treatment emulsion, yet it is still hindered due to the membrane fouling problem. Lu *et al.* (2016) fabricated the ceramic membrane by a pre-coated dynamic membrane using Fe_2O_3 that acted as protection and filtration membrane. It significantly reduced the ceramic membrane fouling by increasing 10% of the flux recovery rate after four filtration cycles. The pre-coated Fe_2O_3 showed a good performance as it is simple and efficient strategy to reduce the ceramic membrane fouling. The addition of Fe_2O_3 had increased the modified ceramic membrane hydrophilicity by almost 50% from its original water contact angle, which was from 39.9 ± 2.0° to 26.6 ± 1.6°.

In this present work, 0.2 wt% of Fe_2O_3 was mixed in the host polymer PVDF. This work achieved water flux of 46.7 L/m^2.h and oil rejection of 97.7%. The water flux and oil rejection performances of the MMM prepared in this work exhibited comparable results with those of previous studies. This indicated that the PVDF mixed with Fe_2O_3 can be considered as one of the promising candidates for oily wastewater treatment. However, several improvements have to be made in order to compete with the present technologies in oily wastewater treatment.

Table 1 Membrane for oily wastewater treatment reported by previous studies.

Material	Performance		Reference
	Water Flux (L/m^2.h)	Oil Rejection (%)	
PES/HMO/TiO_2	43.4	99.5	Lai *et al.*, 2017
Chitosan/PFO-PVDF SiNPs	26.8	99.9	Wang and Lin, 2017
PVDF/PC	28.6	97.8	Masuelli, 2015
Ceramic+Fe_2O_3	-	97.8	Lu *et al.*, 2016
PVDF/ Fe_2O_3	46.7	97.7	This work

In addition, biodegradable polymers can also be considered as a host polymer due to their non-toxic nature, readily available and inexpensiveness, in which they are rarely used (Risica *et al.*, 2010). Paixão and Balaban (2010) discovered guar gum as an alternative material for the treatment of oily water treatment by conventional methods. Guar gum is a natural polymer of low cost and high hydrophilicity. The membrane from this guar gum material managed to remove 90% of 100-ppm oily water. Meanwhile, Cheng *et al.* (2017) fabricated a membrane from renewable marine resources (tunicate shells). The high occupancy of hydroxyl groups in the tunicate cellulose nanocrystals (TCNCs) created membranes that were superhydrophilic, with the attainment of underwater superoleophobic wettability properties. The pore size of the membrane was determined by the weight percentage of the said biodegradable polymer, resulting in water flux of 1,700 L/m^2.h and rejection rate of more than 90%. Referring to the aforementioned literature, the material used in producing the membrane is important as the characteristic of the membrane depends on the main material utilized.

CONCLUSION

The MMM was succesfully fabricated by employing 0.2 wt% of Fe_2O_3 as the nanoparticles in PVDF. The addition of this inorganic material had improved the porosity of the membrane that eventually induced better hydrophilicity compared to its neat membrane. The MMM membrane exhibited water flux of 46 L/m^2.h, which was 20% higher than the neat PVDF. While for oil rejection, both polymers managed to obtain oil rejection higher than 94%. In order to obtain membrane with high performance in oily wastewater treatment, the wetting properties (hydrophilic and oleophobic) of the membrane must be taken into account. It is believed that membrane with hydrophilic surface will induce high flux and oil rejection rates that are comparable with the present technologies.

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