Effect of various oil/water emulsion concentration towards PVDF/HMO mixed matrix membrane performance

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Abstract: Meeting environmental quality standard for water and freshwater requires the use of innovative technologies, such as membrane technology for treating oily wastewater. Nevertheless, polymeric membrane require modification, as it is incapable of separating or removing oil molecules from oily wastewater. As such, this study incorporated the hydrous manganese dioxide (HMO) with polyvinylidene fluoride (PVDF) to attain mixed matrix membrane (MMM) for separation of various oil/water emulsion concentration feeds (50 ppm, 100 ppm, 500 ppm and 1000 ppm) by using lubricant oil. It was observed that the addition of HMO in MMM had altered the membrane surface morphology, as well as the wetting properties. The presence of HMO in MMM had increased the membrane hydrophilicity, as it reduced the water contact angle value by up to 40%. Apart from that, the MMM was able to increase the oleophobicity of the membrane by increasing 35% of the oil contact angle value. Both pristine PVDF membrane and PVDF/HMO MMM showed a flux decline with increasing oil/water emulsion concentration but managed to achieve oil rejection percentage greater than 93%.

1. Introduction

Oily wastewater that is rich hydrocarbon can have a negative impact on ecological resources and their functions, such as surface and groundwater resources, aquatic system, and human health. Moreover, there is poor biodegradability of oil in a natural ecosystem, which hinders the biological function in environment to the prolonged presence of oil components [7, 10]. Hence, it is necessary to remove oil components from wastewater prior to their discharge according to the standard limits set by the regulatory bodies. Membrane technology is a favourable candidate with very promising potential. However, polymeric membrane is unable to compete with the present technology due to its disadvantages, such as easy to foul during operation [15]. Therefore, enhancement is necessary to improve the membrane performance. One encouraging alternative is the incorporation of nanoparticles in a polymeric membrane matrix. The addition of nanoparticles in membrane could alter the natural characteristics of the host polymer [3, 13, 14], for example, the wetting properties of a membrane, as well as its surface roughness, and membrane morphology, this also improves the membrane antifouling performance. Generally, most applied polymers are hydrophobic; in order for them to be applicable in oily wastewater treatment for the acquirement of clean water, the membrane must be hydrophilic and have oleophobic wetting properties.
Ahmad et al [1] investigated the effect of bentonite nanoclay weight percentage towards the ultrafiltration mixed matrix membrane (MMM) by using polyvinyl chloride (PVC) as host polymer. The ultrafiltration MMM was fabricated to study the efficacy and permeate flux performance of the membrane to separate oily wastewater with zero salinity and at 35,000 ppm salinity. The low-cost bentonite nanoparticles were chosen as they can enhance the membrane hydrophilicity and antifouling behavior [9]. The bentonite nanoclay had varied for the four different weight percentages (2, 4, 6 and 8 wt%) where 6 wt% was found to be optima. The water contact angles for pristine PVC membrane and PVC/bentonite (6 wt%) MMM were obtained at 74.9° and 68.4°, respectively. This proved that the presence of bentonite nanoclay in the MMM have enhanced the membrane hydrophilicity. Furthermore, this membrane hydrophilicity had induced better water permeation, as the pure water fluxes for pristine PVC membrane and MMM were attained at approximately 171 L/m²·h and 412 L/m²·h, respectively. The PVC/bentonite (6 wt%) was further studied by comparing the oil rejection percentage and permeate flux in zero salinity (oil rejection of 97.0% and permeate flux at 186 L/m²·h) and 35,000 ppm salinity (oil rejection of 92.5% and permeate flux at 94 L/m²·h) in 200 ppm of oil/water emulsion concentration.

In addition, Nasrollahi et al [14] incorporated copper oxide (CuO) with polyethersulfone (PES) to study the effect of the hydrophilic nanoparticles in MMM through the addition of polyvinyl pyrrolidone (PVP) via phase inversion method. The CuO nanoparticles were expected to improve the membrane hydrophilicity, porosity, and surface properties [2]. The water contact angles of pristine PES and PES/CuO MMM were obtained at 69.8° and 61.9°, respectively. Result showed that the membrane hydrophilicity of the MMM had increased at about 12% compared with that of its pristine membrane. The pure water fluxes performance of the pristine PES and PES/CuO MMM was observed at 533 L/m²·h and 870 L/m²·h, respectively. The presence of hydroxyl groups in MMM contributed to better hydrophilicity, as well as to the water flux performance [8]. Apart from that, the addition of CuO in MMM (11.3nm) had resulted in smoother membrane surface compared with that in pristine membrane (31.5 nm). The 0.1wt% CuO was the optima amount in this study, as it exhibited the best antifouling flux recovery ratio (FRR) of 60% due to the low surface roughness value of the MMM. Membrane with high surface roughness value may be prone to fouling issue and incompatibility in its application in oily wastewater treatment [4, 17].

In this study, polyvinylidene fluoride (PVDF) was used as the host polymer. However, the natural characteristics of PVDF membrane without further modification make direct application impossible in oily wastewater treatment. Thus, the addition of nanoparticles were seen as one option to fabricate membrane with high hydrophilicity and oleophobicity for the purpose of ease of application [13]. Recently, various nanoparticles have been applied to gain the required propensity apart from its wetting properties. Hydrous manganese dioxide (HMO) was utilized in this study due to the high amount of hydroxyl groups that could improve the surface roughness, high affinity between water molecules and membrane surface, and repellency of oil molecules [5]. Previously, Lai et al [11] studied ratio of HMO and TiO₂ incorporated into polyethersulfone (PES), where the optimum ratio was HMO:TiO₂ at 0.75:0.25 that was 17.31 wt% of HMO. The HMO increased MMM hydrophilicity, however the water flux performance was quite low (28.48 L/m²·h) although the oil/water emulsion used was only 500 ppm. It is believed that the addition of nanoparticles in MMM indeed improved the wetting hydrophilicity, however the oleophobicity of the membrane was not observed in their study. Thus, based on our previous study [5], the optimum amount of HMO incorporated in PVDF was evaluated by using 500 ppm oil/water emulsion concentration as feed with pure water flux of 402 L/m²·h. In addition, the oleophobicity of the membrane were tested to show the MMM resistance towards oil droplet. Greater amount of oil/water emulsion concentration in feed is to be further tested in this work in order to see the improvement made by addition of HMO. At the same time, this paper would also like to prove that low oil/water emulsion concentration can easily be separated by this fabricated MMM. The objective of this work is to investigate the effect of various oil/water emulsion concentration towards the performance of PVDF/HMO MMM and its pristine PVDF membrane. It is understood that the PVDF/HMO membrane can achieve higher pure water flux and attain improved antifouling resistance compared with that via pristine PVDF membrane. This is owing to the presence of hydroxyl (−OH) functional groups in the HMO nanoparticles that increases the membrane hydrophilicity and enhances membrane resistance towards the adhesion of oil droplets on the membrane surface.
2. Materials and methods

2.1 Materials
Polyvinylidene fluoride (PVDF, Kynar® 760) pellets (Arkema Inc., Philadelphia, USA) was used as the host polymer, while N-Methyl-2-Pyrroldione (NMP) (Merck, > 99%) was used as solvent to generate a homogenous dope solution. The HMO nanoparticles were synthesized using manganese (II) sulfate monohydrate (MnSO₄·H₂O), potassium permanganate (KMnO₄) and sodium hydroxide (NaOH); all of which were obtained from Merck.

2.2. Synthesis of HMO nanoparticles
HMO nanoparticles were formed via the oxidation of manganese ions via an applied method in Parida et al [16]. Potassium permanganate (KMnO₄) was dissolved in deionized water, followed by adding 1M of sodium hydroxide (NaOH) until the pH reached 12.5. This solution was then added drop-wise into the MnSO₄·H₂O solution with deionized water under vigorous stirring. Then, a brown precipitate was obtained, which showed the presence of hydrorous manganese oxide (HMO). The HMO was washed with deionized water until it reached a neutral pH, where it was then left for several weeks for aging purposes. Finally, the nanoparticles product was dried at 65°C and stored in a dry place.

2.3. Fabrication of composite membrane
The MMM was prepared by phase inversion technique, where 18 wt% and 10 wt% of PVDF polymer and HMO nanoparticles, respectively, were stirred in NMP at 60°C for 24 h. The polymer and nanoparticles was added gradually to avoid precipitation. After a homogenous solution was obtained, the dope solution was placed in sonicator in order to remove the bubbles that had formed during stirring. The pristine PVDF membrane was prepared with the same preparation method without the addition of HMO nanoparticles. The nomenclatures of the resultant membrane were given in the form of PVDF_feed as the pristine membrane and HMO_feed as the PVDF/HMO MMM (i.e. PVDF_50ppm, PVDF_100ppm, PVDF_500ppm, PVDF_1000ppm, HMO_50ppm, HMO_100ppm, HMO_500ppm and HMO_1000ppm).

The flat sheet membrane was fabricated via the casting method. 20 ml of dope solution was poured onto a clean glass plate, where a roller glass was used to obtain the flat sheet membrane. The cast membrane with glass plate was immersed into tap water for phase-inversion. The membrane was naturally delaminated from glass plate and transferred to another coagulation bath. The membrane then went through a post-treatment prior to being dried in oven at 40°C for 24 h. Every membrane was tested with three different samples, and three readings were taken for each sample.

2.4. Characterization
The cross-section morphologies of the membrane were inspected using a Scanning Electron Microscope (SEM; JEOL JSM-5610LV model). Deionized water and lubricant oil were utilized as probe liquid for water contact angle and oil contact angle goniometers respectively (OCA 15Pro, DataPhysics). The membrane porosity was measured using Equation 1, which is the gravimetric method.

\[
\varepsilon = \frac{\omega_1 - \omega_2}{\rho \times l \times d_{\text{w}}}
\]  

(1)

where \(\omega_1\) is the wet membrane weigh, \(\omega_2\) is the dry membrane weight, \(A\) is the membrane effective area (m²), \(d_{\text{w}}\) is the water density (0.998 g/cm³), and \(l\) is the membrane thickness (m). The membrane was immersed in deionized water for 4h to ensure that the water is fully occupied within the membrane pores, where it was then dried using filter paper and weighed. Next, the membranes were put inside an oven overnight before it was weighed again.

The Guerout-Elfond-Ferry equation was employed to evaluate the mean pore radius \(r_m\) of the membrane, as shown in Eq. 2:
\[ r_m = \sqrt{\frac{(2.9 - 1.75 \varepsilon) \times 8 \eta l Q}{e \times A \times \Delta P}} \]  

(2)

where \( \eta \) is the water viscosity \((8.9 \times 10^{-4} \text{ Pa.s})\), \( l \) is the membrane thickness \((\text{m})\), \( Q \) is the volume of the permeate pure water per unit time \((\text{m}^3/\text{s})\), \( A \) is the membrane effective area, and \( \Delta P \) is the operating pressure \((\text{Pa})\). The membrane pore size (diameter) may be derived by multiplying \( r \) by 2.

2.5. Preparation of oily feed solution

Lubricant oil, sodium dodecyl sulfate (SDS), and deionized water were mixed to prepare the various oily feed solutions \((50 \text{ ppm}, 100 \text{ ppm}, 500 \text{ ppm} \text{ and } 1000 \text{ ppm})\). The surfactant -SDS was used to stabilize the oil/water emulsion. Lubricant oil -to- SDS in oil/water emulsion ratio was 9:1 \((\text{w/w})\).

2.6. Membrane performance test

The pure water flux was attained from a cross-flow system. Prior to flux determination, all membranes were compacted at 2 bar until a steady-state condition was achieved. Subsequently, the equation (Eq. 3) below was used to calculate the pure water flux \((J_w, \text{L/m}^2 \cdot \text{h})\) at an ambient pressure of 1 bar:

\[ J_w = \frac{Q}{A \times \Delta T} \]  

(3)

where, \( Q \) is the volume of permeate collected over a specific time \((\text{L})\), \( A \) is the membrane effective surface area \((\text{m}^2)\), and \( \Delta T \) is the sampling time \((\text{h})\). Additionally, Eq. 3 was employed to calculate the permeate flux during the treatment of the oil/water emulsion. The membrane oil rejection rate \((R)\) was determined as per Eq. (4). The efficacy of the membranes’ separation of oil molecules from oil/water emulsion was calculated using the equation below:

\[ R = \left( 1 - \frac{C_p}{C_f} \right) \times 100 \]  

(4)

where, \( R \) is the process of rejection ultrafiltration \((\%)\), \( C_p \) is the concentration of the permeate \((\%)\), and \( C_f \) is the concentration of feed \((\%)\). The oil concentration was determined by UV–Vis spectrophotometer (Model UV-3101PC) at a wavelength of 320 nm, 304 nm, 293 nm and 292 nm for 1000 ppm, 500 ppm, 100 ppm and 50 ppm, respectively.

3. Results and discussion

3.1. Membrane surface morphology

The membrane cross-section morphology of pristine PVDF and PVDF/HMO membrane is shown in Figure 1. Both membranes showed typical asymmetric structure that had resulted from the phase inversion process. The top and bottom parts of the membrane showed a thin layer of porous sub-layer and finger-like structure lying within the cross-section membrane. The finger-like structure of pristine membrane was slightly different from that in the MMM due to the presence of the HMO nanoparticles in MMM. The existence of HMO nanoparticles in the PVDF/HMO MMM had led to high exchange rates between the solvent and non-solvent during phase inversion surface, compared with that in pristine PVDF membrane, in which the exchange rates were delayed [13]. These exchange rates were determined by the solvent emerging from the membrane, where membrane with high hydrophilicity tends to remove solvent faster than hydrophobic membrane can [8]. The difference morphology structure of MMM from pristine membrane induced a high water flux performance and affinity between the membrane and water molecules. As the addition of HMO nanoparticles in the MMM had increased its hydrophilicity, the tendency of oil droplets from assembling on the membrane surface and within the membrane pores is also reduced. This statement was further discussed in section 3.2.
3.2. Membrane wetting properties

The wetting properties play a dominant role behind the membrane oil/water emulsion separation and its antifouling performance. Table 1 present the details of membrane wetting properties, which are water and oil contact angle for PVDF membrane and MMM. The water and oil contact angle of pristine membrane is 99.3° and 0°, respectively. The wetting properties value of pristine membrane shows that the membrane was hydrophobic and oleophilic, as they are the natural characteristics of a PVDF membrane [7]. When oil was dropped onto the membrane surface, the oil immediately dispersed into the membrane in less than two seconds, which made it impossible to measure the angle of the oil droplets. Meanwhile, the presence of HMO nanoparticles in MMM was altering the membrane’s wetting properties. The MMM showed hydrophilic and oleophobic characteristics for water and oil contact angle of 58.7° and 35.1°, respectively. The water droplet exhibited a lower water contact angle value when dropped onto the membrane surface, which shows that the presence of HMO nanoparticles had increased the affinity between the membrane surface and water molecules. Moreover, the tendency of oil molecules penetration into the membrane was reduced as the oil contact angle value was higher than that in pristine membrane. The hydroxyl groups of HMO in the modified membrane formed a hydrogen bonding and resulted to hydration, where it lowered the surface energy as a consequence of the membrane surface becoming oleophobic [12]. By default, the presence of hydroxyl functional groups from the HMO will contribute to the changes of MMM wetting properties and ensure the practical application of MMM in oily wastewater treatment.

Table 1. Wetting properties of pristine PVDF membrane and PVDF/HMO MMM.

| Membrane              | PVDF    | PVDF/HMO |
|-----------------------|---------|----------|
| Water contact angle   | 99.3    | 58.7     |
| Oil contact angle     | 0       | 35.1     |
3.3. Water flux and oil rejection

The pure water flux performances for pristine PVDF membrane (42 L/m²·h) and PVDF/HMO MMM (402 L/m²·h) have been discussed in a previous work, where the modified membrane had achieved almost 10 times higher flux than PVDF membrane [5]. In this study, further performance was studied, where various feed oil/water emulsion concentrations of 50 ppm, 100 ppm, 500 ppm, and 1000 ppm were used. Both membranes showed oil/water rejection percentage greater than 93%; however, the water flux decreased with increasing oil/water emulsion concentration feed. Pristine membrane showed decreasing flux beginning from 39.23 L/m²·h, 32.19 L/m²·h, 26.55 L/m²·h, and eventually 5.79 L/m²·h for 50 ppm, 100 ppm, 500 ppm, and 1000 ppm of oil/water emulsion concentration, respectively. The decrement in flux was due to the cake layer formation on the membrane surface and membrane pore blockage by the oil droplets [18]. Around 85% of flux had declined from 50 ppm to 1000 ppm of feed concentration. Increasing oil/water concentration also increased the oil molecules in the feed concentration. Thus, more oil droplets were able to easily penetrate the membrane pores, leading to pore blockage due to the oleophilic characteristics of the pristine membrane wetting properties [15].

In addition, the hydrophobic nature of the PVDF makes it almost impractical for the water molecule to pass through the membrane. In different circumstances, the presence of HMO in the MMM exhibited higher flux compared with that in unmodified membrane. The fluxes obtained were 288.44 L/m²·h, 196.93 L/m²·h, 53.26 L/m²·h, and 37.80 L/m²·h for oil/water emulsion feed concentrations of 50 ppm, 100 ppm, 500 ppm, and 1000 ppm, respectively. Although the flux filtration for MMM declined with increasing oil/water emulsion, the result of oil/water separation flux still showed higher compared with pristine membrane. The addition of HMO in MMM had increased the membrane filtration flux as it improved the MMM hydrophilicity and membrane oleophobicity owing to the existence of hydroxyl groups in the nanoparticles. This is attributed by the longer time taken by oil molecules to disperse or assemble on the membrane surface, which can slow down the formation of cake layer formation and MMM hydrophilicity, thus demonstrating a greater flux filtration performance. Furthermore, the HMO functional groups in the MMM had induced low membrane surface roughness, as high surface roughness value is prone to fouling issue [6].

![Graph](image-url)
Figure 2. Oil/water emulsion filtration flux at various feed concentration for a) PVDF membrane b) PVDF/HMO MMM.

4. Conclusion
In this work, various lubricant oil/water emulsion concentration feeds were tested by comparing pristine PVDF membrane with PVDF/HMO MMM filtration performance. The PVDF/HMO MMM was successfully fabricated via the incorporation of HMO nanoparticles with PVDF polymer. The SEM images showed that the presence of HMO in MMM acted as modifier by altering the membrane morphology and increased the membrane hydrophilicity and oleophobicity. The altered membrane morphology had eased the water molecules to pass through the membrane. The PVDF/HMO MMM (water contact angle: 58.7° and oil contact angle: 35.1°) had obtained higher hydrophilicity and oleophobicity than pristine PVDF membrane (water contact angle: 99.3° and oil contact angle: 0°) due to the presence of hydroxyl functional groups from the HMO nanoparticles. In addition, the oleophobic characteristic had lowered the possibility of oil droplets assembling on the membrane surface. For separation flux performance, pristine PVDF membrane showed a lower flux, as the PVDF faced higher chances of fouling due to its hydrophobic and oleophilic nature. The flux separation performances for 50 ppm, 100 ppm, 500 ppm, and 1000 ppm for pristine membrane were 39.23 L/m²·h, 32.19 L/m²·h, 26.55 L/m²·h, and 5.79 L/m²·h, respectively; while that for PVDF/HMO MMM were 288.44 L/m²·h, 196.93 L/m²·h, 53.26 L/m²·h, and 37.80 L/m²·h, respectively. The oleophilicity characteristic of the PVDF had attracted oil droplets into attaching themselves to the membrane, thereby easily causing pore blockage. In addition, PVDF/HMO MMM can achieve a good flux value even at high oil/water emulsion concentration. This study revealed the potential application of HMO nanoparticles in oily wastewater treatment.

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References

[1] Ahmad T, Guria C and Mandal A 2018 *Process. Saf. Environ. Prot.* **116** 703-17
[2] Baghbanzadeh M, Rana D, Matsuura T and Lan C Q 2015 *Desalination* **369** 75-84
[3] Deng Y, Zhang G, Bai R, Shen S, Zhou X and Wyman I 2019 *J. Membr. Sci.* **569** 60-70
[4] Islam M S, McCutcheon J R and Rahaman M S 2017 *J. Membr. Sci.* **537** 297-309
[5] Ismail N, Salleh W, Awang N, Ahmad S, Rosman N, Sazali N and Ismail A 2019 *Chem. Eng. Comm.* 1-11
[6] Ismail N, Salleh W, Hasbullah H, Aziz F, Awang N, Ahmad S, Rosman N and Ismail A *IOP Conf. Ser.: Mater. Sci. Eng.* **736** 052004
[7] Ismail N H, Salleh W N W, Ismail A F, Hasbullah H, Yusof N, Aziz F and Jaafar J 2020 *Sep. Purif. Technol.* **233** 116007
[8] Ismail N H, Salleh W N W, Rosman N, Awang N A, Hasbullah H, Aziz F and Yusof N 2019 *Malaysian J. Fund. Appl. Sci.* **15**(5) 703-07
[9] Kumar S, Guria C and Mandal A 2015 *Sep. Purif. Technol.* **150** 145-58
[10] Kundu P and Mishra I M 2018 *T Rev. Chem. Eng.* **35**(1) 73-108
[11] Lai G, Yusob M, Lau W, Gohari R J, Emadzadeh D, Ismail A, Goh P, Isloor A and Arzhandi M R-D 2017 *Sep. Purif. Technol.* **178** 113-21
[12] Makanjuola O, Ahmed F, Janajreh I and Hashaikeh R 2019 *J. Membr. Sci.* **570** 418-26
[13] Moeinzadeh R, Ghadam A G J, Lau W J and Emadzadeh D 2019 *Carbohydr. Polym.* **225** 115212
[14] Nasrollahi N, Aber S, Vatanpour V and Mahmoudi N M 2019 *Mater. Chem. Phys.* **222** 338-50
[15] Otitoju T, Ahmad A and Ooi B 2016 *J. Water. Process. Eng.* **14** 41-59
[16] Parida K, Kanungo S and Sant B 1981 *Electrochim. Acta* **26**(3) 435-43
[17] Shamaei L, Khorshidi B, Islam M A and Sadrzadeh M 2020 *J. Clean. Prod.* **256** 120304
[18] Zhou L, He Y, Shi H, Xiao G, Wang S, Li Z and Chen J 2019 *J. Hazard. Mater.* **380** 120865