Development of antifouling poly(vinylidene fluoride) ultrafiltration membrane with the addition of polyethylene glycol as additive

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Abstract. Poly(vinylidene fluoride) (PVDF) is commonly used to fabricate ultrafiltration (UF) membrane due to its excellent thermal stability and chemical resistance. However, it is hydrophobic and hence has higher fouling tendency due to hydrophobic interaction with foulants. In this study, the antifouling properties of PVDF UF membranes was enhanced through the addition/blending of hydrophilic polyethylene glycol (PEG) of varying molecular weight. The addition of low molecular weight (200 Da, 4000 Da) PEG enhances the membrane’s pure water permeability (from 22.049 L/m² hr bar to 24.791 L/m² hr bar) which could be explained by the improved surface wettability. However, the addition of large PEG (35k Da) on other hand reduces the membrane’s pure water permeability (from 20.408 L/m² hr bar to 9.181 L/m² hr bar), with increasing rejection on humic acid (82.6 % to 98.5 %). This is due to the formation of a denser membrane with narrower surface pores. The membrane synthesized from 20% (w/v) PVDF with the addition of 4 g PEG 4000 Da showed better antifouling characteristic compared to pure PVDF membrane which could be explained by the enhancement of surface hydrophilicity. Nonetheless, the PVDF/PEG composite UF membrane suffered from rejection loss due to the leaching of PEG molecules from the membrane matrix. Lastly, a regeneration test is performed by flushing the used membrane (after the filtration on humic acid) with distilled water for one-hour duration. SEM images on the membrane surface reveals that the deposited humic acid layer was completely removed and the membrane was successfully recovered to its initial state. The results signified that the addition of PEG could enhances the hydrophilicity of the membrane and hence improving the membrane’s antifouling characteristic.

Keywords: Ultrafiltration membrane, Antifouling, Polyethylene glycol, Blending, Additive leaching
1. Introduction
Ultrafiltration (UF) is a pressure-driven membrane which has the pore size ranging from 0.01 µm to 0.1 µm. Ultrafiltration (UF) has been reported for the use in removal of suspended solids, bacteria, viruses, endotoxins and other pathogens from water [1]. During the filtration process, the membrane is prone to lose permeability due to fouling phenomena. Formation of a scale layer on top of membrane and pore blockage imposed higher resistivity to water passage across the membrane, hence reduces the water permeability. A higher pressure is required to retain or elevate the permeation flux. The scale layer formed on top of membrane surface could be removed via chemical or physical approach, however, a membrane suffered from non-reversible fouling could not able to be fully restored to its original condition by any means of washing process [2].

It is generally known that the membrane fouling is usually induced by hydrophobic-hydrophobic interaction. A PVDF membrane is easily suffered from fouling due to its hydrophobic nature. Hydrophilization of the membrane is considered as an effective way to enhance the antifouling characteristic of the membrane [3, 4]. A hydrophilic membrane could be developed through blending the PVDF with hydrophilic additive such as polyethylene glycol (PEG) [5]. In this work, a composite UF membranes that has enhanced antifouling characteristic was prepared through blending of PVDF with PEG of varying molecular weight through non-solvent induced phase separation. The separation performances, fouling characteristic and the changes on physicochemical properties of the membranes were evaluated.

2. Methodology

2.1. Chemicals
Poly(vinylidene fluoride) (PVDF) was purchased from Solvay; polyethylene glycol (PEG) of various molecular weight (200 Da, 4000 Da and 35000 Da) was purchased from Merck; N, N-dimethyl formamide (DMF), humic acid sodium salt and sodium hydroxide were purchased from Sigma Aldrich.

2.2. Membrane preparation
First, a PVDF polymer solution was prepared by dissolving 20% (w/v) of PVDF in DMF with the addition of PEG with varying molecular weight (200 Da, 4000 Da and 35k Da). Then, the solution was evenly spread onto a glass plate taped with polyester fabric using a stainless-steel thin film applicator. The glass plate with polymeric solution was immediately immersed in a water bath. All membranes were kept in distilled water until use.

2.3. Membrane characterization
The membrane surface morphology was characterized using a tabletop SEM (Hitachi, TM3000). The sample was sputter coated with platinum and the imaging was performed under electron accelerating voltage of 10kV. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) (Thermo scientific, Nicolet iS10) was used to identify the functional groups presented in a membrane. The wettability of the membrane surface is determined using a contact angle goniometer (Jikan, CAG-10).

2.4. Membrane’s performance evaluation
The filtration using PVDF membrane was conducted using cross-flow filtration unit. The membranes were evaluated for its pure water permeability, rejection on humic acid and antifouling properties using humic acid as model solute. Prior to permeation test, the membrane was compressed using distilled water at 1.5 bar about 2 hours. Afterwards, the membrane pure water flux (Jw, L/m² hrs) was measured at varying operating pressure from 0.5 bar to 1 bar and the permeability was calculated based on the slope of the flux versus the pressure. Next, the membrane was evaluated for its rejections on humic substances (r, %). After filtration on humic acid for 1 hour, the membrane was flushed using
distilled water under pressure 1 bar and flow rate 1.2 L/min. The water flux was monitored throughout the flushing process.

3. Result and discussion

The FTIR spectra of PVDF/PEG composite membranes prepared from varying PEG molecular weight is illustrated in Fig. 1. The peaks located at 1400 cm\(^{-1}\) is assigned to the -C-F- stretching while the band at 1180 cm\(^{-1}\) is attributed by the -CF\(_2\) group. However, the peak corresponds to hydroxyl groups which covers the range 3600-3300 cm\(^{-1}\) is insignificant for all the membranes, suggest that trace amount of PEG molecules presented in membrane matrix.

![FTIR spectra](image)

Figure 3.1: FTIR spectra of the membrane prepared from (a) 20 g of PVDF only, (b) 20 g of PVDF/4 g of PEG 200 Da, (c) 20 g of PVDF/4 g of PEG 4000 Da, (d) 20 g of PVDF/4 g of PEG 35000 Da.

The contact angle, pure water permeability and rejection of humic acid of the membranes prepared using varying PVDF/PEG composition is summarized in Table 3.1. Pure PVDF membrane recorded the highest contact angle at value of 75°. This infers that the membrane has the least surface wettability, which is not favours water permeation. Addition of PEG with molecular weight 200 Da and 4000 Da reduces the contact angle of membranes to 61.8° and 55° respectively, denotes the enhancement of the membrane surface wettability. However, the addition of PEG 35k Da on other hand elevates the contact angle to 63°. Such observation was explained by the membrane’s surface roughness. It is commonly accepted that a smoother membrane is obtained using a viscous polymeric solution [6]. The PVDF solution containing 4g of 35000 Da is viscous, hence a membrane with smoother surface is produced. A smoother surface leads to higher apparent contact angle according to Wenzel’s equation [7].

In overall, the addition of PEG of low molecular weight (200 Da and 4000 Da) improves the membrane permeability from 19.9 L/m\(^2\) hr bar (pure PVDF membrane) to 24.8 L/m\(^2\) hr bar (composite membrane with the addition of PEG 4000). The improved water permeability was explained based on its surface hydrophilicity. However, composite membrane PVDF/4g PEG 35k Da exhibited the lowest permeability (9.2 L/m\(^2\) hr bar). As explained earlier, the addition of PEG 35000 Da increases the viscosity of the polymeric solution, which subsequently renders a denser membrane. The membrane surface was smoother which reduces the effective surface area for the contact between water and membrane. From Table 3.1, the rejection on humic acid is increasing in the order of PVDF/PEG 200 Da < PVDF < PVDF/PEG 4000 Da < PVDF/PEG 35k Da. It could be explained by the formation of tighter membrane with the increasing of PEG molecular weight. A narrow pore enhances the rejection of humic acid through size exclusion.

Next, the membranes were prepared using varying amount of PEG 4000 Da (from 0 g till 4 g) and their water permeability and rejection on humic acid was determined. Refer to Table 3.1, increasing amount of PEG 4000 Da further reduces the contact angle, however, the pure water permeability was reduced (13.4 L/m\(^2\) hr bar), while the rejection on humic acid is increased to 99%. As mentioned
earlier, the addition of PEG produces a thicker PVDF polymer solution which lead to the formation of tighter and smoother membrane. In conclusion, the membrane prepared using PVDF/4 g PEG 4000 Da was selected to further investigate for its antifouling characteristic using humic acid.

| Membrane composition          | Contact Angle (°) | Pure water permeability (L/m² hr bar) | Rejection on humic acid (%) |
|-------------------------------|-------------------|--------------------------------------|----------------------------|
| 20% (w/v) PVDF                | 74.7              | 19.9                                 | 82.6                       |
| 20% (w/v) PVDF/2g PEG 200Da  | 61.8              | 22.0                                 | 78.7                       |
| 20% (w/v) PVDF/2g PEG 4000Da | 55.0              | 24.8                                 | 83.7                       |
| 20% (w/v) PVDF/2g PEG 35k Da | 63.2              | 9.2                                  | 98.5                       |
| 20% (w/v) PVDF/4g PEG 4000 Da | 53.2              | 13.4                                 | 99.0                       |

Fig. 3.2 and Fig. 3.3 shows the permeate flux recorded during the one hour filtration on humic acid, followed by another hour of flushing the membrane using distilled water. It can be observed from Fig. 3.2 that the pure PVDF membrane has a continuous flux declination during the filtration on humic acid. The membrane retained 78% of its initial flux after the filtration on humic acid for one-hour duration. The membrane was able to recover 87% of its initial permeability after an hour of flushing with distilled water. On other hand, the PVDF/PEG composite membrane shows continuously increment of flux during the filtration on humic acid (Fig. 3.2b). Such observations are rarely reported. The increment of flux suggests the leaching of PEG molecules from the membrane matrix during the filtration process. The leached PEG increases the membrane interior void space and creates a larger pore which promotes water permeation. However, a declination of water permeability during regeneration step suggests that the residual humic acid molecules (was previously presented as cake layer) can be accessed into the interior of the pore which clog the pore and block the water passage.

Figure 3.2: The normalized flux during the filtration on humic acid and flushing using distilled water of (a) pure PVDF membrane and (b) composite membrane synthesized from PVDF/PEG 4000 Da.

Figure 3.3 and Figure 3.4 compares the FTIR spectra between pure PVDF membrane and PVDF/PEG composite membrane before and after filtration of humic acid and after regeneration step. There is an additional peak found in the range of 3700 cm⁻¹ to 2800 cm⁻¹ for PVDF membrane after filtration of humic acid (Figure 3.3b) while there is no peak observed for PEG/PVDF composite membrane in the same range of wavenumber. The new peak is assigned to alcohol OH- stretch and carboxylic OH- stretch, which are the active functional groups presented in humic acid. This signified that the membrane synthesized using PEG/PVDF composite has improved anti-fouling characteristic compared to pristine PVDF membrane. The peak is disappeared after flushing the membrane with
distilled water, indicates that the humic acid accumulated on membrane surface are being removed (Figure 3.3c).

![FTIR spectra of the membranes synthesized using 20 g of PVDF membrane (a) before filtration, (b) after filtration on humic acid for one hour and (c) after flushing with water for one hour.](image)

Figure 3.3: FTIR spectra of the membranes synthesized using 20 g of PVDF membrane (a) before filtration, (b) after filtration on humic acid for one hour and (c) after flushing with water for one hour.

![FTIR spectra of the membrane synthesized using 20 g of PVDF/4 g of PEG 4000 Da membrane (a) before filtration, (b) after filtration on humic acid for one hour and (c) after flushing with water for one hour.](image)

Figure 3.4: FTIR spectra of the membrane synthesized using 20 g of PVDF/4 g of PEG 4000 Da membrane (a) before filtration, (b) after filtration on humic acid for one hour and (c) after flushing with water for one hour.

The surface morphologies of the PVDF/PEG composite membranes is illustrated in Fig. 3.5. There is a formation of humic acid cake layer on top of membrane surface after filtration with humic acid as demonstrated in Fig. 3.5b. The membrane surface is free from any observable cake after flushing with distilled water as shown in Fig. 3.5c. This further signified that the fouling layer of humic acid on membrane surface can be removed through a simple flushing step.
Figure 3.5: SEM image of the surface of membrane synthesized using 20 g of PVDF/4 g of PEG 4000 Da membrane, (a) before filtration, (b) after filtration on humic acid for one hour and (c) after flushing with distilled water for one hour.

Similar to other reported works, the addition of PEG improved the surface wettability and antifouling properties of the PVDF UF membrane. However, it offers some limitations to membrane performances. In this work, we found that the PVDF/PEG composite membrane suffered from flux increment and humic acid rejection declination during the filtration of humic acid. On the contrary, the flux of the composite membrane was declined during the regeneration using distilled water. The findings suggesting the swelling of the composite membrane matrix, which leads to an enlargement of surface pores. It is worth to further investigate how the embedment of PEG could stimulate the swelling of a membrane.

4. Conclusion

A hydrophilic PVDF membrane was produced through the blending of PVDF with PEG of various molecular weight. The membrane with highest hydrophilicity was produced through the blend of 20% (w/v) PVDF with 4 g of PEG 4000 Da. The membrane’s surface wettability is improved with the addition of low molecular weight PEG (200 Da and 4000 Da) initially, however, the contact angle is increased with the addition of larger molecular weight PEG (35k Da). The observation on contact angle reflected on the pure water permeability of membrane. The permeability has been increased from 19.9 L/m² hrs bar to 24.8 L/m² hrs bar with the addition of PEG 4000 Da. However, the permeability is declined to 9.2 L/m² hrs bar with the addition of 4 g of PEG 35k Da. The performance of the membrane was evaluated in terms of permeate flux and rejection on humic acid flux. Surprisingly, the permeation flux of membrane synthesized from PVDF/PEG blend was found to be continuously increased throughout the 1 hr filtration on humic acid. This finding is explained by the leaching phenomenon of PEG molecules from the membrane polymer matrix. The regeneration of the membrane was performed through flushing of the used membrane with distilled water for an hour. SEM images on the PVDF/PEG composite membrane shows the presence of deposited humic acid
cake layer on membrane surface after filtration on humic acid. The deposited layer was successfully removed and the membrane is fully recovered to its initial state after flushing with distilled water for one-hour duration. This lead to conclusion that the membrane with the addition of PEG has improved antifouling characteristic.

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