

# Ultrafiltration Behavior of Organic Mixtures Simulating Sweetwater Solutions: Influence of Membrane Surface and Feed Chemistry

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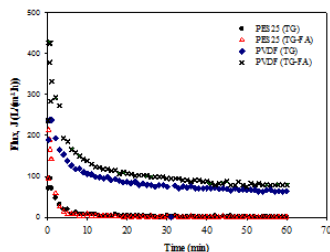
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## Graphical abstract



## Abstract

One of the major drawbacks for the successful of ultrafiltration (UF) during pretreatment of glycerin-rich solution is membrane fouling due to the deposition of triglycerides (TG) and fatty acids (FA). In the present study, attempts were made to examine the filtration behaviour of organic mixtures (oleic acid-triglycerides) compared to single organic solute (triglycerides) contained in synthetic glycerol-water solutions (known as sweetwater). Furthermore, the rejections of individual solutes were studied. The TG-FA mixtures permeated preferentially when compared with single TG which is mainly due to the solubility as well as diffusivity of small fatty acid in the TG-FA mixtures. Furthermore, PVDF membrane provided higher fluxes and experienced less fouling than PES membrane for both cases. In case of PVDF membrane, the rejection of fatty acid was 6.20% while oil rejection in glycerol-water plus TG and TG-FA mixtures was 82.42% and 84.67%, respectively. However, PES membrane underwent higher fatty acid rejection (20.93%) as well as oil rejection in single TG (94.70%) and TG-FA mixtures (91.08%). It is noteworthy that the nature of the membrane and the feed characteristics had a significant effect on the fouling potential and filtration performance.

**Keywords:** Adhesion; ultrafiltration; diffusion; fouling; wettability; triglyceride

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## 1.0 INTRODUCTION

Triglycerides (TG) and long chain fatty acids (FAs) are typically undesirable in the oleochemical and food industry.<sup>1</sup> The removal of TG and fatty acids from glycerine-water solutions is important because of their potential for severe fouling during the clarification process. Both of the solutes were expected to be the predominant cause of severe fouling due to them being smaller in size than the membrane pores. The ability of the solutes to adhere/adsorb on the membrane surface as well as within the pore may reduce the permeate flux dramatically.<sup>2</sup>

In recent years, a considerable amount of attention has been focused on the effects of oil droplets on the flux of ultrafiltration processes.<sup>3-5</sup> However, those investigations focused primarily on the ultrafiltration of solute-solvent systems; thus, considerably less attention has been paid to the pretreatment of TG in aqueous (solute-water) systems. Previously, the ability of various polymeric membranes to separate oil constituents (FFA, DG, MG and TG) from organic solvents has been investigated.<sup>3</sup> In addition, attempts have been carried out to separate FA and TG in the presence of alcohols and they suggest that membrane materials play an important role in the separation of FA and TG.<sup>6</sup> As a matter of fact, membrane

fouling by oil-water mixtures was influenced by the hydrophobicity of the membrane surface and could be reduced by improving the hydrophilicity behavior.<sup>7</sup> Moreover, the performance of dense membranes during the permeation of triglycerides, fatty acids and TG-FA mixtures is dependent on temperature and pressure. In particular, both parameters had a significant effect on the permeation rate of TG and fatty acids.<sup>8</sup>

Therefore, the aim of the present study was to investigate in detail the effects of the membrane surface chemistry and the pH of the feed solution toward the flux decline behavior during ultrafiltration of organic solutes. In fact, the attempt was to gain essential understanding regarding the contribution of single TG and its combination with fatty acids to ultrafiltration performance. The influence of dynamic fouling revealed the trend of the interaction between the membranes and the mixtures of organic solutes and their influence on permeate flux. Specifically, a glycerol-water solution (containing 15% glycerin) was evaluated, and polyethersulphone (PES) membranes with a MWCO of 25 kDa as well as polyvinylidene fluoride (PVDF) membranes with a MWCO of 30 kDa were used.

## 2.0 EXPERIMENTAL

### 2.1 Membranes

Ultrafiltration flat-sheet polymeric membranes based of PES and PVDF materials were purchased from Sterlitech

Corporation and used in the flux decline experiments. Both membranes were of the composite type using proprietary material which was not disclosed by the manufacturer. The maximum operating pressure for PES and PVDF membrane is 10.342 and 2.068 bar, respectively. The properties of the membranes are shown in Table 1.

**Table 1** Properties of membranes

Membrane	Manufacturer	Material	MWCO	Contact angle, $\theta$	Surface property
PES 25	Koch	Polyethersulphone	25000	74.10±0.2	Hydrophobic
PVDF	GE Osmonic	Polyvinylidene fluoride	30000	72.60±3.0	Hydrophobic

### 2.2 Permeation Experiments

Separation performance of PES and PVDF membranes was observed using a stainless steel stirred cell dead-end filtration module as described elsewhere.<sup>9</sup> The experiments were run in the water bath at 40°C, constant pressure of 2.0 bar and also constant stirring rate of 450 RPM to avoid the effect of concentration polarization on the surface. Permeation experiments were carried out using synthetic glycerol–water solutions plus single foulant (TG) and combined foulants (TG–FA). Glycerin (USP, 92.09 g/mol) and oleic acid (282.46 g/mol) purchased from Merck, and commercial TG (RBD Palm Olein, 870 g/mol) were obtained from the local hypermarket. Mixtures of 84% ultrapure water, 15% glycerin, 1% (v/v) TG and 0.003 g/L oleic acid were synthesized and used as a feed solution. The pH of the feed solution was altered between pH 3 to 10 with a few drops of 0.1 M HCl or 0.1 M NaOH and measured with a pH meter (Mettler Toledo). Additionally, the permeate samples were collected within 60 minutes of filtration time and analyzed for oil content with an oil content analyzer (HORIBA) in mg/L. On the other hand, the work of adhesion ( $W_a$ ) of the membrane materials was determined by applying Equation 1:

$$W_a = \gamma_L (\cos \theta + 1), \quad (1)$$

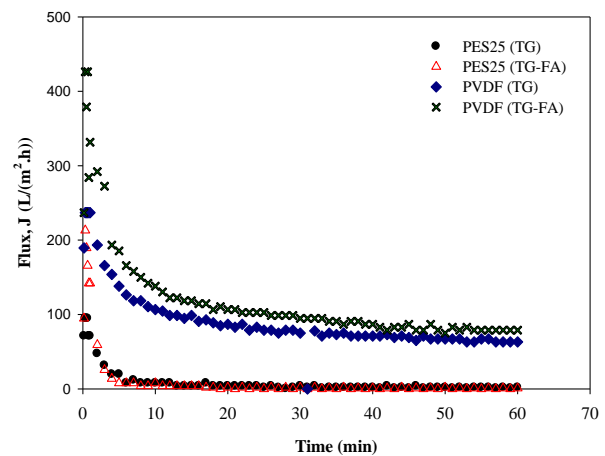
where  $W_a$ ,  $\gamma_L$  and  $\theta$  are the work of adhesion (N/m), the liquid surface tension (N/m) and the contact angle at the solid–liquid interface, respectively.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Effects of Membrane Surface Chemistry

Figure 1 depicts the actual flux ( $J$ ) of a glycerine–water solutions containing single hydrophobic solute (TG) and combined solutes (TG–FA) as a function of time. As shown in Figure 1, the flux declined rapidly during the first 15 min of filtration and constant values were achieved at longer operating times with PES25 membrane. However, for PVDF membrane, the flux decays continuously but slowly moving towards constant values after 40 minutes. Membrane fouling may have occurred at the beginning of the permeation process due to the relatively high flux at the beginning of the run, which resulted in a higher rate of fluid concentration and a rapid increase in the thickness of the fouled layer.<sup>10</sup> Moreover, the stabilisation of the flux at long operating times implied that a gel layer formed on

the membrane surface during the final stages of filtration (15–60 min) due to the presence of wax,<sup>11</sup> which can increase the thickness of the deposited layer on the membrane surface and occlude internal pores. It is inferred that as more particles deposit with time, the flux decreases continuously, but at decreasingly lower rates.<sup>12</sup> Moreover, the larger decline in the actual flux observed for the hydrophobic UF membrane (PES25) was partly due to strong hydrophobic–hydrophobic interactions between the oil droplets and the membrane surface. Hence, the droplets tend to adsorb directly on the hydrophobic membrane surface, resulting in a serious membrane fouling.



**Figure 1** Flux decline for glycerine–water solutions with TG and TG–FA using PES25 and PVDF membranes

On the other hand, the water contact angle for PES25 membrane is 74.10°, which is slightly higher than PVDF membrane (as reported in Table 2). Previously, the researcher suggested that if the contact angle tend to be  $0 < \theta_{o/w} < 90^\circ$  after the deposition of TG/oil, then the oil droplets were definitely pass through the membrane pores.<sup>13</sup> Thus, the PES25 membrane was easily wetted and fouled with oil droplets mainly attributed to low surface tension, and probably enhanced the adhesion between the oil and the membrane material. The aforementioned hypothesis was confirmed by determining the contact angle after fouling and the work of adhesion ( $W_a$ ), as shown in Table 2. In particular, the liquid in a wetted pore requires less energy to pass through the pores and reach the other side of the membrane. In fact, oil droplets are more likely to enter and adhere to the pore walls as well as the surface of the membrane,

which reduces the effective diameter of the pore and causes blockages.<sup>13</sup> As a result, deposited TG form a layer on the surface of the membrane and resist the transport of water. Conversely, with PVDF membranes, the contact angle after fouling with TG increased from 72.60° to 88.30°, leading to slow and incomplete wetting. Thus, due to high surface tension, liquid on non-wetted material would not spontaneously enter the pore and the adhesive forces between the liquid and membrane were relatively weak.<sup>14</sup> As a matter of fact, the adhesive forces between oil and hydrophobic surfaces are much stronger than those of less hydrophobic surfaces.<sup>15</sup> Thus, oil easily adheres to the surface of a hydrophobic membrane, which leads to significant fouling. The work of adhesion ( $W_a$ ) of the membrane materials is presented in Table 2.

It should be noted that the work of adhesion for oil droplets for hydrophobic membrane was approximately  $12.05 \times 10^{-2}$  and  $11.90 \times 10^{-2}$  N/m for TG and TG-FA mixtures, respectively. Further, the adhesion work for PES25 membrane was higher than that of PVDF membrane, which ranged within  $8.08 \times 10^{-2}$  and  $8.30 \times 10^{-2}$  N/m. Evidently, higher  $W_a$  for PES25 membrane was mainly attributed to lower surface tension of the membrane material and induced greater deposition of oil droplets and fatty acid on the hydrophobic membrane surface. Hence, low surface tension might facilitate better oil wetting and could not hold the shape of the oil droplets on the top surface. Thus, the tendency of the oil droplets to adhere on the membrane and near the pore entrance led to severe fouling during clarification of the glycerine-water solutions plus TG and TG-FA mixtures.

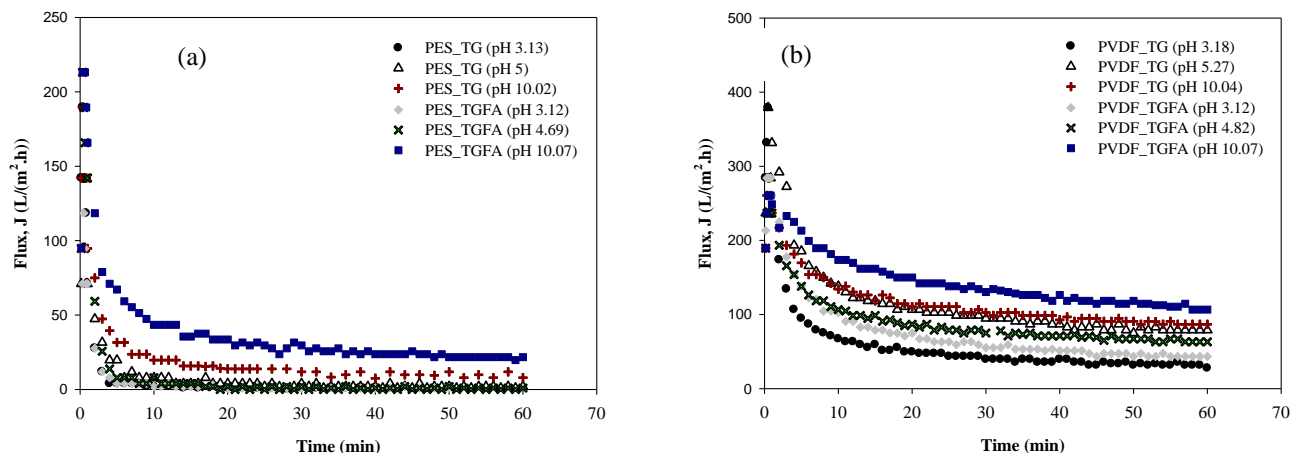
**Table 2** Contact angle and work of adhesion for PES25 and PVDF membranes after fouling

Membrane	Contact angle, $\square$		Work adhesion, $W_a \times 10^{-2}$		
	Clean	After fouling		(N/m)	
		TG	TG-FA	TG	TG-FA
PES25	74.10±0.2	47.60±1.5	49.30±0.2	12.05	11.90
PVDF	72.60±3.0	81.20±2.4	83.00±0.9	8.08	8.30

### 3.2 Effects of pH

Figure 2 depict the actual flux of PES25 and PVDF membranes over time at different feed characteristics, respectively. Specifically, the filtration flux can be seen to be significantly higher with the increase in pH for both types of membrane. It

should be noted that acidic solution led to a severe flux decline across the membrane, whereas basic solution enhanced the permeate flux. The hypothesis was associated with the findings in the literature.<sup>16–18</sup> Hence, the best filtration performance through PES25 and PVDF membranes was found at pH 10.



**Figure 2** Flux decline for glycerine–water plus TG and TG-FA mixtures at different pH solutions by using (a) PES25 and (b) PVDF membranes

To further elucidate the effects of pH on the fouling of PES and PVDF membranes, the wettability of the oil on the membrane was used to assess the electrochemical interactions between the membrane surface and the charged oil droplets, which are strongly influenced by the pH solution. According to Sutzkover-Gutman *et al.*,<sup>18</sup> the charges might exhibit different fouling propensities based on the membrane materials. This means the tendency of solute adsorption could be attributed to the protonation or deprotonation of the surface hydroxyl groups with the pH adjustment. This hypothesis was allied with

Elmofly and Shokir.<sup>19</sup> As reported in the literature, if both interfaces (membrane and oil droplets) are have like charges, then repulsion will occur, which is likely to produce water-wetness.<sup>20</sup> Conversely, if the interfaces have different charges, an attractive force occurs which enhances the oil-wetting of the membrane surface. Evidently, the zeta potential of oil droplets has been estimated by certain studies<sup>21–23</sup> that confirm the droplets were negatively charged, while the zeta potential for PES25 and PVDF membranes are reported elsewhere.<sup>24</sup> The isoelectric points (IEP) for both membranes were found to be at

pH 5.5, thus the PES25 and PVDF membranes were positively charged at pHs below the IEP and vice versa. Therefore, at low pH, the interfaces (the membrane and also the oil droplets) have opposite charges, leading to an attractive force between the surface and the droplets, which promotes the adsorption of oil droplets on the surface as well as in the pores. Consequently, the oil droplets would participate in pore blocking and severely foul the membrane in acidic conditions. In contrast, at higher pHs, the PES25 and PVDF membranes as well as the oil droplets became negatively charged, which enhances the repulsion force and prevents the oil adsorption on the surface. Therefore, alkaline conditions diminish the oil wettability on the membranes and weaken the solute–solute adhesion forces. Therefore, the oil droplets might not adhere/adsorb to the membrane and avoiding plugging the pores, leading to an improved permeate flux and lower fouling. Nevertheless, under acidic and alkaline conditions, the PVDF membrane presented a larger volume of permeate flux than the PES25 membrane (as shown in Figure 2b) due to the lower hydrophobicity of PVDF, which causes strong repulsive forces between the membrane material and the oil droplets. Therefore, the nature of the PVDF membrane may limit the deposition of oil droplets on the pore

walls and reduce pore blockages, which results in a higher permeate flux.

As shown in Table 3, the contact angle values for PES25 membranes were lower at low pH and significantly increased at high pH. A similar trend was observed for PVDF membrane after being fouled with TG and TG–FA mixtures. This indicates that the oil wettability on the membrane was decreasing in basic solutions compared to acidic conditions and applicable for both membrane materials. Nevertheless, it is clear to note that the contact angle values for fouled PES25 membranes are always lower than the clean PES25, while the contact angle values for the fouled PVDF were higher than the clean membrane in both solutions and oppose the trend exhibited by the PES25 membrane. Therefore, it is inferred that the PES25 membrane material was completely wetted by the oil droplets. Moreover, the contact angles for both membranes were allied with the adhesion work in acidic and also alkaline feed solution. It shows that the adhesion work for PES25 membranes was greater than PVDF membrane and ranged from 10.58 to 12.18 N/m. However, the adhesion work for PVDF membrane was considerably lower and ranged within 7.41–8.46 N/m. This implies the propensity of more droplets/solutes to adhere on the PES25 pore wall than on the PVDF membrane.

**Table 3** Measured contact angles and work of adhesion for PES25 and PVDF membranes after filtration for different feed characteristics

Membrane	Feed characteristic	Contact angle, °			Work adhesion	
		Clean	After fouling		$W_a \times 10^{-2}$ (N/m)	
			TG	TG-FA	TG	TG-FA
PES25	Acidic	74.10±0.2	46.20±0.4	47.60±0.7	12.18	12.05
	Alkaline	74.10±0.2	55.30±3.2	62.00±0.8	11.30	10.58
PVDF	Acidic	72.60±3.0	79.90±0.3	80.70±0.5	8.46	8.36
	Alkaline	72.60±3.0	85.80±0.4	88.30±0.3	7.72	7.41

#### 4.0 CONCLUSION

The surface chemistry of the membranes, feed characteristics and solute–solute interaction in the feed solution have a significant effect on the permeate flux during ultrafiltration of combined organic foulants in synthesized sweetwater solutions. The membranes were severely fouled at low pH due to electrostatic interaction between the membrane and the solutes, whereas a higher permeate flux were obtained at basic pH attributable to similar charges in alkaline conditions. The addition of hydrochloric acid or sodium hydroxide into the feed solution contributes mainly to the particle size distribution, which then influences the membrane–solute–solute interaction. Other than that, the presence of fatty acids believed to diffuse easily in the mixture with TG is mainly due to low MW and attribute to the solution–diffusion effect.

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