

## Adsorption Properties of Triglycerides and Long Chain Fatty Acid on UF Membranes: Effect of Membrane Hydrophobicity and Feed Chemistry

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**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). The aim of the present study is to contribute to the better understanding of fouling by TG as well as TG-FA mixtures and their adsorption properties on UF membrane. Additionally, another significant part of this study was the elucidation of the solute-solute interaction in the feed solution. Two UF membranes were used with the membrane materials made from Polyethersulfone (PES) and Polyvinylidene fluoride (PVDF) with MWCO between 5, 20 and 25 kDa for PES, while 30 kDa for PVDF. Static adsorption of TG and TG-FA were investigated at the solution pH values of 3, 7 and 10; for different MWCO. The behavior of solute adsorption was investigated by taking into account the thickness of fouling layer, the percentage of pore reduction and the water RFR. It was observed that the addition of TG into the glycerin-rich solutions caused a significant relative flux reduction (RFR) than TG-FA and this was probably due to the formation of macromolecule on the membrane surface. The RFR was also dependent on the solution chemistry. Adsorption behavior onto membrane surfaces were analyzed by contact angle and SEM images. Overall results revealed that PES membrane exhibited severe fouling and much larger water RFR than PVDF due to its hydrophobicity and surface roughness.

**Key words:** Adsorption, fatty acid, fouling, triglyceride, ultrafiltration

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### INTRODUCTION

Triglyceride (TG) and long chain Fatty Acids (FA) are usual undesirable contaminants of food oils and so removal of them are an important task for the oil industry (Kocherginsky and Grishchenko, 2000). The removal of TG and FA from glycerol-water solution is of commercial importance, because of their potential to severe fouling during membrane clarifications. In fact, its main drawback is fouling which may be caused by concentration polarization and solute adsorption. Cheryan and Rajagopalan (1998) reported that oil droplets may deposited on the membrane surfaces and caused pore blocking as well as cake layer and lead to water resistant. In recent years, considerable attention has been focused to the potential effects of small oil droplets on severe flux decline in an ultrafiltration process (Koike *et al.*, 2002; Subramanian *et al.*, 2004; Garcia *et al.*, 2006). However, the previous investigations were more pronounced to ultrafiltration of solute-solvent system and less attention

has been paid to the pretreatment of TG in solute-water system. Koike *et al.* (2002) demonstrated the ability of different polymeric membrane materials to separate oil constituents (FFA, DG, MG and TG) in organic solvents. They found that all the constituents could be separated using suitable solvents. Attempts have been made by Kumar and Bhowmick (1996) to separate FA and TG in the presence of alcohol. They reported that membrane materials play an important role in determining the separation of FA and TG. Similar trends also reported by Yan *et al.* (2009), membrane fouling caused by oily-water was affected by the surface hydrophilicity. They concluded that the fouling could be reduced to some extent by improving the membrane hydrophilicity. Subramanian *et al.* (2003) reported the performance of dense membranes during the permeation of triglycerides, fatty acid and their mixtures under different temperatures and pressure. They found that both parameters had significant effect to the TG and fatty acid permeation rates.

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The objective of this study was to understand the effect of surface and solution chemistry on the extent of adsorption onto a membrane surface. It was studied by performing static adsorption experiments with TG and TG-FA mixtures on hydrophobic ultrafiltration membranes under different pH. The membrane-solute interactions at different pH was explained by adsorption behavior of TG and TG-FA inside/on PES and PVDF membranes; by calculating the water relative flux reduction after static adsorption. The experimental results of this work showed a noteworthy water flux reduction and changes after static adsorption for the PES membrane at low pH, whereas no significant changes could be observed for high pH and PVDF membrane. Therefore, the present work provides better understanding towards the role of TG and TG-FA mixtures in adsorptive fouling on the membrane during pretreatment of glycerol-water solution.

**MATERIALS AND METHODS**

**Materials: Chemicals, membranes and experimental rig:** The experiments were carried out with a feed solution containing 15% (v/v) glycerin, 0.003 g L<sup>-1</sup> oleic acid and 1% (v/v) TG. Glycerin (USP, 92.09 g mol<sup>-1</sup>) and oleic acid (282.46 g mol<sup>-1</sup>) were purchased from Merck and commercial triglycerides (RBD Palm Olein, 870 g mol<sup>-1</sup>) were obtained from the local hypermarket. The membranes were made of polyethersulfone (PES) and polyvinylidene fluoride (PVDF) and possessed a MWCO of 5 to 25 and 30 kDa, respectively. Experiments were performed using Sterlitech™ HP4750 dead-end ultrafiltration stirred cell, as described in the literature (Amin *et al.*, 2010).

**Adsorptive fouling experiments:** The glycerine-water solutions plus TG and TG-FA mixtures were initially prepared in a separate beaker and stabilized in ultra-pure water at 650 RPM for 40 min. The composition of oleic acid in the mixtures chose based on their maximum solubility in the pure water. It was initially dissolved in 1 liter pure water prior to mix with the solutions. The pH of the feed solution was altered between pH 3 and pH 10 with a few drops of 0.1 M HCl or 0.1 M NaOH by using a pH meter (Mettler Toledo).

The stirred cell was placed in the water bath and the temperature was set constantly at 40°C as this was the temperature selected to perform the fouling experiments. Then, the solutions were added to the cell and the membrane outer surface was exposed to the mixtures for 6 hours without any flux. Homogeneity was achieved by stirring the solution at 450 rpm in order to avoid the effect of concentration polarization. After the experiment was completed, the mixture was removed and the membrane

surface rinsed with pure water twice for 30 sec. The flux of ultra-pure water through the membranes before and after the experiments was determined at TMP 2 bar. The degree of reduction after static adsorption was determined based on Eq. 1:

$$RFR = \left(1 - \frac{J_a}{J_o}\right) \times 100\% \tag{1}$$

where, RFR, J<sub>o</sub> and J<sub>a</sub> are relative flux reduction, ultra-pure water flux before and after adsorption, respectively.

**RESULTS AND DISCUSSION**

**Effect of membrane characteristics and MWCO:** The potential of adsorptive fouling (membrane-solute interactions) during pre-treatment of glycerine-water solutions were investigated by exposing the outer membrane surface to both single solute solution (TG) and combined solute solution (TG-FA). The effect of membrane material with different hydrophobicity behaviours was investigated and the effect of different MWCO was also included. The RFR was used to determine the degree of fouling as well as membrane-solute interactions. All the experimental findings with PES and PVDF UF membranes in contact with TG and TG-FA mixtures signify that there was a significant solute interaction with the membrane. Figure 1 exhibits the water RFR performance for different membrane materials and MWCOs. It can be clearly seen that the membrane material and its nature had a significant impact on the resulting RFR after adsorptive fouling. It is interesting to note that the water RFRs

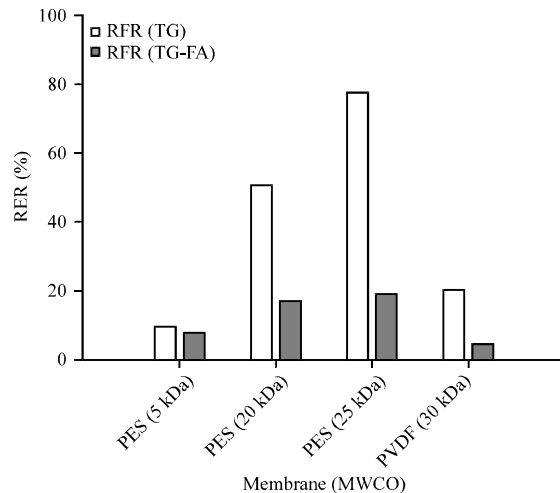


Fig. 1: RFR values of TG and TG-FA mixtures for different membrane material

performance was enormously higher for the PES25 membrane compared to the PVDF membrane.

In fact, some factors such as the membrane-solute interaction and membrane wettability are of utmost importance in fouling behaviour (Srijaroonrat *et al.*, 1999). Since the PES membranes used in this study possess hydrophobicity (oleophilic) behaviour, it might accelerate the adsorption rate of oil droplets on the surface and in the pores, therefore the membrane was easily wetted by the oil.

It was assumed that the oil droplets were quickly deposited and adsorbed on the membrane surface (Chen *et al.*, 2009), causing greater RFR for PES membranes. According to Low and Cheong (2009), the hydrophobic materials were fully wetted and drove the oil droplets to adsorb/stick on the surface. The adsorptive fouling was mainly attributed to the electrostatic interaction between the surface and the solutes, leading to better adhesion force of the droplets on the membrane surface. Thereby, it would facilitate the membrane fouling and result in higher RFR. Conversely, the PVDF membrane had relatively low water RFR for solutes, TG and TG-FA mixtures. This might be due to large MWCO and probably higher porosity of PVDF membrane.

Likewise, it is clearly observed from Fig. 1 that the effect of adsorptive fouling of TG and TG-FA mixtures contained in glycerine-rich solutions on water flux was significantly influenced by the membrane MWCO. In all solutions, the RFR values increased as the membrane cut-off increased. The water RFRs follow the sequence as follows: PES 5<PES 20<PES 25, suggesting that PES membranes with larger pores were more susceptible to adsorptive fouling than the smaller ones. The severe fouling for larger cut-off was probably due to the formation of a wax layer on the membrane surface with the oil droplets coalescences. Apart from that, the small droplets were participating in the pore sealing and occlude the membrane pores and led to severe fouling (Ohya *et al.*, 1998; He *et al.*, 2005). Therefore, as the larger pores become sufficiently clogged, then the solutes deposit onto the surface and form cake which results in a higher RFR. Moreover, the adsorption of the small solutes in the pores would reduce the pore size and increase the water resistance to pass through the membrane (Lindau *et al.*, 1995). Consequently, the percentage of water-relative flux reduction would be higher. The aforementioned hypothesis would be verified with the analysis of pore reduction. The comparison of pore reduction and the thickness of the fouling layer for different MWCO were estimated based on Eq. 2 and 3.

$$d_{m,f} = \left( d_{m,o} \cdot \frac{R_m}{R_f} \right) \tag{2}$$

where,  $d_{m,f}$  and  $d_{m,o}$  are mean pore diameter of the fouled and clean membrane (nm), while  $R_m$  and  $R_f$  are the resistance of the clean and fouled membrane ( $m^{-1}$ ), respectively (Hwang and Sz, 2010).

$$l_a = r_i \left[ 1 - \left( \frac{PWP_f}{PWP_i} \right)^{0.25} \right] \tag{3}$$

where  $l_a$  and  $r_i$  are adsorbed layer thickness (nm) and initial pore size (nm), whereas  $PWP_f$  and  $PWP_i$  are pure water permeability of the fouled and clean membrane ( $L/m^2.h.bar$ ), respectively (Dal-Cin *et al.*, 1995.).

Table 1 reports the percentage of pore reduction (%) as well as the thickness of fouling layer ( $l_a$ ) for PES and PVDF membranes after adsorptive fouling of TG and TG-FA mixtures. Obviously, the thickness of the cake layer was getting thicker as the MWCO increased and similar performance was experienced in pore reduction. It should be noted that the fouling layer was getting thicker from 0.065 to 0.585 nm as the MWCO was getting larger from 5 to 25 kDa. Similarly, after the adsorption of TG, the pore size of PES 5, 20 and 25 kDa was reduced about 7.10, 17.59 and 27.64%, respectively from the initial size. Nevertheless, since PVDF membrane underwent less adsorptive fouling, the thickness of the fouling layer was 0.261 nm which is thinner than PES 25 kDa. Further, the pore size reduced about 15.19% from the original size which is lower than the PES25 membrane. It is interesting to note that the membranes experienced a similar trend after being exposed to glycerine-water solutions plus TG-FA mixtures. However, it is noticeable that TG-FA mixtures suffer a small percentage of pore reduction and thin fouling layer.

According to Table 1, the thickness of the oily layer on the surface fell in the range of 0.028 to 0.327 nm, slightly thinner compared to TG, while the thickness of the oily layer was 0.148 nm for the PVDF membrane. Moreover, the pore reduction was considerably lower than those estimated for single solute TG. The findings were associated with the water RFRs as explained previously. This phenomenon indicates that PES membrane was severely fouled with TG and most likely dominated by the combination of pore blocking and oily layer formation on the surface. Conversely, the TG-FA mixture was expected to infiltrate the membrane pores and stick to the wall instead of seal the pore entrance. This is mainly due to the small particle size as compared to the size of TG in the solution. As a result, the membranes endure less adsorptive fouling with mixed solutes (TG-FA mixtures).

**Effect of pH feed solution:** Figure 2 exhibits the effect of feed characteristic on the adsorption potential of single

Table 1: Estimation of fouling layer thickness and pore reduction (%) for different MWCO after fouling

Membranes	PES						PVDF	
	5 kDa		20 kDa		25 kDa		30 kDa	
	TG	TG-FA	TG	TG-FA	TG	TG-FA	TG	TG-FA
$r_p$ (nm)	1.83	1.83	2.90	2.90	3.13	3.13	3.32	3.32
$d_{m,o}$ (nm)	3.66	3.66	5.80	5.80	6.26	6.26	6.65	6.65
$d_{m,r}$ (nm)	3.40	3.55	4.78	5.67	4.53	5.01	5.64	6.07
$l_s$ (nm)	0.065	0.028	0.263	0.034	0.585	0.327	0.261	0.148
Pore reduction (%)	7.10	3.01	17.59	2.24	27.64	19.97	15.19	8.72

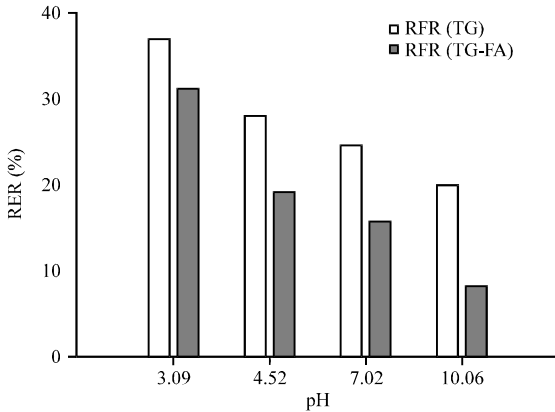


Fig. 2: Performance of water RFR after fouling at different pH

solute (TG) and combined solutes (TG-FA mixtures) on PES25 membranes. It is noted that the RFR values reduced from 37 to 20% and 31 to 8% for TG and TG-FA, respectively as the pH increased from pH 3 to 10. Basic pH reduced the water RFR, whereas acidic feed solution contributed to greater RFR, indicating that solute adsorption was more considerable at lower pH.

The extent of oil adsorption at different pHs depends on the type of interactions taking place between the oil and the surface charge properties of the membrane (Chakrabarty *et al.*, 2008). Literature reported that the oil droplets were negatively charged (Lobo *et al.*, 2006; Zhang *et al.*, 2009), while both of the membranes were positively charged below the IEP point as exhibited in Fig. 3. At low pH feed solution, both of the solutes and the membrane surface have different charges, consequently enhancing the electrostatic interaction. For that reason, the oil droplets and fatty acids tend to adsorb on the membrane surface and severely fouled the membrane. Similar findings were reported in previous studies (Al-Jeshi and Neville, 2008; Zhang *et al.*, 2009). On the other hand, both of the membrane materials and the droplets possess similar charges in basic feed solution which enhances the repulsive force between the surface and the solutes. Therefore, the electrostatic repulsion may possibly prevent the deposition of oil droplets on the

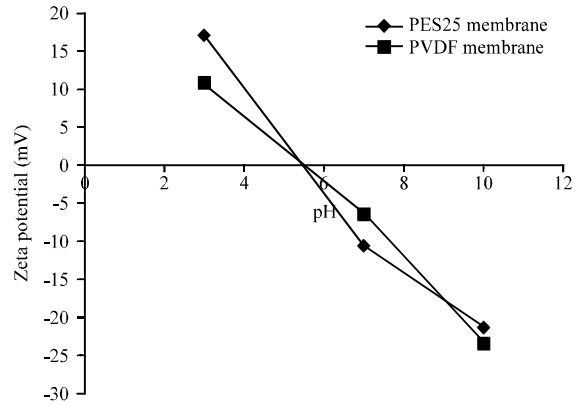


Fig. 3: pH dependence of the zeta potential for PES25 and PVDF membranes

membrane surface and inhibit the formation of a wax layer on the surface, leading to lower RFR values.

### CONCLUSION

The severe adsorptive fouling during pretreatment of glycerin rich solution has been investigated and it was due primarily to the deposition or adhesion of TG and FA on the membrane surface. The following results were obtained. The extent of adsorption of TG and TG-FA are significantly affected by the nature of the membrane and solution chemistry. The porosity and hydrophobicity of membrane affects the adsorption properties and a greater degree of RFR was seen with PES membranes (larger cut-off) compared to PVDF membrane. It might be due to the potential of small solutes participate in pore plugging as well as develop a fouling layer on the surface. Moreover, the rate of adsorption was much greater with mixed solutes (TG-FA) than single solute (TG) which is due to higher solution-diffusion interaction of small FA with TG in the mixtures and then accelerate their deposition to the pore wall and pore surface. The adsorption of the solutes onto membrane is getting higher in acidic condition due to electrostatic interaction between the membrane and the solutes, whereas the tendency of weak adsorption occurred in basic solution which is due to increased

electrostatic repulsion. Therefore, this work contribute to a better understanding of inevitably adsorptive fouling in oleochemical processing due to adsorption/adhesion of small solutes like TG and FA which are contained in the glycerine rich solution.

#### ACKNOWLEDGMENTS

The authors of this work wish to gratefully acknowledge the financial support for this work by the UKM Research Grant (FRGS) through the project no. UKM-KK-03-FRGS0115-2010.

#### REFERENCES

- Al-Jeshi, S. and A. Neville, 2008. An experimental evaluation of reverse osmosis membrane performance in oily water. *Desalination*, 228: 287-294.
- Amin, I.N.H.M., A.W. Mohammad, M. Markom, L.C. Peng and N. Hilal, 2010. Flux decline study during ultrafiltration of glycerin-rich fatty acid solutions. *J. Membrane Sci.*, 351: 75-86.
- Chakrabarty, B., A.K. Ghoshal and M.K. Purkait, 2008. Ultrafiltration of stable oil-in-water emulsion by polysulfone membrane. *J. Membr. Sci.*, 325: 427-437.
- Chen, W., J. Peng, Y. Su, L. Zheng, L. Wang and Z. Jiang, 2009. Separation of oil/water emulsion using Pluronic F127 modified polyethersulfone ultrafiltration membranes. *Sep. Purif. Technol.*, 66: 591-597.
- Cheryan, M. and N. Rajagopalan, 1998. Membrane processing of oily streams. *Wastewater treatment and waste reduction. J. Membrane Sci.*, 151: 13-28.
- Dal-Cin, M.M., C.N. Striez, T.A. Tweddle, C.E. Capes, F. Mcllellan and H. Buisson, 1995. Effect of adsorptive fouling on membrane performance: Case study with a pulp mill effluent. *Desalination*, 101: 155-167.
- Garcia, A., S. Alvarez, F. Riera, R. Alvarez and J. Coca, 2006. Sunflower oil miscella degumming with polyethersulfone membranes: Effect of process conditions and MWCO on fluxes and rejections. *J. Food Eng.*, 74: 516-522.
- He, Y., P. Xu, C. Li and B. Zhang, 2005. High-concentration food wastewater treatment by an anaerobic membrane bioreactor. *Water Res.*, 39: 4110-4118.
- Hwang, K.J. and P.Y. Sz, 2010. Filtration characteristics and membrane fouling in cross-flow microfiltration of BSA/dextran binary suspension. *J. Membr. Sci.*, 347: 75-82.
- Kocherginsky, N.M. and A.B. Grishchenko, 2000. Mass transfer of long chain fatty acids through liquid-liquid interface stabilized by porous membrane. *Sep. Purif. Technol.*, 20: 197-208.
- Koike, S., R. Subramanian, H. Nabetani and M. Nakajima, 2002. Separation of oil constituents in organic solvents using polymeric membranes. *J. Am. Oil Chemists Soc.*, 79: 937-942.
- Kumar, N.S.K. and D.N. Bhowmick, 1996. Separation of fatty acids/triacylglycerol by membranes. *J. Am. Oil Chemists Soc.*, 73: 399-401.
- Lindau, J., A.S. Jonsson and R. Wimmerstedt, 1995. The influence of a low-molecular hydrophobic solute on the flux of polysulphone ultrafiltration membranes with different cut-off. *J. Membr. Sci.*, 106: 9-16.
- Lobo, A., A. Cambiella, J.M. Benito, C. Pazos and J. Coca, 2006. Ultrafiltration of oil-in-water emulsions with ceramic membranes influence of pH and crossflow velocity. *J. Membr. Sci.*, 278: 328-334.
- Low, S.C. and K.T. Cheong, 2009. Polymeric membrane application for bio-diesel transesterification. *Proceedings of the 1st AUN/SEED-Net Regional Workshop, March 11-13, 2009, Bandung, Indonesia.*
- Ohya, H., J.J. Kim, A. Chinen, M. Aihara and S.I. Semenova *et al.*, 1998. Effects of pore size on separation mechanisms of microfiltration of oily water, using porous glass tubular membrane. *J. Membr. Sci.*, 145: 1-14.
- Srijaroonrat, P., E. Julien and Y. Aurelle, 1999. Unstable secondary oil/water emulsion treatment using ultrafiltration: Fouling control by backflushing. *J. Membr. Sci.*, 159: 11-20.
- Subramanian, R., K.S.M.S. Raghavarao, M. Nakajima, H. Nabetani, T. Yamaguchi and T. Kimura, 2003. Application of dense membrane theory for differential permeation of vegetable oil constituents. *J. Food Eng.*, 60: 249-256.
- Subramanian, R., M. Nakajima, K.S.M.S. Raghavarao and T. Kimura, 2004. Processing vegetable oils using nonporous denser polymeric composite membranes. *J. Am. Oil Chemists Soc.*, 81: 313-322.
- Yan, L., S. Hong, M.L. Li and Y.S. Li, 2009. Application of the Al<sub>2</sub>O<sub>3</sub>-PVDF nanocomposite tubular ultrafiltration (UF) membrane for oily wastewater treatment and its antifouling research. *Sep. Purif. Technol.*, 66: 347-352.
- Zhang, Q., Y. Fan and N. Xu, 2009. Effect of the surface properties on filtration performance of Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> composite membrane. *Sep. Purif. Technol.*, 66: 306-312.