Fouling of Ultrafiltration Membrane during Adsorption of Long Chain Fatty Acid in Glycerine Solutions

(Pengotoran Membran Ultraturasan semasa Penjerapan Asid Lemak Rantai Panjang di dalam Larutan Gliserin)

ABDUL WAHAB MOHAMMAD* & INDOK NURUL HASYIMAH MOHD AMIN

ABSTRACT

Membrane fouling caused by the adsorption of fatty acids limits the application of membrane technology in oleochemical industry especially for the pretreatment of glycerin-rich solution. The aim of the work presented in this paper was to understand the adsorptive fouling of palm oil based fatty acid on ultrafiltration membranes. The influence of solution pH, molecular weight cut-off (MWCO) and hydrophobicity of the membrane were studied. Oleic acid was used as a foulant, representing the long chain palm oil based fatty acid in glycerol–water solution. The outer membrane exposed to the mixtures for 6 h without pressure. The stirring speed was set at 300 rpm and polyethersulfone (PES) membranes with MWCO of 5, 20 and 25 kDa were used. The adsorptive fouling was determined using the relative flux reduction (RFR) method. It is demonstrated in this study that PES membranes are susceptible to the deposition of fatty acids on the membrane surface and pores. The fouling phenomenon at low pH is more severe than that of high pH due to the attractive force between solutes and the membrane. The PES membranes after adsorption were characterized by contact angle and Fourier transform infrared (FTIR), while the surface was visualized with scanning electron microscopy (SEM).

Keywords: Adsorption; fatty acid; fouling; glycerin; ultrafiltration

ABSTRAK

Pengotoran membran yang disebabkan oleh penjerapan asid lemak telah mengehadkan aplikasi teknologi membran dalam industri oleokimia terutamanya untuk penjernihan larutan kaya gliserin. Tujuan utama kajian ini dijalankan adalah untuk memahami pengotoran terjerap terhadap membran ultraturasan yang disebabkan oleh asid lemak rantai panjang berasaskan minyak kelapa sawit. Kesan beberapa faktor seperti pH, nilai potongan berat molekul (MWCO) dan kimia permukaan membran (sifat hidrofobik) telah dikaji. Asid olik yang mewakili asid lemak rantai panjang berasaskan minyak kelapa sawit telah digunakan sebagai bahan larut. Permukaan membran telah didedahkan kepada larutan selama enam jam tanpa faktor tekanan membran. Kelajuan pengacau telah digunakan. Pengotoran terjerap ini dinilai dengan menggunakan pengurangan fluks relatif (RFR). Melalui kajian ini, didapati asid lemak mudah melekat di atas permukaan membran PES dan juga di dalam liang membran tersebut. Fenomena pengotoran pada pH rendah lebih teruk berbanding pada keadaan pH tinggi yang disebabkan oleh daya tarikan antara bahan larut dan membran. Perubahan struktur pada permukaan membran selepas pengotoran telah dianalisis menggunakan sudut sesentuh, FTIR dan juga SEM.

Kata kunci: Asid lemak; gliserin; pengotoran; penjerapan; ultraturasan

INTRODUCTION

Glycerin is the major byproduct from hydrolysis process in oleochemical plants. However, the glycerin-rich solution contains various impurities such as free fatty acids, unreacted mono-, di- and triglycerides, inorganic salts, a variety of 'matter organic non-glycerol' (MONG) and water which comprises nearly 85% from the total composition in the solution (Burshe et al. 1999; Khairnar & Pangarkar 2004). Before evaporation and distillation for water removal, there is a need to remove fatty acids as well as other impurities. However, it was noted that severe fouling is encountered when membranes were utilized for treating small and low molecular-weight hydrophobic solutes like fatty acids (Byhlin & Jönsson 2002; Jönsson 1998). The membrane fouling occured when the small fatty acids retained and adsorb on the membrane surface (Jönsson & Jönsson 1995).

Beside hydrolysis process, small and hydrophobic solute like fatty acids presents in most downstream byproducts of oleochemical plants and edible oil processing. For example, glycerol and fatty acid may come directly from the transesterification process of fats and oil (Taufiq-Yap et al. 2011). These fatty acids act as principle impurities in the oil that can adversely affect the end-product quality as well as shorten the shelf life (Subramanian et al. 2001). Although previous literatures has provided understanding into low molecular weight and hydrophobic fatty acid fouling, nevertheless, there is still less attention paid to the potential of long hydrocarbon chain fatty acid to membrane fouling. Even though their concentration in the mixture was quite low, conversely it might lead to severe fouling due to limited solubility in the mixture (Jönsson 1998). As a matter of fact, the solubility of fatty acid in the mixture was influenced by the hydrocarbon chain length, inferred that the long chain fatty acid result to minimum solubility in the mixture. Additionally, most of the fouling studies in the past concentrated more on pore blocking by large solutes as well as the build-up of a cake layer. However, not much consideration has been given to the potential of small hydrophobic solutes to blocking mechanism (Jönsson et al. 1997).

Several studies however have investigated membrane fouling during ultrafiltration of fatty acid (Brinck et al. 2000; Jönsson & Jönsson 1995; Lindau et al. 1995). The resistance in membranes arises due to the adsorption of fatty acids as soon as membranes are in contact with feed containing a small amount of fatty acids. Brinck et al. (2000) reported that the solution pH define the membrane-solute interaction and further quantify the retention of the solute on the membrane surface as well as the flux of the solution. On the other hand, surface chemistry of membranes is another important factor in the filtration of solution containing fatty acids. The hydrophilicity of membrane surface reduces fouling by fatty acids (Lindau & Jönsson 1999). Lindau et al. (1995) presented a study of fouling by adsorption of octanoic acid solution and found that the flux of hydrophobic polysulfone membrane decreased with the increasing concentration of the fatty acid. However, the adsorption did not affect the permeability of a hydrophilic regenerated cellulose membrane. In another investigation, the marked flux decline in the separation of octanoic solution was observed to be affected by membrane molecular weight cut-off (Lindau et al. 1998). In addition, Priyananda and Chen (2006) reported on the role of protein as a binder of fatty acid for reducing adsorptive fouling during ultrafiltration of protein-fatty acid mixtures. They used caprylic acid as the foulant and found that the binding surface is very large in comparison with the specific binding at hydorophobic condition.

The aim of the present work was to study the solutemembrane interactions (adsorption) during ultrafiltration of a solution containing long chain fatty acids. Attempts have been made to study the characteristics of adsorptive fouling by fatty acids using polyethersulfone (PES) ultrafiltration membranes during the clarification of glycerin-rich solution. An extensive study has been carried out to observe the effect of pH, molecular weight cut-off (MWCO) and nature of the fatty acid itself on the relative flux reduction. The experimental results of this work indicated significant water flux reductions after 6 h exposure to the glycerinwater-fatty acid mixture.

MATERIALS AND METHODS

MATERIALS: CHEMICALS, MEMBRANES AND EXPERIMENTAL RIG

Oleic acid was purchased from Merck and used as fouling substance in this study, while glycerol (99.5% USP) acquired from Sigma was added in the mixture. Chemicals were used as received. The properties of oleic acid and the glycerol are listed in Table 1. Three commercially flat sheet polymeric membranes made of PES, obtained from Sterlitech Corporation were used in the adsorption experiments. The properties of the membranes were presented in Table 2. All new membranes were soaked in pure water overnight prior to each run. The membranes was removed from the stirred cell and rinsed with pure water once the experiment was completed. Experiments were performed using Sterlitech[™] HP4750 dead-end ultrafiltration stirred cell, as described in the literature (Amin et al. 2010).

ADSORPTIVE FOULING EXPERIMENTS

The composition of oleic acid in the mixture was chosen based on its maximum solubility in the pure water as displayed in Table 1, while for glycerol was 15% (v/v). It was initially dissolved in 1 L pure water prior to mix with the glycerol. The pH of the feed solution was varied between pH3 and pH10 with a few drops of 0.1 M HCl or 0.1 M NaOH. The pH of the solutions was measured with a pH meter (Mettler Toledo). However, the pH of the feed solution for the effect of MWCO was fixed to the original pH of the solution without any adjustment (pH5.09).

The membrane was compacted with pure water prior to the experiments at 2 bars for 30 min without stirring effect. This is to avoid the effect of compaction process during the experiments. Then, glycerol-water mixture with fatty acid was added to the cell and the membrane outer surface was exposed to the mixture for 6 h (as shown in Figure 1) at 300 rpm without any flux. After the experiment was completed, the mixture was removed and the membrane surface was rinsed with pure water twice for 30 s. The flux of ultra-pure water through the membranes before and after

TABLE 1. The	properties	of oleic	acid and	glycerin
--------------	------------	----------	----------	----------

Solutes	Formula molecule	MW (g/mol)	Solubility in water (g/L)
Oleic acid	C _{18:1}	282.46	0.003ª
Glycerin	C _{3:0}	92.09	Soluble

^a solubility of pure substance in 1 liter pure water

TABLE 2. The properties of membranes

Membrane	Manufacturer	Material	MWCO (Da)	Contact angle, θ	Surface property
PES 5	GE Osmonic	Polyethersulfone	5 000	72.0	Hydrophobic
PES 20	GE Osmonic	Polyethersulfone	20 000	68.1	Hydrophobic
PES 25	Koch	Polyethersulfone	25 000	74.1	Hydrophobic



Adsorption time (hour)

FIGURE 1. Effect of exposure time on water RFR after static adsorption

the experiments was determined at 2 bars. The performance of the membranes after static adsorption was determined quantitatively using (1):

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

where RFR, J_o and J_a are relative flux reduction, water flux before and after adsorption, respectively. All experiments were repeated twice. The influence of pH solution and different molecular weight cut–off (MWCO) to adsorptive fouling were evaluated for this study.

CHARACTERIZATIONS OF FRESH AND FOULED MEMBRANES

The changes occurred to the PES membranes after filtration of glycerol–water and fatty acid solution mixture were analyzed using several analytical methods. The hydrophobicity behavior of the fouled PES membrane was characterized using drop shape analysis system (Easy Drop KRUSS). The membranes were cut into small size before placed on a thin glass plate with 3 μ L of water drops were injected at the rate of 30 μ L/min onto the membrane surface. Then, the reading was recorded within 30 s. Additionally, the absorbance of fatty acid on the membrane surface was analyzed using Fourier transform infrared (FTIR) while the morphology of the membrane surface

was visualized by scanning electron microscopy (SEM). The membrane samples were frozen in liquid nitrogen for a few min before fractured and then coated with gold before analyzing by SEM. All the samples were dried at room temperature before the analysis.

RESULTS AND DISCUSSION

EFFECT OF MEMBRANE CHARACTERISTIC AND MWCO

The difference in water RFR of PES membrane for different cut-offs (5, 20 and 25 kDa) are illustrated in Figure 2. The tendency of greater solute adsorption on membrane surface was noted when PES 25 kDa was used followed by PES 20 kDa and less pronounced for PES with small MWCO (PES 5 kDa). This implies that severe adsorptive fouling occurred on the larger MWCO membrane compared with the smaller cut-off membrane. The RFR of the PES 25 kDa is 3.9%, significantly higher and susceptible to fatty acid adsorption compared with PES 20 kDa. A plausible elucidation of the greater RFR of the PES 25 kDa membrane is internal adsorptive fouling onto the pore wall caused by the deposition/adsorption of long chain oleic acid. It might be explained by the ability of the low molecular weight fatty acid which is hundred times smaller than the membrane pores to pass through the pores. Thus, the fatty acid molecules can easily adsorb in the pores. However, the



FIGURE 2. Effect of MWCO to RFR after adsorptive fouling

adsorption was in small quantities and the rest of oleic acid formed a cake layer and completely covered on the surface, hence leading to greater hydraulic resistance to the pure water flux. Further, it might be explained by the effect of oleic acid structure which forms a V-shape in the middle of carbon chain due to the existence of cis-functional group. Thus, it was easily folded and filled in the middle of the pores which allowed inner pore blockage and reduced pore size. Similar trend was reported by Dal-Chin et al. (1995) and Li and Chen (2004). Therefore, it is reasonable to assume that the adsorption of oleic acid to the pore wall might reduce the pore radius probably due to monolayer adsorption. Consequently, constant exposures to the solution within longer time possibly imply the tendency of multilayer adsorption and lead to formation of thin layer on the membrane surface. Therefore, pore blockage and cake layer become dominant and display higher water RFR. As a matter of fact, the reduction of the fouled membrane pore size and the thickness of the fouled layer were estimated by applying the Hagen-Poiseuille law as shown in (2) and (3), respectively;

$$d_{m,f} = \left(d_{m \cdot o} \ 2 \cdot \frac{R_m}{R_f} \right)^{0.5},\tag{2}$$

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 & 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_o are adsorbed layer thickness and initial pore size (m), whereas PWP_f and PWP_i are pure water permeability of the fouled and clean membrane (L/m².h.bar), respectively (Dal-Cin et al. 1995). Table 3

exhibits the measurement of fouled layer thickness as well as the mean pore diameter for clean membrane and also after fouled with oleic acid for different MWCO. All measurements were estimated based on the resistance and pure water permeability. It should be noted from Table 3 that as the MWCO increased, the pore reduction and the fouled layer thickness were considerably increased. This coincided with the RFR values as discussed previously, inferring that larger MWCO (PES25) was susceptible to severe fouling. The mean pore diameter of PES 5kDa reduces to 0.27% from the clean membrane after adsorption with oleic acid. Nevertheless, the percent age reduction getting higher up to 0.86% and 1.60% for PES 20 and 25kDa, respectively. Moreover, the fouled layer thickness (l_{a}) also displayed similar trend with the mean pore diameter after deposition of fatty acid. The accumulation of oleic acid on the membrane surface thickens the fouling layer from 0.002 nm on the PES5 to 0.013 nm on PES20. Nevertheless, the fouling layer was more significant with PES25 with a thicker adsorption layer up to 0.026 nm. The severity of PES membrane with larger cut-off mainly attributed to the pore blockage which further clogged into the membrane pores and resulted in pore reduction. As time passed, the pore plugging was slowly discontinued and at this level, the formation of thin layer close to the pore entrance began to dominate. However, the fouling of PES membranes with small MWCO (5 and 20kDa) was considerable probably due to the pore blocking instead of cake layer. It is inferred that the pore plugging was dominant during the 6 h adsorption than the formation of fouling layer.

Figure 3 visualizes the fouled PES membranes for different MWCO after 6 h exposure to glycerol–water with fatty acid (original condition, pH5). All images were taken at the same magnification of 1000×. It was clearly observed that the small solute fatty acids adsorb on the membrane surface. Comparing the SEM images as displayed in Figure 3(a) and 3(b), revealed that more fatty acids adsorb onto

Membranes		PES	
Wembranes	5 kDa	20 kDa	25 kDa
$r_p (\mathrm{nm})^a$	1.83	2.90	3.13
$d_{m,o}$ (nm)	3.66	5.80	6.26
d_{mf} (nm)	3.65	5.75	6.16
l_a (nm)	0.002	0.013	0.026
pore reduction (%)	0.27	0.86	1.60

TABLE 3. Fouled layer thickness and fouled membrane mean pore size for different MWCO

^a Determined from hydraulic radius (Jönsson et al. 1997)

the larger cut off membrane and continuously dominated the surface area. Conversely, fewer solutes were adsorbed on the PES 5kDa. This is consistent with the RFR values of PES 20kDa which was higher than PES 5kDa as discussed in the previous section, inferring that the adsorptive fouling mainly affected by the membrane cut–off. It is worth noting that the solutes aggregated and only covered a part of the PES 5 kDa, thereby facilitating pore sealing. In contrast, the solutes deposited on the PES 20kDa in a finger–like strips, initially form a thin layer and gradually cover the membrane surface. Therefore, the high RFR value of PES 20kDa was mostly attributed to the pore blocking and cake formation.

Additionally, in a case of PES 25kDa, obviously the solutes fouled the membrane. It is noted that the membrane surface was completely covered by the fatty acid and revealed that great amount of solutes were well-distributed over the membrane surface. According to Figure 3(c), the long chain fatty acid observed to overlap each other, in which a cake layer is formed caused by solutes accumulation on the surface. The structure of the layer was found to be sticky, thicker and more compact than that observed in Figure 3(b). The adsorption of fatty acid probably occurred at the pore entrance and resulted in a reduction of the pore size and lead to significant RFR value. The dense layer observed for the PES 25 kDa was consistent with higher RFR value and coincided with findings reported by Li and Chen (2004), who found the severe fouling due to humic acid with larger cut-off rather than small cut-off membranes. It might be explained by the fact that larger pores probably allow the fatty acids to enter the pores easily, led to pore blocking and cake layer formation. Consequently, those membranes with larger pores might allow the small fatty acid to enter the membrane pore and adsorb to the pore wall and slowly form a layer on the top. It is likely attributed to pore plugging and formation of fouling layer on membrane surfaces instead of only pore sealing with small MWCO.

The identification of functional groups for fouled PES membrane was verified by IR spectroscopy. Figure 4 exhibits the FTIR spectrum of fouled PES membrane with fatty acid for different MWCO. The broad absorbance at a band 3500 cm⁻¹ has been ascribed to the stretching modes of hydroxyl groups (–OH) and carboxyl groups of fatty



FIGURE 3. Analysis of SEM for different MWCOs (a) PES 5 kDa (b) PES 20 kDa and (c) PES 25 kDa

acid retained by the membrane. Moreover, the fouled PES membranes have 2 small bands of the frequency 2800 cm⁻¹, can be ascribed to stretch vibration of CH₂ scissors indicating the presence of unsaturated fatty acid on the membrane surface. It should be noted that the PES 5kDa

illustrated higher signal absorbance at this band when compared with both PES 20 and 25kDa membranes. It might imply the tendency of the small solutes to deposit on the membrane surface and susceptible to adsorptive fouling with small cut–off membranes rather than penetrate into the membrane pore and assist the pore blockage. The strong fingerprint region at the wavenumber 1700 cm⁻¹ was assigned to the stretching band of carbonyl group (C=O), indicating the typical band of fatty acid exists on the membrane surface. The band was significantly revealed in all MWCO membranes as depicted in Figure 4. Hence, this spectrum supports that PES membranes were completely fouled with the deposition of fatty acid.

EFFECT OF FEED CHARACTERISTIC (PH SOLUTION)

Figure 5 depicts the effect of pH on membrane RFR after the adsorption of fatty acid on PES 25kDa membrane. The water flux of the membranes is significantly influenced by the exposure to the glycerol–water mixture with oleic acid at different pH. It was noticeable that the RFR value reduced from 33% to 6.2% when the solution pH rises from pH3.18 to pH9.95. The observation may be due to the dissociation changes of fatty acid. The addition of HCl acid would increase the percentage of undissociated fatty acid in the solution as shown in Figure 6. The dissociation percentage of oleic acid was determined by (4) (Brinck et al. 2000):

$$\frac{[HA]}{C_{tot}} = \frac{I}{I + 10^{pH - pKa}},\tag{4}$$

where, C_{tot} is total amount of acid, $[HA]+[A^{-}]$ and pKa is dissociation constant (pKa_{oleic} 5.02 at 25°C). It is clearly observed that the oleic acid is mainly undissociated at acidic conditions, thus the whole molecule behaves

as hydrophobic solute. Hence, reducing the pH would facilitate the attractive forces between the foulant and membrane surface which mainly due to hydrophobic interactions and lead to more adsorption on the membrane surface. As a result, the PES membrane underwent higher RFR at acidic solutions.

However, the RFR value reduces to 6.2% in alkaline solution due to the full dissociation of oleic acid. Similar trend was confirmed with the finding reported by Mohammadi and Esmaeelifar (2005). At higher pH, the fatty acid would act as a surfactant molecule and might induce a negative charge to the membrane. Consequently, the negative charge causes repulsive forces between the membrane and the solutes to increase (Priyananda & Chen 2006) and result in continuous decrease in fatty acid adsorption on PES membranes (Jones & O' Melia 2000). Therefore, it will reduce the deposition of fatty acid on the membrane surface, leading to low water RFR at higher pH values. The dotted line plot in Figure 5 shows the effect of pH on pure water flux after adsorption. It can be observed that the flux increased significantly as the pH increased from 3.18 to 9.95. It might be explained by the fact that alkaline solution will reduce the formation of cake layer on the membrane surface, thus it may reduce the water resistance to pass through the membrane pores.

To reveal the nature of the adsorption, several analyses have been performed to characterize PES membrane after exposure to the mixture for 6 h. The surface of the membranes was examined with SEM before and after fatty acid adsorption. Figure 7 depicts the SEM images of clean and oleic acid–fouled PES membrane at different feed characteristic. It was noted from Figure 7(b)–7(d) that fatty acid formed a new layer in finger-like strips after interacting with PES membrane outer surface. It might be explained by the molecular shape of oleic acid,



Wavenumbers (cm⁻¹)

FIGURE 4. Analysis of FTIR spectrums for different MWCO



FIGURE 5. Effect of pH to RFR and water flux after adsorption (PES 25kDa membrane)



FIGURE 6. Percentage of fatty acid dissociation at different pH

which is more like a long straight hydrocarbon chain with a V-shape in the middle of structure. The thickness of the cake layer will depend on the carbon number in the chain length, which means the long chain fatty acid lead to denser cake to be formed on the surface. Severe fatty acid deposition was seen on the PES membrane surfaces at pH3.18 (Figure 7(b)), coinciding with the RFR results. The fouled membrane images were clearly found that the fatty acids were uniformly distributed and almost covered the membrane surface at low pH. The layer apparently more compact, overlapping to each other and observed to form a thick gel-like layer on the top surface and causes greater RFR. Conversely, the fouling layer in alkaline condition as revealed in Figure 7(d) was much lighter than in acidic, and thinly scattered on the PES membrane surface. Fewer fatty acid adsorbed on the membrane at high pH compared to Figure 7(b)-7(c). As reported earlier, the possible reason is full dissociation of oleic acid at basic solution and allows their conversion into

ions and subsequently reducing the adsorption from the membrane surface. Hence, the cake layer as depicted in Figure 7(d) seems like thinner and sparsely disseminated on the surface.

On the other hand, analysis of FTIR was used to verify the adsorptive fouling detection on the membrane. It was reported in the literature that the main functional group of C=O for fatty acid would give strong absorbance at 1690–1750 cm⁻¹ (Puro et al. 2011). Figure 8 revealed that the C=O stretching band was found at 1644 cm⁻¹ for all types of feed solution, inferred that mostly fatty acids contribute large amount at 1644 cm⁻¹. The absence of the fatty acid functional group at 1690–1750 cm⁻¹ might be due to the unevenly spread on the membrane surface. Other than that, the presence of fatty acid on the PES membrane could be confirmed by carefully examining the CH₂ scissors at 1487 cm⁻¹ and C–O stretching at 1152 cm⁻¹. Moreover, it was found that the typical peaks of hydrocarbon at the band 2928 cm⁻¹ as revealed by the





Fouled PES 25 kDa (pH 5.09)

FIGURE 7. Analysis of SEM for different pH after adsorption (a) clean PES (b) fouled PES at pH3.18 (c) fouled PES at pH5.09 and (d) fouled PES at pH9.95



Wavenumbers (cm⁻¹)

FIGURE 8. Analysis of FTIR spectrums at different pH after adsorption

fresh PES membrane was also observed in the fouled membrane at all pH values. Even though the fouled membrane at all pH solutions displayed a small band at 2928 cm⁻¹, suggesting that CH (CH₂ asymmetric) stretching of unsaturated fatty acid chains appeared on the fouled membrane surface. Thus, this finding clearly indicated the importance of FTIR analysis in the studies of weakly adsorbed fatty acid.

Moreover, Figure 9 shows the contact angle values of fouled PES 25 membrane after adsorptive fouling at different feed characteristic. It should be noted that contact angle values increased at low pH and significantly reduced at high pH, inferring that the hydrophobicity behavior after adsorption influenced by the changes in pH. The PES membranes were positively charged in acid solution (17.04 mV) and vice versa (Amin et al.



FIGURE 9. Analysis of contact angle at different pH after adsorption

2011). Since the fatty acid behaved as hydrophobic solute in nature, then it might enhanced the hydrophobic interaction between the membrane surface and the solutes in acid solution and improve the hydrophobicity of PES25 membrane. However, in alkaline solution, similar charge between the membrane and the solutes would induce the repulsion force and weaken the tendency of fatty acid to adsorb on the membrane surface.

CONCLUSION

The major drawback during clarification of glycerol water mixture was primarily due to the adsorption of the fatty acid on the membrane surface and to the pore wall. The influence of feed solution and membrane MWCO strongly affected the performance of flux reduction as well as representing the importance of solute-membrane interaction on the overall fouling behavior. The greater fatty acid adsorption on the membrane surface occurred at low pH than at high pH due to the greater undissociation of low molecular weight fatty acid in acidic solution. Furthermore, the extent of fouling was much higher with the larger molecular weight cut-off membranes. A further increase in the membrane MWCO would enhanced the hydraulic resistance to flow provided by the fatty acid deposit on the larger cut-off membranes. Thus, the finding from this study provide essential insights into fouling phenomenon governing long chain and low molecular weight fatty acids solutes during ultrafiltration process.

ACKNOWLEDGEMENT

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

REFERENCES

- Amin, I.N.H.M., Mohammad, A.W., Markom, M., Leo, C.P. & Hilal, N. 2010. Flux decline study during ultrafiltration of glycerin-rich fatty acid solutions. *Journal of Membrane Science* 351(1-2): 75-86.
- Amin, I.N.H.M., Mohammad, A.W. & Markom, M. 2011. Influence of triglycerides on fouling of glycerol-water with ultrafiltration membranes. *Industrial & Engineering Chemistry Research* 50: 7520-7526.
- Brinck, J., Jönsson, A.-S., Jönsson, B. & Lindau, J. 2000. Influence of pH on the adsorptive fouling of ultrafiltration membranes by fatty acid. *Journal of Membrane Science* 164(1-2): 187-194.
- Burshe, M.C., Sawant, S.B. & Pangarkar, V.G. 1999. Dehydration of glycerin-water mixtures by pervaporation. *Journal of the American Oil Chemists' Society* 76(2): 209-214.
- Byhlin, H. & Jönsson, A-S. 2002. Influence of adsorption and concentration polarisation on membrane performance during ultrafiltration of a non-ionic surfactant. *Desalination* 151: 21-31.
- Dal-Cin, M.M., Striez, C.N., Tweddle, T.A., Capes, C.E., McLellan, F. & Buisson, H. 1995. Effect of adsorptive fouling on membrane performance: Case study with a pulp mill effluent. *Desalination* 101(2): 155-167.
- Hwang, K-J. & Sz, P-Y. 2010. Filtration characteristics and membrane fouling in cross-flow microfiltration of BSA/ dextran binary suspension. *Journal of Membrane Science* 347(1-2): 75-82.
- Jones, K.L. & O' Melia, C.R. 2000. Protein and humic acid adsorption onto hydrophilic membrane surfaces: Effects of pH and ionic strength. *Journal of Membrane Science* 165: 31-46.
- Jönsson, A-S. 1998. Fouling during ultrafiltration of a low molecular weight hydrophobic solute. *Separation Science* and Technology 33(4): 503-516.
- Jönsson, C. & Jönsson, A-S. 1995. Influence of membrane material on the adsorptive fouling of ultrafiltration membranes. *Journal of Membrane Science* 108(1-2): 79-87.

- Jönsson, A-S., Lindau, J., Wimmerstedt, R., Brinck, J. & Jönsson, B. 1997. Influence of the concentration of a low-molecular organic solute on the flux reduction of a polyethersulfone ultrafiltration membrane. *Journal of Membrane Science* 135(1): 117-128.
- Khairnar, D.B. & Pangarkar, V.G. 2004. Dehydration of glycerin/ water mixtures by pervaporation using homo and copolymer membranes. *Journal of the American Oil Chemists' Society* 81(5): 505-510.
- Li, C-W. & Chen, Y-S. 2004. Fouling of UF membrane by humic substance: Effects of molecular weight and powder-activated carbon (PAC) pre-treatment. *Desalination* 170(1): 59-67.
- Lindau, J. & Jönsson, A-S. 1999. Adsorptive fouling of modified and unmodified commercial polymeric ultrafiltration membranes. *Journal of Membrane Science* 160(1): 65-76.
- Lindau, J., Jonsson, A-S. & Bottino, A. 1998. Flux reduction of ultrafiltration membranes with different cut-off due to adsorption of a low-molecular-weight hydrophobic solutecorrelation between flux decline and pore size. *Journal of Membrane Science* 149(1): 11-20.
- Lindau, J., Jonsson, A-S. & Wimmerstedt, R. 1995. The influence of a low-molecular hydrophobic solute on the flux of polysulfone ultrafiltration membranes with different cut-off. *Journal of Membrane Science* 106(1-2): 9-16.
- Mohammadi, T. & Esmaeelifar, A. 2005. Wastewater treatment of a vegetable oil factory by a hybrid ultrafiltration-activated carbon process. *Journal of Membrane Science* 254(1-2): 129-137.
- Priyananda, P. & Chen, V. 2006. Flux decline during ultrafiltration of protein-fatty acid mixtures. *Journal of Membrane Science* 273(1-2): 58-67.

- Puro, L., Kallioinen, M., Manttari, M. & Nyström, M. 2011. Evaluation of behavior and fouling potential of wood extractives in ultrafiltration of pulp and paper mill process water. *Journal of Membrane Science* 368(1-2): 150-158.
- Subramanian, R., Raghavarao, K.S.M.S., Nabetani, H., Nakajima, M., Kimura, T. & Maekawa, T. 2001. Differential permeation of oil constituents in nonporous denser polymeric membranes. *Journal of Membrane Science* 187(1-2): 57-69.
- Taufiq-Yap, Y.H., Abdullah, N.F. & Basri, M. 2011. Biodiesel production via transesterification of palm oil using NaOH/ Al₂O₃ catalysts. *Sains Malaysiana* 40(6): 587-594.

Abdul Wahab Mohammad*

Department of Chemical and Process Engineering Faculty of Engineering and Built Environment

Universiti Kebangsaan Malaysia

43600 UKM Bangi, Selangor D.E.

Malaysia

Indok Nurul Hasyimah Mohd Amin Section of Chemical Engineering Technology Universiti Kuala Lumpur Malaysian Institute of Chemical & Bioengineering Technology 78000 Alor Gajah, Melaka Malaysia

*Corresponding author; e-mail: wahabm@vlsi.eng.ukm.my

Received: 2 August 2012 Accepted: 15 October 2012