PERFORMANCE OF POLYMERIC MEMBRANES FOR PHOSPHOLIPID REMOVAL FROM RESIDUAL PALM FIBRE OIL/HEXANE MISCELLA

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ABSTRACT

Palm pressed fibre, a by-product from the processing of crude palm oil contains about 5%-8% residual oil (on dry basis). The oil contains a high amount of minor components such as phospholipids, carotenes and vitamin E. This study investigates the ability of polymeric membranes to remove phospholipid from residual palm fibre oil/hexane miscella. The performance of 10 kDa polyethersulphone (PES), 20 kDa PES and 30 kDa polyvinylidene fluoride (PVDF) membranes were evaluated. A detailed evaluation on 30 kDa PVDF showed that permeate flux increases with the increase of operating pressure, temperature and agitation speed. Increasing operating pressure from 2 to 6 bar with a temperature of 40^oC and speed of 300 rpm resulted in the retention of phospholipids from 81% to 95%. The resistance of the membrane due to concentration polarisation ranged from 30.6 to 97.0 x 10^{12} m^{-1} which gave 79% - 84% of total resistance values indicating significant influence on the permeate flux. A complete 2^3 experimental design indicated statistically that the increased pressure, temperature and agitation speed resulted in a higher permeate flux. An increase in pressure and agitation speed also increased the retention of phospholipid. However, the regression model obtained from this study showed that the temperature had a negative effect on the retention of phospholipid.

INTRODUCTION

The production of Malaysian palm oil has gradually increased over the years which has also resulted in an increase of by-products as well as waste. The main by-products and wastes produced from the processing of crude palm oil are the empty fruit

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bunch (EFB), palm oil mill effluent (POME), palm pressed fibre and palm shell. During processing, a certain amount of residual oil still remains in the palm pressed fibre after the mesocarp oil is extracted. In view of the large amount of palm pressed fibre produced in the palm oil milling process, the loss of oil is considerable. The residual oil is reported to contain a high level of minor components such as phospholipids, vitamin E and carotenes (Choo *et al.*, 1996). Phospholipid can be a valuable by-product which has potential as a multifunctional additive for food, pharmaceutical and industrial applications (Endre and Szuhaj, 1996). However, in the vegetable oil refining process, phospholipids are one of the undesired impurities which should be removed

so as to avoid undue darkening of the oil during deodorisation at a high temperature.

Over the years, the interest in the pressure-driven membrane processes, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) has grown rapidly in various applications in the oils and fats industry. The attractions of these processes are due to their advantages, which include low operating temperatures without loss of nutrients and low energy requirements without the need for phase change, which can consequently reduce energy cost (Subramanian *et al.*, 2004). A number of studies have been carried out on the use of ultrafiltration for vegetable oils applications. Those studies include the rejection of phospholipids and carotenoids from mixtures of vegetable oils such as soyabean, sunflower and rapeseed with a solvent, hexane recovery from oil miscella, vapour recovery, condensate return, degumming, hydrogenation catalyst recovery, waste-water treatment and remove trace metals from the oil (Subramanian *et al.*, 2004; Raman *et al.*, 1994; Koseoglu and Engelgau, 1990).

The small difference in molecular weight of phospholipids (about 800 Daltons) and triacyglycerols (about 900 Daltons) makes the separation by membrane to be quite difficult. Gupta (1977) reported that in non-polar media like hexane or neutral oil, phospholipid molecules tend to form reverse micelles with an average molecular weight (MW) of 20 000 Daltons or more. In the oil extraction process, hexane is commonly used as solvent. Thus, the separation of phospholipids by using appropriate membranes is possible in non-aqueous streams such as vegetable and oil/hexane miscella.

The membrane separation process, which can simultaneously concentrate, fractionate and purify products, thus offers an alternative method to recover valuable components, as well as reject unwanted impurities from residual palm fibre oil. To our knowledge, extensive investigations have been carried out for refining soyabean, sunflower, rapeseed and groundnuts oils using the membrane process, but only a few studies have been conducted where the membrane process for phospholipid removal from palm oil was adopted. Pagliero *et al.* (2007) investigated the use of the polyvinylidene flouride (PVDF) membrane to recover solvent from sunflower degummed oil/hexane miscellas. Ribeiro *et al.* (2006) has carried out work on polymeric membranes for solvent recovery from soyabean/oil miscella. In this work, ultrafiltration polymeric membranes were investigated under various operating conditions for their performance in terms of permeate flux, fouling and phospholipid retention during permeation where residual palm pressed fibre oil/hexane miscella were used.

MATERIALS AND METHODS

Samples

Palm pressed fibre was obtained from a nearby palm oil mill. The residual palm fibre oil was extracted from palm pressed fibre by using a laboratory-scale Soxhlet apparatus. Hexane was used as the solvent. The oil concentration in the residual palm fibre oil/hexane miscella was maintained at 10% by controlling the evaporation of the solvent in a rotary evaporator (Rotavapor, Buchi R-210, Switzerland). All solvents and chemicals used were of analytical grade, and were purchased from Merck, J T Baker or Ajax Chemicals.

Membrane

Three flat-sheet polymeric membranes were initially evaluated. The characteristics of the membranes are shown in *Table 1*. The membrane was conditioned before use to minimise the solvent effect on the membrane structure. The conditioning of the membrane was done by soaking the membrane with hexane for a period of 24 hr.

TABLE 1. CHARACTERISTICS OF MEMBRANES

Parameter	Membrane		
	PES	**PES**	**PVDF**
Membrane type	Flat-sheet	Flat-sheet	Flat-sheet
Material	Polyethersulphone	Polyethersulphone	Polyvinylidene fluoride
Manufacturer	Koch (USA)	GE Osmonics (USA)	GE Osmonics (USA)
MWCO	10 kDa	20 kDa	30 kDa
Contact angle[a]	71.3 ± 0.83	80.5 ± 0.54	83.0 ± 0.41
pH range (25°C)	2-10	2-11	1-11

Note: [a] Measured using a Drop Shape Analysis.
PES - polyethersulphone.
PVDF - polyvinylidene fluoride.

The contact angle was determined by using a Drop Shape Analysis (Kruss, Germany). The structure morphology of the membrane was investigated by scanning electron microscopy (Hitachi TM 1000, Tokyo, Japan). A Perkin-Elmer Spectrum One FTIR Spectrometer (Connecticut, USA) was used to determine the spectra of the membrane.

Filtration Apparatus

The ultrafiltration experiment was performed using a stirred dead-end cell as shown in *Figure 1*. The temperature of the experiment was controlled by a thermostatic controlled water bath. All experiments were performed in batch mode by filling up the cell with 300 ml of residual palm fibre oil/hexane miscella (10% of oil concentration). Permeate and retentate samples were collected and the permeate flow rate was measured in regular time intervals. The effects of operating conditions (temperature, pressure and agitation speed) on membrane performance were carried out only for the best membrane, which showed better performance in the preliminary experiments. In this study, the temperature used ranged from 30°C to 50°C; pressure varied from 2 to 6 bar and stirring speed ranged from 200 to 400 rpm.
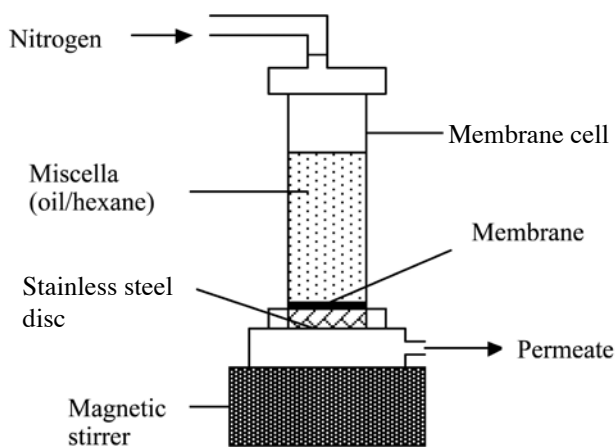

Figure 1. Membrane apparatus.

Analytical Method

Phosphorus was analysed according to the PORIM Test Method (1995), by charring and ashing the sample in the presence of magnesium oxide, followed by spectrophotometric measurement as phosphovanadomolybdic complex. The test solution was measured at 400 nm using a UV-Vis spectrophotometer (UV mini 1240, Shimadzu, Tokyo, Japan). The phospholipid content in palm oil is calculated by multiplying the phosphorus content by a factor of 25 (Goh *et al.*, 1982).

Performance Parameters

The performance of the membrane used is expressed in terms of phospholipid retention and permeate flux. The permeate flux (J) is expressed according to the following equation:

$$J = \frac{V}{t.A} \quad \text{Equation (1)}$$

where J is the permeate flux (l/m^2 hr), V the collected volume of permeate (l), t the filtration time (hr) and A the membrane surface area (m^2).

The percentage of phospholipid retention can be determined from Equation (2):

$$R(\%) = \left(1 - \frac{C_P}{C_F}\right) \times 100 \quad \text{Equation (2)}$$

where C_P and C_F are the concentration of component in permeate and feed, respectively.

The volume concentration ratio (VCR) is defined as follows:

$$VCR = \frac{V_F}{V_R} \quad \text{Equation (3)}$$

where V_F and V_R are the initial feed volume and retentate volume, respectively.

Experimental Design and Statistical Analysis

A statistical design based on the response surface methodology (RSM) was used to evaluate the effect of three independent variables; X_1 (pressure), X_2 (temperature) and X_3 (agitation speed), on two dependent (response) variables; Y_1 (permeate flux) and Y_2 (% phospholipid retention) at VCR of 2.0. A complete 2^3 experimental design was performed with three independent variables at five levels of each variable. The coded and actual values of the independent variables in the experimental design are shown in *Table 2*.

The matrix of experimental design with 20 treatments as shown in *Table 3* was used for determining the regression coefficients and statistical significance of models terms. The centre points were repeated six times in order to measure the repeatability of the method (Montgomery, 2001). All experiments were carried out in duplicate and

TABLE 2. CODED AND ACTUAL LEVELS OF INDEPENDENT VARIABLES USED IN THE EXPERIMENTAL DESIGN

Variables	Levels				
	-1.682	-1	0	+1	+1.682
X_1 = Pressure (bar)	0.64	2	4	6	7.36
X_2 = Temperature (°C)	23.18	30	40	50	56.82
X_3 = Speed (rpm)	131.82	200	300	400	468.18

TABLE 3. PERMEATE FLUX AND RETENTION OF PHOSPHOLIPID ACCORDING TO A 2^3 COMPLETE DESIGN OF EXPERIMENT

Run	Independent variable			Response variable	
	Pressure (bar) (X_1)	Temperature (°C) (X_2)	Speed (rpm) (X_3)	Flux* (l/m² hr)	Phospholipid retention* (%)
1	4	40	300	56.29 ± 2.45	80.45 ± 1.91
2	2	50	200	30.93 ± 2.02	79.65 ± 0.78
3	6	30	200	34.02 ± 2.88	91.15 ± 0.64
4	2	30	200	36.42 ± 3.07	84.00 ± 0.71
5	4	40	300	47.89 ± 0.92	82.70 ± 0.71
6	4	40	131.82	31.98 ± 4.44	80.80 ± 1.27
7	6	50	400	72.30 ± 4.56	91.60 ± 0.71
8	6	30	400	54.71 ± 1.89	92.45 ± 1.77
9	0.64	40	300	35.98 ± 1.63	73.50 ± 1.13
10	2	30	400	38.26 ± 5.81	83.70 ± 0.14
11	4	23.18	300	41.49 ± 1.65	89.65 ± 6.43
12	4	40	468.18	49.90 ± 1.92	86.80 ± 3.82
13	4	56.82	300	59.78 ± 3.07	84.00 ± 1.70
14	4	40	300	48.70 ± 0.88	79.55 ± 2.47
15	4	40	300	50.24 ± 1.44	78.65 ± 0.64
16	6	50	200	50.35 ± 1.45	78.80 ± 0.85
17	7.36	40	300	59.48 ± 2.64	93.20 ± 1.41
18	2	50	400	54.57 ± 2.98	81.25 ± 1.34
19	4	40	300	49.47 ± 2.24	83.30 ± 3.54
20	4	40	300	49.85 ± 1.85	78.75 ± 0.64

Note: *Mean ± standard deviation of two experiments.

means values of the data are reported. The predicted regression equation developed for the evaluation variables is as follows:

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3$$

Equation (4)

where Y is the response variable; b_0, b_1, b_2, b_3, b_{11}, b_{22}, b_{33}... are regression coefficients and X_1, X_2 and X_3 are uncoded values for pressure, temperature and agitation speed, respectively. The analysis of variance (ANOVA) was performed to determine the effect and regression coefficients of individual linear, quadratic and interaction terms. The experimental design was statistically analysed using the Minitab version 14 statistical package (Minitab Inc., PA, USA) software.

Resistance Values

The resistance-in-series model (Cheryan, 1986) was used to determine the resistance values for the membrane studied. The relationship between permeate flux, pressure and resistance can be described by Darcy's law as follows:

$$J = \frac{\Delta P}{\mu . R_T} = \frac{\Delta P}{\mu . (R_M + R_F + R_P)}$$

Equation (5)

where J is the permeation flux of miscella, ΔP is the applied pressure, μ is the dynamic viscosity of miscella, R_T is the total resistance, R_M is the resistance of clean membrane, R_F is the resistance caused by fouling and R_P is the resistance due to concentration polarisation. The resistance value was expressed in m^{-1}.

The resistance of the membrane (R_M) was determined before miscella filtration by measuring hexane flux through the clean membrane as follows:

$$R_M = \frac{\Delta P}{\mu_h J_h}$$

Equation (6)

where J_h is the pure hexane flux through the clean membrane and μ_h is the dynamic viscosity of hexane. Resistance due to fouling (R_F) was calculated from

the hexane flux through the fouled membrane after miscella filtration:

$$R_M + R_F = \frac{\Delta P}{\mu_h J_H}$$

Equation (7)

By rearranging Equation (7), the R_F is expressed as:

$$R_F = \frac{\Delta P}{\mu_h J_H} - R_M$$

Equation (8)

where J_H is the hexane flux through the fouled membrane and μ_h is the viscosity of hexane. Resistance due to polarisation concentration (R_P) can be derived from Equation (5):

$$R_P = R_T - R_M - R_F$$

Equation (9)

RESULTS AND DISCUSSION

Membrane Selection

Initial screening was performed at 40ºC and agitation of 300 rpm. The flux and phospholipid retention of PES 10 kDa, PES 20 kDa and PVDF 30 kDa membranes are shown in *Figure 2*. The phospholipid retention of PES 10 kDa, PES 20 kDa and PVDF 30 kDa were 86%, 60% and 80%, respectively. Comparing membranes with the same material (PES 10 kDa and PES 20 kDa) which exhibited higher phospholipid retention for PES 10 kDa indicates that most of the reverse micelles formed in the residual palm fibre oil/hexane stream were larger than the molecular weight cut off (MWCO) value of the PES 10 kDa that restricted the solutes to pass through the membrane. The MWCO membrane was reported to play an important role in increasing solute rejection (Gupta and Muralidhara, 2002).

The PVDF 30 kDa membrane had the highest overall flux (184.8 l/m² hr), followed by PES 20 kDa (78.1 l/m² hr), and PES 10 kDa (61.1 l/m² hr). Both PVDF 30 kDa and PES 20 kDa membranes were operated at the same pressure (3 bar). However, for the PES 10 kDa membrane, no permeate was obtained when tested at the initial operating pressure at 3 bar. The experiment for PES 10 kDa was continued by gradually increasing the operating pressure until the permeate came out at 27 bar and the obtained permeate flux was 61.1 l/m² hr. The overall permeate flux for each membrane was taken for a period of 60 min. Results on the flux and phospholipid retention of PES 10 kDa presented in *Figure 2* were achieved at the highest operating pressure (27 bar) as compared to the other two membranes. The contact angle measurement was used to determine the hydrophobicity of the membrane surface. A higher contact angle indicates
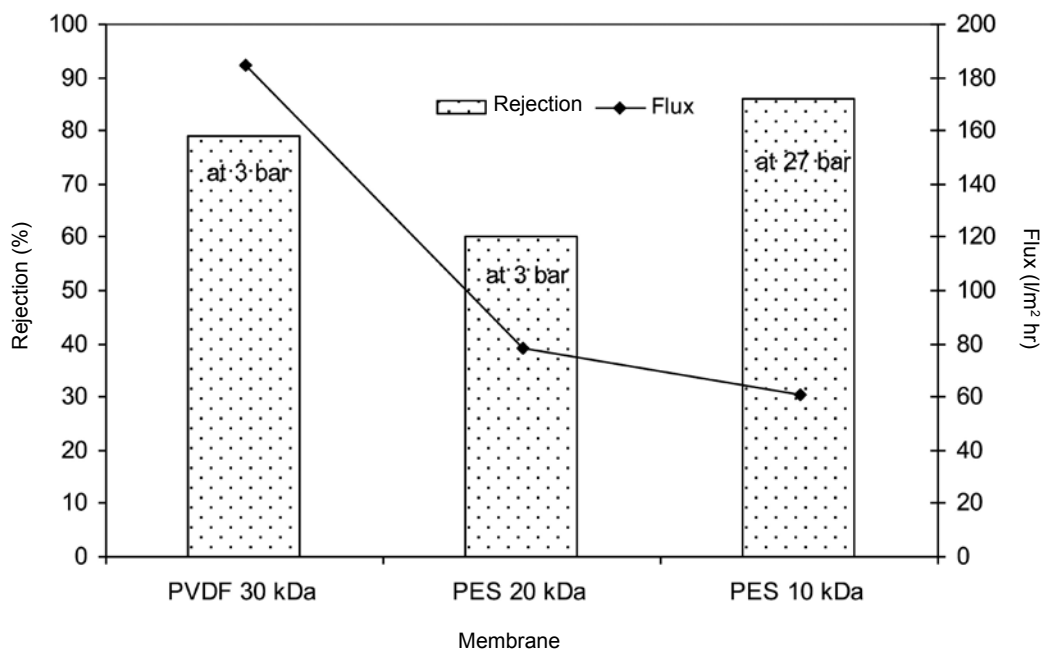
Note: PES - polyethersulphone.
PVDF - polyvinylidene fluoride.

Figure 2. Performance of membrane tested on residual palm fibre oil/hexane miscella.

a greater hydrophobicity of the material. Non-polar solvents such as n-hexane with low viscosity, low surface tension and low polarity index are expected to have a high flux with hydrophobic membranes (Van Der Bruggen *et al.*, 2006). In this study, the PVDF 30 kDa was found to be the most hydrophobic membrane with the contact angle of 83.0° (*Table 1*) and it had the largest molecular weight cut off which resulted in the high flux as compared to the other membranes. Thus, the PVDF 30 kDa membrane was selected for further investigation as the percentage phospholipid retention was above 80% and it gave the highest flux with low operating pressure.

The Effect of Operating Pressure on Miscella Permeate Flux

Figure 3 illustrates the permeate flux of miscella as a function of time at different pressure. The initial flux at 2, 4 and 6 bar when filtered at 40°C and 300 rpm was 112, 123 and 147 l/m² hr, respectively. The increase in permeation flux with the increase of operating pressure is expected as has been reported in literature (Garcia *et al.*, 2006). It was noted that at all studied operating pressures (2, 4 and 6 bar), the permeate flux declined rapidly at the initial stage, then gradually declined until after 60 min of filtration, the flux started to stabilise. This result shows that the permeate flux as a function of time exhibited three stages of flux decline: a sharp decrease in flux at the beginning stage of filtration, reduction in the decreased permeate rate at the second stage and a move towards stabilisation at later stage. A similar trend in flux decline was observed in other studies (Márcia *et al.*, 2008; Pagleiro *et al.*, 2001). This flux behaviour is probably linked to the fouling

phenomenon in the dead end filtration that suggests that the permeation process is affected by the solute compaction on the surface of the membrane or within the membrane pores. As explained by Cheryan (1986), a layer of rejected molecules (gel-polarised layer) deposits on the membrane surface, and the flow process is highly dependent on the consolidation of this layer.

The Effect of Operating Temperature on Miscella Permeate Flux

Increasing the operating temperature from 30°C to 50°C with constant pressure at 3 bar showed an increase of the permeate flux as illustrated in *Figure 4*. The initial permeate flux at 30°C, 40°C and 50°C was 97, 102 and 110 l/m² hr, respectively. These results indicate that a higher temperature reduces the viscosity of miscella, which lead to an increase in permeate flux. The negative dependence of viscosity on temperature has been reported in literature (Noureddini *et al.*, 1992). As temperature increases, the intermolecular forces between the liquid molecules decrease which make the flow of the fluid to be easier and faster. High temperature will also increase fluid diffusivity and both viscosity and diffusivity effects can influence the permeate flux. Results from *Figure 4* show that after operating for 10, 30 and 90 min at 30°C and 300 rpm, the permeate flux of the miscella gradually declined from 97 l/m² hr to 84, 69 and 45 l/m² hr, respectively. Similar fouling trends were observed for the other two temperature conditions (40°C and 50°C).

This study used hexane as solvent and in order to avoid significant solvent losses during processing, the filtration test was carried out below the boiling
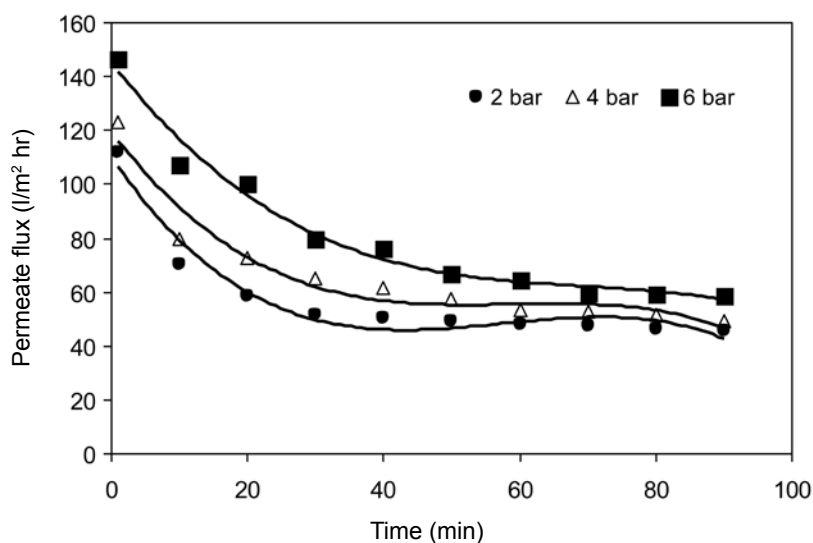

Figure 3. Permeate flux of residual palm fibre oil/hexane miscella through polyvinylidene fluoride (PVDF) 30 kD membrane at different pressures. Temperature: 40°C; agitation speed: 300 rpm.
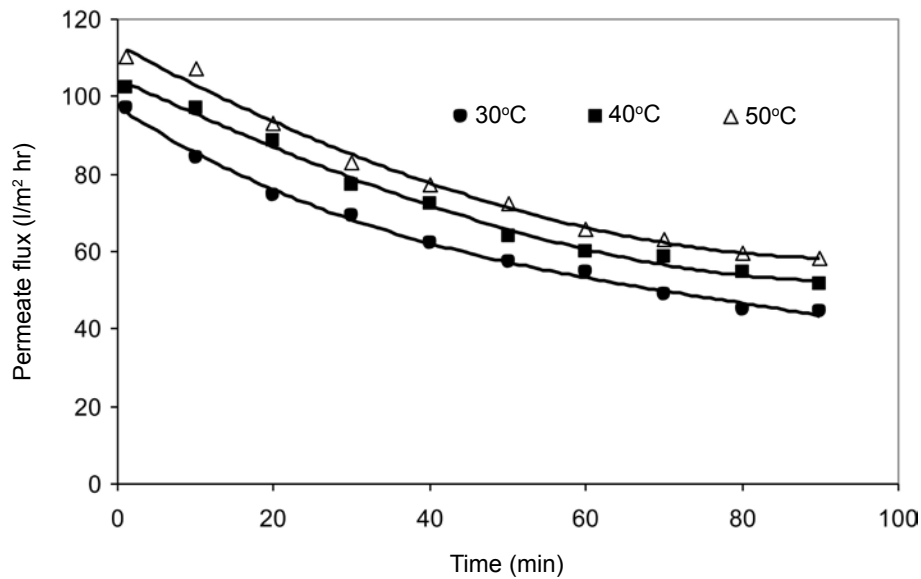
Figure 4. Permeate flux of residual palm fibre oil/hexane miscella through polyvinylidene fluoride (PVDF) 30 kD membrane at different temperatures. Pressure: 3 bar; agitation speed: 300 rpm.

point of hexane (69°C). It was also to minimise the change in miscella concentration due to the vaporisation of hexane. Although in commercial applications, a high permeate flux is desired and can be achieved with a high operating temperature, it is noted that a higher temperature implies an increase in energy consumption, which would lead to a higher operating cost. Another consideration is that the quality of oil and the heat-sensitive components in oil, which have nutritional values might be affected by the high temperature.

The Effect of Agitation Speed on Miscella Permeate Flux

Figure 5 presents the effect of agitation speed on permeate flux. As observed, increasing the speed from 200 rpm to 400 rpm with constant temperature at 40°C and pressure at 3 bar gave an increase of permeate flux from 88 to 123 l/m² hr indicating that at the higher speed of the stirred cell, the permeate flux increased. A high agitation rate and the mixing of the fluid near the membrane will create turbulence that will sweep away the accumulated solute and reduces the thickness of the boundary layer on the membrane surface, as reported in earlier studies (Garcia *et al.*, 2006; Lin *et al.*, 1997). Cheryan (1986) also reported that the use of a high recirculation rate in UF of a solution with a low viscosity reduces the polarisation phenomena. As shown in *Figure 5*, it was observed that the permeate flux gradually declined when filtering the residual fibre oil/hexane miscella through the PVDF membrane for the entire

duration of the test. At 200 rpm, the flux declined from 88 to 41 l/m² hr after 90 min of filtration. Agitation at the speed of 300 rpm showed a similar trend of flux decline.

The Effect of Operating Conditions on Phospholipid Retention

In *Table 4*, all ranges of the studied pressure and temperature showed that the *%R* of phospholipid was higher than 80%. This validates the high selectivity of the PVDF membrane for phospholipid removal from crude sunflower and soyabean oil filtration, where more than 95% of phospholipid retention was observed (Pagliero *et al.*, 2007). It was found that at 30°C, increasing the pressure from 2 to 6 bar resulted in a higher phospholipid retention from 86% to 94%. The agitation speed was kept constant at 300 rpm for all runs. Similar trends were

TABLE 4. PERCENTAGE RETENTION OF PHOSPHOLIPID

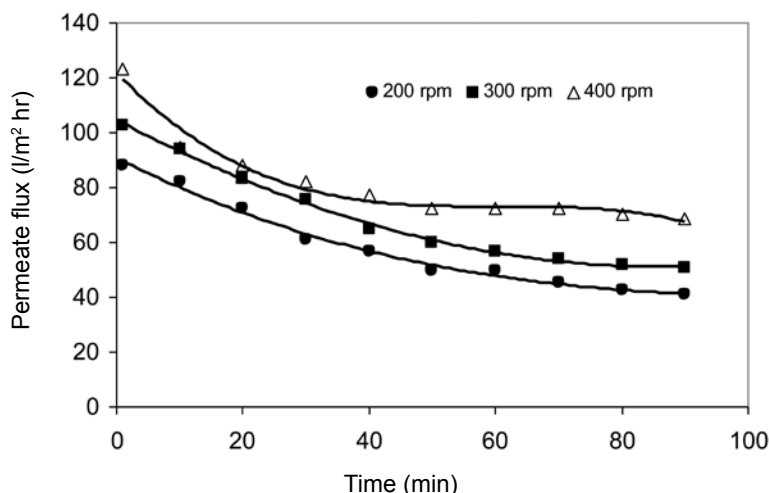| Temperature (⁰C)	Pressure (bar)	Phospholipid (%R)
30	2	86.0
	4	91.4
	6	94.3
40	2	81.0
	4	88.7
	6	95.0
50	2	81.0
	4	86.4
	6	93.2

Figure 5. Permeate flux of residual palm fibre oil/hexane miscella through polyvinylidene fluoride (PVDF) 30 kD membrane at different agitation speeds. Pressure: 3 bar; temperature: 40ºC.

observed at temperatures of 40ºC and 50ºC where the permeate flux increase from 81% to 95% and from 81% to 93%, respectively. It was noted that phospholipid retention increased with an increase in pressure, which could be due to the greater retention of solute on the surface and/or within the membrane and a higher solute compaction of the membrane that had occurred at a higher pressure. Moura *et al.* (2005) reported that filtering soyabean oil/hexane with PES membrane at a pressure higher than 2 bar reduced the average diameter of its pores and caused them to clog, thus bringing about an increase in phospholipid removal. A study by Márcia *et al.* (2008) on the usage of 0.05 µm pore diameter ceramic membrane for the filtration of corn oil/hexane miscellas showed a similar response whereby the retention of phospholipid increased with the transmembrane pressure.

Resistances

Table 5 shows the values of total resistance (R_T), membrane resistance (R_M), resistance due to fouling (R_F) and resistance due to concentration polarisation (R_P) at pressures of 2, 4 and 6 bar. In this study, the temperature and agitation speed were kept constant at 40ºC and 300 rpm, respectively. At operating pressure of 2 bar, the values for R_T, R_M, R_F and R_P

were 38.6×10^{12}, 1.2×10^{12}, 6.7×10^{12} and 30.6×10^{12} m^{-1}, respectively. Operating at a higher pressure of 6 bar resulted in higher total resistance (115.8×10^{12} m^{-1}), membrane resistance (3.7×10^{12} m^{-1}), fouling resistance (15.0×10^{12} m^{-1}) and polarisation resistance (97.0×10^{12} m^{-1}). The high resistance values at a higher pressure could be explained by the accumulation and compaction of solute molecules on the membrane surface resulting in a thicker or denser solute layer. These occurrences contributed to higher resistance values and limiting the movement of the solute molecules. The resistance that gave the highest contribution was concentration polarisation (about 79%), which demonstrated its major influence in the process. The membrane resistance of the PVDF membrane in the resistance-in-series model is less than 3.5% and seems to be insignificant as compared to the concentration polarisation. Kim *et al.* (2002) working with a polyimide sheet membrane (20 kDa) and soyabean oil miscella found total resistance values between 25 and 62×10^{12} m^{-1} and the membrane resistance values between 3 and 5×10^{12}. Márcia *et al.* (2008) working on corn oil/hexane extract using ceramic membrane (0.05 µm) also found major resistance contributions from the polarised layer.

Concentration polarisation as indicated by Lin *et al.* (1997) arises when the rejected compounds tend to form fairly viscous and gelatinous-type layers on

TABLE 5. RESISTANCE VALUES

Pressure (bar)	R_T (x 10¹² m⁻¹)	R_M (x 10¹² m⁻¹)	R_F (x 10¹² m⁻¹)	R_P (x 10¹² m⁻¹)
2	38.62	1.25	6.75	30.62
4	75.42	2.09	13.22	60.11
6	115.80	3.76	15.02	97.02

the membrane. The occurrence of fouling resistance, which was in the range of 6.7 and 15.0 x 10^{12} m^{-1} for the studied operating pressure (2 - 6 bar) could be due to the accumulation and deposition of solutes on the membrane surface and/or the crystallisation of oil molecules within the pores of membrane.

Statistical Analysis

Tables 6 and *7* illustrate the statistical regression models and coefficient of determination (R^2) for the permeate flux and the percentage retention of phospholipid, respectively at VCR = 2. The parameters from the analysis were reduced and those with a confidence level of above 95% ($p \leq 0.05$) were considered as significant. The following regression models Equations (10) and (11) were obtained for the three independent variables (X_1: pressure; X_2: temperature; X_3: agitation speed), and the response variables (Y_1: permeate flux; Y_2: retention of phopholipid):

$$Y_1 = 49.83 + 6.64\,X_2 + 5.53\,X_2 + 7.20\,X_3 - 3.22\,X_3^2 + 2.89\,X_1\,X_2 + 2.88\,X_2\,X_3$$

Equation (10)

$$Y_2 = 80.51 + 5.01\,X_1 - 1.44\,X_2 + 1.14\,X_3 + 1.33\,X_1^2 + 2.56\,X_2^2 + 1.49\,X_3^2$$

Equation (11)

It was confirmed from Equation (10) that pressure, temperature and speed had a positive effect on the permeate flux. Besides the linear fraction, the quadratic and interaction between parameters also contributed towards a significant effect on the permeate flux. As shown in *Table 3*,

TABLE 6. REGRESSION COEFFICIENTS, R² AND PROBABILITY VALUES OF THE REGRESSION MODEL AND STATISTICAL ANALYSIS FOR THE PERMEATE FLUX

Regression term	Permeate flux (l/m² hr)	
	Coefficient	Probability (*p*-value)*
Intercept (b_0)	49.333	0.000
Pressure (b_1)	6.643	0.000
Temperature (b_2)	5.528	0.000
Speed (b_3)	7.195	0.000
Speed² (b_{33})	-3.225	0.006
Pressure/temperature (b_{12})	2.887	0.048
Temperature/speed (b_{23})	2.883	0.048
R^2	0.917	-
Regression	-	0.000
Lack-of-fit	-	0.249

Note: * The *p*-value less than 0.05 is significantly different at 95% level.

TABLE 7. REGRESSION COEFFICIENTS, R² AND PROBABILITY VALUES OF THE REGRESSION MODEL AND STATISTICAL ANALYSIS FOR THE RETENTION OF PHOSPHOLIPID

Regression term	Phospholipid retention (%)	
	Coefficient	Probability (*p*-value)*
Intercept (b_0)	80.513	0.000
Pressure (b_1)	5.011	0.000
Temperature (b_2)	-1.435	0.013
Speed (b_3)	1.142	0.040
Pressure² (b_{11})	1.334	0.017
Temperature² (b_{22})	2.562	0.000
Speed² (b_{33})	1.493	0.009
R^2	0.921	-
Regression	-	0.000
Lack-of-fit	-	0.653

Note: *The *p*-value less than 0.05 is significantly different at 95% level.

increasing the pressure from the lowest level (-1.682) to the highest level (+1.682) resulted in an increase of permeate flux from 35.98 to 59.48 l/m^2 hr. The highest permeate flux (72.30 l/m^2 hr) was observed for the experiment with the maximum level (+1) for all the three independent variables. The regression model for phospholipids [Equation (11)] indicated the positive effect of pressure and agitation speed, and the negative effect of temperature for the retention of phospholipid. The interaction between the variables of pressure, temperature and speed has no significant effect on the retention of phospholipid. The retention of phospholipid as shown in *Table 3* was above 88% for the experiment with the high operating pressure (6 bar).

A shown in *Tables 6* and *7*, the coefficients of determination (R^2) for the permeate flux and the percentage of phospholipid retention were 0.917 and 0.921, respectively. These results illustrate that the response surface models can explain more than 90% of the variation in permeate flux and percentage retention of phospholipid. The R^2 values of the permeate flux and percentage retention of phospholipid are sufficiently high, meaning that the regression models can be used to predict the response. The fitness of the model which was determined by the lack-of-fit value was not statistically significant ($p > 0.05$) for both cases, indicating that the two regression models were sufficient for predicting the effect of independent variables on response variations (Montgomery, 2001).

CHARACTERISTICS OF MEMBRANE

Fourier Transform Infrared Spectroscopy

The Fourier transform infrared spectroscopy (FTIR) spectrums of clean and fouled PVDF membranes at 650 – 4000 cm^{-1} are presented in *Figure 6*. Both clean and fouled membranes showed almost identical spectral patterns with slightly different intensities. The spectra of both membranes exhibited bands at 3300, 1180 and 1400 cm^{-1} which refers to the stretching of C-H, C-C and C-F groups, respectively. For the fouled membrane, it was observed that the spectra showed an additional peak at 1740 cm^{-1} with very low intensity. The presence of this peak which refers to carbonyl group (C=O), indicates the presence of oil molecules in the fouled membrane. It was noted that all functional groups in the clean membrane are also present in the fouled membrane, except for the difference in transmittance intensity. This suggests that the functional groups in the fouled membrane have not been degraded by hexane,
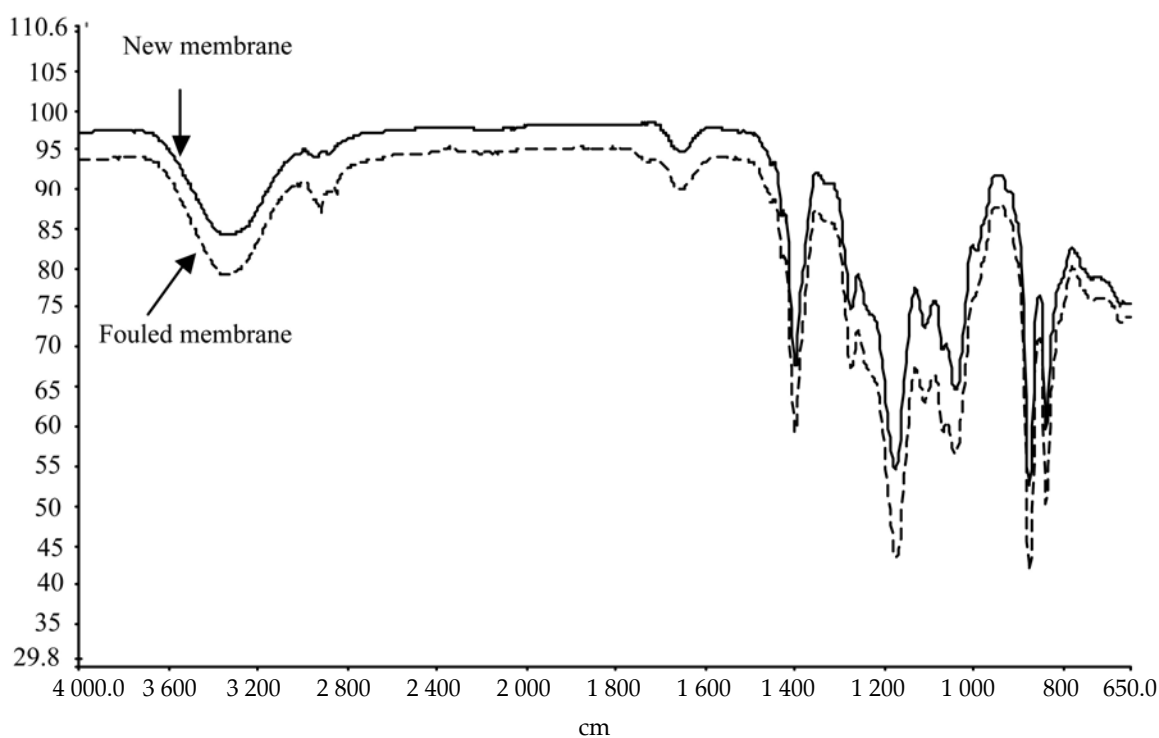

Figure 6. Fourier transform infrared spectroscopy of polyvinylidene fluoride 30 kD membrane (new and fouled membranes).

but the reduction in intensity could be due to the foulants deposited on the membrane that affects the intensity measurement.

Scanning Electron Microscopy

Figure 7 shows the scanning electron microscopy (SEM) of the PVDF membrane structure before and after permeation at 40°C. The results show no changes on the surface of the membrane. From the cross-section view, it was observed that there was a slight morphological modification at the top layer of the membrane, which could be due to membrane-solvent interaction that ended up with membrane structural changes.
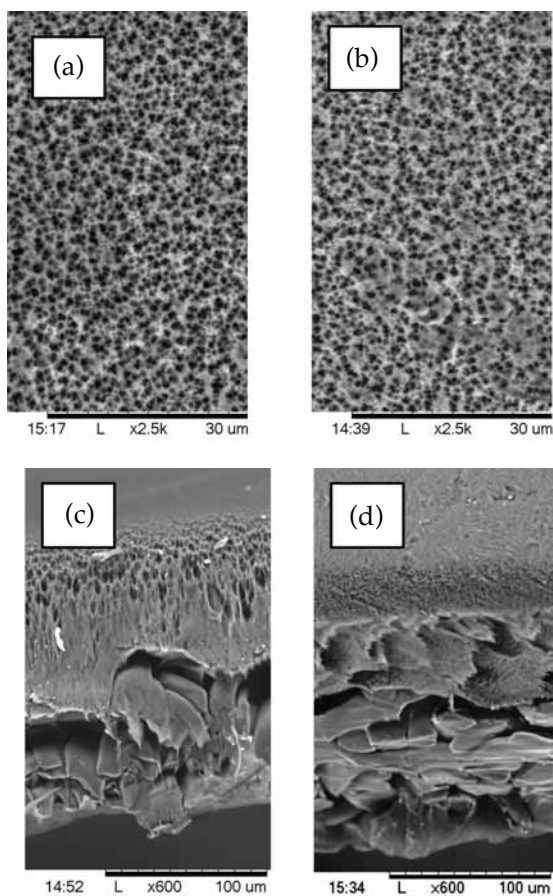

Figure 7. Morphology of polyvinylidence flouride 30 kD membrane: (a) clean (surface), (b) used (surface), (c) clean (cross-section), (d) used (cross-section).

CONCLUSION

The results indicate that the PVDF 30 kDa can be effectively used to retain phospholipid from residual palm fibre oil/hexane miscella. About 80% to 95% of the phospholipid retention was observed within the range of operations studied. This study

of the permeate flux showed that by increasing the operating conditions such as pressure, temperature and agitation speed would lead to an increase in flux. The filtration of miscella at different pressures exhibited three stages of flux decline over processing time, which indicated the fouling of the PVDF membrane. Operating at different temperatures and agitation speeds showed a similar trend in flux decline where the flux gradually declined through out the processing period. The total resistance of the PVDF membrane when operating at a pressure of 2 – 6 bar and fixed conditions at 40°C and 300 rpm were in the range of 38 and 115 x 10^{12} m^{-1}. The resistance due to the membrane is insignificant as compared to resistance due to concentration polarisation, which gave the highest contribution to the value of permeate flux. Based on the regression model for permeate flux, it was verified that the increase in pressure, temperature and agitation speed led to an increase in permeate flux. The interaction between pressure/temperature and temperature/speed also gave no significant effect on the permeate flux. The regression model for the percentage retention of phospholipid indicated the negative effect of temperature and the positive effect on pressure and agitation speed.

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