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C2 : Ultrafiltration Membrane for Degumming of Crude Palm Oil-Isopropanol Mixture

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ULTRAFILTRATION MEMBRANE FOR DEGUMMING OF CRUDE PALM OIL-ISOPROPANOL MIXTURE

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Abstract

This research performed separation of crude palm oil-isopropanol mixture by laboratory made flat-sheets Polyethersulfone ultrafiltration. Flux profiles confirmed that the increase of crude palm oil concentration resulted on lower fluxes. Moreover, increase the temperature from 30 ^{o}C to 45 ^{o}C initially generated raising the flux but further decrease when feed temperature is raised from 40 ^{o}C to 45 ^{o}C. Ultrafiltration of crude palm oil-isopropanol mixture at crude oil concentration of 30% and 40% is able to reject more than 99% phospholipids and nearly 93% phospholipids, respectively. However, separation of free fatty acid by this process is ineffective due to the small size of free fatty acids. Evaluation of blocking mechanism by Hermia model proposed that the standard and intermediate blocking were the dominant mechanisms at filtration of crude palm oil at a concentration of 30 and 40% and 50 and 60%, respectively.

Keywords: crude palm oil, ultrafiltration, degumming

INTRODUCTION

Crude vegetable oil is a raw material to produce edible vegetable oil. Some examples of crude vegetable oil comprise crude palm oil, crude soybean oil, crude corn oil, crude coconut oil, crude sunflower oil and crude castor oil[1]. Indonesia is one of the biggest producer of crude

palm oil, followed by Malaysia, Thailand, Colombia and Nigeria. Compared to other oilseed crops, palm oil produces more oil product[2]. Compared to other vegetable oil, the palm oil is preferrable as a substantial cost saving on many application[3]. Crude Palm Oil (CPO) is widely used in various food and industrial product manufacturing processes such as ice cream, frying oils, shortening, cosmetics, toothpaste, biodiesel and much more[4]. CPO is extracted from the ripe mesocarp of the fruit of oil palm tree (*Elaeis guineensis*), by a various method such as mechanical pressing followed by solid-liquid extraction [2].

The crude oil extracted from palm oil fruit also rich in palmitic acid, β-carotene, vitamin E and some undesirable compounds, such as phospholipids, free fatty acid (FFA), pigments, and protein[5-6]. CPO composed of a vast number of triglycerides (TAGs) and 6% of diglycerides (DAGs) naturally consist of FFA[7]. Industrial rules expect that high-quality oil must contain more than 95% of neutral TAGs and 0.5% or less FFA, for some reason the limit also decrease to less than 0.1% [2,8].

Complex refining process comprised degumming, neutralization, bleaching, and deodorization are performed to achieve the desired requirement. The first step of refining process is degumming, has a function to remove phospholipids and mucilaginous gums. Conventional degumming methods by using water and acid posses numerous drawback due to its high energy consumption, oil loss, loss of nutrients, and requirement of large water quantities [9-11].

Membrane-based filtration process is a promising method for palm oil refining. Membrane filtration provides low energy consumption, chemicals addition and almost no loss of natural oil[12-14]. Previous study of oil refining using membrane performed to eliminate unwanted components [3,14-16]. Membrane ultrafiltration combine with the solvent such as hexane is one of the most used methods for oil degumming[12,14,17-18]. Similar molecular weights of triglycerides and phospholipids (about 900 and 700 Da, respectively), could interfere with their

separation process by membrane technology. Phospholipids tend to form reverse micelles in non-polar media like hexane or crude oil, because of its amphiphilic properties[17,19]. This unique feature of phospholipid micelles increase its average molecular weight from 700 kDa to around 20 kDa or more[12,14]. Then, ultrafiltration (UF) membrane separated the micelle from the solvent-oil mixture, and the phospholipid was retained by the UF membrane[20]. However, the primary challenge in the use of membranes especially ultrafiltration is the existance of phenomena called fouling. Fouling is an irreversible membrane change caused by specific physical and chemical interactions between the membrane and the various components present in the process flow. Fouling membrane represents by decreasing of the permeate flux due to the effect of blocking on the surface as well as inside the membrane pores[21-22].

Fundamental studies of fouling mechanisms on ultrafiltration membranes have been performed for coconut cream[23], organic compounds[24], whey models[25] and PEG[26]. In more detail, the fundamental studies focusing on the fouling mechanism in ultrafiltration for oil degumming or separation of oil components are limited only for degumming corn oil[18, 27], crude sunflower and soybean oil [14]. This study emphasized on the fundamental and comprehensive analysis of the influence of oil solvents and micelle on fouling mechanism models. Specifically, this study addressed novelty finding on analysis of fouling model, fouling mechanism and fouling constant occurring on ultrafiltration for degumming CPO.

MATERIALS AND METHODS

Materials

Main raw materials used for this experiment was Crude Palm Oil from Kalimantan, Indonesia and iso-propanol (Merck) as a solvent. The ultrafiltration membrane was a Polyethersulphone (PES) flatseet membrane,

Membrane Characterization

The membrane was characterized for its permeability, surface structure, and specific functional group. Membrane permeability was determined by determining membrane flux of distilled water or iso-propanol into the membrane module at various operating pressures (1-3 bar). The fluxes were calculated according to the sample volume (V), the sampling time (t) as well as the membrane surface area (A). The volumetric permeate flow rate (υ) was calculated by equation (1):

$$\upsilon = \frac{V}{t} \quad (1)$$

Further, the flux was determined by equation (2):

$$J = \frac{1}{A}\, x\, v \quad (2)$$

Membrane surface and cross-sectional structure was characterized by Scanning Electron Microscopy (SEM, FEI Type Inspect-S50).

Evaluation of UF Membrane Performance for Degumming of CPO-Isopropanol Mixture

The ultrafiltration performance was examined by a laboratory-made cell filtration based on total recycle model as illustrated in Figure 1. The total recycle model involved returning the permeate and retentate flow back to the feed tank to maintain equivalent concentration during the process.

Figure 1. Schematic of Ultrafiltration Cell with Total Recycle Operation

Micelle solution was prepared by mixing CPO with isopropanol with ratios of CPO were 30%, 40%, 50%, 60% weight of the solution. The filtration cell was operated at 1 Bar for 120 minutes , and before be returned back to the feed tank, permeate was collected every 5 minutes to determine flux and concentration of phospolipids/fatty acid. Feed temperature was varied to

30°C, 35°C, 40°C, and 45°C in order to investigate the effect of temperature on UF performance. The feed tank was equipped with a temperature regulator and magnetic stirrer for homogenization of oil micelle. Membrane performance was evaluated in the term of permeate flux and phospolipid/ free fatty acid rejection. Similar to permeability determination, the permeate fluxes (J, L/m^{2}h) were calculated based on equation (2).

Rejections of phospolipid and free fatty acid were determined based on the concentration of phospolipid/ free atty acid in feed (C_f) and phospolipid/ free fatty acid concentration in permeate (C_p). Rejection is calculated according to equation (3).

$$R = \frac{C_f \, x \, C_p}{C_f} \qquad (3)$$

Characterization of CPO and Permeate

Specific characteristics of CPO and permeate included phospholipid and Free Fatty Acid (FFA) content. Phospholipid was expressed as total phosphorus, and were analyzed according to AOAC Ca 12-55 method. Determination of FFA was performed by acid-base titration method[14].

Blocking Mechanism

Blocking mechanism of CPO- Isopropanol ultrafiltration was studied according to Hermia's model. This model has been previously applied for fouling mechanism evaluation of konjac glucomannan separation[28], ultrafiltration of model dye wastewater[29] and ultrafiltration of dye solution[30]. The Hermia's model describes the mechanism of membrane fouling based on blocking filtration law, consisting of complete pore blocking, standard pore blocking and intermediate pore blocking and cake filtration. The blocking law filtration is expressed in the term of permeate time and filtration time and developed for dead-end filtration as shown in equation (3)[31]:

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \tag{3}$$

where t is filtration time, and V is the permeate volume, k is constant, and n is a value illustrating the different fouling mechanism.

The values of n are described as follows: complete blocking having n value of 2, intermediate blocking is represented with n = 1, the standard blocking illustrated with n = 1.5 and the cake layer formation has n value of 0. In the complete blocking model, it is assumed that each solute participated in blocking the entrance of the membrane pores completely. For intermediate blocking, it is assumed that every solute stays on previously deposited solute. Standard blocking considers the deposition of each solute to the internal pore wall. The cake layer formation applied based on the accumulation of the solute on the membrane surface in the cake form[32]. The Hermia's model was then linearized based on the n value for each model using fitting equation (4) to (7) regarding permeate flux versus time as presented in the following.

For Complete Blocking (n = 2) :

$$\ln J = \ln J_0 - k_c t \tag{4}$$

For Intermediate Blocking (n = 1) :

$$\frac{1}{J} = \frac{1}{J_0} + k_i t \tag{5}$$

For Standard Blocking (n = 1.5) :

$$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + k_s t \tag{6}$$

For Cake/Layer Formation (n = 0) :

$$\frac{1}{J^2} = \frac{1}{J_0^2} + k_{cf}t \quad (7)$$

Where k_c, k_i, k_s and k_{cf} are constants for complete blocking, intermediate blocking and cake/layer formation, respectively.

RESULT AND DISCUSSION

Water and Solvent Permeability

Flux profile of water and isopropanol at various pressure for the UF membrane is presented in Figure 2.

Figure 2. Flux Profile of Isopropanol and Water at Pressure of 1-3 bar

The figure shows an increase of water and isopropanol flux with the rise of pressure from 1 – 3 bar. According to linerization regression (y = mx) of water and isopropanol flux in the figure, it is found that the water permeability and isopropanol permeability are 44,19 L/m^2. hr and 62,69 L/m^2. hr, respectively. This is surprising since the water is predicted having permeability higher than the ethanol due to the water characteristic as the most polar solvent. The result is in contrast with de Melo et al.[33] confirming that lower solvent polarity result on permeation decrease. In addition, the prepared polyethersulphone membrane had a characteristic as hydrophilic membranes especially due to the addition of polyvinylpyrrolidone (PVP) and polyethene glycols (PEG)[34]. With the hydrophilic characteristic of the PES membrane, the water permeation is expected higher than isopropanol. A solvent characteristics such as viscosity, surface tension and polarity as well as the molar volume of the solvent had an effect on the transport of solvent by the membrane[35-36]. According to the physical-chemical

characteristics of solvent (viscosity and interfacial tension), the isopropanol flux should be below the water flux. However, the phenomenon is not found in this research, presumably that there is the specific interaction of the membrane and the solvent. A similar result was observed by Araki et al.[37]. The high permeability of isopropanol indicates that the conditioning process (immersing in the isopropanol) creating less hydrophilic of the PES membrane. The alteration of the hydrophobic characteristic is generated due to the transformation of the hydrophilic and hydrophobic site of the membrane and resulting on higher permeability of the isopropanol. Water permeation has a correlation with the hydrophilic characteristic (hydrogen bonding formation) of the membrane. When alcohol such as isopropanol is permeated, the hydrogen bonding formation is less and contributing in low water flux.

Permeate Flux

Profile of permeate flux showing flux versus time is presented in Figure 3.

Figure 3 Permeate Flux Profile in Ultrafiltration of CPO-Isopropanol Mixture at Various Concentration of CPO (Feed Temperature is 19 ^{o}C, Trans Membrane Pressure of 1 bar)

The figure shows there is a flux decline during filtration of solvent and CPO mixtures. A significant flux falling-off is observed during the first 5 minutes of filtration, followed by a flux reduction deceleration rate and finally, flux is steady. The three-steps behaviours were also perceived by de Souza et al. [11] in filtration of corn oil/hexane micelle, Pagliero et al. [14] for soybean oil/micelle filtration and Penha et al.[38] in filtration of marracuba oil/n-hexane mixture. The initial flux decline is caused by a phenomenon called polarization concentration, while the following flux reduction was as a result of membrane fouling. Comparable performances were reported for oil/hexane mixture permeation through UF membrane using sunflower oil[39] as well as coconut oil, groundnut oil, mustard oil, sunflower oil and rice bran oil [36, 40]. In addition,

it was reported that the flux reduction at the beginning of sunflower oil-n-hexane filtration was concentration polarization phenomenon and a gel layer formation on the membrane surface[39]. Moreover, the flux drop at the end of filtration was due to deposition of gel on the membrane surface [14,38,41]. The deposited layer could be formed due to phospholipids retained on the membrane surface and pores plugging [14, 42].

Figure 3 also confirms an increase of oil concentration leads to more reduction of flux. This decrease takes place due to an increase of oil concentration results on a solution viscosity increase. With the rise of viscosity, smaller flux is obtained since the permeability is influenced by the viscosity[35]. In addition, the lower flux is obtained as a result of polarized/gel layer formation. When the oil concentration is higher, the layer is larger and generate larger resistance to the flux permeation [33,36,41]. As elucidated by Kim et al.[41], convective solute transport to the membrane produces a sharp gradient of concentration inside the boundary layer. Due to diffusion, a solute back-transport into the bulk is taken place, and a close-packed arrangement of solute is formed. As a consequence, no more solute can be accomodated, and the mobility of solutes is restricted.

Scanning Electron Microscope images of the fouled membrane as displayed in Figure 4 confirms a foulant layer on the membrane surface is present.

Figure 4. Scanning Electron Microscope Images of Clean Membranes (1a) Surface (2a) Cross-Sectional Structure and Fouled Membrane after ultrafiltration of 30% CPO-Solvent mixture (1b) Surface (2b) Cross-Sectional Structure at magnification of 10.000x

Figure 5 displays the effect of feed temperature on initial and final permeate flux.

Figure 5. The effect of feed temperature on Initial and Final Flux at pressure of 1 bar and CPO concentration of 30%

Based on the figure, it indicates that increase mixture temperature from 30 to 35 ^{o}C has effect on higher flux permeate. This was expected due to the decrease of viscosity or increase of phospholipid diffusion on the membrane pores. However, with further temperature increase (from 40 to 45 ^{o}C) leads on flux decrease and the reduction of viscosity do not have an effect on the flux. This result is close to Kim et al. [41] confirming that the operating temperature at 40 ^{o}C was suitable for degumming of soybean extract then above the temperature of 40^{o}C, the flux decreased. Flux declining is predicted due to the fouling on the membrane surface as a result of solid denaturation or gelatinisation of solid as well as insoluble salts precipitation at high temperature[43].

Phospholipid and Free Fatty Acid Rejection

Membrane selectivity is represented as rejection indicating membrane ability to reject or remove of a feed compound. Micelles will be formed when phospholipids are dispersed in water. A mixture of phospholipids in a non-polar solvent such as isopropanol formed reverse micelles having the average molecular weight of 20.000 daltons (10-200 nm)[43]. Based on its pore size, ultrafiltration rejects compound having a molecular weight in the range of 300-500.000 Dalton. Hence, in the phospholipids-isopropanol system, the phospholipid is expected to be retained in the retentate, and the permeate comprises the oil and isopropanol. In contrast to phospholipids, the molecular weight of free fatty acid and triglyceride is similar. The triglycerides and free fatty acids (FFA) have a molecular weight of 800 Da and 300 Da, respectively[9]. Comparing to ultrafiltration pore size, separation of FFA is challenging due to low selectivity and results in low rejection value. Rejection of phospholipid and FFA at various CPO concentration is displayed in Table 1.

Table 1 Rejection of Phospholipid and Fatty Acid at Various CPO Concentration at pressure of 1 bar and Feed Temperature of 29 ^{o}C

The table shows rejection of phospholipids is significantly higher than the fatty acids. This is noticeable since the molecular weight of micelle phospholipids are considerably greater than the free fatty acids. The phospholipids rejection is found greater than 99% at CPO concentration of 30% and slightly reduced to nearly 93% with increase of CPO concentration to 40%. The reduction of phospholipid rejection is more obvious with the increase of CPO concentration to 50%. In addition, a similar trend is shown when the feed temperature is raised. The rejection of both phospholipids and FFA is declined with higher temperature from 30oC to 40oC as presented in Table 2.

Table 2 Rejection of Phospholipid and Fatty Acid at Various Feed Temperature at pressure of 1 bar and CPO Concentration of 30 %

Blocking Mechanism by Hermia Model

In this research, Hermia's model was applied in order to evaluate the blocking mechanism during ultrafiltration of CPO-Isopropanol mixture at various feed CPO concentration. Fouling mechanism represented by blocking mechanism is identified by fitting the experimental data into the Hermia's linearized equation (equation (4) to equation (7). The fitting of experimental data to the four type Hermia's model is shown in Figure 6, and the corresponding correlation coefficient (R^2) is listed in Table 3.

Figure 6 Fitting of experimental data (feed temperature of 30^{o}C, pressure at 1 bar) to Hermia's model: (a) complete blocking (b) Standard blocking (c) Intermediate blocking (d) cake/gel layer formation

Table 3 R^2 value of Blocking Mechanism based on Hermia's Model.

According to the table, two dominant blocking mechanisms are found, the standard blocking and the intermediate blocking. At low concentration of CPO (30% and 40%), the blocking mechanism is dominated by standard blocking. In contrast, at higher concentration of CPO (50 and 60%), the intermediate blocking are the dominant mechanism. The standard blocking assumes that each solute is deposited into the internal pore wall. In the intermediate blocking, it is proposed that every solute stays on the previously deposited solutes.

Proposed standard blocking and intermediate blocking mechanism in UF of CPO-Isopropanol is illustrated in Figure 7.

Figure 7. Schemcatic Illustration of (a) Intermediate Blocking (b) Standard Blocking Mechanism in UF of CPO-Isopropanol Mixture

According to the Figure 7a, large particles accumulated on the membrane surface and blocked the membrane pores were tryglycerides. Large particles formed at high concentration of CPO was firstly presumably as phospolipid-isopropanol micelle due to their large size and potential to block the pores. However, this assumption is in contradictive with the phospolipid rejection. If the large parcticles were the agglomeration of phospolipis micelle then the rejection at high CPO concentration should be larger. Hence, it can be assumed that at high concentration of CPO, not all the phospolipids generated micelle with isopropanol. This confirmed why the phospolipid rejection at high concentration of CPO was lower. Then the larger particles accumulated on the membrane surface were predicted as other oil compound such as tryglycerides.

In addition, Figure 7b presents that at low concentration of CPO, the dominat fouling mechanism was the standard blocking, representing small particles attached inside the

membrane pore and providing pore constriction (reducing of pore size). Compound that possibly blocking inside the membrane pores was the fatty acid since the size of fatty acid was smaller than the phospolipid-isopropanol micelle. At low concentration of CPO, sufficient amount of phospolipid-isopropanol micelles were formed and with pore constriction provided high rejection of phospolipid. On the other hand, small molecules such as fatty acid can enter the membrane pores.

Conclusion

This research performed separation of crude palm oil-isopropanol mixture by laboratory made flat-sheets Polyethersulfone ultrafiltration. Flux profiles confirmed that the increase of crude palm oil concentration resulted on lower fluxes. Moreover, increasing the temperature from 30 ^{o}C to 45 ^{o}C initially generated raising the flux but further decrease when feed temperature is raised from 40 ^{o}C to 45 ^{o}C. Ultrafiltration of crude palm oil-isopropanol mixture at crude oil concentration of 30% and 40% is able to reject more than 99% phospholipids and nearly 93% phospholipids, respectively. However, separation of free fatty acid by this process is ineffective due to the small size of free fatty acids. Evaluation of blocking mechanism by Hermia model proposed that the standard blocking and intermediate blocking were the dominant mechanisms at filtration of crude palm oil at a low concentration (30% and 40%) and high concentration (50 and 60%), respectively.

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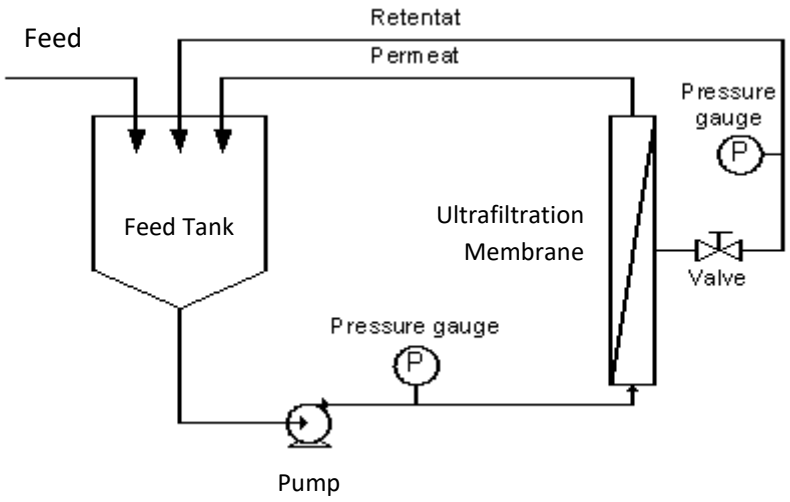


Figure 1. Schematic of Ultrafiltration Cell with Total Recycle Operation

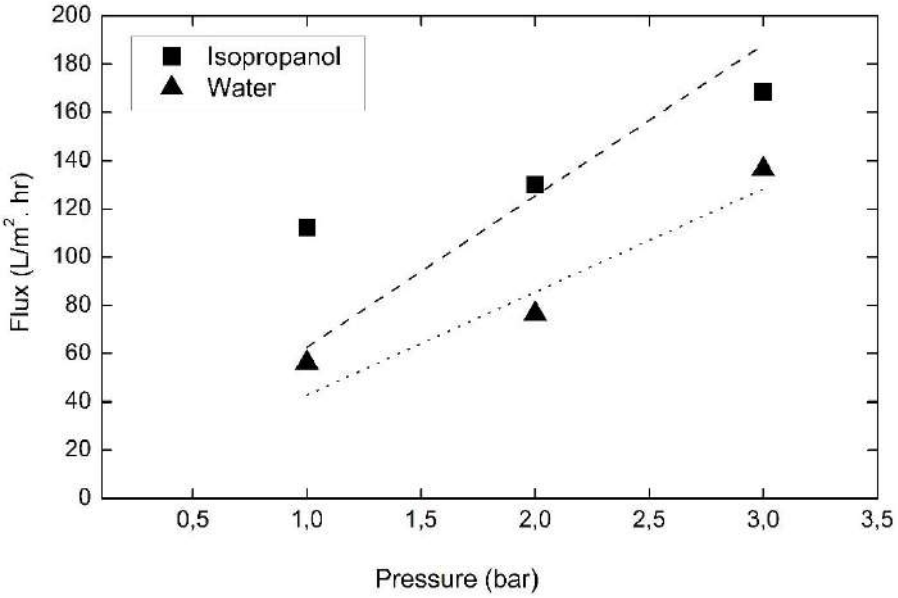


Figure 2. Flux Profile of Isopropanol and Water at Pressure of 1-3 bar

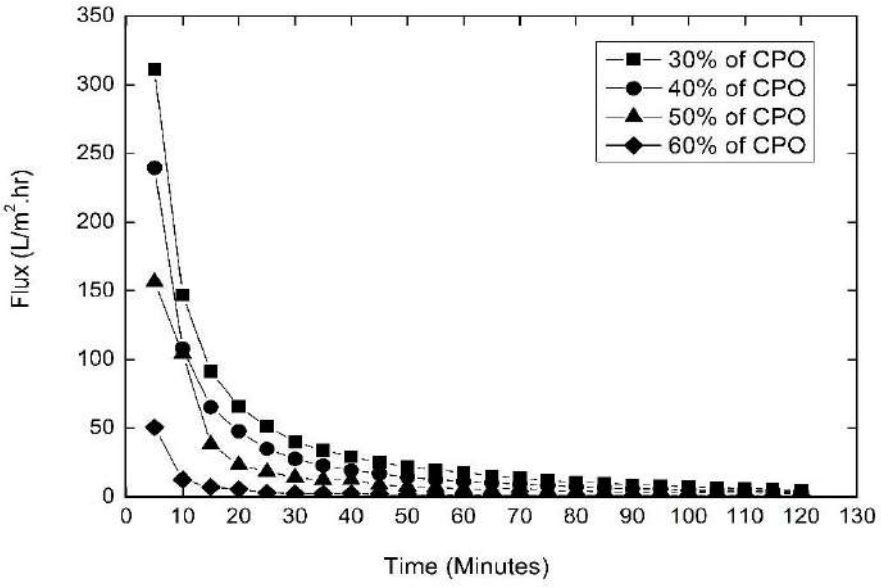
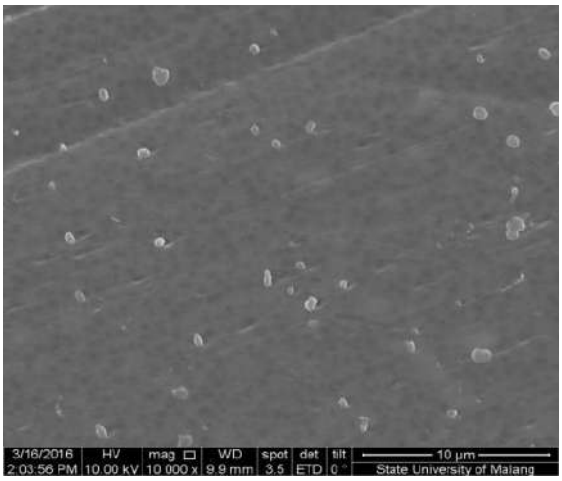
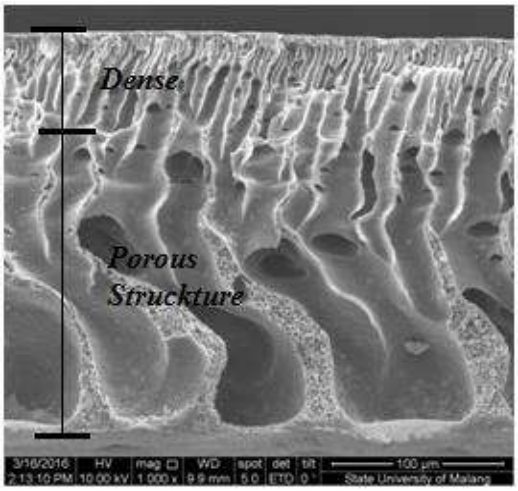


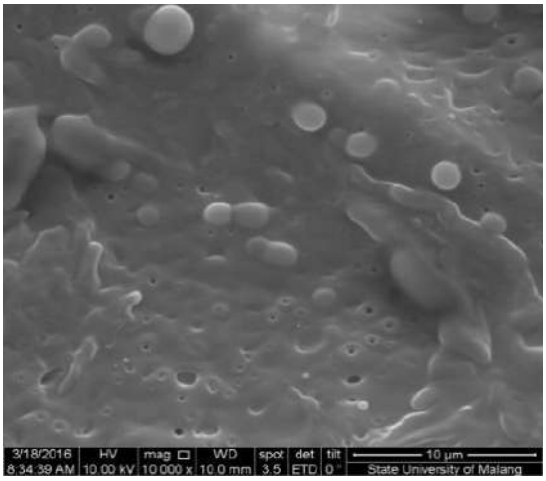
Figure 3 Permeate Flux Profile in Ultrafiltration of CPO-Isopropanol Mixture at Various



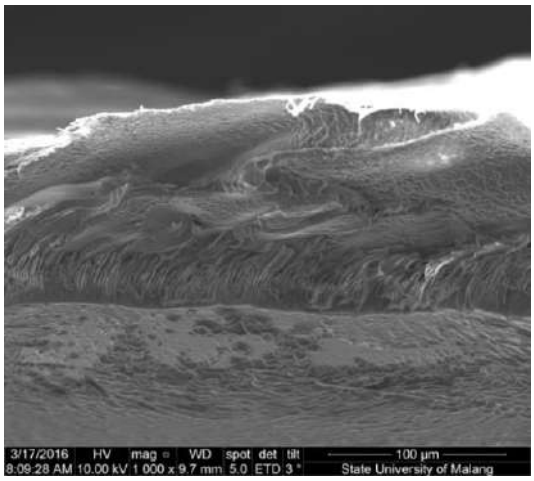
(1a)



(2a)



(1b)



(2b)

Figure 4. Scanning Electron Microscope Images of Clean Membranes (1a) Surface (2a) Cross-Sectional Structure and Fouled Membrane after ultrafiltration of 30% CPO-Solvent mixture (1b) Surface (2b) Cross-Sectional Structure at magnification of 10.000x

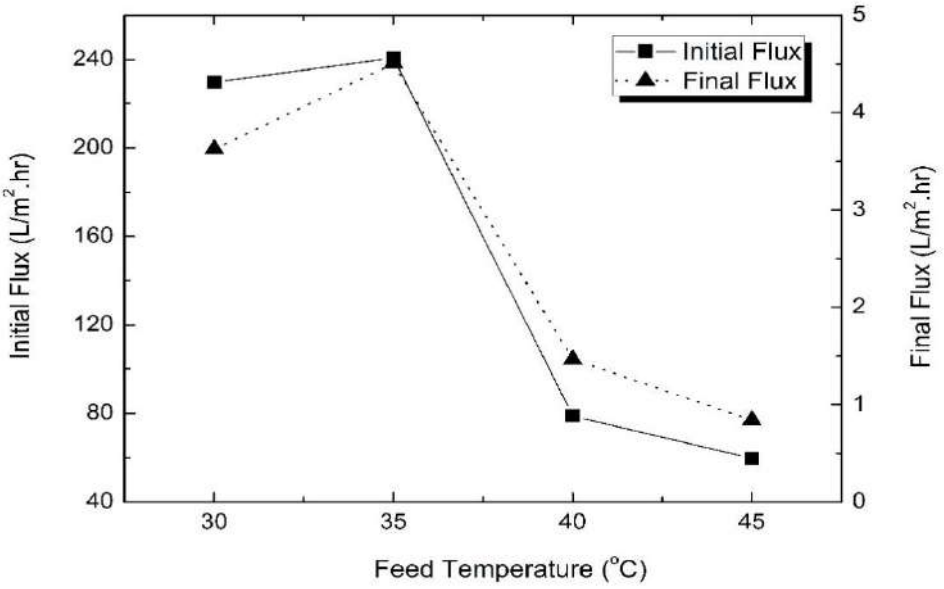


Figure 5. The effect of feed temperature on Initial and Final Flux at pressure of 1 bar and CPO concentration of 30%

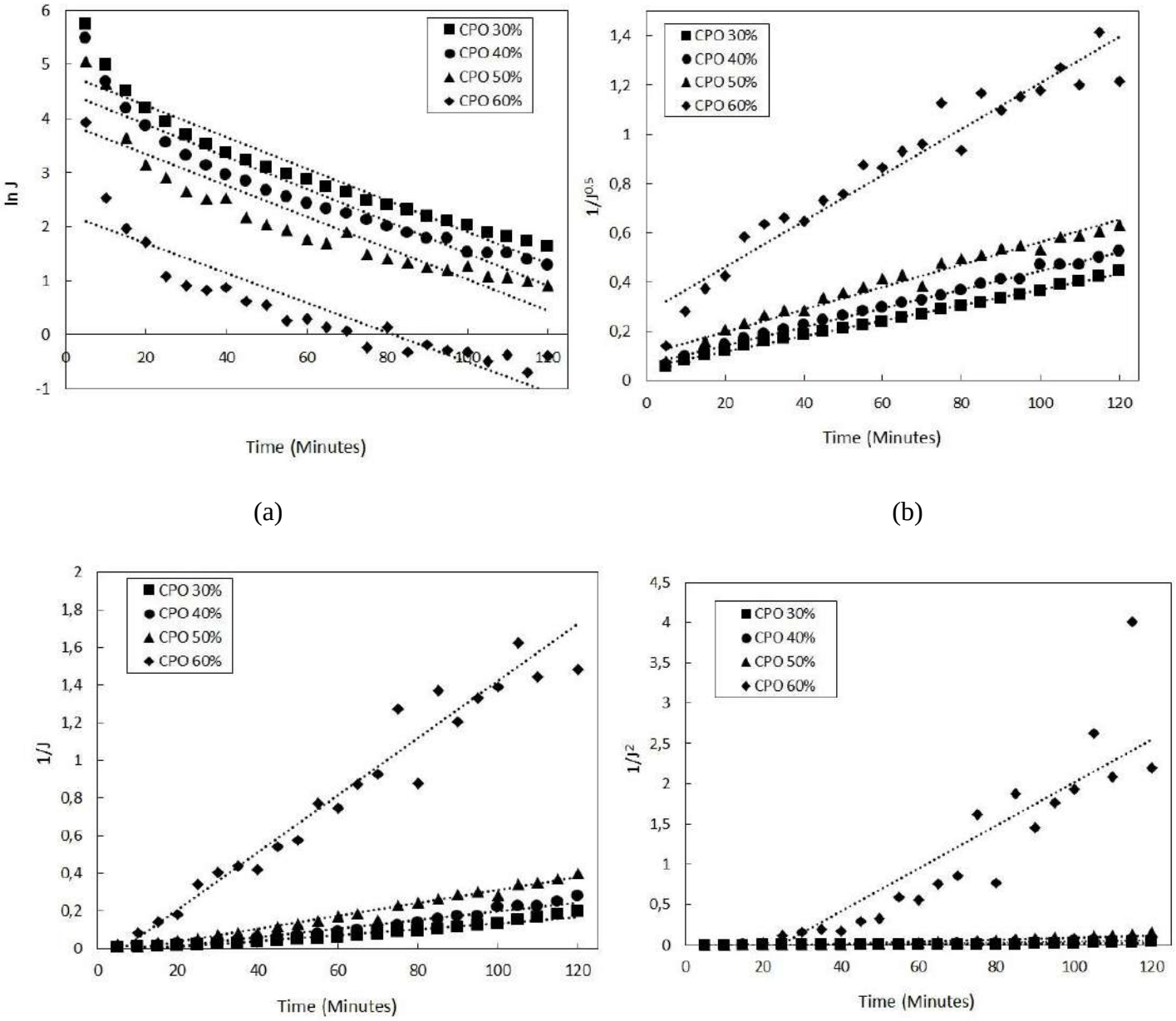
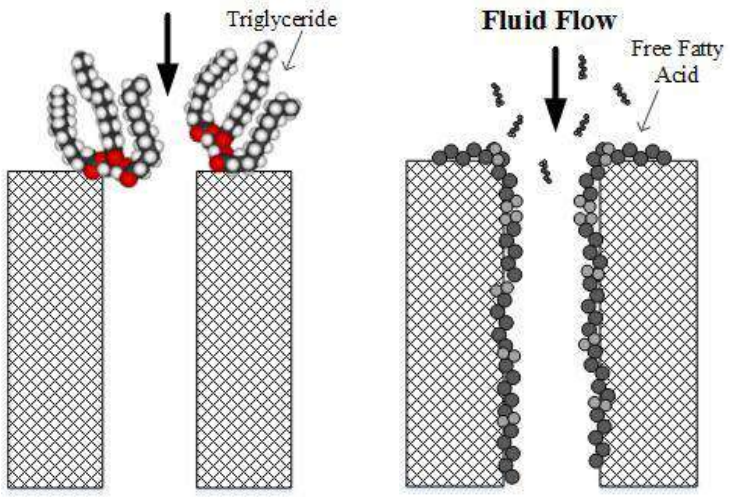


Figure 6 Fitting of experimental data (feed temperature of 30ºC, pressure at 1 bar) to Hermia's model: (a) complete blocking (b) Standard blocking (c) Intermediate blocking (d) cake/gel layer formation



(a) (b)

Figure 7. Schemcatic Illustration of (a) Intermediate Blocking (b) Standard Blocking Mechanism in UF of CPO-Isopropanol Mixture

Table 1 Rejection of Phospholipid and Fatty Acid at Various CPO Concentration at pressure of 1 bar and Feed Temperature of 29 ^{o}C

CPO Concentration	Phospholipid Rejection (%)	Free Fatty Acid Rejection (%)
30%	>99,21	16
40%	92,93	13
50%	37,52	9

Table 2 Rejection of Phospholipid and Fatty Acid at Various Feed Temperature at pressure of 1 bar and CPO Concentration of 30 %

Feed Concentration	Phospholipid Rejection (%)	Free Fatty Acid Rejection (%)
30^{O}C	92,93	13
35^{O}C	86,60	7,168
40^{O}C	73,94	10,24

Table 3 R^2 value of Blocking Mechanism based on Hermia's Model.

	R^2			
	Complete Blocking	**Intermediate Blocking**	**Standard Blocking**	**Cake/ Gel Formation**
CPO 30%	0,9186	0,9512	**0,9971**	0,7755
CPO 40%	0,9022	0,9618	**0,9953**	0,8053
CPO 50%	0,8354	**0,9811**	0,9737	0.8769
CPO 60%	0,7797	**0,9432**	0,9394	0,8052

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[CABEQ] Official notification upon submission of MS 1244 by CABEQ Editorial board

1 message

cabeq@pbf.hr <cabeq@pbf.hr> 30 October 2017 at 20:01
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Dear author,

Thank you for submission of your manuscript

MS number: MS 1244
Authors: N. Aryanti
Title: ULTRAFILTRATION MEMBRANE FOR DEGUMMING OF CRUDE PALM OIL-ISOPROPANOL MIXTURE
to Chemical and Biochemical Eng. Q. Journal.

Your manuscript will be reviewed by at least two international experts in the field of your research, and their evaluation will be E-mailed to your address.

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cabeq@pbf.hr <cabeq@pbf.hr> 29 December 2017 at 16:04
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Based on the reviewers evaluation your manuscript MS 1244 should be revised before publication in Chemical and Biochemical Engineering Q. Journal.

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In my opinion this manuscript should (please check the appropriate line) be published:

Number	**1244**
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Title	Ultrafiltration Membrane for Degumming of Crude Palm Oil-Isopropanol Mixture

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1. Original scientific paper x
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Review:

1. **Flat-sheet polyethersulfone UF membrane was laboratory made. Authors mentioned that the membrane was characterized for permeability, surface structure and specific functional group. Nevertheless only SEM was used for surface structure. SEM is good for taking pictures but with this kind of picture there is no a lot of possibilities to conclude about surface structure. Also where are results about specific functional group? If this is "home" made membrane more is necessary for characterization. For example MWCO what is crucial for UF membranes and the method is not very hard.**
2. **Why authors used 1 bar for working pressure? Why not also higher since UF can go up to 10 bar? Maybe it is hard to decide about working pressure if you don't have enough characteristics.**

Minor comment:

There are a lot of mistakes through the paper:

1. **full name for PEG on first mention**
2. **missing "h" in flatseet membrane**
3. **put English words in Fig. 1**
4. **small B in 1 bar**
5. **symbols must be italic – like J, C, t, V etc. through whole paper**
6. **two different explanation for Fig. 5 in the text-**
7. **a lot of mistakes with "°C" through the paper**

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Title	ULTRAFILTRATION MEMBRANE FOR DEGUMMING OF CRUDE PALM OIL-ISOPROPANOL MIXTURE

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1. **Original scientific paper X**
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Review:

The content of the paper "**ULTRAFILTRATION MEMBRANE FOR DEGUMMING OF CRUDE PALM OIL-ISOPROPANOL MIXTURE"** is relevant to Chemical and Biochemical Engineering Quarterly. The subject is well chosen and the methods used appropriate. There are many papers published about application of ultrafiltration in refining various oils, which also includes crude palm oil as the media but surprisingly those dealing with palm oil are not included in references of this paper. Novelty of this paper is in thorough analysis of fouling mechanism of the membrane by ingredients of crude palm oil and the results obtained here are valuable and deserve publishing. However, this paper needs major revision before publishing. Quality of the presentation of the results is rather low and needs improvement in many aspects since in its present form it does not have sufficient quality for publishing in Chemical and Biochemical Engineering Quarterly.

The major problems in the manuscript are:

1. English language used in the paper is rather poor. There are serious grammar errors and style problems throughout the text. It is difficult to understand the meaning of some sentences at some places in the text. A thorough correction is necessary and a native speaker as an editor should be involved.
2. Authors cited many papers but omitted several that deals with membrane filtration in refining of crude palm oil:
    a. PERFORMANCE OF POLYMERIC MEMBRANES FOR PHOSPHOLIPID REMOVAL FROM RESIDUAL PALM FIBRE OIL/HEXANE MISCELLA By: Abd Majid, Rusnani; Mohamad, Abdul Wahab; May, Choo Yuen JOURNAL OF OIL PALM RESEARCH (25) 2 (2013) 253-264
    b. Deacidification of crude palm oil using PVA-crosslinked PVDF membrane by Azmi, R. A.; Goh, P. S.; Ismail, A. F.; et al. in JOURNAL OF FOOD ENGINEERING 166 (2015) 165-173 which deals with similar topic.
    c. DEACIDIFICATION OF PALM OIL USING SOLVENT EXTRACTION INTEGRATED WITH MEMBRANE TECHNOLOGY By: Lai, S. O.; Heng, S. L.; Chong, K. C.; et al JURNAL TEKNOLOGI 78 (12) (2016)
    d. Non Dispersive Chemical Deacidification of Crude Palm Oil in Hollow Fiber Membrane Contactor By: Purwasasmita, Mubiar; Nabu, Eryk Bone Pratama; Khoiruddin; et al.JOURNAL OF ENGINEERING AND TECHNOLOGICAL SCIENCES 47 (4) (2015) 426-446
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    f. Membrane processing of crude palm oil By: Arora, S; Manjula, S; Krishna, AGG; et al. DESALINATION 191 (1-3) (2006) 454-466

I suggest shortening the existing reference list to more closely related research and including some of the papers listed above.

3. Abstract is completely the same as Conclusions, which is blatant neglect of the economy of the paper and the purpose of those chapters in a research paper.
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5. Fig.1 needs improvement in both graphical presentation and legend, which is currently not in English.
6. Caption of Fig. 4 suggests that there are 4 figures (1a, 1b, 2a and 2b) within the same figure, but there are only 3 figures in the end of the manuscript.
7. Volumetric flow rate is usually denoted as Q and not 'υ'.
8. Equation 3 has an error. '*' should be replaced by '-'.
9. Page 3: 'This unique feature of phospholipid micelles increase its average molecular weight from 700 kDa to around 20 kDa or more'. This is not an increase.
10. Fig. 7 can be omitted. It takes too much space while providing limited amount of information.

Gmail **Nita Aryanti <nita.aryanti@gmail.com>**

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Thank you for your revised manuscript "ULTRAFILTRATION MEMBRANE FOR DEGUMMING OF CRUDE PALM OIL-ISOPROPANOL MIXTURE". You will be notified on the outcome of the review process in next few days.

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RESPONSE TO REVIEW 1244

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   We have sent the manuscript to the professional proof reader (Enago) for English improvement.

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Paper number f has been previously cited (referrence number 3). Paper number a-e have been cited in the referrence (referrence number 13-17)

3. Abstract is completely the same as Conclusions, which is blatant neglect of the economy of the paper and the purpose of those chapters in a research paper.

   Abstract has been modified and Conclusion has been completely changed.

4. Important information in the experimental methods about the membrane and laboratory ultrafiltration unit are missing. It is not clear who and how produced the membrane. Some technical information about membrane area, pore size, type of pump and pressure gauge used etc. are vital for clear description of the experimental conditions. It is not possible to recreate fully this experiment from the information provided.

   We provide information of the membrane preparation. We used similar method with the previously published paper and hence we only add the referrence to prepare the membrane.

   Technical information about membrane and other supporting equipment are given. (Membrane pore size in MWCO, type of pump, pressure gauge)

5. Fig.1 needs improvement in both graphical presentation and legend, which is currently not in English.

   The figure has been changed with new image.

6. Caption of Fig. 4 suggests that there are 4 figures (1a, 1b, 2a and 2b) within the same figure, but there are only 3 figures in the end of the manuscript.

   There are 4 Figure in Fig.4 (now Fig 4 is transformed as Fig 5).

7. Volumetric flow rate is usually denoted as Q and not 'υ'.

   Volumetric rate has been changed to Q

8. Equation 3 has an error. '*' should be replaced by '-'.

   The equation has been changed.

9. Page 3: 'This unique feature of phospholipid micelles increase its average molecular weight from 700 kDa to around 20 kDa or more'. This is not an increase.

   The molecular weight should be 700 Da not 700 kDa. Correction has been made

10. Fig. 7 can be omitted. It takes too much space while providing limited amount of information.

    We provide Fig.7 (now is labelled as Fiure 8) to clearly visualize the reader who are not familiar with the model in order.

RESPONSE TO REVIEW 1244

Major comments:

1. Flat-sheet polyethersulfone UF membrane was laboratory made. Authors mentioned that the membrane was characterized for permeability, surface structure and specific functional group. Nevertheless only SEM was used for surface structure. SEM is good for taking pictures but with this kind of picture there is no a lot of possibilities to conclude about surface structure. Also where are results about specific functional group? If this is "home" made membrane more is necessary for characterization. For example MWCO what is crucial for UF membranes and the method is not very hard.
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   "Bar" have been changed into "bar"
5. symbols must be italic – like J, C, t, V etc. through whole paper
   All symbols have been written in italic
6. two different explanation for Fig. 5 in the text-

Two different explanation due to we found two different phenomena with the increase of temperature. So it was presumed that there was a temperature limitation for the ultrafiltration of CPO.

7. a lot of mistakes with "°C" through the paper

   Mistakes with ^{o}C have been changed.

Revision - 1:
22 Maret 2018

ULTRAFILTRATION MEMBRANE FOR DEGUMMING OF CRUDE PALM OIL-ISOPROPANOL MIXTURE

Nita Aryanti*, Dyah Hesti Wardhani, Aininu Nafiunisa

Department of Chemical Engineering, Diponegoro University

Kampus Undip Tembalang, Jl. Prof. Soedarto, SH, Semarang, Indonesia-50275

Email: nita.aryanti@che.undip.ac.id,

*corresponding author

Abstract

Membrane technology such as ultrafiltration has been applied for crude palm oil degumming. The method is an alternative of conventional technology of crude palm oil degumming due to its lower energy consumption, no chemicals addition is required and almost no loss of natural oil. This research performed separation of crude palm oil-isopropanol mixture by laboratory made flat-sheets Polyethersulfone ultrafiltration. Flux profiles confirmed that the increase of crude palm oil concentration resulted on lower fluxes. Moreover, increased the temperature from 30 ^{o}C to 45 ^{o}C initially generated raising the flux but further decreased when feed temperature was raised from 40 ^{o}C to 45 ^{o}C. Ultrafiltration of crude palm oil-isopropanol mixture at crude oil concentration of 30% and 40% was able to reject more than 99% phospholipids and nearly 93% phospholipids, respectively. However, separation of free fatty acid by this process was ineffective due to the small size of free fatty acids. Evaluation of blocking mechanism by Hermia model proposed that the standard and intermediate blocking were the dominant mechanisms at filtration of crude palm oil at a concentration of 30 and 40% and 50 and 60%, respectively.

Keywords: crude palm oil, ultrafiltration, degumming

INTRODUCTION

Crude vegetable oil is a raw material to produce edible vegetable oil. Some examples of crude vegetable oil comprise crude palm oil, crude soybean oil, crude corn oil, crude coconut oil, crude sunflower oil and crude castor oil[1]. Indonesia is one of the biggest producer of crude palm oil, followed by Malaysia, Thailand, Colombia and Nigeria. Compared to other oilseed crops, palm oil produces more oil product[2]. Compared to other vegetable oil, the palm oil is preferrable as a substantial cost saving on many application[3]. Crude Palm Oil (CPO) is widely used in various food and industrial product manufacturing processes such as ice cream, frying oils, shortening, cosmetics, toothpaste, biodiesel and much more[4]. CPO is extracted from the ripe mesocarp of the fruit of oil palm tree (*Elaeis guineensis*), by a various method such as mechanical pressing followed by solid-liquid extraction [2].

The crude oil extracted from palm oil fruit also rich in palmitic acid, β-carotene, vitamin E and some undesirable compounds, such as phospholipids, free fatty acid (FFA), pigments, and protein[5-6]. CPO composed of a vast number of triglycerides (TAGs) and 6% of diglycerides (DAGs) naturally consist of FFA[7]. Industrial rules expect that high-quality oil must contain more than 95% of neutral TAGs and 0.5% or less FFA, for some reason the limit also decrease to less than 0.1% [2,8].

Complex refining process comprised degumming, neutralization, bleaching, and deodorization are performed to achieve the desired requirement. The first step of refining process is degumming, has a function to remove phospholipids and mucilaginous gums. Conventional degumming methods by using water and acid posses numerous drawback due to its high energy consumption, oil loss, loss of nutrients, and requirement of large water quantities [9-10]. Membrane-based filtration process is a promising method for palm oil refining. Membrane filtration provides low energy consumption, without chemicals addition and almost

no loss of natural oil[11-12]. Previous studies of crude palm oil refining by using membrane filtration have been evaluated[3,13-17]. Arora et al.[3] evaluated degumming of crude palm oil and crude palm olein with hexane solvent to remove phospolipids, lovibond colour value, carotenoid, major tocopherols and tocotrienols as well as major fatty acids. Ong et al.[13] studied ultrafiltration of crude palm oil degumming for the removal of phospolipids, carotene, lovibond colour, free fatty acid and volatile matters. Lai et al.[14] performed research on deacidification of model fatty system of crude palm oil by various solvents and nanofiltration. On the other hand, Polyvinylidene fluoride (PVDF) has been modified with polyvinyl alcohol (PVA) cross-linked as ultrafiltration membrane in deacidification of CPO[15]. Deacidification of deacidification of CPO using aqueous NaOH solution in hollow fiber membrane contactor by Purwasasmita et al.[16]. Furthermore, hexane solvent combined with ultrafiltration membrane has been applied to remove phospolipids from residual palm oil fiber[17].

Similar molecular weights of triglycerides and phospholipids (about 900 and 700 Da, respectively), could interfere with their separation process by membrane technology. Phospholipids tend to form reverse micelles in non-polar media like hexane or crude oil, because of its amphiphilic properties[18,19]. This unique feature of phospholipid micelles increase their average molecular weight from 700 Da to more than 20 kDa[12], which are significantly different from the triglycerides. As a result, the ultrafiltration (UF) membrane is able to separate the micelle from the solvent-oil mixture, and the phospholipid was retained by the UF membrane[20]. However, the primary challenge in the use of membranes especially ultrafiltration is the existance of phenomena called fouling. Fouling is an irreversible membrane change caused by specific physical and chemical interactions between the membrane and the various components present in the process flow. Fouling membrane represents by decreasing of the permeate flux due to the effect of blocking on the surface as well as inside the membrane pores[21-22]. As detail investigation of fouling is essential and there is no research studied on

membrane fouling in degumming of crude palm oil, this research is primarily focused on flux decline study as well as fouling mechanism in degumming of crude palm oil by ultrafiltration.

Fundamental studies of fouling mechanisms on ultrafiltration membranes have been performed for coconut cream[23], organic compounds[24], whey models[25] and PolyEthylene Glycol (PEG)[26]. In more detail, the fundamental studies focusing on the fouling mechanism in ultrafiltration for oil degumming or separation of oil components are limited only for degumming corn oil[18, 27], crude sunflower and soybean oil [14]. This study emphasized on the fundamental and comprehensive analysis of the influence of oil solvents and micelle on fouling mechanism models. Specifically, this study addressed novelty finding on analysis of fouling model and fouling mechanism in ultrafiltration for degumming CPO.

MATERIALS AND METHODS

Materials

Main raw materials used for this experiment was Crude Palm Oil from Kalimantan, Indonesia and iso-propanol (Merck) as a solvent. The ultrafiltration membrane was a laboratory made Polyethersulphone (PES) flatsheet membrane. The PEG material was Veradel PESU 3100P (Solvay, Singapore). The membrane was prepared by a non-solvent induced phase separation method with PolyEthylene Glycol (PEG) as the additive and N-Methyl Pyrrolidone (NMP) as the solvent[28].

Membrane Characterization

The membrane was characterized for its molecular weight cut-off (MWCO), permeability, surface structure and specific functional groups. In this research, PEGs (from Sigma-Aldrich) having molecular weight of 4kDa, 6kDa, 12kDa, 20kDa and 35kDa were used for determining membrane's MWCO. The PEG solution was prepared in 1 wt-% concentration and then

filtrated in a dead-end filtration cell. PEG concentration in the permeate was analyze by handheld digital refractometer (PAL-91S, ATAGO, Japan) and PEG molecular weights vs PEG rejections were plotted. The MWCO of membrane was estimated based on the lowest molecular weight of solute (in Dalton or KDa) in which 90% of the solute is rejected by the membrane. According to the rejection profiles, the MWCO of the membrane was found as 20 kDa.

Membrane permeability was evaluated by determining membrane flux of distilled water or iso-propanol into the membrane module at various operating pressures (1-3 bar). The fluxes were calculated according to the sample volume (V), the sampling time (t) as well as the membrane surface area (A). The volumetric permeate flow rate (Q) was calculated by equation (1):

$$Q = \frac{V}{t} \quad (1)$$

Further, the flux (J) was determined by equation (2):

$$J = \frac{1}{A}\, x\, Q \quad (2)$$

Membrane surface and cross-sectional structure was characterized by Scanning Electron Microscopy (SEM, FEI Type Inspect-S50). Specific functional groups of the membrane were determined by FTIR Spectroscopy (Prestige-21, Shimadzu, Japan).

Evaluation of UF Membrane Performance for Degumming of CPO-Isopropanol Mixture

The ultrafiltration performance was examined by a laboratory-made cell filtration with total recycle model as illustrated in Figure 1.

Figure 1. Schematic of Ultrafiltration Cell with Total Recycle Operation

The cell filtration was equipped with centrifugal pump (Kemflow, with nominal flow rate 1.0 LPM, maximum pump output of 110 psi, maximum inlet pressure of 60 psi) as the feed pump,

gate valves, pressure gauge (JAKO, with maximum pressure of 150 psi) and a stainless steel ultrafiltration housing. The total recycle model involved returning the permeate and retentate flow back to the feed tank to maintain equivalent concentration during the process. All experimental runs were conducted at room temperature (29 ± 2 ^{o}C). Before starting the experiments, membranes were first compacted by filtering water through the membrane at a pressure of 1 bar for 60 minutes. For each run, a new circular membrane sheet with an effective area of 13.85 cm^2 was used.

Figure 1. Schematic of Ultrafiltration Cell with Total Recycle Operation

Miscela solution was prepared by mixing CPO with isopropanol with ratios of CPO were 30%, 40%, 50%, 60% weight of the solution. The filtration cell was operated at 1 bar for 120 minutes , and before be returned back to the feed tank, permeate was collected every 5 minutes to determine flux and concentration of phospolipids/fatty acid. Feed temperature was varied to 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, and 45 ^{o}C in order to investigate the effect of temperature on UF performance. The feed tank was equipped with a temperature regulator and magnetic stirrer for homogenization of oil micelle. Membrane performance was evaluated in the term of permeate flux and phospolipid/ free fatty acid rejection. Permeate fluxes (J) were determined by weighing the volume of permeate collected at 5 minute intervals for 120 minutes and calculated by using equation (3).

$$J = \frac{W}{A\,x\,t} \tag{3}$$

where W representing total weight of permeate, A is the membrane area and t is a time interval. Rejections of phospolipid and free fatty acid were determined based on the concentration of phospolipid/ free atty acid in feed (C_f) and phospolipid/free fatty acid concentration in permeate (C_p). Rejection is calculated according to equation (4).

$$R = \frac{C_f - C_p}{C_f} \quad (4)$$

Characterization of CPO and Permeate

Specific characteristics of CPO and permeate included phospholipid and Free Fatty Acid (FFA) content. Phospholipid was expressed as total phosphorus, and were analyzed according to AOAC Ca 12-55 method. Determination of FFA was performed by acid-base titration method[14].

Blocking Mechanism

Blocking mechanism of CPO- Isopropanol ultrafiltration was studied according to Hermia's model. This model has been previously applied for fouling mechanism evaluation of dye solution ultrafiltration[28], konjac glucomannan separation[29] and ultrafiltration of model dye wastewater[30]. The Hermia's model describes the mechanism of membrane fouling based on blocking filtration law, consisting of complete pore blocking, standard pore blocking and intermediate pore blocking and cake filtration. The blocking law filtration is expressed in the term of permeate time and filtration time and developed for dead-end filtration as shown in equation (5)[31]:

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \quad (5)$$

where *t* is filtration time, and *V* is the permeate volume, *k* is constant, and *n* is a value illustrating the different fouling mechanism.

The values of *n* are described as follows: complete blocking having *n* value of 2, intermediate blocking is represented with *n* = 1, the standard blocking illustrated with *n* = 1.5 and the cake

layer formation has *n* value of 0. In the complete blocking model, it is assumed that each solute participated in blocking the entrance of the membrane pores completely. For intermediate blocking, it is assumed that every solute stays on previously deposited solute. Standard blocking considers the deposition of each solute to the internal pore wall. The cake layer formation applied based on the accumulation of the solute on the membrane surface in the cake form[32]. The Hermia's model was then linearized based on the *n* value for each model using fitting equation (6) to (9) regarding permeate flux versus time as presented in the following.

For Complete Blocking ($n = 2$) :

$$\ln J = \ln J_0 - k_c t \tag{6}$$

For Intermediate Blocking ($n = 1$) :

$$\frac{1}{J} = \frac{1}{J_0} + k_i t \tag{7}$$

For Standard Blocking ($n = 1.5$) :

$$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + k_s t \tag{8}$$

For Cake/Layer Formation ($n = 0$) :

$$\frac{1}{J^2} = \frac{1}{J_0^{\,2}} + k_{cf} t \tag{9}$$

Where k_c, k_i, k_s and k_{cf} are constants for complete blocking, intermediate blocking and cake/layer formation, respectively.

RESULT AND DISCUSSION

Water and Solvent Permeability

Flux profile of water and isopropanol at various pressure for the UF membrane is presented in Figure 2.

Figure 2. Flux Profile of Isopropanol and Water at Pressure of 1-3 bar

The figure shows an increase of water and isopropanol flux with the rise of pressure from 1 – 3 bar. According to linerization regression ($y = mx$) of water and isopropanol flux in the figure, it is found that the water permeability and isopropanol permeability are 44,19 L/m^2. hr and 62,69 L/m^2. hr, respectively. This is surprising since the water is predicted having permeability higher than the ethanol due to the water characteristic as the most polar solvent. The result is in contrast with de Melo et al.[33] confirming that lower solvent polarity result on permeation decrease. In addition, the prepared polyethersulphone membrane had a characteristic as hydrophilic membranes especially due to the addition of polyvinylpyrrolidone (PVP) and PolyEthylene Glycol (PEG)[34]. With the hydrophilic characteristic of the PES membrane, the water permeation is expected higher than isopropanol. A solvent characteristics such as viscosity, surface tension and polarity as well as the molar volume of the solvent had an effect on the transport of solvent by the membrane[35-36]. According to the physical-chemical characteristics of solvent (viscosity and interfacial tension), the isopropanol flux should be below the water flux. However, the phenomenon is not found in this research, presumably that there is the specific interaction of the membrane and the solvent. A similar result was observed

by Araki et al.[37]. The high permeability of isopropanol indicates that the conditioning process (immersing in the isopropanol) creating less hydrophilic of the PES membrane. The alteration of the hydrophobic characteristic is generated due to the transformation of the hydrophilic and hydrophobic site of the membrane and resulting on higher permeability of the isopropanol. Water permeation has a correlation with the hydrophilic characteristic (hydrogen bonding formation) of the membrane. When alcohol such as isopropanol is permeated, the hydrogen bonding formation is less and contributing in low water flux.

Specific Functional Groups

Specific functional groups of the membrane is shown in Figure 3.

Figure 3. FT-IR Spectra of the Membrane confirming Specific Functional Groups

According to the figure, characteristics of PES membrane is determined by peaks at 1492.9 and 1589.3 cm^{-1}. Moreover, the peaks of 1161.15 and 1172.7 cm^{-1} show a symmetric stretching sulfur SO_2. In more detail, Table 1 lists other specific functional group of the membrane.

Table 1 Specific Functional Groups as shown in FT-IR Spectra

Based on the table, the specific functional groups were matched with the chemical structure of main membrane materials. Beside of the PES characteristic, the O-H bonding vibration, C-H asymmetric, C-C stretching in Benzene ring and -C-O-C- bonding are representation of bonds in the polymer of PEG.

Permeate Flux

Profile of permeate flux showing flux versus time is presented in Figure 4.

Figure 4 Permeate Flux Profile in Ultrafiltration of CPO-Isopropanol Mixture at Various Concentration of CPO (Feed Temperature is 30 ^oC, Trans Membrane Pressure of 1 bar)

The figure shows there is a flux decline during filtration of solvent and CPO mixtures. A significant flux falling-off is observed during the first 5 minutes of filtration, followed by a flux reduction deceleration rate and finally, flux is steady. The three-steps behaviours were also perceived by Penha et al.[38] in filtration of marracuba oil/n-hexane mixture. The initial flux decline is caused by a phenomenon called polarization concentration, while the following flux reduction was as a result of membrane fouling. Comparable performances were reported for oil/hexane mixture permeation through UF membrane using sunflower oil[39] as well as coconut oil, groundnut oil, mustard oil, sunflower oil and rice bran oil [36, 40]. In addition, it was reported that the flux reduction at the beginning of sunflower oil-n-hexane filtration was concentration polarization phenomenon and a gel layer formation on the membrane surface[39]. Moreover, the flux drop at the end of filtration was due to deposition of gel on the membrane surface [38,41,42]. The deposited layer could be formed due to phospholipids retained on the membrane surface and pores plugging [14, 43].

Figure 4 also confirms an increase of oil concentration leads to more reduction of flux. This decrease takes place due to an increase of oil concentration results on a solution viscosity increase. With the rise of viscosity, smaller flux is obtained since the permeability is influenced by the viscosity[35]. In addition, the lower flux is obtained as a result of polarized/gel layer formation. When the oil concentration is higher, the layer is more significant and generate larger resistance to the flux permeation [33,36,41]. As elucidated by Kim et al.[41], convective solute transport to the membrane produces a sharp gradient of concentration inside the boundary layer. Due to diffusion, a solute back-transport into the bulk is taken place, and a close-packed arrangement of solute is formed. As a consequence, no more solute can be accommodated, and the mobility of solutes is restricted.

Scanning Electron Microscope images of the fouled membrane as displayed in Figure 5 confirms a foulant layer on the membrane surface is present.

Figure 5. Scanning Electron Microscope Images of Clean Membranes (1a) Surface (2a) Cross-Sectional Structure and Fouled Membrane after ultrafiltration of 30% CPO-Solvent mixture (1b) Surface (2b) Cross-Sectional Structure at magnification of 10.000x

Figure 6 displays the effect of feed temperature on initial and final permeate flux.

Figure 6. The effect of feed temperature on Initial and Final Flux at pressure of 1 bar and CPO concentration of 30%

Based on the figure, it indicates that increase mixture temperature from 30 to 35 ^{o}C has an effect on higher flux permeate. This was expected due to the decrease of viscosity or increase of phospholipid diffusion on the membrane pores. However, with further temperature increase (from 40 to 45 ^{o}C) leads on flux decrease and the reduction of viscosity do not have an effect on the flux. This result is closed to Kim et al. [41] confirming that the operating temperature at 40 ^{o}C was suitable for degumming of soybean extract then above the temperature of 40 ^{o}C, the flux decreased. Flux declining is predicted due to the fouling on the membrane surface as a result of solid denaturation or gelatinisation of solid as well as insoluble salts precipitation at high temperature[44].

Phospholipid and Free Fatty Acid Rejection

Membrane selectivity is represented as rejection indicating membrane ability to reject or remove from a feed compound. Micelles will be formed when phospholipids are dispersed in water. A mixture of phospholipids in a non-polar solvent such as isopropanol formed reverse

micelles having the average molecular weight more than 20.000 daltons[44]. Based on its pore size, ultrafiltration rejects compound having a molecular weight in the range of 300-500.000 Dalton. Hence, in the phospholipids-isopropanol system, the phospholipid is expected to be retained in the retentate, and the permeate comprises the oil and isopropanol. In contrast to phospholipids, the molecular weight of free fatty acid and triglyceride is similar. The triglycerides and free fatty acids (FFA) have a molecular weight of 800 Da and 300 Da, respectively[9]. Comparing to ultrafiltration pore size, separation of FFA is challenging due to low selectivity and results in low rejection value. Rejection of phospholipid and FFA at various CPO concentration is displayed in Table 2.

Table 2 Rejection of Phospholipid and Fatty Acid at Various CPO Concentration at pressure of 1 bar and Feed Temperature of 30 ^{o}C

The table shows rejection of phospholipids is significantly higher than the fatty acids. This is noticeable since the molecular weight of micelle phospholipids are considerably higher than the free fatty acids. The phospholipids rejection is found greater than 99% at CPO concentration of 30% and slightly reduced to nearly 93% with increase of CPO concentration to 40%. The reduction of phospholipid rejection is more obvious with the increase of CPO concentration to 50%. In addition, a similar trend is shown when the feed temperature is raised. The rejection of both phospholipids and FFA is declined with higher temperature from 30 ^{o}C to 40 ^{o}C as presented in Table 3.

Table 3 Rejection of Phospholipid and Fatty Acid at Various Feed Temperature at pressure of 1 bar and CPO Concentration of 30 %

Blocking Mechanism by Hermia Model

In this research, Hermia's model was applied in order to evaluate the blocking mechanism during ultrafiltration of CPO-Isopropanol mixture at various feed CPO concentration. Fouling mechanism represented by blocking mechanism is identified by fitting the experimental data into the Hermia's linearized equation (equation (4) to equation (7). The fitting of experimental data to the four type Hermia's model is shown in Figure 7, and the corresponding correlation coefficient (R^2) is listed in Table 4.

Figure 7 Fitting of experimental data (feed temperature of 30 ^oC, pressure at 1 bar) to Hermia's model: (a) complete blocking (b) Standard blocking (c) Intermediate blocking (d) cake/gel layer formation

Table 4 R^2 value of Blocking Mechanism based on Hermia's Model.

According to the table, two dominant blocking mechanisms are found, the standard blocking and the intermediate blocking. At low concentration of CPO (30% and 40%), the blocking mechanism is dominated by standard blocking. In contrast, at higher concentration of CPO (50 and 60%), the intermediate blocking are the dominant mechanism. The standard blocking assumes that each solute is deposited into the internal pore wall. In the intermediate blocking, it is proposed that every solute stays on the previously deposited solutes.

Proposed standard blocking and intermediate blocking mechanism in UF of CPO-Isopropanol is illustrated in Figure 8.

Figure 8. Schematic Illustration of (a) Intermediate Blocking (b) Standard Blocking Mechanism in UF of CPO-Isopropanol Mixture

According to the Figure 8a, large particles accumulated on the membrane surface and blocked the membrane pores were triglycerides. Large particles formed at high concentration of CPO was firstly presumably as phospholipid-isopropanol micelle due to their large size and potential to block the pores. However, this assumption is in contradictive with the phospholipid rejection. If the large particles were the agglomeration of phospholipids micelle then the rejection at high CPO concentration should be larger. Hence, it can be assumed that at high concentration of CPO, not all the phospholipids generated micelle with isopropanol. This confirmed why the phospholipid rejection at high concentration of CPO was lower. Then the larger particles accumulated on the membrane surface were predicted as other oil compound such as triglycerides.

In addition, Figure 8b presents that at low concentration of CPO, the dominant fouling mechanism was the standard blocking, representing small particles attached inside the membrane pore and providing pore constriction (reducing of pore size). Compound that is possibly blocking inside the membrane pores was the fatty acid since the size of fatty acid was smaller than the phospholipid-isopropanol micelle. At low concentration of CPO, sufficient amount of phospholipid-isopropanol micelles were formed and with pore constriction provided high rejection of phospholipid. On the other hand, small molecules such as fatty acid can enter the membrane pores.

Conclusion

Phospholipid separation and free fatty acid removal of crude palm oil have been performed by using of polyethersulphone ultrafiltration membrane. In general, lower fluxes were obtained with the increase of crude palm oil concentration. Raising feed temperature from 30 ^{o}C to 40 ^{o}C result in lower permeate flux, but with further feed temperature increase to 45 ^{o}C decreased

the permeate flux. The phospholipid rejection was in the range of 93%-99%. However, the removal of fatty acid was unsuccessful. Flux decrease due to membrane fouling was evaluated based on Hermia model confirming that there were two dominant mechanisms observed, the standard blocking and intermediate blocking models.

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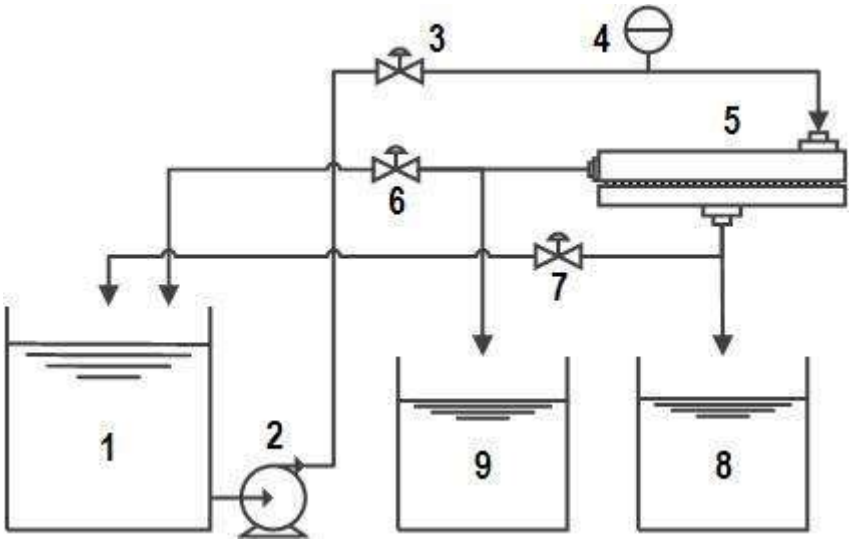


Figure 1. Schematic of Ultrafiltration Cell with Total Recycle Operation : (1). Feed Tank, (2) Feed Pump, (3) Feed Valve (4) Pressure Gauge (5) Ultrafiltration housing (6) Retentate valve (7) Permeate valve (8) Permeate tank (9) Retentate Tank

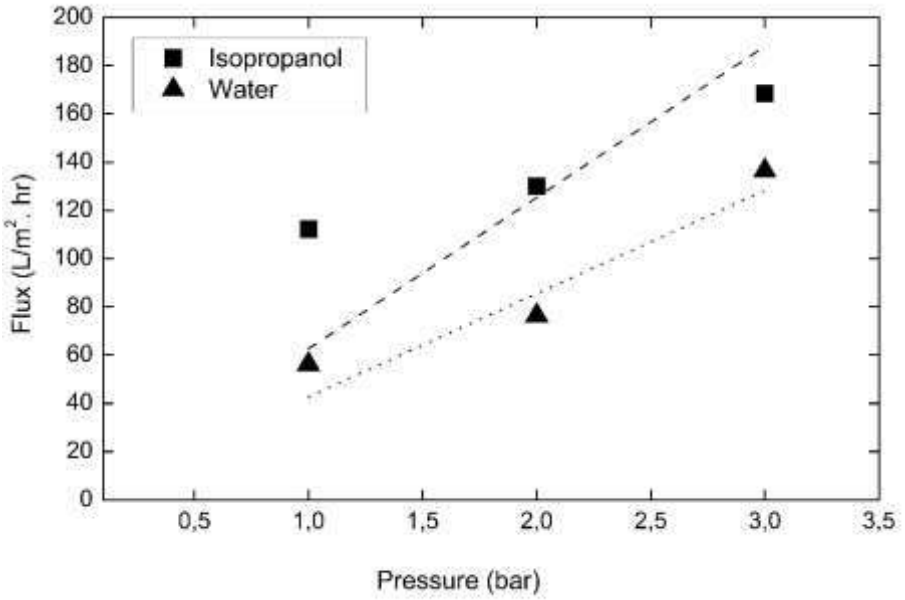


Figure 2. Flux Profile of Isopropanol and Water at Pressure of 1-3 bar

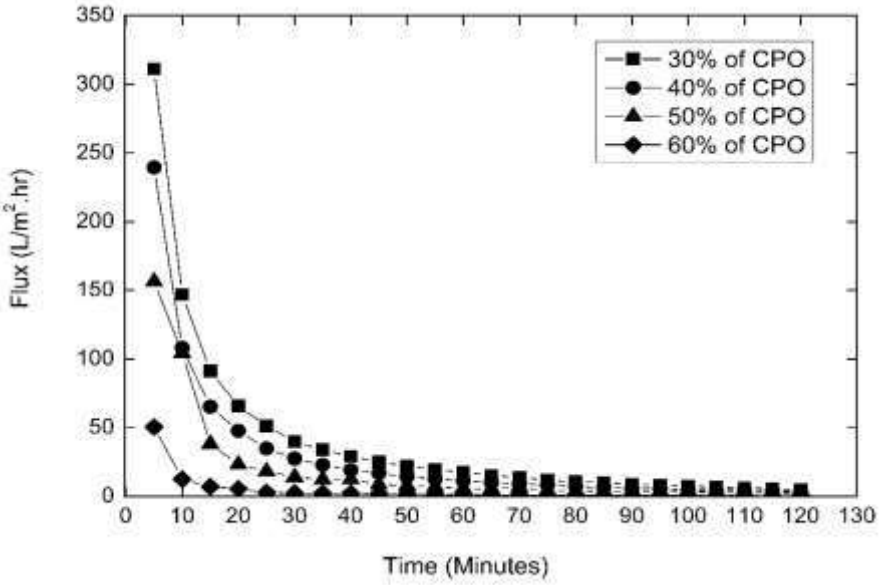


Figure 4 Permeate Flux Profile in Ultrafiltration of CPO-Isopropanol Mixture at Various Concentration of CPO (Feed Temperature is 30 ^{o}C, Trans Membrane Pressure of 1 bar)

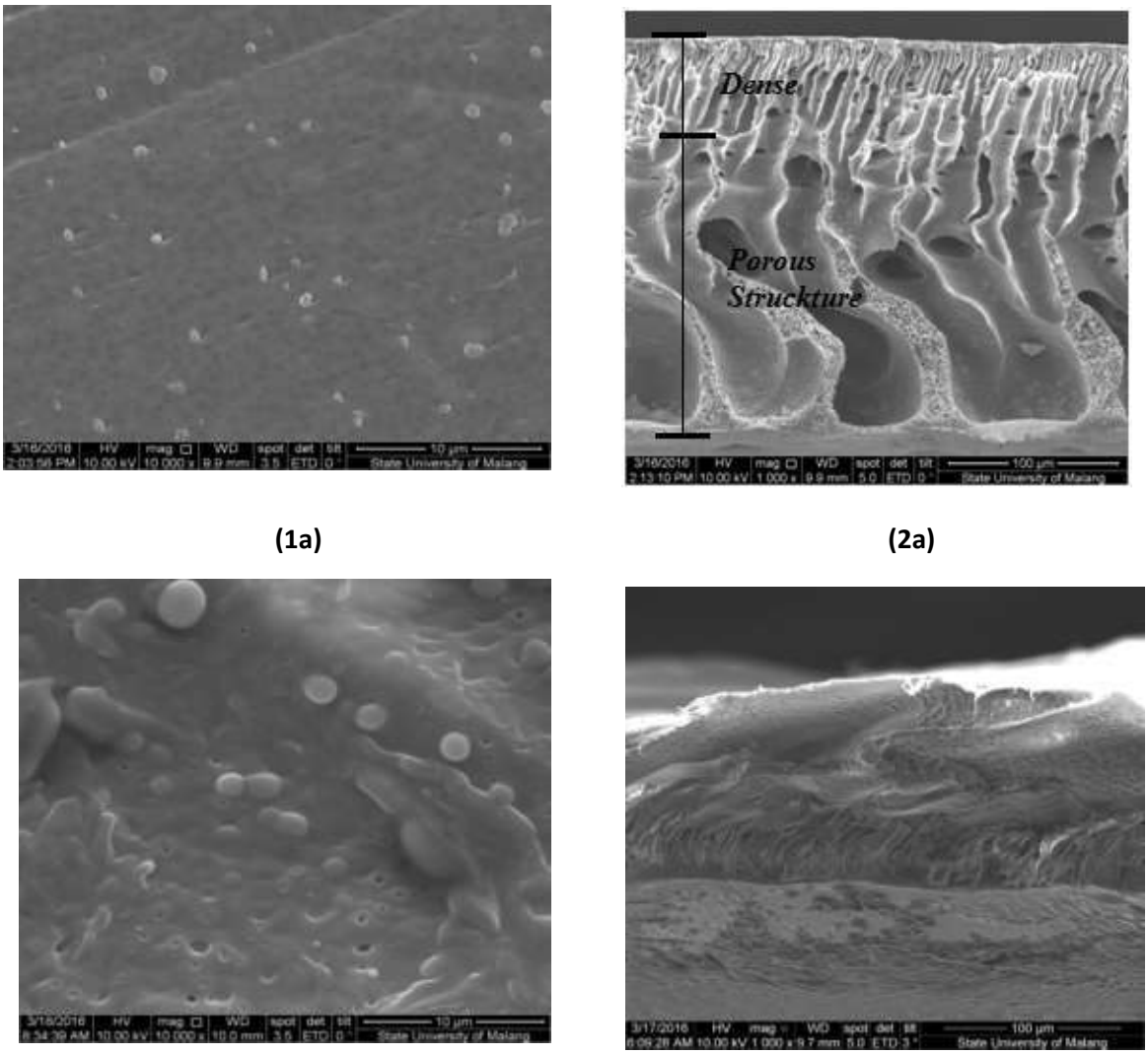


Figure 5. Scanning Electron Microscope Images of Clean Membranes (1a) Surface (2a) Cross-Sectional Structure and Fouled Membrane after ultrafiltration of 30% CPO-Solvent mixture (1b) Surface (2b) Cross-Sectional Structure at magnification of 10.000x

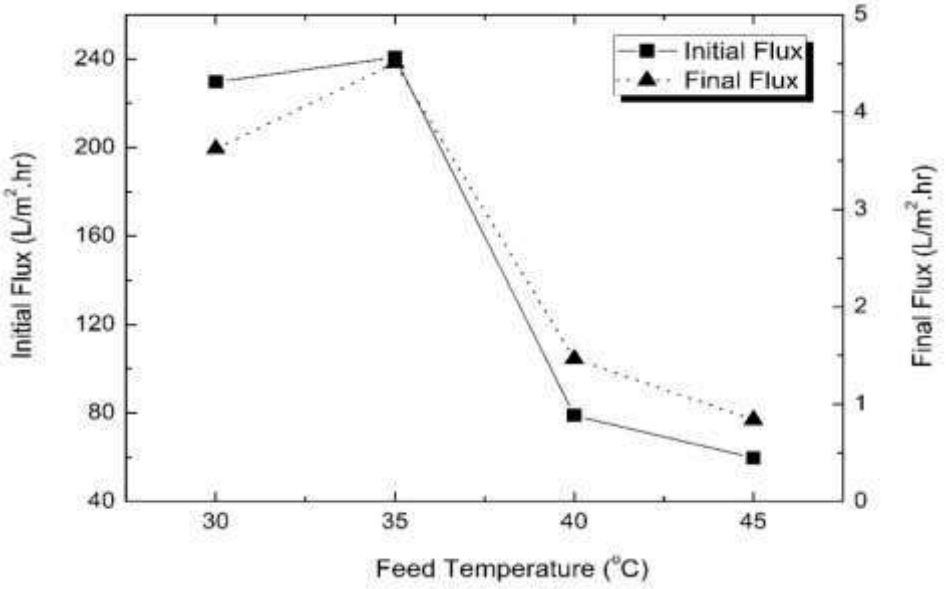


Figure 6. The effect of feed temperature on Initial and Final Flux at pressure of 1 bar and CPO concentration of 30%

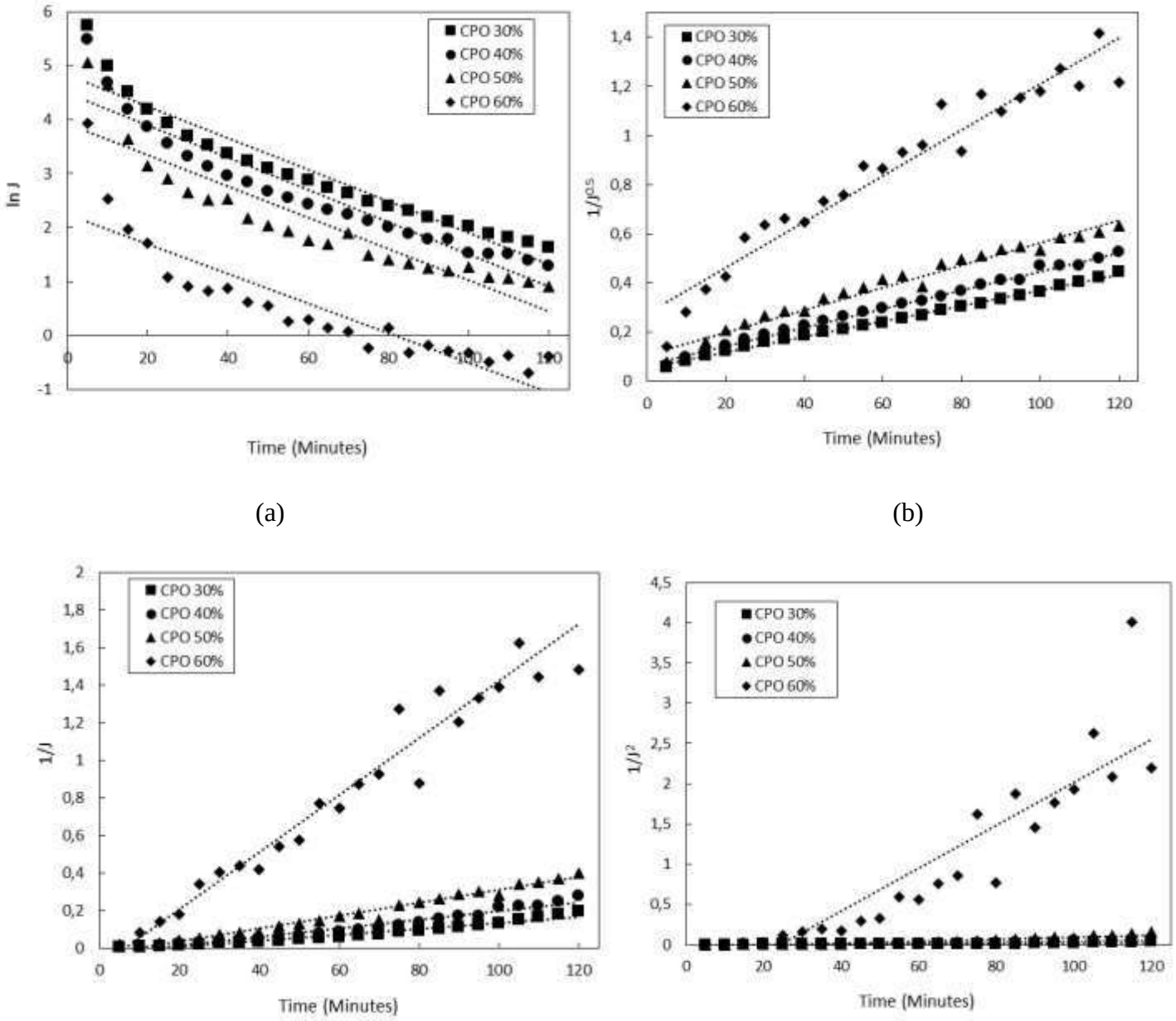
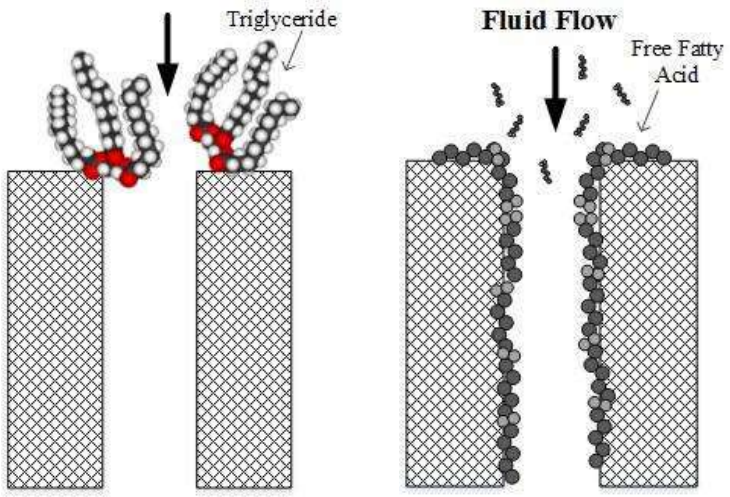


Figure 7 Fitting of experimental data (feed temperature of 30 ^{o}C, pressure at 1 bar) to Hermia's model: (a) complete blocking (b) Standard blocking (c) Intermediate blocking (d) cake/gel layer formation



(a) (b)

Figure 8. Schematic Illustration of (a) Intermediate Blocking (b) Standard Blocking Mechanism in UF of CPO-Isopropanol Mixture

Table 1 Specific Functional Groups as shown in FT-IR Spectra

Absorbance Peaks (cm^{-1})	Specific Functional Groups
1492.9 and 1589.3	Aromatic compounds (C-C streching)
1219.01 and 1261.4	Aromatic ether compounds
849.2 and 862.2	Para substituted Benzene
1074.3, 1093.6 and 1114.8	-C-O-C- bonding
2872.01 and 2926.01	C-H asymmetric bonding
3375.43 and 3475.73	O-H alcohol bonding

Table 2 Rejection of Phospholipid and Fatty Acid at Various CPO Concentration at pressure of 1 Bar and Feed Temperature of 30 ^{o}C

CPO Concentration	Phospholipid Rejection (%)	Free Fatty Acid Rejection (%)
30%	>99,21	16
40%	92,93	13
50%	37,52	9

Table 3 Rejection of Phospholipid and Fatty Acid at Various Feed Temperature at pressure of 1 bar and CPO Concentration of 30 %

Feed Concentration	Phospholipid Rejection (%)	Free Fatty Acid Rejection (%)
30 ^{O}C	92,93	13
35 ^{O}C	86,60	7,168
40 ^{O}C	73,94	10,24

Table 4 R^2 value of Blocking Mechanism based on Hermia's Model.

	R^2			
	Complete Blocking	**Intermediate Blocking**	**Standard Blocking**	**Cake/ Gel Formation**
CPO 30%	0,9186	0,9512	**0,9971**	0,7755
CPO 40%	0,9022	0,9618	**0,9953**	0,8053
CPO 50%	0,8354	**0,9811**	0,9737	0.8769
CPO 60%	0,7797	**0,9432**	0,9394	0,8052

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I cannot estimate scientific impact of the research on the filed (out of my research interest). Performed experiments is simple, methodology used is common, experimental results are evaluated using common procedures; for me it looks as unambitious professional paper. Similar researches were conducted on similar compounds (please see reference list of the manuscript and Introduction section), therefore, I think manuscript should be neglected. Manuscript is not written according to the guidelines and even single CABEQ article is not cited in the references.

Author responses:

Membrane experimental procedure is usually simple and common but this fulfill the standard of membrane filtration procedure.

The research performed detail investigation of crude palm oil degumming. Eventhough previous researches on degumming have been performed. We add information on type of oil in degumming by membrane at the introduction section. However, specific on crude palm oil degumming is very limited. Arora et al., 2005 performed degumming of crude palm oil by using hexane solvent, but the research was mainly focused on retention of several oil compound. In our research we used isopropanol solvent and polyethersulphone membrane. In addition, we evaluated the blocking mechanism of crude palm oil degumming with proposed schematic mechanism of CPO-Isopropanol mixture, which is one of the manuscript novelty. We add some sentences in the manuscript to emphasise the novelty. Some corrections are highlighted in yellow colour.

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Ultrafiltration Membrane for Degumming of Crude Palm Oil-Isopropanol Mixture

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Abstract

Ultrafiltration (UF) is a membrane technology that has been applied for crude palm oil (CPO) degumming. It is considered as an alternative for the conventional CPO degumming technology because of its lower energy consumption, no need for the addition of chemicals, and almost no loss of natural oil. In this research, we separated a CPO-isopropanol mixture via laboratory-made flat-sheet polyethersulfone (PES) UF. Flux profiles confirmed that the increase of the CPO concentration resulted in lower fluxes. However, increasing the temperature from 30°C to 45°C initially raised the flux, but it was further decreased when the feed temperature was raised from 40°C to 45°C. Using UF of the CPO-isopropanol mixture at crude oil concentrations of 30% and 40%, we were able to reject more than 99% phospholipids and nearly 93% phospholipids, respectively. However, the separation of free fatty acids using this process was ineffective due to the small size of the free fatty acids. Through the evaluation of the blocking mechanism in the Hermia model, it was proposed that the standard and intermediate blocking were the dominant mechanisms of filtration of CPO at a concentration of 30 and 40% and 50 and 60%, respectively.

Keywords: crude palm oil, ultrafiltration, degumming

INTRODUCTION

Crude vegetable oil is a raw material used in the production of edible vegetable oil. Some examples of crude vegetable oils include crude palm oil (CPO), crude soybean oil, crude corn oil, crude coconut oil, crude sunflower oil, and crude castor oil[1]. Indonesia is one of the largest producers of CPO, followed by Malaysia, Thailand, Colombia, and Nigeria. Compared to other oilseed crops, palm oil produces more oil products[2]. And compared to other vegetable oils, it is preferable in many applications as it is substantially cost-effective[3]. CPO is widely used in various food and industrial products' manufacturing processes, such as ice cream, frying oils, shortening, cosmetics, toothpastes, and biodiesel[4]. CPO is extracted from the ripe mesocarp of the fruit of oil palm trees (*Elaeis guineensis*) through various methods, such as mechanical pressing followed by solid–liquid extraction[2].

The crude oil extracted from palm oil fruits is also rich in palmitic acid, β-carotene, and vitamin E, along with some undesirable compounds such as phospholipids, free fatty acid (FFA), pigments, and proteins[5-6]. CPO is composed of a vast number of triglycerides (TAGs) and 6% diglycerides (DAGs) that naturally consist of FFA[7]. Industrial regulations expect that high-quality oil must contain more than 95% neutral TAGs and 0.5% or less FFA; for some reason, the limit also decreases to less than 0.1%[2,8].

Complex refining processes including degumming, neutralization, bleaching, and deodorization are performed to achieve the desired requirement. The first step in the refining process is degumming, whose function is to remove phospholipids and mucilaginous gums. Conventional degumming methods using water and acids possess numerous drawbacks due to the high energy consumption, oil loss, loss of nutrients, and requirement for large water quantities[9-10]. The membrane-based filtration process is a promising method for refining palm oil. Membrane filtration provides low energy consumption, without the addition of chemicals

and with almost no loss of natural oil[11-12]. Previous studies on CPO refining using membrane filtration have been evaluated[3,13-17]. Arora et al.[3] evaluated the degumming of CPO and crude palm olein with a hexane solvent to remove phospholipids, Lovibond color value, carotenoids, major tocopherols and tocotrienols, and major fatty acids. Ong et al.[13] studied ultrafiltration (UF) of CPO degumming for the removal of phospholipids, carotenes, Lovibond color, FFAs, and volatile matter. Lai et al.[14] performed research on the deacidification of a model fatty system of CPO using various solvents and nanofiltration. On the other hand, polyvinylidene fluoride (PVDF) has been modified with polyvinyl alcohol (PVA) cross-linked as a UF membrane in the deacidification of CPO[15]. Deacidification of CPO using an aqueous NaOH solution in a hollow fiber membrane contactor was carried out by Purwasasmita et al.[16]. Furthermore, a hexane solvent combined with a UF membrane has been applied to remove phospholipids from residual palm oil fibers[17].

Similar molecular weights of TAGs and phospholipids (about 900 and 700 Da, respectively) can interfere with their separation process using membrane technology. Phospholipids tend to form reverse micelles in nonpolar media like hexane or crude oil because of their amphiphilic properties[18,19]. This unique feature of phospholipid micelles increases their average molecular weight from 700 Da to around 20 kDa or even more [12], which is significantly different from TAGs. As a result, the UF membrane is able to separate the micelles from the solvent–oil mixture, and the phospholipids were retained by the UF membrane [20]. However, the primary challenge in the use of membranes, especially UF, is the existence of a phenomenon called fouling. Fouling is an irreversible membrane change that is caused by specific physical and chemical interactions between the membrane and the various components present in the process flow. Membrane fouling is represented by a decrease of the permeate flux due to the effect of blocking on the surface as well as inside the membrane pores[21-22]. As it is essential to have a detailed investigation on fouling and there is no research investigating

membrane fouling in the degumming of crude palm oil, this research is primarily focused on studying the flux decline as well as the fouling mechanism in the degumming of CPO by UF.

Fundamental studies on fouling mechanisms on UF membranes have been performed for coconut cream[23], organic compounds[24], whey models[25], and polyethylene glycol (PEG)[26]. In more detail, the fundamental studies focusing on the fouling mechanism in UF for oil degumming or separation of oil components are limited only for degumming corn oil[18-27], crude sunflower oil, and soybean oil[14]. This study placed emphasis on the fundamental and comprehensive analysis of the influence of oil solvents and micelles on fouling mechanism models. Specifically, this study addressed a novelty finding on the analysis of the fouling model and fouling mechanism in UF for degumming CPO.

MATERIALS AND METHODS

Materials

The main raw materials used in this experiment were CPO (Kalimantan, Indonesia) and isopropanol (Merck) as a solvent. The UF membrane was a laboratory-made polyethersulfone (PES) flat-sheet membrane. The PEG material was Veradel PESU 3100P (Solvay, Singapore). The membrane was prepared via a non-solvent-induced phase separation method with PEG as the additive and N-methyl-2-pyrrolidone (NMP) as the solvent[28].

Membrane Characterization

The membrane was characterized for its molecular weight cut-off (MWCO), pore size, permeability, surface structure, and specific functional groups. The MWCO of the membrane represents the lowest molecular weight of solute (in Daltons), in which 90% of the solute is rejected by the membrane. The MWCO value is evaluated to describe the pore size distribution and retention capabilities of membranes. In this work, solute rejection experiments were

performed using PEG (from Sigma-Aldrich) as polymer solute with various molecular weights (MWs) of 4, 6, 12 and 20 kDa. The PEG solution was prepared in 1 wt.% concentration and then filtrated in a dead-end filtration cell. The permeate samples were analyzed using a digital handheld refractometer (PAL-91S, ATAGO, Japan). Plots of MW versus solute rejection were created, and then the MW corresponding to 90% rejection was estimated as MWCO of the membrane. The MWCO of the laboratory-made membrane was found as 20 kDa.

Membrane permeability was evaluated by determining the membrane flux of distilled water or isopropanol in the membrane module at various operating pressures (1–3 bar). The fluxes were calculated according to the sample volume (V), the sampling time (t), and the membrane surface area (A). The volumetric permeate flow rate (Q) was calculated by

$$Q = \frac{V}{t} \quad (1)$$

Further, the flux (J) was determined by:

$$J = \frac{1}{A}\, x\, Q \quad (2)$$

The membrane's surface and cross-sectional structure was characterized using scanning electron microscopy (SEM, FEI Type Inspect-S50). The specific functional groups of the membrane were determined using FTIR Spectroscopy (Prestige-21, Shimadzu, Japan).

Evaluation of UF Membrane Performance for Degumming of the CPO-Isopropanol Mixture

The UF performance was examined using laboratory-made cell filtration based on the total recycle model as illustrated in Figure 1.

Figure 1. Schematic of Ultrafiltration Cell with Total Recycle Operation

The cell filtration was equipped with centrifugal pump (Kemflow, with nominal flow rate 1.0 LPM, maximum pump output of 110 psi, maximum inlet pressure of 60 psi) as the feed pump, gate valves, pressure gauge (JAKO, with maximum pressure of 150 psi) and a stainless steel ultrafiltration housing. The total recycle model involved returning the permeate and retentate flow back to the feed tank to maintain equivalent concentration during the process. All experimental runs were conducted at room temperature (29 ± 2°C). Before starting the experiments, membranes were first compacted by filtering water through the membrane at a pressure of 1 bar for 60 min. For each run, a new circular membrane sheet with an effective area of 13.85 cm^2 was used.

Figure 1. Schematic of the UF cell with total recycle operation.

A micellar solution was prepared by mixing CPO with isopropanol with ratios of CPO of 30%, 40%, 50%, and 60% weight of the solution. The filtration cell was operated at 1 bar for 120 min, and before returning it back to the feed tank, the permeate was collected every 5 min to determine the flux and concentration of phospholipids/fatty acids. The feed temperature was varied—30°C, 35°C, 40°C, and 45°C—in order to investigate the effect of temperature on UF performance. The feed tank was equipped with a temperature regulator and a magnetic stirrer for homogenization of oil micelles. Membrane performance was evaluated in terms of permeate flux and phospholipid/FFA rejection. Permeate fluxes (J) were determined by weighing the volume of the permeate collected at 5 min intervals for 120 min and calculated using

$$J = \frac{W}{A\,x\,t} \tag{3}$$

where W represents the total weight of the permeate, A is the membrane area, and t is the time interval.

Rejection of phospholipids and FFAs was determined on the basis of the concentration of phospholipids/FFAs in the feed (C_f) and in the permeate (C_p). Rejection is calculated according to

$$R = \frac{C_f - C_p}{C_f} \quad (4)$$

Characterization of CPO and Permeate

The specific characteristics of CPO and permeate included the phospholipid and FFA content. Phospholipids were expressed as total phosphorus and were analyzed according to the AOAC Ca 12-55 method. Determination of FFA was performed via the acid–base titration method[14].

Blocking Mechanism

The blocking mechanism of CPO-isopropanol UF was studied according to Hermia's model. This model has been previously applied for the evaluation of the fouling mechanism of dye solution UF[28], konjac glucomannan separation[29], and UF of model dye wastewater[30]. Hermia's model describes the mechanism of membrane fouling on the basis of the blocking filtration law, consisting of complete pore blocking, standard pore blocking, and intermediate pore blocking and cake filtration. The blocking law filtration is expressed in terms of permeation time and filtration time and was developed for dead-end filtration as shown in[31]:

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \quad (5)$$

where t is the filtration time, V is the permeate volume, k is a constant, and n is a value illustrating the different fouling mechanisms.

The values of n are described as follows: complete blocking with n = 2, intermediate blocking with n = 1, standard blocking with n = 1.5, and cake layer formation with n = 0. In the complete blocking model, it is assumed that each solute participated in blocking the entrance of the membrane pores completely. In intermediate blocking, it is assumed that every solute stays on the previously deposited solutes. Standard blocking considers the deposition of each solute to the internal pore wall. The cake layer formation occurs due to the accumulation of the solute on the membrane surface in a cake form[32]. Hermia's model was then linearized on the basis of the n value for each model by fitting equations (6) to (9) regarding the permeate flux versus time as presented in the following.

For Complete Blocking (n = 2) :

$$\ln J = \ln J_0 - k_c t \tag{6}$$

For Intermediate Blocking (n = 1) :

$$\frac{1}{J} = \frac{1}{J_0} + k_i t \tag{7}$$

For Standard Blocking (n = 1.5) :

$$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + k_s t \tag{8}$$

For Cake/Layer Formation (n = 0) :

$$\frac{1}{J^2} = \frac{1}{J_0^{\,2}} + k_{cf} t \tag{9}$$

Here, k_c, k_i, k_s, and k_{cf} are constants for complete blocking, intermediate blocking, standard blocking, and cake layer formation, respectively.

RESULT AND DISCUSSION

Water and Solvent Permeability

The flux profile of water and isopropanol at various pressures for the UF membrane is presented in Figure 2.

Figure 2. Flux Profile of Isopropanol and Water at Pressure of 1-3 bar

The figure shows an increase of water and isopropanol flux with the rise of pressure from 1 to 3 bar. According to the linearization regression ($y = mx$) of water and isopropanol flux in the figure, it was found that the water permeability and isopropanol permeability are 44.19 $L/m^2 \cdot h$ and 62.69 $L/m^2 \cdot h$, respectively. This is surprising since water is predicted to have permeability higher than that of ethanol due to the fact that water is the most polar solvent. This result is in contrast with de Melo et al.[33], confirming that lower solvent polarity results in a decrease in permeation. In addition, the prepared PES membrane had the characteristics of hydrophilic membranes especially because of the addition of polyvinylpyrrolidone (PVP) and PEG[34]. With the hydrophilic characteristic of the PES membrane, water permeation is expected to be higher than that of isopropanol. Solvent characteristics, such as viscosity, surface tension, and polarity, as well as the molar volume of the solvent, have an effect on the transport of the solvent by the membrane[35-36]. According to the physicochemical characteristics of the solvent (viscosity and interfacial tension), the isopropanol flux should be below the water flux. However, this phenomenon was not observed in this research, presumably because there is a specific interaction between the membrane and the solvent. A similar result was observed by Araki et al.[37]. The high permeability of isopropanol indicates that the conditioning process (immersing in isopropanol) created a less hydrophilic PES membrane. The alteration of the

hydrophobic characteristic is caused by the transformation of the hydrophilic and hydrophobic sites of the membrane, resulting in the higher permeability of isopropanol. Water permeation is correlated to the hydrophilic characteristic (hydrogen bond formation) of the membrane. When an alcohol such as isopropanol is permeated, the hydrogen bond formation becomes less, contributing to a low water flux.

Specific Functional Groups

Specific functional groups of the membrane is shown in Figure 3.

Figure 3. FT-IR Spectra of the Membrane confirming Specific Functional Groups

According to the figure, characteristics of PES membrane are determined by peaks at 1492.9 and 1589.3 cm^{-1}. Moreover, the peaks of 1161.15 and 1172.7 cm^{-1} show a symmetric stretching sulfur SO_2. In more detail, Table 1 lists other specific functional group of the membrane.

Table 1 Specific Functional Groups as shown in FT-IR Spectra

Based on the table, the specific functional groups were matched with the chemical structure of main membrane materials. Beside the PES characteristic, the O-H bonding vibration, C-H asymmetric, C-C stretching in Benzene ring and -C-O-C- bonding are representation of bonds in the polymer of PEG.

Permeate Flux

The profile of the permeate flux showing flux versus time is presented in Figure 4.

Figure 4 Permeate flux profile in the UF of the CPO-isopropanol mixture at various concentrations of CPO (feed temperature: 19°C, transmembrane pressure: 1 bar).

The figure shows that there is a flux decline during the filtration of the solvent and CPO mixtures. A significant flux fall-off was observed during the first 5 min of filtration, followed by a flux reduction deceleration rate, and then finally the flux becomes steady. A three-step behavior was also perceived by Penha et al.[38] during the filtration of maracuja oil/*n*-hexane mixture. The initial flux decline is caused by a phenomenon called polarization concentration, whereas the following flux reduction is a result of membrane fouling. Comparable performances were reported for oil/hexane mixture permeation through the UF membrane using sunflower oil[39] as well as coconut oil, groundnut oil, mustard oil, sunflower oil, and rice bran oil [36-40]. In addition, it was reported that the flux reduction at the beginning of the sunflower oil–*n*-hexane filtration was type of concentration polarization phenomenon and gel layer formation on the membrane surface[39]. Moreover, the flux drop at the end of the filtration was due to the deposition of a gel on the membrane surface [38, 41, 42]. The deposited layer is formed because of the phospholipids retained on the membrane surface and pores plugging[14,43].

Figure 4 also confirms that the increase of oil concentration leads to a higher reduction of flux. This decrease takes place due to an increase of oil concentration, resulting in the increase of solution viscosity. With the rise of viscosity, a smaller flux is obtained since the permeability is influenced by the viscosity[35]. In addition, a lower flux is obtained as a result of polarized/gel layer formation. When the oil concentration is higher, the layer becomes larger and generates larger resistance to the flux permeation[33,36,41]. As elucidated by Kim et al.[41], convective solute transport to the membrane produces a sharp gradient of concentration inside the boundary layer. Because of diffusion, solute back-transport into the bulk takes place, and a close-packed arrangement of the solute is formed. As a consequence, no more solute can be accommodated, and the mobility of solutes is restricted.

Scanning electron microscopy images of the fouled membrane, as displayed in Figure 4, confirm that a foulant layer on the membrane's surface is present.

Figure 5. Scanning Electron Microscope Images at magnification of 10.000x: Clean Membranes (1a- Surface), (2a- Cross-Sectional Structure) and Fouled Membrane after ultrafiltration of 30% CPO-Solvent mixture (1b-Surface), (2b-Cross-Sectional Structure)

Figure 6 displays the effect of feed temperature on the initial and final permeate flux.

Figure 6. The effect of feed temperature on the initial and final flux at a pressure of 1 bar and CPO concentration of 30%.

Based on the figure, it is indicated that increasing the mixture temperature from 30 to 35°C has an effect on the higher flux permeate. This was expected due to the decrease of viscosity or the increase of phospholipid diffusion on the membrane pores. However, a further temperature increase (from 40 to 45°C) leads to a decrease in flux, but the reduction of viscosity does not have an effect on the flux. This result is close to that of Kim et al.[41], confirming that the operating temperature of 40°C was suitable for the degumming of soybean extract; above the temperature of 40°C, the flux decreased. A decline in flux is predicted because of the fouling on the membrane surface as a result of solid denaturation or gelatinization as well as insoluble salts precipitation at a high temperature[44].

Phospholipid and FFA Rejection

Membrane selectivity is represented as rejection, indicating the membrane's ability to reject or remove a feed compound. Micelles are formed when phospholipids are dispersed in water. The mixture of phospholipids in a nonpolar solvent such as isopropanol formed reverse micelles having an average molecular weight of 20,000 Daltons (10–200 nm)[44]. Based on the pore size, UF rejects compounds having a molecular weight in the range of 300–500,000

Daltons. Hence, in the phospholipids-isopropanol system, phospholipids are expected to be retained in the retentate, and the permeate comprises the oil and isopropanol. In contrast to phospholipids, the MWs of FFAs and TAGs are similar. TAGs and FFAs have a molecular weight of 800 Da and 300 Da, respectively[9]. Compared to the UF pore size, the separation of FFAs is challenging due to the low selectivity and it results in a low rejection value. Rejection of phospholipids and FFAs at various CPO concentrations is displayed in Table 2.

Table 2 Rejection of Phospholipid and Fatty Acid at Various CPO Concentration at a pressure of 1 bar and Feed Temperature of 30 ^{o}C

The table shows that rejection of phospholipids is significantly higher than of fatty acids. This is noticeable since the molecular weight of micelle phospholipids is considerably greater than of FFAs. The phospholipids' rejection is found to be greater than 99% at a CPO concentration of 30% and slightly reduced to nearly 93% with the increase of CPO concentration to 40%. The reduction of phospholipid rejection becomes more obvious with the increase of CPO concentration to 50%. In addition, a similar trend is shown when the feed temperature is raised. The rejection of both phospholipids and FFAs declines at higher temperatures from 30°C to 40°C as presented in Table 3.

Table 3 Rejection of Phospholipid and Fatty Acid at Various Feed Temperature at a pressure of 1 bar and CPO Concentration of 30 %

Blocking Mechanism by Hermia's Model

In this research, Hermia's model was applied in order to evaluate the blocking mechanism during UF of the CPO-isopropanol mixture at various feed CPO concentrations. The fouling

mechanism represented by the blocking mechanism is identified by fitting the experimental data into Hermia's linearized equation [equations (4) to (7)]. The fitting of experimental data to the four-type Hermia model is shown in Figure 7, and the corresponding correlation coefficients (R^2) are listed in Table 4.

Figure 7 Fitting of experimental data (feed temperature: 30°C, pressure: 1 bar) to Hermia's model: (a) complete blocking, (b) standard blocking, (c) intermediate blocking, and (d) cake/gel layer formation.

Table 4 R^2 values of the blocking mechanism based on Hermia's model.

According to the table, two dominant blocking mechanisms are found: standard blocking and intermediate blocking. At low concentrations of CPO (30% and 40%), the blocking mechanism is dominated by standard blocking. In contrast, at higher concentrations of CPO (50 and 60%), the intermediate blocking is the dominant mechanism. Standard blocking assumes that each solute is deposited into the internal pore wall. In intermediate blocking, it is proposed that every solute stays on the previously deposited solutes.

The proposed standard blocking and intermediate blocking mechanisms in UF of CPO-isopropanol are illustrated in Figure 8.

Figure 8. Schematic illustration of (a) intermediate blocking and (b) standard blocking mechanisms in UF of the CPO-isopropanol mixture.

According to Figure 8(a), the large particles that accumulated on the membrane surface and blocked the membrane pores were TAGs. The large particles that formed at a high concentration of CPO were first presumed to be phospholipid-isopropanol micelles because of their large size and potential to block the pores. However, this assumption is in contradiction

with phospholipid rejection. If the large particles were an agglomeration of phospholipid micelles, then rejection at high CPO concentrations should be larger. Hence, it can be assumed that, at high concentrations of CPO, not all phospholipids generate micelles with isopropanol. This confirms why phospholipid rejection at high concentrations of CPO was lower. Hence, the larger particles that accumulated on the membrane surface were predicted to be other oil compounds such as TAGs.

In addition, Figure 8(b) shows that, at low concentrations of CPO, the dominant fouling mechanism was standard blocking, representing small particles attached inside the membrane pore and causing pore constriction (reduction of pore size). The compound that was possibly blocking the membrane pores is fatty acid, since the size of fatty acids is smaller than of the phospholipid-isopropanol micelles. At low concentrations of CPO, a sufficient amount of phospholipid-isopropanol micelles was formed, with pore constriction providing high rejection of phospholipids. On the other hand, small molecules such as fatty acids can enter the membrane pores.

Conclusion

Phospholipids separation and FFAs removal in CPO have been performed using a PES UF membrane. In general, lower fluxes were obtained with the increase of CPO concentration. Raising the feed temperature from 30°C to 40°C resulted in a lower permeate flux, but further feed temperature increase to 45°C decreased the permeate flux. The phospholipid rejection rate was in the range 93–99%. However, the removal of fatty acids was unsuccessful. The decrease of flux due to membrane fouling was evaluated on the basis of Hermia's model, confirming that there were two dominant mechanisms observed: standard blocking and intermediate blocking.

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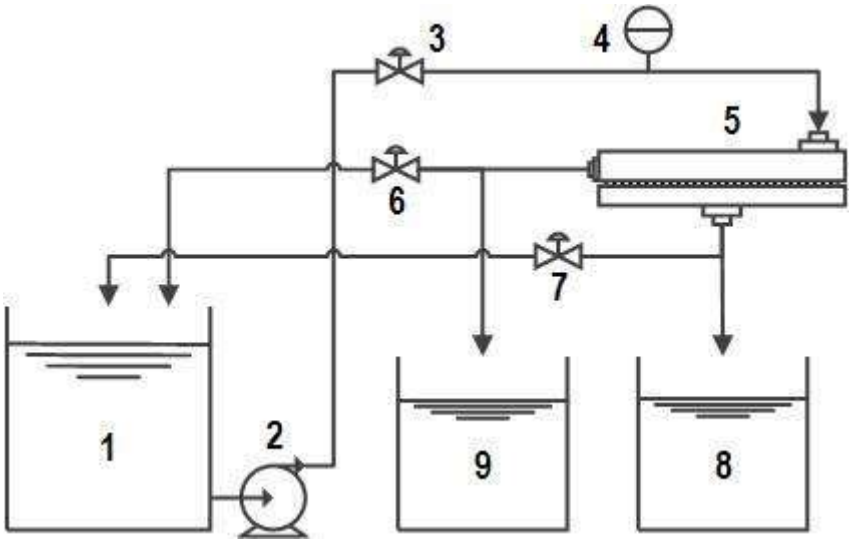


Figure 1. Schematic of Ultrafiltration Cell with Total Recycle Operation : (1). Feed Tank, (2) Feed Pump, (3) Feed Valve (4) Pressure Gauge (5) Ultrafiltration housing (6) Retentate valve (7) Permeate valve (8) Permeate tank (9) Retentate Tank

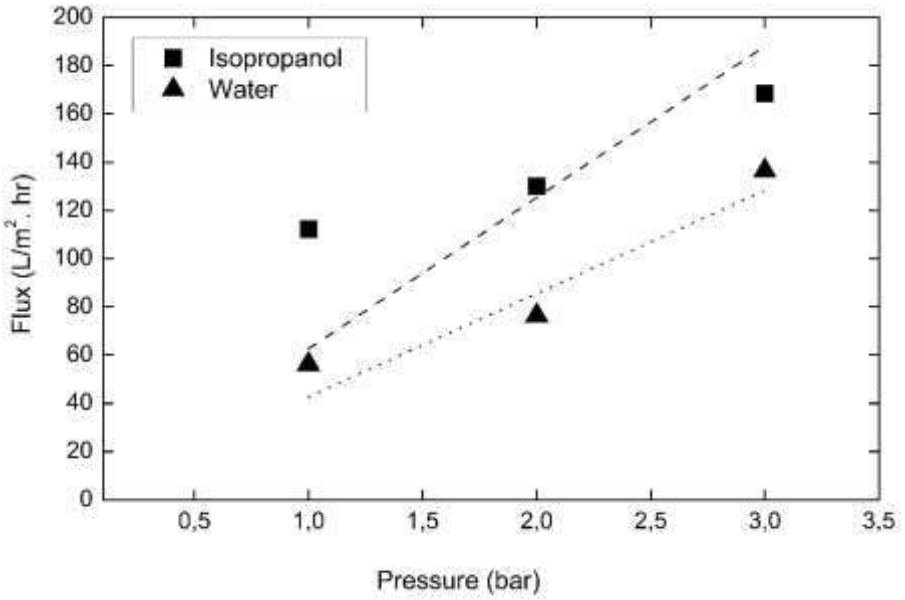


Figure 2. Flux Profile of Isopropanol and Water at Pressure of 1-3 bar

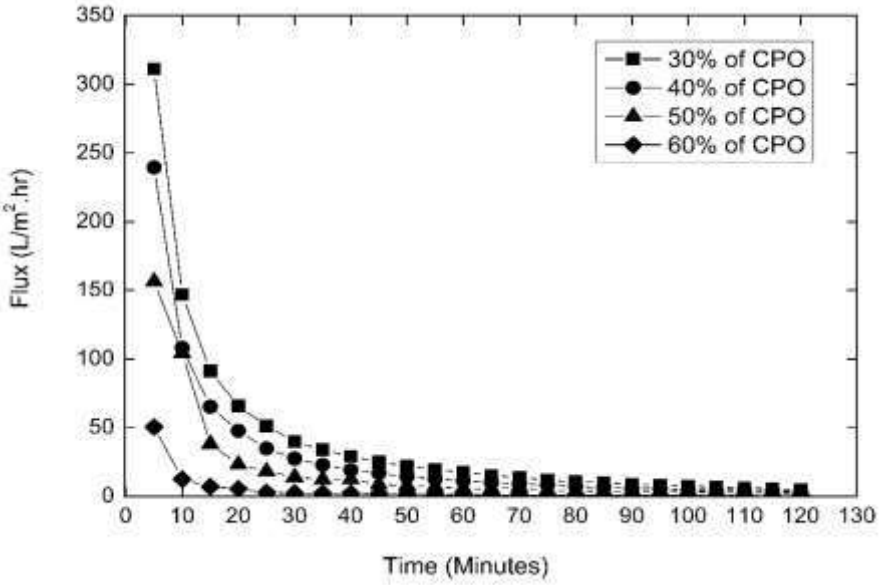
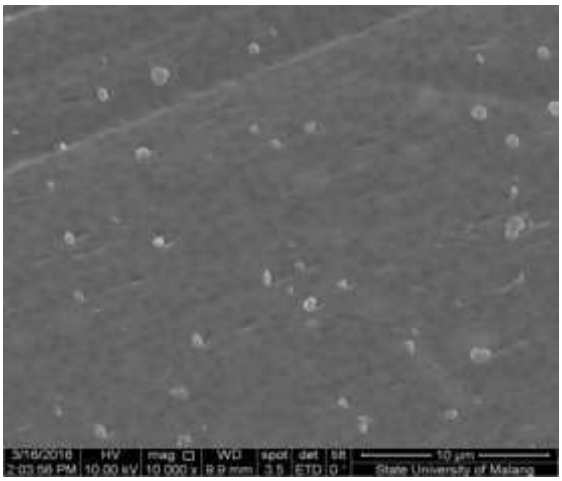


Figure 4 Permeate flux profile in the UF of the CPO-isopropanol mixture at various concentrations of CPO (feed temperature: 19°C, transmembrane pressure: 1 bar).



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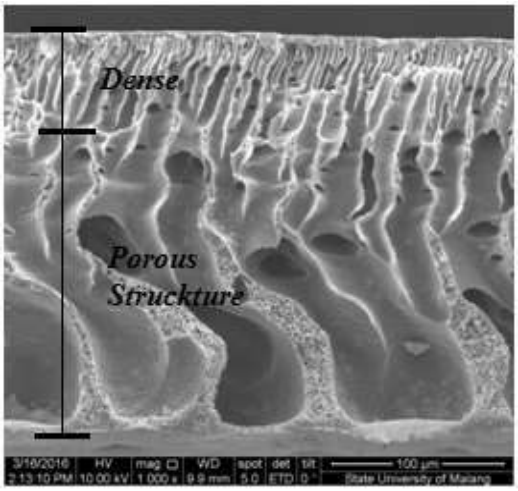

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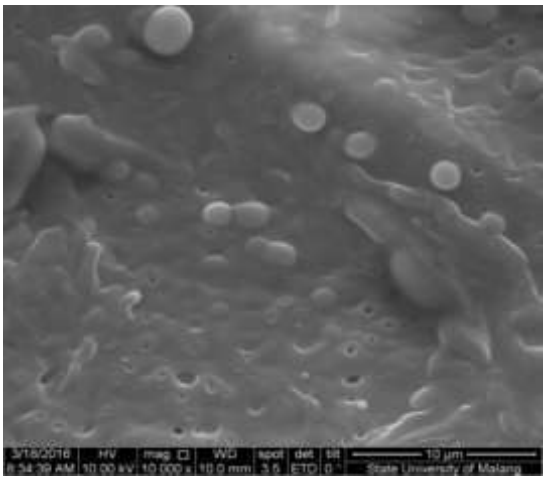

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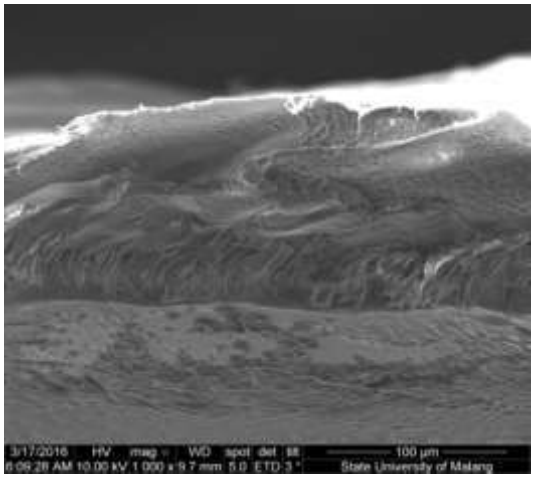


(2b)

Figure 5. Scanning Electron Microscope Images at magnification of 10.000x: Clean Membranes (1a- Surface), (2a- Cross-Sectional Structure) and Fouled Membrane after ultrafiltration of 30% CPO-Solvent mixture (1b-Surface), (2b-Cross-Sectional Structure)

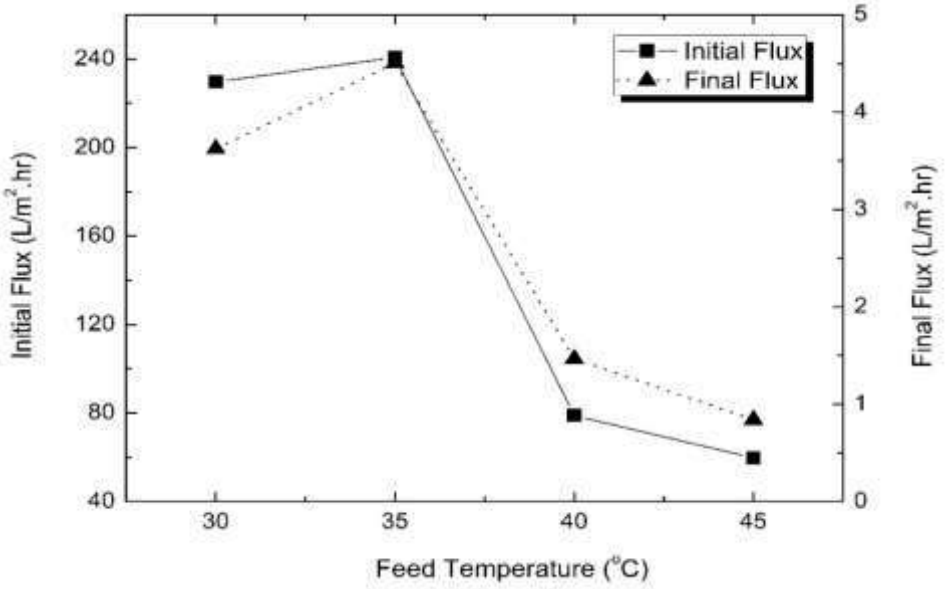


Figure 6. The effect of feed temperature on the initial and final flux at a pressure of 1 bar and CPO concentration of 30%.

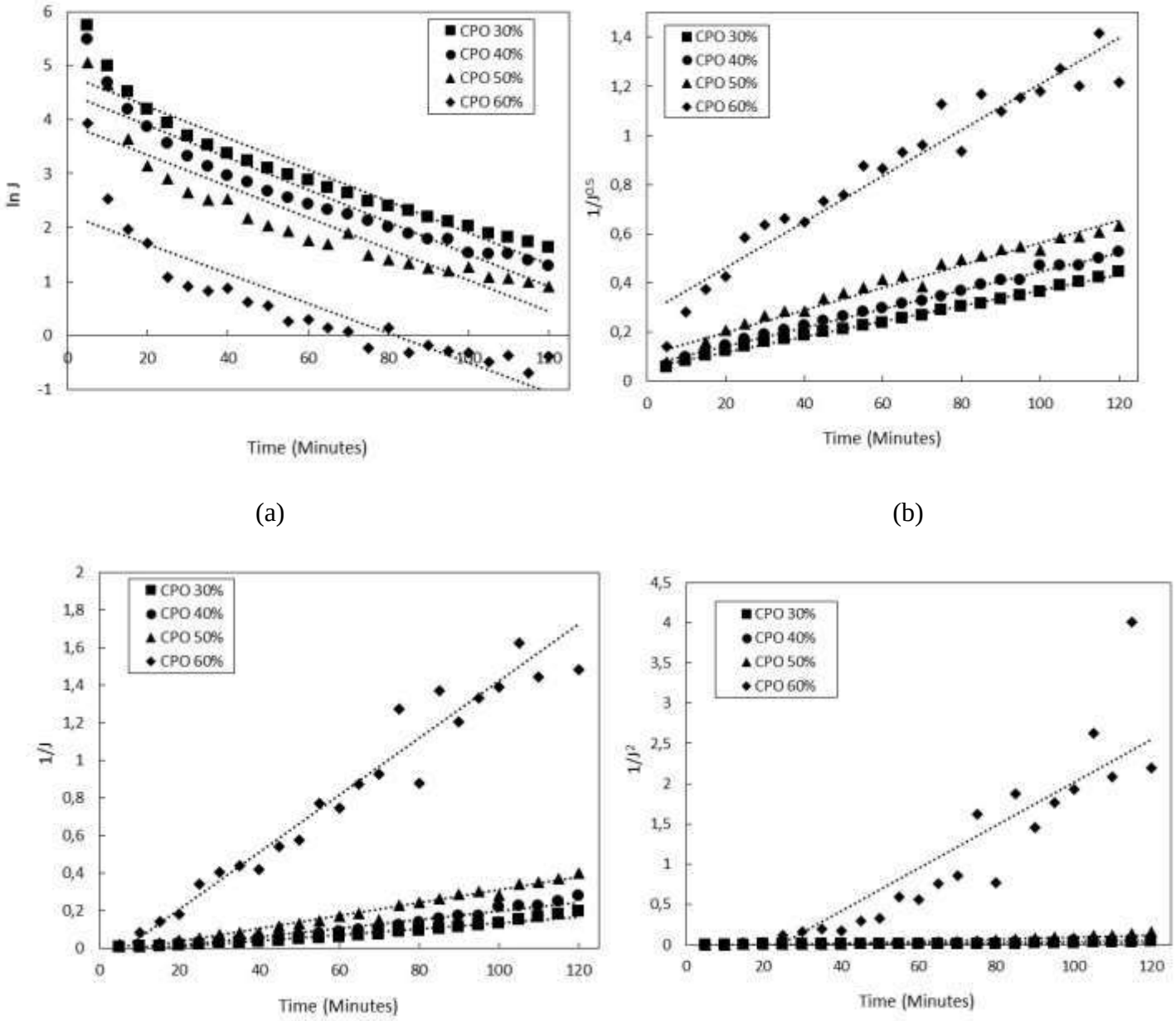
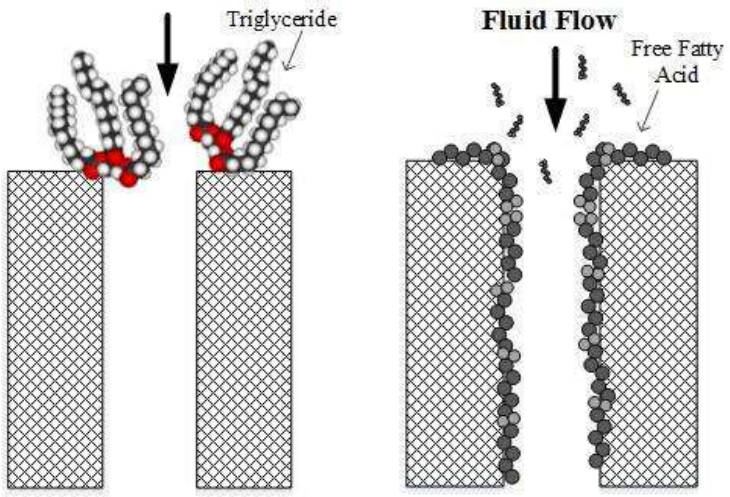


Figure 7 Fitting of experimental data (feed temperature: 30°C, pressure: 1 bar) to Hermia's model: (a) complete blocking, (b) standard blocking, (c) intermediate blocking, and (d) cake/gel layer formation.



(a) (b)

Figure 8. Schematic illustration of (a) intermediate blocking and (b) standard blocking mechanisms in UF of the CPO-isopropanol mixture.

Table 1 Specific Functional Groups as shown in FT-IR Spectra

Absorbance Peaks (cm^{-1})	Specific Functional Groups
1492.9 and 1589.3	Aromatic compounds (C-C streching)
1219.01 and 1261.4	Aromatic ether compounds
849.2 and 862.2	Para substituted Benzene
1074.3, 1093.6 and 1114.8	-C-O-C- bonding
2872.01 and 2926.01	C-H asymmetric bonding
3375.43 and 3475.73	O-H alcohol bonding

Table 2 Rejection of Phospholipid and Fatty Acid at Various CPO Concentration at pressure of 1 Bar and Feed Temperature of 30 ^{o}C

CPO Concentration	Phospholipid Rejection (%)	Free Fatty Acid Rejection (%)
30%	>99,21	16
40%	92,93	13
50%	37,52	9

Table 3 Rejection of Phospholipid and Fatty Acid at Various Feed Temperature at pressure of 1 bar and CPO Concentration of 30 %

Feed Concentration	Phospholipid Rejection (%)	Free Fatty Acid Rejection (%)
30 ^{O}C	92,93	13
35 ^{O}C	86,60	7,168
40 ^{O}C	73,94	10,24

Table 4 R^2 values of the blocking mechanism based on Hermia's model.

	R^2			
	Complete Blocking	**Intermediate Blocking**	**Standard Blocking**	**Cake/ Gel Formation**
CPO 30%	0,9186	0,9512	**0,9971**	0,7755
CPO 40%	0,9022	0,9618	**0,9953**	0,8053
CPO 50%	0,8354	**0,9811**	0,9737	0.8769
CPO 60%	0,7797	**0,9432**	0,9394	0,8052

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N. Aryanti <nita.aryanti@gmail.com> 4 April 2018 at 15:53
To: Tamara Jurina <tlekic@pbf.hr>

Dear editor CABEQ,

I apologize for the revised manuscript. I sent the wrong version of the revised manuscript. Here I also send the correct version (Enago CBEQ-Manuscript Total Revised.docx) and letter from enago confirming that I sent it to the professional English editing service.
Apologize for any inconvenience.
Many thanks

Regards,
Nita
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--
Nita Aryanti, Ph.D
Department of Chemical Engineering, Diponegoro University
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tamara.jurina@pbf.hr <tamara.jurina@pbf.hr> 8 April 2018 at 13:16
To: "N. Aryanti" <nita.aryanti@gmail.com>

Dear Nita Aryanti,

received, thank you very much.
I will forward your e-mail to Co-Editors-In-Chief and let you know their decision.
Sincerely,

Tamara Jurina
Assistant Editor
[Quoted text hidden]

Gmail

Nita Aryanti <nita.aryanti@gmail.com>

request for revision of MS 1244 CABEQ journal

2 messages

tamara.jurina@pbf.hr <tamara.jurina@pbf.hr> 5 July 2018 at 18:39
To: nita.aryanti@gmail.com

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Please find here attached reviews of your revised manuscript MS 1244. Please find attached your revised version together with Editors' comments. Based on the reviewers evaluation and Editors' comments, your revised manuscript should be revised again before publication in Chemical and Biochemical Engineering Q. Journal.

Your revised version should be submitted with a separate document with answers for each reviewer and a list of accounted corrections and adjustments. The authors are obliged to accept all the comments and to correct the text accordingly. Otherwise the manuscript will be rejected.

Please confirm your decision to resubmit a revised document in two weeks (from today).

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Prof. Marko Rogosic
Prof. Bruno Zelic
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Tamara Jurina, PhD
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Gmail Nita Aryanti <nita.aryanti@gmail.com>

Revision of MS 1244 CABEQ journal

2 messages

N. Aryanti <nita.aryanti@gmail.com> 18 July 2018 at 13:23
To: tamara.jurina@pbf.hr

Dear editor,

Please kindly find our revision according to the comments of the reviewer and editor. We also send our response to the reviewer.
We accepted all comments and corrected the manuscript.
In the revised manuscript, we replied comment form the editor in the comment form and corrected them. We highlighted the correction in the blue highlight.

NITA

On 5 July 2018 at 18:39, <tamara.jurina@pbf.hr> wrote:

> Dear authors,
>
> Please find here attached reviews of your revised manuscript MS 1244.
> Please find attached your revised version together with Editors' comments.
> Based on the reviewers evaluation and Editors' comments, your revised manuscript should be revised again before publication in Chemical and Biochemical Engineering Q. Journal.
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> Your revised version should be submitted with a separate document with answers for each reviewer and a list of accounted corrections and adjustments. The authors are obliged to accept all the comments and to correct the text accordingly. Otherwise the manuscript will be rejected.
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> Please confirm your decision to resubmit a revised document in two weeks (from today).
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Number	**1244**
Authors	**Nita Aryanti, Dyah Hesti Wardhani, Aininu Nafiunisa**
Title	Ultrafiltration Membrane for Degumming of Crude Palm Oil-Isopropanol Mixture

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2. **Fig. 1 – it is not showing total recycling mode since authors have permeate and retentate tank**
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7. **There is no Fig. 3.**
8. **Be careful about decimal places in Table 2 and 3. Authors wrote 0 to 3 decimal places.**

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Review:

Manuscript "**ULTRAFILTRATION MEMBRANE FOR DEGUMMING OF CRUDE PALM OIL-ISOPROPANOL MIXTURE"** in its improved form is still relevant to Chemical and Biochemical Engineering Quarterly. The subject is well chosen and the methods used appropriate. As I stated in previous review, novelty of this paper is in thorough analysis of fouling mechanism of the membrane by ingredients of crude palm oil and the results obtained here are valuable and deserve publishing. However, this manuscript still needs major revision before publishing. Quality of the presentation of the results is still rather low and needs improvement since in its present form it does not have sufficient quality for publishing in Chemical and Biochemical Engineering Quarterly. My comments are listed below.

1. Laboratory set-up for ultrafiltration presented on the Fig. 1 cannot be correct. Authors claim they worked in total recycle mode of operation but setup on the Fig. does not allow for such a mode because permeate could not be recycled. There are significant differences from the laboratory setup which had been submitted in previous version of this manuscript which cast some doubt whether authors are serious and responsible scientists. Changing the procedure of an experimental setup during reviewing process is not acceptable in my opinion.
2. One of the trend lines on the figure 2 is clearly not a trend line that represents the set of data for isopropanol. This also cast some doubt on authors' ability to analyze their data correctly.
3. Data on the Fig. 6 should be expanded with data of initial and final flux for 30% CPO from the Fig. 4. Including data for the temperature of 19^{o}C would show expanded trend of flux behavior over wider temperature range and probably change the current conclusion about temperature influence on flux.
4. Chapter in the manuscript is called "Result and discussion" which is not in concordance with the Instructions to authors from the Journal.

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7. **There is no Fig. 3.**
8. **Be careful about decimal places in Table 2 and 3. Authors wrote 0 to 3 decimal places.**

Responses :

Thank you for your comments. Our responses are listed in the following.

1. We measured the MWCO based on PEG rejection. The value of PEG rejection as well as MWCO of the membrane is now listed in Result and Discussion (New table : Table 1)

2. We apologize for the Figure. Actually, we tried to redraw the figure for better visualization. However, we made fatal mistake in placing the valve so the figure was not showing the total recycling. As also suggested by the Journal editor, we changed the figure with the old-version image and correcting the non-English text in the figure.

3. Psi has changed into SI unit, bar

4. The Fig 2 is only one in the text.

5. We corrected the linearization for isopropanol

6. At the previous statement, we assumed according to the addition of PVP and PEG. In order to chech the hydrophobic/hydrophilic character, we measured the water-membrane contact angle by using contac angle meter and the result is listed in Table 1.

7. We added FTIR image as Fig. 3

8. We changed decimal place in Table 2 and Table 3 (now is Table 3 and Table 4) into 2 decimal places.

Review:

Manuscript "**ULTRAFILTRATION MEMBRANE FOR DEGUMMING OF CRUDE PALM OIL-ISOPROPANOL MIXTURE"** in its improved form is still relevant to Chemical and Biochemical Engineering Quarterly. The subject is well chosen and the methods used appropriate. As I stated in previous review, novelty of this paper is in thorough analysis of fouling mechanism of the membrane by ingredients of crude palm oil and the results obtained here are valuable and deserve publishing. However, this manuscript still needs major revision before publishing. Quality of the presentation of the results is still rather low and needs improvement since in its present form it does not have sufficient quality for publishing in Chemical and Biochemical Engineering Quarterly. My comments are listed below.

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RESPONSES:

Thank you very much for your comments which are very significant for improvement of our article. Our responses are listed in the following.

1. Yes. We made mistake in re-drawing the laboratory set-up. Actually, we were tried to make better visualization for the image. However, we made fatal mistake on the valve placement and hence the figure was definitely not representing total recycle mode. As also suggested by the Journal editor, we changed the figure with the old-version image and correcting the non-English text in the figure.

2. Yes..we made wrong linearization for isopropanol. We corrected the trend line for isopropanol.

3. In Fig. 4, the feed temperature was written as 19 ^{o}C, apologize for the typo.. The temperature was supposed to be 29 ^{o}C since our minimum set-up temperature was only 28 ^{o}C. We could not reduce the temperature to 19 ^{o}C. However, we has expand the data in Fig 6 with temperature of 29 ^{o}C. In fig. 6, the initial flux

representing the flux after 10 minutes of filtration and we expanded data in Fig 6 based on data in Fig.4 as suggested.

5. We checked the instruction to author of the journal and it is stated that the structure of the article can be divided into: Introduction – Material and Methods – Results-Discussion-Conclusions. However, it is also writtent that "*A combined Results and Discussion section is often appropriate*".

Manuscript Revision -3:
18 Juli 2018

Ultrafiltration Membrane for Degumming of Crude Palm Oil-Isopropanol Mixture

Nita Aryanti*, Dyah Hesti Wardhani, Aininu Nafiunisa

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Email: nita.aryanti@che.undip.ac.id,

*Corresponding Author

Abstract

Ultrafiltration (UF) is a membrane technology that has been applied for crude palm oil (CPO) degumming. It is considered as an alternative for the conventional CPO degumming technology because of its lower energy consumption, no need for the addition of chemicals,and almost no loss of natural oil. In this research, we separated a CPO-isopropanol mixture via laboratory-made flat-sheet polyethersulfone (PES) UF. Flux profiles confirmed that the increase of the CPO concentration resulted in lower fluxes. However, increasing the temperature from 30°C to 45°C initially raised the flux, but it was further decreased when the feed temperature was raised from 40°C to 45°C. Using UF of the CPO-isopropanol mixture at crude oil concentrations of 30% and 40%, we were able to reject more than 99% phospholipids and nearly 93% phospholipids, respectively. However, the separation of free fatty acids using this process was ineffective due to the small size of the free fatty acids. Through the evaluation of the blocking mechanism in the Hermia model, it was proposed that the standard and intermediate blocking were the dominant mechanisms of filtration of CPO at a concentration of 30 and 40% and 50 and 60%, respectively.

Keywords: crude palm oil, ultrafiltration, degumming

INTRODUCTION

Crude vegetable oil is a raw material used in the production of edible vegetable oil. Some examples of crude vegetable oils include crude palm oil (CPO), crude soybean oil, crude corn oil, crude coconut oil, crude sunflower oil, and crude castor oil[1]. Indonesia is one of the largest producers of CPO, followed by Malaysia, Thailand, Colombia, and Nigeria. Compared to other oilseed crops, palm oil produces more oilproducts[2]. And compared to other vegetable oils, it is preferable in many applications as it is substantially cost-effective[3]. CPO is widely used in various food and industrial products' manufacturing processes, such as ice cream, frying oils, shortening, cosmetics, toothpastes, and biodiesel[4]. CPO is extracted from the ripemesocarp of the fruit of oil palm trees (*Elaeisguineensis*) through various methods, such as mechanical pressing followed by solid–liquid extraction[2].

The crude oil extracted from palm oil fruits is also rich in palmitic acid, β-carotene, and vitamin E, along with some undesirable compounds such as phospholipids, free fatty acid (FFA), pigments, and proteins[5-6]. CPO is composed of a vast number of triglycerides (TAGs) and 6% diglycerides (DAGs) that naturally consist of FFA[7]. Industrial regulations expect that high-quality oil must contain more than 95% neutral TAGs and 0.5% or less FFA; for some reason, the limit also decreases to less than 0.1%[2,8].

Complex refining processes includingdegumming, neutralization, bleaching, and deodorization are performed to achieve the desired requirement. The first step in the refining process is degumming,whose function is to remove phospholipids and mucilaginous gums. Conventional degumming methods using water and acids possess numerous drawbacks due to the high energy consumption, oil loss, loss of nutrients, and requirement for large water quantities[9-10]. The membrane-basedfiltration process is a promising method for refining palm oil. Membrane filtration provides low energy consumption, without the addition of chemicals

and with almost no loss of natural oil[11-12]. Previous studies on CPO refining using membrane filtration have been evaluated[3,13-17]. Arora et al.[3]evaluated the degumming of CPO and crude palm olein with a hexane solvent to remove phospholipids, Lovibond color value, carotenoids, major tocopherols and tocotrienols, and major fatty acids. Ong et al.[13]studied ultrafiltration (UF) of CPO degumming for the removal of phospholipids, carotenes, Lovibond color, FFAs, and volatile matter. Lai et al.[14]performed research on the deacidification of a model fatty system of CPO using various solvents and nanofiltration. On the other hand, polyvinylidene fluoride (PVDF) has been modified with polyvinyl alcohol (PVA) cross-linked as a UF membrane in thedeacidification of CPO[15].Deacidification of CPO using an aqueous NaOH solution in a hollow fiber membrane contactor was carried out by Purwasasmitaet al.[16]. Furthermore, a hexane solvent combined with a UF membrane has been applied to remove phospholipids from residual palm oil fibers[17].

Similar molecular weights of TAGs and phospholipids (about 900 and 700 Da, respectively) can interfere with their separation process using membrane technology. Phospholipids tend to form reverse micelles in nonpolar media like hexane or crude oil because of their amphiphilic properties[18,19]. This unique feature of phospholipid micelles increases their average molecular weight from 700 Da to around 20 kDa or even more [12], which is significantly different from TAGs. As a result, theUF membrane is able to separate the micelles from the solvent–oil mixture, and the phospholipids were retained by the UF membrane [20]. However, the primary challenge in the use of membranes, especially UF, is the existence of a phenomenon called fouling. Fouling is an irreversible membrane change that is caused by specific physical and chemical interactions between the membrane and the various components present in the process flow. Membrane fouling is represented by a decrease of the permeate flux due to the effect of blocking on the surface as well as inside the membrane pores[21-22]. As it is essential to have a detailed investigation on fouling and there is no research

investigating membrane fouling in the degumming of crude palm oil, this research is primarily focused on studying the flux decline as well as the fouling mechanism in the degumming of CPO by UF.

Fundamental studies on fouling mechanisms on UF membranes have been performed for coconut cream[23], organic compounds[24], whey models[25], and polyethylene glycol (PEG)[26]. In more detail,the fundamental studies focusing on the fouling mechanism in UF for oil degumming or separation of oil components are limited only for degumming corn oil[18-27], crude sunflower oil, and soybean oil[14]. This study placed emphasis on the fundamental and comprehensive analysis of the influence of oil solvents and micelles on fouling mechanism models. Specifically, this study addressed a novelty findingon the analysis of the fouling model and fouling mechanism in UF for degumming CPO.

MATERIALS AND METHODS

Materials

The main raw materials used in this experiment were CPO (Kalimantan, Indonesia) and isopropanol (Merck) as a solvent. The UF membrane was a laboratory-made polyethersulfone (PES) flat-sheet membrane. The PEG material was Veradel PESU 3100P (Solvay, Singapore). The membrane was prepared via a non-solvent-induced phase separation method with PEG as the additive and N-methyl-2-pyrrolidone (NMP) as the solvent[28].

Membrane Characterization

The membrane was characterized for its molecular weight cut-off (MWCO), pore size, permeability, surface structure, and specific functional groups. The MWCO of the membrane represents the lowest molecular weight of solute (in Daltons), in which 90% of the solute is rejected by the membrane. The MWCO value is evaluated to describe the pore size

distribution and retention capabilities of membranes. In this work, solute rejection experiments were performed using PEG (from Sigma-Aldrich)as polymer solute with various molecular weights (MWs) of 4, 6, 12 and 20 kDa. The PEG solution was prepared in 1 wt.% concentration and then filtrated in a dead-end filtration cell. The permeate samples were analyzed using a digital handheld refractometer (PAL-91S, ATAGO, Japan). Plots of MW versus solute rejection were created, and then the MW corresponding to 90% rejection was estimated as MWCO of the membrane. The MWCO of the laboratory-made membrane was found as 20 kDa.

Membrane permeability wasevaluated by determining the membrane flux ofdistilled water or isopropanol in the membrane module at various operating pressures (1–3 bar). The fluxeswere calculated according to the sample volume (*V*), the sampling time (*t*), and the membrane surface area (*A*). The volumetric permeate flow rate (*Q*) was calculated by

$$Q = \frac{V}{t} \quad (1)$$

Further, the flux(*J*) was determined by:

$$J = \frac{1}{A}\, x\, Q \quad (2)$$

The membrane's surface and cross-sectional structure was characterized using scanning electron microscopy (SEM, FEI Type Inspect-S50). The specific functional groups of the membrane were determined using FTIR Spectroscopy (Prestige-21, Shimadzu, Japan).

Evaluation of UF Membrane Performance for Degumming of the CPO-Isopropanol Mixture

The UF performance wasexamined using laboratory-made cell filtration based on thetotal recycle model as illustrated in Figure 1.

Figure 1. Schematic of Ultrafiltration Cell with Total Recycle Operation

The cell filtration was equipped with centrifugal pump (Kemflow, with nominal flow rate 1.0 LPM, maximum pump output of 110 psi, maximum inlet pressure of 60 psi)as the feed pump, gate valves, pressure gauge (JAKO, with maximum pressure of 150 psi) and a stainless steel ultrafiltration housing. The total recycle model involved returning the permeate and retentate flow back to the feed tank to maintain equivalent concentration during the process. All experimental runs were conducted at room temperature (29 ± 2°C). Before starting the experiments, membranes were first compacted by filtering water through the membrane at a pressure of 1 bar for 60 min. For each run, a new circular membrane sheet with an effective area of 13.85 cm^2 was used.

Figure 1.Schematic of the UF cell with total recycle operation.

A micellar solution was prepared by mixing CPO with isopropanolwith ratios of CPO of 30%, 40%, 50%, and 60% weight of the solution. The filtration cell was operated at 1 barfor 120 min, and before returning it back to the feed tank, the permeate wascollected every 5 min to determine the flux and concentration of phospholipids/fatty acids. The feed temperature was varied—30°C, 35°C, 40°C, and 45°C—in order to investigate the effect of temperature on UF performance. The feed tank was equipped with a temperature regulator and a magnetic stirrer for homogenization of oil micelles. Membrane performance was evaluated in terms of permeate flux and phospholipid/FFA rejection. Permeate fluxes (*J*) were determined by weighing the volume of the permeate collected at 5 min intervals for 120 min and calculated using

$$J = \frac{W}{A\,x\,t} \tag{3}$$

where*W*represents the total weight of the permeate, *A* is the membrane area, and *t* is the time interval.

Rejection of phospholipids and FFAs was determined on the basis of the concentration of phospholipids/FFAs in the feed (C_f) and in the permeate (C_p). Rejection is calculated according to

$$R = \frac{C_f - C_p}{C_f} \quad (4)$$

Characterization of CPO and Permeate

The specific characteristics of CPO and permeate included the phospholipid and FFA content. Phospholipids were expressed as total phosphorus and were analyzed according to the AOAC Ca 12-55 method. Determination of FFAwas performed via the acid–base titration method[14].

Blocking Mechanism

The blocking mechanism of CPO-isopropanol UF was studied according to Hermia's model. This model has been previously applied for the evaluation of the fouling mechanism of dye solution UF[28],konjacglucomannanseparation[29], and UF of model dye wastewater[30]. Hermia's model describes the mechanism of membrane fouling on the basis of the blocking filtration law, consisting of complete pore blocking, standard pore blocking, and intermediate pore blocking and cake filtration. The blocking law filtration is expressed in terms of permeation time and filtration time and was developed for dead-end filtration as shown in[31]:

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \quad (5)$$

where*t* is the filtration time, *V* is the permeate volume, *k* is a constant, and *n* is a value illustrating the different fouling mechanisms.

The values of *n* are described as follows: complete blocking with*n*= 2, intermediate blocking with *n* = 1, standard blocking with *n* = 1.5, and cake layer formation with*n*= 0. In the complete blocking model, it is assumed that each solute participated in blocking the entrance of the membrane pores completely. In intermediate blocking, it is assumed that every solute stays on the previously deposited solutes. Standard blocking considers the deposition of each solute to the internal pore wall. The cake layer formation occurs due to the accumulation of the solute on the membrane surface in a cake form[32]. Hermia's model was then linearized on the basis of the *n* value for each model by fitting equations (6) to (9) regarding thepermeate flux versus time as presented in the following.

For Complete Blocking (*n* = 2) :

$$\ln J = \ln J_0 - k_c t \tag{6}$$

For Intermediate Blocking (*n* = 1) :

$$\frac{1}{J} = \frac{1}{J_0} + k_i t \tag{7}$$

For Standard Blocking (*n* = 1.5) :

$$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + k_s t \tag{8}$$

For Cake/Layer Formation (*n* = 0) :

$$\frac{1}{J^2} = \frac{1}{J_0^2} + k_{cf}t \quad (9)$$

Here, k_c, k_i, k_s, and $k_{cf}$are constants for complete blocking, intermediate blocking, standard blocking, and cake layer formation, respectively.

RESULT AND DISCUSSION

Water and SolventPermeability

The flux profile of water and isopropanol at various pressures for the UF membrane is presented in Figure 2.

Figure 2. Flux Profile of Isopropanol and Water at Pressure of 1-3 bar

The figure shows an increase of water and isopropanol flux with the rise of pressure from 1 to 3 bar. According to the linearization regression ($y = mx$) of water and isopropanol flux in the figure, it was found that the water permeability and isopropanol permeability are 44.19 L/m^2·h and 62.69 L/m^2·h, respectively. This is surprising since water is predicted to have permeability higher than that of ethanol due to the fact that water is the most polar solvent. This result is in contrast with de Meloet al.[33], confirming that lower solvent polarity results in a decrease in permeation. In addition, the prepared PES membrane had the characteristics of hydrophilic membranes especially because of the addition of polyvinylpyrrolidone (PVP) and PEG[34]. With the hydrophilic characteristic of the PES membrane, water permeation is expected to be higher than that of isopropanol. Solvent characteristics, such as viscosity, surface tension, and polarity, as well as the molar volume of the solvent, have an effect on the transport of the solvent by the membrane[35-36]. According to the physicochemical characteristics of the solvent (viscosity and interfacial tension), the isopropanol flux should

be below the water flux. However, this phenomenon was not observed in this research, presumably because there is a specific interaction between the membrane and the solvent. A similar result was observed by Araki et al.[37]. The high permeability of isopropanol indicates that the conditioning process (immersing in isopropanol) created a less hydrophilic PES membrane. The alteration of the hydrophobic characteristic is caused by the transformation of the hydrophilic and hydrophobic sites of the membrane, resulting in the higher permeability of isopropanol. Water permeation is correlated to the hydrophilic characteristic (hydrogen bond formation) of the membrane. When an alcohol such as isopropanol is permeated, the hydrogen bond formation becomes less, contributing to a low water flux.

Specific Functional Groups

Specific functional groups of the membrane is shown in Figure 3.

Figure 3.FT-IR Spectra of the Membrane confirming Specific Functional Groups

According to the figure, characteristics of PES membrane are determined by peaks at 1492.9 and 1589.3 cm^{-1}. Moreover, the peaks of 1161.15 and 1172.7 cm^{-1}show a symmetric stretching sulfur SO_2. In more detail, Table 1 lists otherspecific functional group of the membrane.

Table 1 Specific Functional Groups as shown in FT-IR Spectra

Based on the table, the specific functional groups were matched with the chemical structure of main membrane materials. Beside the PES characteristic, the O-H bonding vibration, C-H asymmetric, C-C stretching in Benzene ring and -C-O-C- bonding arerepresentation of bonds in the polymer of PEG.

Permeate Flux

The profile of the permeate flux showing flux versus time is presented in Figure 4.

Figure 4Permeate flux profile in the UF of the CPO-isopropanol mixture at various concentrations of CPO (feed temperature: 19°C, transmembrane pressure: 1 bar).

The figure shows that there is a flux decline during the filtration of the solvent and CPO mixtures. A significant flux fall-off was observed during the first 5 min of filtration, followed by a flux reduction deceleration rate, and then finally the flux becomes steady. A three-step behavior was also perceived by Penha et al.[38] during the filtration of maracuja oil/*n*-hexane mixture. The initial flux decline is caused by a phenomenon called polarization concentration, whereas the following flux reduction is a result of membrane fouling. Comparable performances were reported for oil/hexane mixture permeation through the UF membrane using sunflower oil[39]as well as coconut oil, groundnut oil, mustard oil, sunflower oil, and rice bran oil [36-40].In addition, it was reported that the flux reduction at the beginning of the sunflower oil–*n*-hexane filtration was type of concentration polarization phenomenon and gel layer formation on the membrane surface[39]. Moreover, the flux drop at the end of the filtration was due to the deposition of a gel on the membrane surface [38, 41, 42]. The deposited layer is formed because of the phospholipids retained on the membrane surface and pores plugging[14,43].

Figure 4 also confirms that the increase of oil concentration leads to a higher reduction of flux. This decrease takes place due to an increase of oil concentration, resulting in the increase of solution viscosity. With the rise of viscosity, a smaller flux is obtained since the permeability is influenced by the viscosity[35]. In addition, a lower flux is obtained as a result of polarized/gel layer formation. When the oil concentration is higher, the layer becomes larger and generates larger resistance to the flux permeation[33,36,41]. As elucidated by Kim et al.[41], convective solute transport to the membrane produces a sharp gradient of concentration

inside the boundary layer. Because of diffusion, solute back-transport into the bulk takes place, and a close-packed arrangement of the solute is formed. As a consequence, no more solute can be accommodated, and the mobility of solutes is restricted.

Scanning electron microscopy images of the fouled membrane, as displayed in Figure 4, confirm that a foulant layer on the membrane's surface is present.

Figure 5. Scanning Electron Microscope Images at magnification of 10.000x: Clean Membranes (1a- Surface), (2a- Cross-Sectional Structure) and Fouled Membrane after ultrafiltration of 30% CPO-Solvent mixture(1b-Surface), (2b-Cross-Sectional Structure)

Figure 6 displays the effect of feed temperature on the initial and final permeate flux.

Figure 6. The effect of feed temperature on the initial and final flux at a pressure of 1 bar and CPO concentration of 30%.

Based on the figure, it is indicated that increasing the mixture temperature from 30 to 35°C has an effect on the higher flux permeate. This was expected due to the decrease of viscosity or the increase of phospholipid diffusion on the membrane pores. However, a further temperature increase (from 40 to 45°C) leads to a decrease in flux, but the reduction of viscosity does not have an effect on the flux. This result is close to that of Kim et al.[41], confirming that the operating temperature of 40°C was suitable for the degumming of soybean extract; above the temperature of 40°C, the flux decreased. A decline in flux is predicted because of the fouling on the membrane surface as a result of solid denaturation or gelatinization as well as insoluble salts precipitation at a high temperature[44].

Phospholipid and FFA Rejection

Membrane selectivity is represented as rejection, indicating the membrane's ability to reject or remove a feed compound. Micelles are formed when phospholipids are dispersed in water. The mixture of phospholipids in a nonpolar solvent such as isopropanol formed reverse micelles having an average molecular weight of 20,000 Daltons (10–200 nm)[44]. Based on the pore size, UF rejects compounds having a molecular weight in the range of 300–500,000 Daltons. Hence, in the phospholipids-isopropanol system, phospholipids are expected to be retained in the retentate, and the permeate comprises the oil and isopropanol. In contrast to phospholipids, the MWs of FFAs and TAGs are similar. TAGs and FFAs have a molecular weight of 800 Da and 300 Da, respectively[9]. Compared to the UF pore size, the separation of FFAs is challenging due to the low selectivity and it results in a low rejection value. Rejection of phospholipids and FFAs at various CPO concentrations is displayed in Table 2.

Table 2 Rejection of Phospholipid and Fatty Acid at Various CPO Concentration at a pressure of 1 bar and Feed Temperature of 30^{o}C

The table shows that rejection of phospholipids is significantly higher than of fatty acids. This is noticeable since the molecular weight of micelle phospholipids is considerably greater than of FFAs. The phospholipids' rejection is found to be greater than 99% at a CPO concentration of 30% and slightly reduced to nearly 93% with the increase of CPO concentration to 40%. The reduction of phospholipid rejection becomes more obvious with the increase of CPO concentration to 50%. In addition, a similar trend is shown when the feed temperature is raised. The rejection of both phospholipids and FFAs declines at higher temperatures from 30°C to 40°C as presented in Table 3.

Table 3 Rejection of Phospholipid and Fatty Acid at Various Feed Temperature at apressure of 1 bar and CPO Concentration of 30 %

Blocking Mechanism by Hermia's Model

In this research, Hermia's model was applied in order to evaluate the blocking mechanism during UF of the CPO-isopropanol mixture at various feed CPO concentrations. The fouling mechanism represented by the blocking mechanism is identified by fitting the experimental data into Hermia's linearized equation [equations (4) to (7)]. The fitting of experimental data to the four-type Hermia model is shown in Figure 7, and the corresponding correlation coefficients (R^2) are listed in Table 4.

Figure 7Fitting of experimental data (feed temperature: 30°C, pressure: 1 bar) to Hermia's model: (a) complete blocking, (b) standard blocking, (c) intermediate blocking, and (d) cake/gel layer formation.

Table 4R^2values of the blocking mechanism based on Hermia's model.

According to the table, two dominant blocking mechanisms are found: standard blocking and intermediate blocking. At low concentrations of CPO (30% and 40%), the blocking mechanism is dominated by standard blocking. In contrast, at higher concentrations of CPO (50 and 60%), the intermediate blocking is the dominant mechanism. Standard blocking assumes that each solute is deposited into the internal pore wall. In intermediate blocking, it is proposed that every solute stays on the previously deposited solutes.

The proposed standard blocking and intermediate blocking mechanisms in UF of CPO-isopropanol are illustrated in Figure 8.

Figure 8. Schematic illustration of (a) intermediate blocking and (b) standard blocking mechanisms in UF of the CPO-isopropanol mixture.

According to Figure 8(a), the large particles that accumulated on the membrane surface and blocked the membrane pores were TAGs. The large particles that formed at a high concentration of CPO were first presumed to be phospholipid-isopropanol micelles because of their large size and potential to block the pores. However, this assumption is in contradiction with phospholipid rejection. If the large particles were an agglomeration of phospholipid micelles, then rejection at high CPO concentrations should be larger. Hence, it can be assumed that, at high concentrations of CPO, not all phospholipids generate micelles with isopropanol. This confirms why phospholipid rejection at high concentrations of CPO was lower. Hence, the larger particles that accumulated on the membrane surface were predicted to be other oil compounds such as TAGs.

In addition, Figure 8(b) shows that, at low concentrations of CPO, the dominant fouling mechanism was standard blocking, representing small particles attached inside the membrane pore and causing pore constriction (reduction of pore size). The compound that was possibly blocking the membrane pores is fatty acid, since the size of fatty acids is smaller than of the phospholipid-isopropanol micelles. At low concentrations of CPO, a sufficient amount of phospholipid-isopropanol micelles was formed, with pore constriction providing high rejection of phospholipids. On the other hand, small molecules such as fatty acids can enter the membrane pores.

Conclusion

Phospholipids separation and FFAs removal in CPO have been performed using a PES UF membrane. In general, lower fluxes were obtained with the increase of CPO concentration. Raising the feed temperature from 30°C to 40°C resulted in a lower permeate flux, but further feed temperature increase to 45°C decreased the permeate flux. The phospholipid rejection rate was in the range 93–99%. However, the removal of fatty acids was unsuccessful. The decrease of flux due to membrane fouling was evaluated on the basis of Hermia's model, confirming that there were two dominant mechanisms observed: standard blocking and intermediate blocking.

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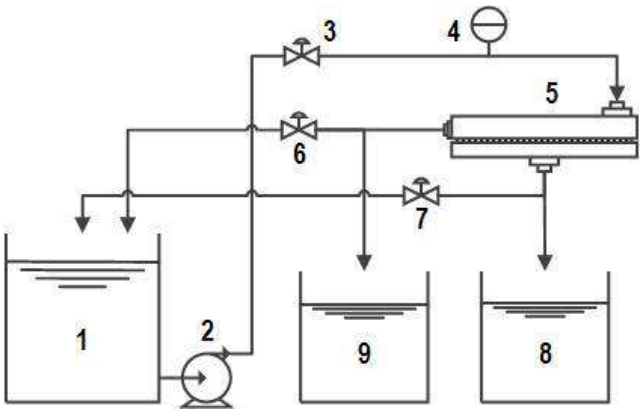

Figure 1. Schematic of Ultrafiltration Cell with Total Recycle Operation : (1). Feed Tank, (2) Feed Pump, (3) Feed Valve (4) Pressure Gauge (5) Ultrafiltration housing (6) Retentate valve (7) Permeate valve (8) Permeate tank (9) Retentate Tank

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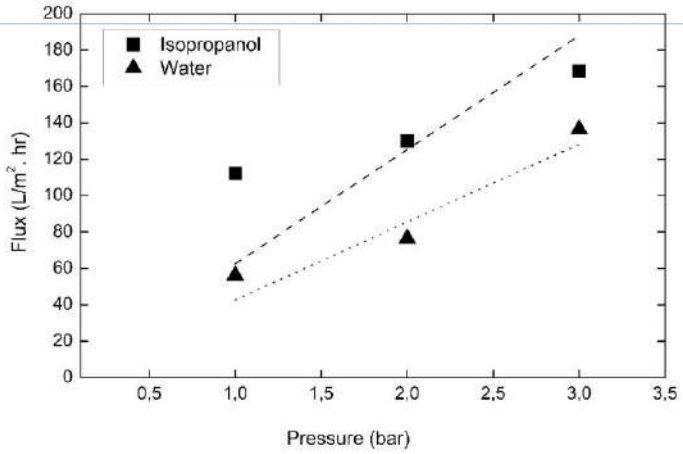

Figure 2. Flux Profile of Isopropanol and Water at Pressure of 1-3 bar

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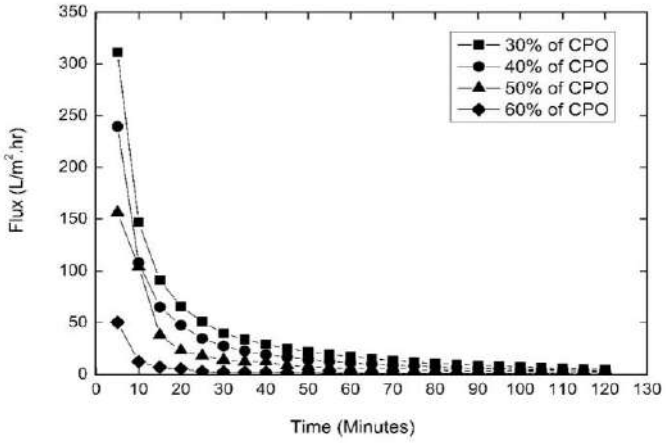
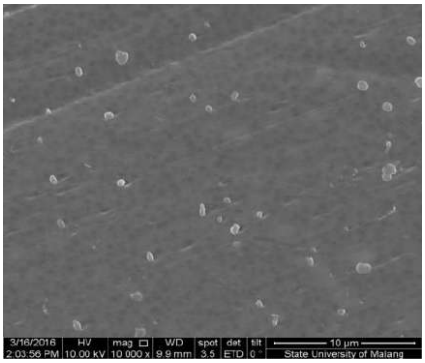


Figure 4 Permeate flux profile in the UF of the CPO-isopropanol mixture at various concentrations of CPO (feed temperature: 19°C, transmembrane pressure: 1 bar).



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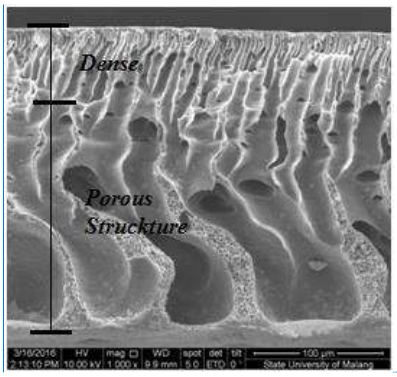

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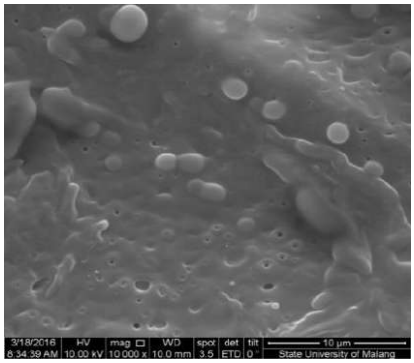

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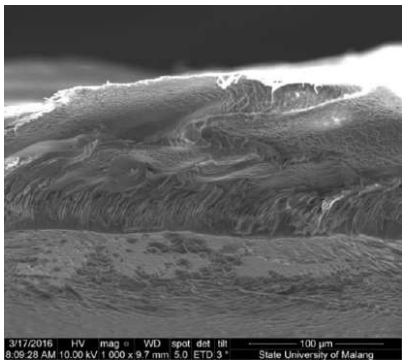


(2b)

Figure 5. Scanning Electron Microscope Images at magnification of 10.000x: Clean Membranes (1a- Surface), (2a- Cross-Sectional Structure) and Fouled Membrane after ultrafiltration of 30% CPO-Solvent mixture(1b-Surface), (2b-Cross-Sectional Structure)

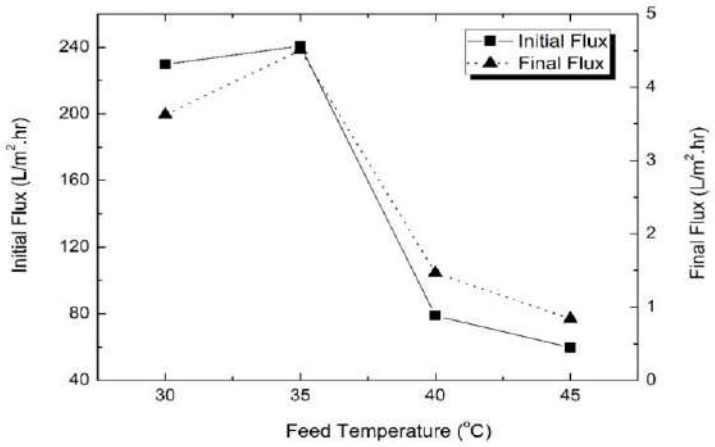


Figure 6. The effect of feed temperature on the initial and final flux at a pressure of 1 bar and CPO concentration of 30%.

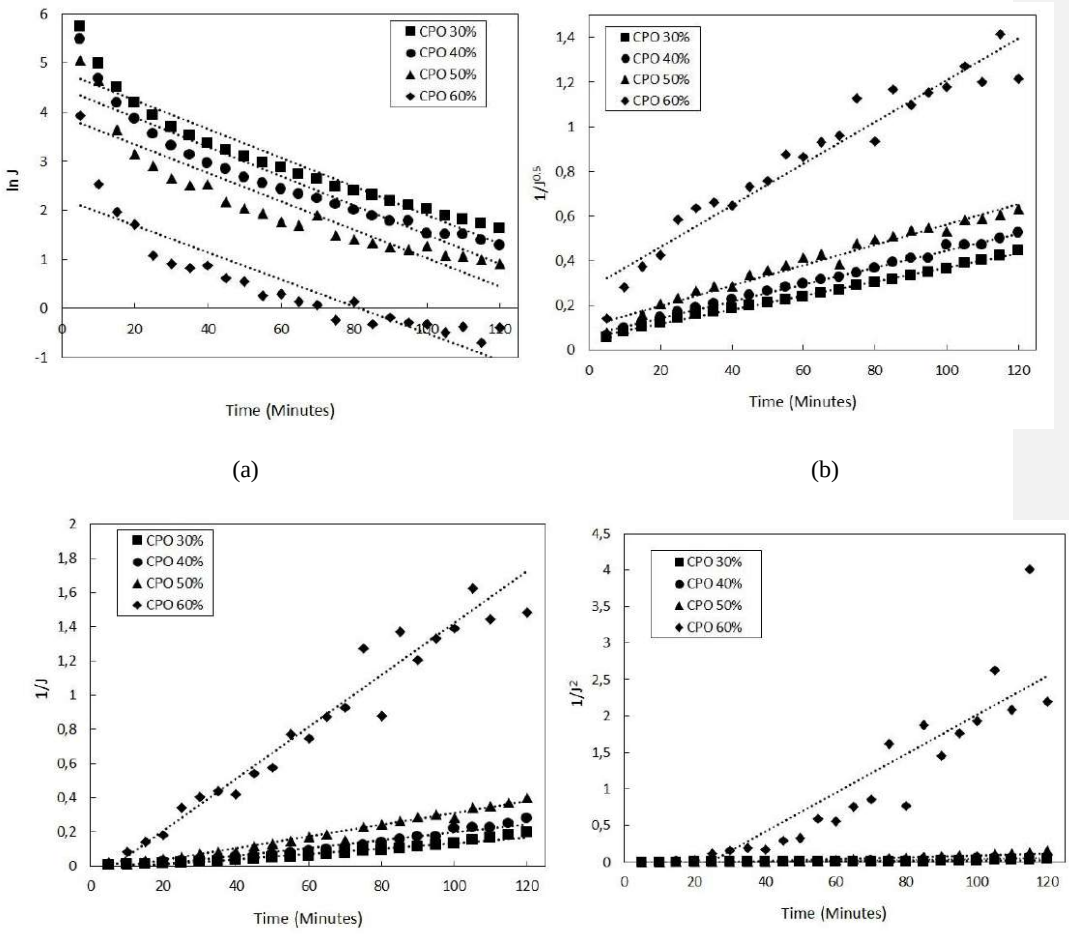
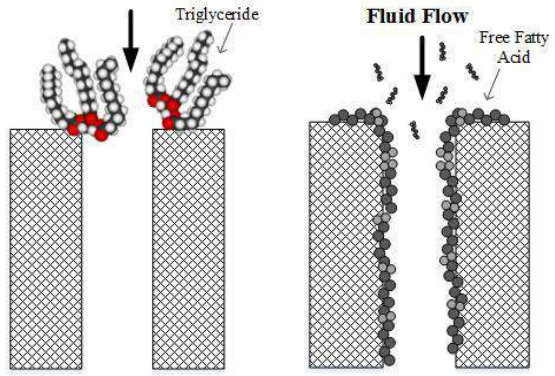


Figure 7Fitting of experimental data (feed temperature: 30°C, pressure: 1 bar) to Hermia's model: (a) complete blocking, (b) standard blocking, (c) intermediate blocking, and (d) cake/gel layer formation.



(a) (b)

Figure 8. Schematic illustration of (a) intermediate blocking and (b) standard blocking mechanisms in UF of the CPO-isopropanol mixture.

Table 1 Specific Functional Groups as shown in FT-IR Spectra

Absorbance Peaks (cm^{-1})	Specific Functional Groups
1492.9 and 1589.3	Aromatic compounds (C-C streching)
1219.01 and 1261.4	Aromatic ether compounds
849.2 and 862.2	Para substituted Benzene
1074.3, 1093.6 and 1114.8	-C-O-C- bonding
2872.01 and 2926.01	C-H asymmetric bonding
3375.43 and 3475.73	O-H alcohol bonding

Table 2 Rejection of Phospholipid and Fatty Acid at Various CPO Concentration at pressure of 1 Bar and Feed Temperature of 30^{o}C

CPO Concentration	Phospholipid Rejection (%)	Free Fatty Acid Rejection (%)
30%	>99,21	16
40%	92,93	13
50%	37,52	9

Table 3 Rejection of Phospholipid and Fatty Acid at Various Feed Temperature at pressure of 1 bar and CPO Concentration of 30 %

Feed Concentration	Phospholipid Rejection (%)	Free Fatty Acid Rejection (%)
30^{O}C	92,93	13
35^{O}C	86,60	7,168
40^{O}C	73,94	10,24

Table 4R^2values of the blocking mechanism based on Hermia's model.

	R^2			
	Complete Blocking	**Intermediate Blocking**	**Standard Blocking**	**Cake/ Gel Formation**
CPO 30%	0,9186	0,9512	**0,9971**	0,7755
CPO 40%	0,9022	0,9618	**0,9953**	0,8053
CPO 50%	0,8354	**0,9811**	0,9737	0.8769
CPO 60%	0,7797	**0,9432**	0,9394	0,8052

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Ultrafiltration Membrane for Degumming of Crude Palm Oil-Isopropanol Mixture

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Abstract

Ultrafiltration (UF) is a membrane technology that has been applied for crude palm oil (CPO) degumming. It is considered as an alternative for the conventional CPO degumming technology because of its lower energy consumption, no need for the addition of chemicals, and almost no loss of natural oil. In this research, we separated a CPO-isopropanol mixture via laboratory-made flat-sheet polyethersulfone (PES) UF. Flux profiles confirmed that the increase of in the CPO concentration resulted in lower fluxes. However, increasing the temperature from 30 °C to 45 °C initially raised the flux, but it was further decreased when the feed temperature was raised from 40 °C to 45 °C. Using UF of the CPO-isopropanol mixture at crude oil concentrations of 30 % and 40 %, we were able to reject more than 99 %

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phospholipids and nearly 93 % phospholipids, respectively. However, the separation of free fatty acids using this process was ineffective due to the small size of ~~the~~ free fatty acids. Through the evaluation of the blocking mechanism in the Hermia model, it was proposed that the standard and intermediate blocking were the dominant mechanisms of filtration of CPO at a concentration of 30 and 40 %, and 50 and 60 %, respectively.

Keywords: crude palm oil, ultrafiltration, degumming

Introduction

Crude vegetable oil is a raw material used in the production of edible vegetable oil. Some examples of crude vegetable oils include crude palm oil (CPO), crude soybean oil, crude corn oil, crude coconut oil, crude sunflower oil, and crude castor oil[1]. Indonesia is one of the largest producers of CPO, followed by Malaysia, Thailand, Colombia, and Nigeria. Compared to other oilseed crops, palm oil produces more oil products[2]. ~~And c~~Compared to other vegetable oils, it is preferable in many applications as it is substantially cost-effective[3]. CPO is widely used in various food and industrial products' manufacturing processes, such as ice cream, frying oils, shortening, cosmetics, toothpastes, and biodiesel[4]. CPO is extracted from the ripe mesocarp of the fruit of oil palm trees (*Elaeis guineensis*) through various methods, such as mechanical pressing followed by solid–liquid extraction[2].

The crude oil extracted from palm oil fruits is also rich in palmitic acid, β-carotene, and vitamin E, along with some undesirable compounds, such as phospholipids, free fatty acids (FFA), pigments, and proteins[5-6]. CPO is composed of a vast number of triglycerides (TAGs) and 6 % diglycerides (DAGs) that naturally consist of FFA[7]. Industrial regulations expect that high-quality oil must contain more than 95 % neutral TAGs and 0.5 % or less FFA; for some reason, the limit also decreases to less than 0.1 %[2,8].

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Complex refining processes including degumming, neutralization, bleaching, and deodorization are performed to ~~achieve~~ meet the desired requirement. The first step in the refining process is degumming, ~~whose~~ the function of which is to remove phospholipids and mucilaginous gums. Conventional degumming methods using water and acids possess numerous drawbacks due to the high energy consumption, oil loss, loss of nutrients, and requirement for large water quantities[9-10]. The membrane-based filtration process is a promising method for refining palm oil. Membrane filtration provides low energy consumption, without the addition of chemicals and with almost no loss of natural oil[11-12]. Previous studies on CPO refining using membrane filtration have been evaluated[3,13-17]. Arora *et al.*[3] evaluated the degumming of CPO and crude palm olein with a hexane solvent to remove phospholipids, Lovibond color value, carotenoids, major tocopherols and tocotrienols, and major fatty acids. Ong *et al.*[13] studied ultrafiltration (UF) of CPO degumming for the removal of phospholipids, carotenes, Lovibond color, FFAs, and volatile matter. Lai *et al.*[14] performed research on the deacidification of a model fatty system of CPO using various solvents and nanofiltration. On the other hand, polyvinylidene fluoride (PVDF) has been modified with polyvinyl alcohol (PVA) cross-linked as a UF membrane in the deacidification of CPO[15]. Deacidification of CPO using an aqueous NaOH solution in a hollow fiber membrane contactor was carried out by Purwasasmita *et al.*[16]. Furthermore, a hexane solvent combined with a UF membrane has been applied to remove phospholipids from residual palm oil fibers[17].

Similar molecular weights of TAGs and phospholipids (about 900 and 700 Da, respectively) can interfere with their separation process using membrane technology. Phospholipids tend to form reverse micelles in nonpolar media like hexane or crude oil because of their amphiphilic properties[18,19]. This unique feature of phospholipid micelles increases their average molecular weight from 700 Da to around 20 kDa or even more[12].

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which is significantly different from TAGs. As a result, the UF membrane is able to separate the micelles from the solvent–oil mixture, and the phospholipids ~~were~~ are retained by the UF membrane~~.~~[20]. However, the primary challenge in the use of membranes, especially UF, is the existence of a phenomenon called fouling. Fouling is an irreversible membrane change that is caused by specific physical and chemical interactions between the membrane and the various components present in the process flow. Membrane fouling is represented by a decrease ~~of~~ in the permeate flux due to the effect of blocking on the surface as well as inside the membrane pores[21-22]. As it is essential to have a detailed investigation on fouling and there is no research investigating membrane fouling in the degumming of crude palm oil, this research is ~~primarily~~ focused primarily on studying the flux decline as well as the fouling mechanism in the degumming of CPO by UF.

Fundamental studies on fouling mechanisms on UF membranes have been performed for coconut cream[23], organic compounds[24], whey models[25], and polyethylene glycol (PEG)[26]. In more detail, the fundamental studies focusing on the fouling mechanism in UF for oil degumming or separation of oil components are limited only for degumming corn oil[18-27], crude sunflower oil, and soybean oil[14]. This study placed emphasis on the fundamental and comprehensive analysis of the influence of oil solvents and micelles on fouling mechanism models. Specifically, this study addressed a novelty finding ~~on~~ in the analysis of the fouling model and fouling mechanism in UF for degumming CPO.

Materials aAnd mMethods

Materials

The main raw materials used in this experiment were CPO (Kalimantan, Indonesia) and isopropanol (Merck) as a solvent. The UF membrane was a laboratory-made polyethersulfone (PES) flat-sheet membrane. The PEG material was Veradel PESU 3100P (Solvay,

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Singapore). The membrane was prepared via a non-solvent-induced phase separation method with PEG as the additive and N-methyl-2-pyrrolidone (NMP) as the solvent[28].

Membrane ~~Characterization~~characterization

The membrane was characterized for its molecular weight cut-off (MWCO), contact angle, permeability, surface structure, and specific functional groups. The MWCO of the membrane represents the lowest molecular weight of solute (in Daltons), in which 90 % of the solute is rejected by the membrane. The MWCO value is evaluated to describe the pore size distribution and retention capabilities of membranes. In this work, solute rejection experiments were performed using PEG (from Sigma-Aldrich) as polymer solute with various molecular weights (MWs) of 2, 6, 12, 20 and 35kDa. The PEG solution was prepared in 1 wt.% concentration and then filtrated in a dead-end filtration cell. The permeate samples were analyzed using a digital handheld refractometer (PAL-91S, ATAGO, Japan). Plots of MW versus solute rejection were created, and then the MW corresponding to 90 % rejection was estimated as MWCO of the membrane. The hydrophobic/hydrophilic character of the membrane was determined by measuring the water-membrane contact angle (θ). The water-membrane contact angle values of the prepared membrane were measured using water contact angle meter (RACE contact angle ~~mater~~meter, Japan) using deionized water as a probe liquid.

Membrane permeability was evaluated by determining the membrane flux of distilled water or isopropanol in the membrane module at various operating pressures (1–3 bar). The fluxes were calculated according to the sample volume (V), the sampling time (t), and the membrane surface area (A). The volumetric permeate flow rate (Q) was calculated by

$$Q = \frac{V}{t} \quad (1)$$

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Further, the flux (J) was determined by:

$$J = \frac{1}{A} \cdot \frac{dV}{dt} Q \quad (2)$$

The membrane's surface and the cross-sectional structure were characterized using scanning electron microscopy (SEM, FEI Type Inspect-S50). The specific functional groups of the membrane were determined using FTIR Spectroscopy (Prestige-21, Shimadzu, Japan).

Evaluation of UF Membrane performance for degumming of the CPO-~~Isopropanol~~ isopropanol ~~Mixture~~mixture

The UF performance was examined using laboratory-made cell filtration based on the total recycle model as illustrated in ~~Figure~~ Fig. 1.

Figure 1. Schematic of ultrafiltration cell with total recycle operation

The cell filtration was equipped with a centrifugal pump (Kemflow, with nominal flow rate 1.0 LPM, maximum pump output of 7.58 bar, ~~the~~ maximum inlet pressure of 4.14 bar) as the feed pump, gate valves, pressure gauge (JAKO, with maximum pressure of 10.34 bar) and a stainless steel ultrafiltration housing. The total recycle model involved returning the permeate and retentate flow back to the feed tank to maintain equivalent concentration during the process. All experimental runs were conducted at room temperature (29 ± 2 °C). Before starting the experiments, membranes were first compacted by filtering water through the membrane at a pressure of 1 bar for 60 min. For each run, a new circular membrane sheet with an effective area of 13.85 cm^2 was used.

~~Figure 1 Schematic of the UF cell with total recycle operation.~~

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A micellar solution was prepared by mixing CPO with isopropanol with ratios of CPO of 30 %, 40 %, 50 %, and 60 % weight of the solution. The filtration cell was operated at 1 bar for 120 min, and before returning it back to the feed tank, the permeate was collected every 5 min to determine the flux and concentration of phospholipids/fatty acids. The feed temperature was varied—30 °C, 35 °C, 40 °C, and 45 °C—in order to investigate the effect of temperature on UF performance. The feed tank was equipped with a temperature regulator and a magnetic stirrer for homogenization of oil micelles. Membrane performance was evaluated in terms of permeate flux and phospholipid/FFA rejection. Permeate fluxes (J) were determined by weighing the volume of the permeate collected at ~~5~~ 5-min intervals for 120 min and calculated using

$$J = \frac{W}{A \times t} \quad (3)$$

Where W represents the total weight of the permeate, A is the membrane area, and t is the time interval.

Rejection of phospholipids and FFAs was determined on the basis of the concentration of phospholipids/FFAs in the feed (C_f) and in the permeate (C_p). Rejection is calculated according to

$$R = \frac{C_f - C_p}{C_f} \quad (4)$$

Characterization of CPO and ~~Permeate~~permeate

The specific characteristics of CPO and permeate included the phospholipid and FFA content. Phospholipids were expressed as total phosphorus and ~~were~~ analyzed according to the AOAC Ca 12-55 method. Determination of FFA was performed via the acid-base titration method[14].

Blocking mMechanism

The blocking mechanism of CPO-isopropanol UF was studied according to Hermia's model. This model has been previously applied for the evaluation of the fouling mechanism of dye solution UF[28], konjac glucomannan separation[29], and UF of model dye wastewater[30]. Hermia's model describes the mechanism of membrane fouling on the basis of the blocking filtration law, consisting of complete pore blocking, standard pore blocking, and intermediate pore blocking and cake filtration. The blocking law filtration is expressed in terms of permeation time and filtration time, and was developed for dead-end filtration as shown in[31]:

$$\frac{\mathrm{d}^2 t}{\mathrm{d}V^2} = k\left(\frac{\mathrm{d}t}{\mathrm{d}V}\right)^n \quad (5)$$

Wherewhere t is the filtration time, V is the permeate volume, k is a constant, and n is a value illustrating the different fouling mechanisms.

The values of n are described as follows: complete blocking with n = 2, intermediate blocking with n = 1, standard blocking with n = 1.5, and cake layer formation with n = 0. In the complete blocking model, it is assumed that each solute participated in blocking the entrance of the membrane pores completely. In intermediate blocking, it is assumed that every solute stays on the previously deposited solutes. Standard blocking considers the deposition of each solute to on the internal pore wall. The cake layer formation occurs due to the accumulation of the solute on the membrane surface in a cake form[32]. Hermia's model was then linearized on the basis of the n value for each model by fitting equations (6) to (9) regarding the permeate flux versus time, as presented in the following.

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For Complete Blocking (n = 2)-:

$$\ln J = \ln J_0 - k_c t \quad (6)$$

For Intermediate Blocking (n = 1)-:

$$\frac{1}{J} = \frac{1}{J_0} + k_i t \quad (7)$$

For Standard Blocking (n = 1.5)-:

$$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + k_s t \quad (8)$$

For Cake/Layer Formation (n = 0)-:

$$\frac{1}{J^2} = \frac{1}{J_0^2} + k_{cf} t \quad (9)$$

Here, k_c, k_i, k_s, and k_{cf} are constants for complete blocking, intermediate blocking, standard blocking, and cake layer formation, respectively.

Rresults and discussion

Membrane ~~Characteristic~~cCharacteristics

Table 1 shows the characterization results of the synthesized membranes confirming PEG rejections, MWCO, contact angle, and permeabilities.

Table 1 ~~Characteristic~~ Characteristics of the ~~Synthesized~~ synthesized PES ~~Membrane~~membrane

~~Further, detail~~Details of the flux water and isopropanol flux profiles at various pressures for the UF membrane ~~is~~ are presented in Fig.~~ure~~ 2.

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Figure 2. Flux profile of isopropanol and water at pressure of 1-3 bar

The figure shows an increase ~~of~~ in water and isopropanol flux with the rise of pressure from 1 to 3 bar. According to the linearization regression ($y = mx$) of water and isopropanol flux in the figure, it was found that the water permeability and isopropanol permeability ~~are~~ were 42.77 L ~~/m^2~~m^{-2} ~~-~~h^{-1} and 63.58 L ~~/m^2~~m^{-2} ~~-~~h^{-1}, respectively. This is surprising, since water is predicted to have permeability higher than that of ethanol ~~due to the fact that~~which is why water is the most polar solvent. This result is in contrast with de Meloet *et al.*[33], confirming that lower solvent polarity results in a decrease in permeation. In addition, the prepared PES membrane had the characteristics of hydrophilic membranes represented by the contact angle value as listed in Table 1, especially because of the addition of polyvinylpyrrolidone (PVP) and PEG[34]. With the hydrophilic characteristic of the PES membrane, water permeation is expected to be higher than that of isopropanol. Solvent characteristics, such as viscosity, surface tension, and polarity, as well as the molar volume of the solvent, have an effect on the transport of the solvent by the membrane[35-36]. According to the physicochemical characteristics of the solvent (viscosity and interfacial tension), the isopropanol flux should be below the water flux. However, this phenomenon was not observed in this research, presumably because there ~~is~~ was a specific interaction between the membrane and the solvent. A similar result was observed by Araki *et al.*[37]. The high permeability of isopropanol indicates that the conditioning process (immersing in isopropanol) created a less hydrophilic PES membrane. The alteration of the hydrophobic characteristic is caused by the transformation of the hydrophilic and hydrophobic sites of the membrane, resulting in the higher permeability of isopropanol. Water permeation is correlated to the hydrophilic characteristic (hydrogen bond formation) of the membrane. When an alcohol such as

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isopropanol is permeated, the hydrogen bond formation becomes less, contributing to a low water flux.

Specific ~~Functional~~ functional ~~Groups~~groups

Specific functional groups of the membrane are shown in ~~Figure~~ Fig. 3.

Figure 3. FT-IR Spectra of the ~~Membrane~~ membrane confirming ~~Specific~~ specific ~~Functional~~ functional ~~Groups~~groups

According to the figure, characteristics of the PES membrane are determined by peaks at 1492.9 and 1589.3 cm^{-1}. Moreover, the peaks of 1161.15 and 1172.7 cm^{-1} show a symmetric stretching sulfur SO_2. In more detail, Table 2 lists other specific functional groups of the membrane.

Table 2 Specific ~~Functional~~ functional ~~Groups~~ groups as shown in FT-IR ~~Spectra~~spectra

Based on the table, the specific functional groups were matched with the chemical structure of main membrane materials. Beside the PES characteristic, the O-H bonding vibration, C-H asymmetric, C-C stretching in ~~Benzene~~ benzene ring and -C-O-C- bonding are representation of bonds in the polymer of PEG.

Permeate ~~f~~Flux

The profile of the permeate flux showing flux versus time is presented in ~~Figure~~ Fig. 4.

Figure 4 Permeate flux profile in the UF of the CPO-isopropanol mixture at various concentrations of CPO (feed temperature: 29 °C, transmembrane pressure: 1 bar)~~.~~

The figure shows that there is a flux decline during the filtration of the solvent and CPO mixtures. A significant flux fall-off was observed during the first 5 min of filtration, followed

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by a flux reduction deceleration rate, and then finally the flux ~~becomes~~ became steady. A three-step behavior was also perceived by Penha *et al.*[38] during the filtration of maracuja oil/*n*-hexane mixture. The initial flux decline is caused by a phenomenon called polarization concentration, whereas the following flux reduction is a result of membrane fouling. Comparable performances were reported for oil/hexane mixture permeation through the UF membrane using sunflower oil[39] as well as coconut oil, groundnut oil, mustard oil, sunflower oil, and rice bran oil [36-40]. In addition, it was reported that the flux reduction at the beginning of the sunflower oil–*n*-hexane filtration was type of concentration polarization phenomenon and gel layer formation on the membrane surface[39]. Moreover, the flux drop at the end of the filtration was due to the deposition of a gel on the membrane surface[38,-41,-42]. The deposited layer is formed because of the phospholipids retained on the membrane surface and pores plugging[14,43].

~~Figure~~ Fig. 4 also confirms that the increase in oil concentration leads to a higher reduction ~~of~~ in flux. This decrease takes place due to an increase ~~of~~ in oil concentration, resulting in the increase ~~of~~ in solution viscosity. With the rise of viscosity, a smaller flux is obtained since the permeability is influenced by the viscosity[35]. In addition, a lower flux is obtained as a result of polarized/gel layer formation. When the oil concentration is higher, the layer becomes larger and generates larger resistance to the flux permeation[33,36,41]. As elucidated by Kim *et al.*[41], convective solute transport to the membrane produces a sharp gradient of concentration inside the boundary layer. Because of diffusion, solute back-transport into the bulk takes place, and a close-packed arrangement of the solute is formed. As a consequence, no more solute can be accommodated, and the mobility of solutes is restricted.

Scanning electron microscopy images of the fouled membrane, as displayed in ~~Figure~~ Fig. 5, confirm that a foulant layer on the membrane's surface is present.

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Figure 5~~.~~ ~~Scanning Electron Microscope~~SEM ~~Images~~ images at magnification of 10~~,~~000x: Clean ~~Membranes~~ membranes (1a- Surface), (2a- Cross-~~Sectional~~ sectional ~~Structure~~structure) and ~~Fouled~~ fouled ~~Membrane~~ membrane after ultrafiltration of 30 % CPO-~~Solvent~~ solvent mixture (1b-Surface), (2b-Cross-~~Sectional~~ sectional ~~Structure~~structure)

~~Figure~~ Fig. 6 displays the effect of feed temperature on the initial and final permeate flux.

Figure 6~~.~~ ~~The e~~Effect of feed temperature on the initial and final flux at a pressure of 1 bar and CPO concentration of 30 %~~.~~

~~Based on the figure, it is indicated that~~The figure suggests that the ~~increasing~~ increase in the mixture temperature from 29 to 35 °C ~~has~~ had an effect on the higher flux permeate. This was expected due to the decrease ~~of~~ in viscosity or the increase ~~of~~ in phospholipid diffusion on the membrane pores. However, a further temperature increase (from 40 to 45 °C) ~~leads~~ led to a decrease in flux, but the reduction ~~of~~ in viscosity ~~does not have an~~had no effect on the flux. This result is close to that of Kim *et al.*[41], confirming that the operating temperature of 40 °C was suitable for the degumming of soybean extract; above the temperature of 40 °C, the flux decreased. A decline in flux is predicted because of the fouling on the membrane surface as a result of solid denaturation or gelatinization, as well as insoluble salts precipitation at a high temperature[44].

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Phospholipid and FFA ~~Rejection~~rejection

Membrane selectivity is represented as rejection, indicating the membrane's ability to reject or remove a feed compound. Micelles are formed when phospholipids are dispersed in water. The mixture of phospholipids in a nonpolar solvent such as isopropanol formed reverse micelles having an average molecular weight of 20,000 Daltons (10–200 nm)[44]. Based on the pore size, UF rejects compounds having a molecular weight in the range of 300–500,000 Daltons. Hence, in the phospholipids-isopropanol system, phospholipids are expected to be retained in the retentate, and the permeate comprises the oil and isopropanol. In contrast to phospholipids, the MWs of FFAs and TAGs are similar. TAGs and FFAs have a molecular weight of 800 Da and 300 Da, respectively[9]. Compared to the UF pore size, the separation of FFAs is challenging due to the low selectivity, and it results in a low rejection value. Rejection of phospholipids and FFAs at various CPO concentrations ~~are~~ is displayed in Table 3.

Table 3 Rejection of ~~Phospholipid~~ phospholipid and ~~Fatty~~ fatty ~~Acid~~ acids at ~~Various~~ various CPO ~~Concentration~~ concentrations at a pressure of 1 bar and ~~Feed~~ feed ~~Temperature~~ temperature of 30 °C

The table shows that rejection of phospholipids is significantly higher than that of fatty acids. This is noticeable since the molecular weight of micelle phospholipids is considerably greater than that of FFAs. The phospholipids' rejection is found to be greater than 99 % at a CPO concentration of 30 %, and slightly reduced to nearly 93 % with the increase ~~of~~ in CPO concentration to 40 %. The reduction of phospholipid rejection becomes more obvious with the increase ~~of~~ in CPO concentration to 50 %. In addition, a similar trend is shown when the

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feed temperature is raised. The rejection of both phospholipids and FFAs declines at higher temperatures from 30 °C to 40 °C, as presented in Table 5.

Table 5 Rejection of ~~Phospholipid~~ phospholipid and ~~Fatty~~ fatty ~~Acid~~ acids at ~~Various~~ various ~~Feed~~ feed ~~Temperature~~ temperatures at a pressure of 1 bar and CPO ~~Concentration~~ concentration of 30 %

Blocking ~~Mechanism~~ mechanism by Hermia's ~~Model~~model

In this research, Hermia's model was applied in order to evaluate the blocking mechanism during UF of the CPO-isopropanol mixture at various feed CPO concentrations. The fouling mechanism represented by the blocking mechanism is identified by fitting the experimental data into Hermia's linearized equation [equations (4) to (7)]. The fitting of experimental data to the four-type Hermia model is shown in ~~Figure~~ Fig. 7, and the corresponding correlation coefficients (R^2) are listed in Table 4.

Figure 7 Fitting of experimental data (feed temperature: 30 °C, pressure: 1 bar) to Hermia's model: (a) complete blocking, (b) standard blocking, (c) intermediate blocking, and (d) cake/gel layer formation.

Table 4 R^2 values of the blocking mechanism based on Hermia's model.

According to the table, two dominant blocking mechanisms are found: standard blocking and intermediate blocking. At low concentrations of CPO (30 % and 40 %), the blocking mechanism is dominated by standard blocking. In contrast, at higher concentrations of CPO

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(50 % and 60 %), the intermediate blocking is the dominant mechanism. Standard blocking assumes that each solute is deposited into the internal pore wall. In intermediate blocking, it is proposed that every solute ~~stays~~ remains on the previously deposited solutes.

The proposed standard blocking and intermediate blocking mechanisms in UF of CPO-isopropanol are illustrated in ~~Figure~~ Fig. 8.

Figure 8. Schematic illustration of (a) intermediate blocking and (b) standard blocking mechanisms in UF of the CPO-isopropanol mixture.

According to ~~Figure~~ Fig. 8(a), the large particles that accumulated on the membrane surface and blocked the membrane pores were TAGs. The large particles that formed at a high concentration of CPO were first presumed to be phospholipid-isopropanol micelles because of their large size and potential to block the pores. However, this assumption is in contradiction with phospholipid rejection. If the large particles were an agglomeration of phospholipid micelles, then rejection at high CPO concentrations should be ~~larger~~greater. Hence, it can be assumed that, at high concentrations of CPO, not all phospholipids generate micelles with isopropanol. This confirms why phospholipid rejection at high concentrations of CPO was lower. Hence, the larger particles that accumulated on the membrane surface were predicted to be other oil compounds such as TAGs.

In addition, ~~Figure~~ Fig. 8(b) shows that, at low concentrations of CPO, the dominant fouling mechanism was standard blocking, representing small particles attached inside the membrane pore, and causing pore constriction (reduction ~~of~~ in pore size). The compound that was possibly blocking the membrane pores ~~is~~was fatty acid, since ~~the size of~~ fatty acids ~~is~~ are smaller than ~~of the~~ phospholipid-isopropanol micelles. At low concentrations of CPO, a sufficient amount of phospholipid-isopropanol micelles was formed, with pore constriction

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providing high rejection of phospholipids. On the other hand, small molecules such as fatty acids can enter the membrane pores.

Conclusions

Phospholipids separation and FFAs removal in CPO have been performed using a PES UF membrane. In general, lower fluxes were obtained with the increase ~~of~~ in CPO concentration. Raising the feed temperature from 30 °C to 40 °C resulted in a lower permeate flux, but further feed temperature increase to 45 °C decreased the permeate flux. The phospholipid rejection rate was in the range 93–99 %. However, the removal of fatty acids was unsuccessful. The decrease ~~of~~ in flux due to membrane fouling was evaluated on the basis of Hermia's model, confirming that there were two dominant mechanisms observed: standard blocking and intermediate blocking.

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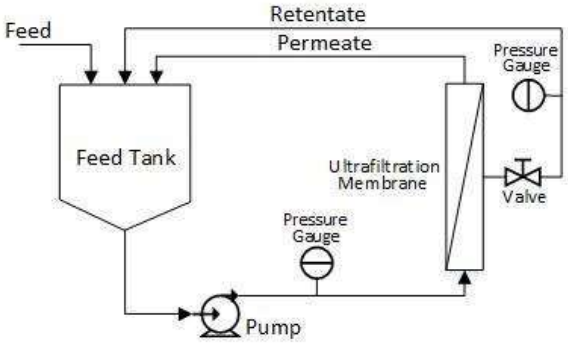

Figure 1. Schematic of Ultrafiltration ultrafiltration Cell cell with Total total Recycle recycle Operationoperation

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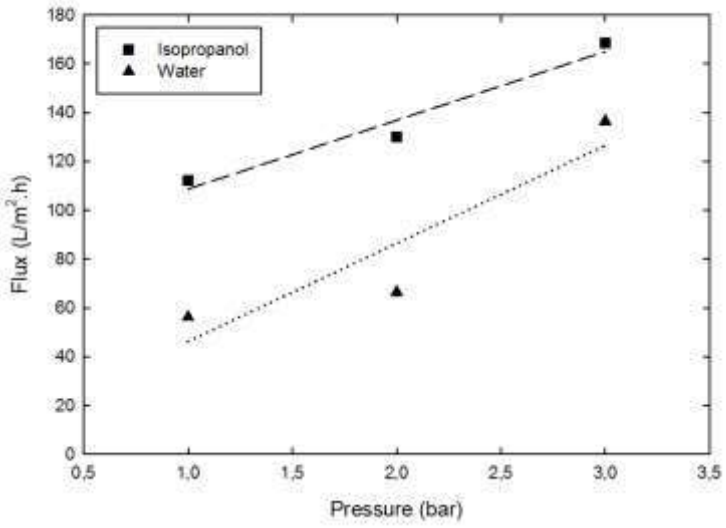

Figure 2. ~~Flux Profile profile of Isopropanol isopropanol and Water water at Pressure pressure of 1-3 bar~~

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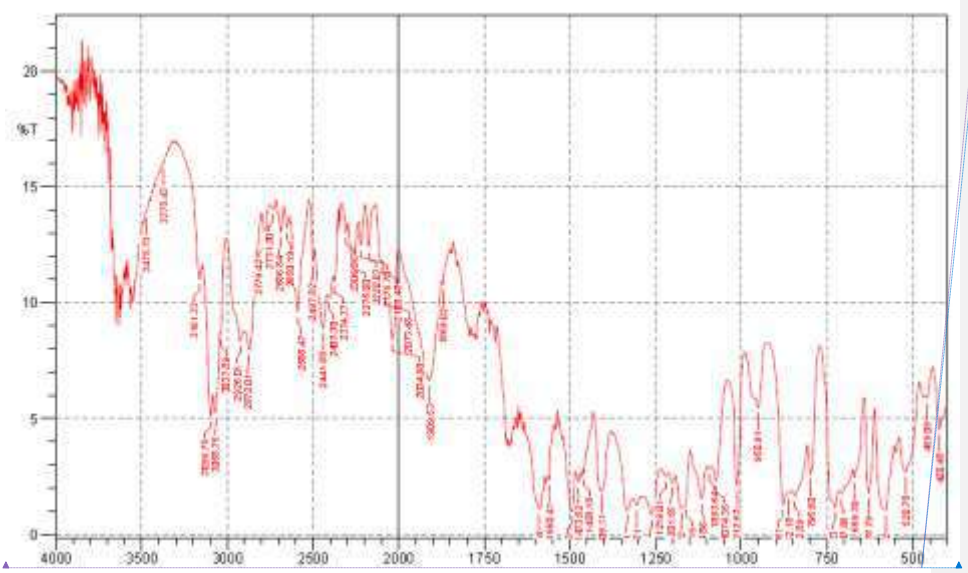

Figure 3. FT-IR Spectra of the Membrane membrane confirming Specific specific Functional functional Groupsgroups.

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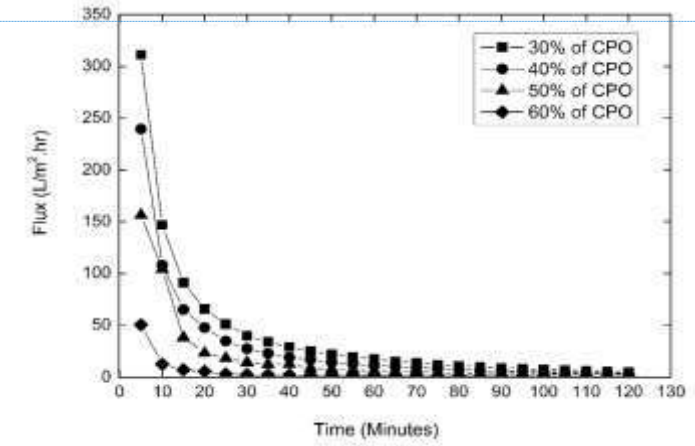

Figure 4 ~~Permeate flux profile in the UF of the CPO-isopropanol mixture at various concentrations of CPO (feed temperature: 29°C, transmembrane pressure: 1 bar).~~

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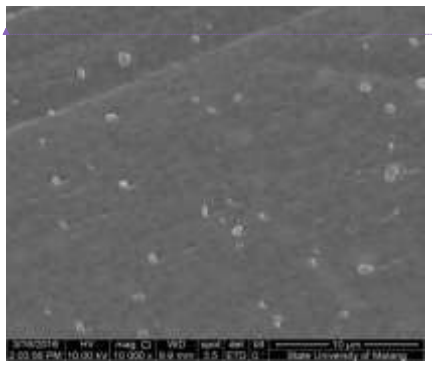

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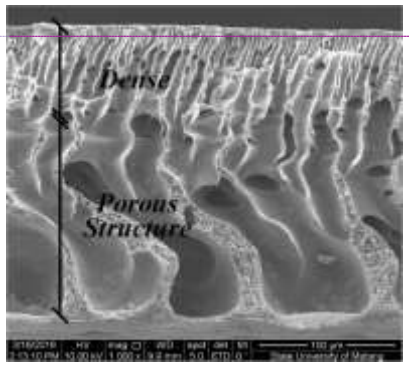

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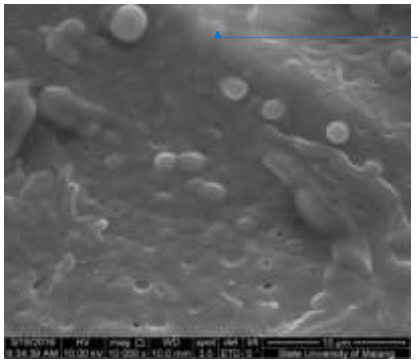

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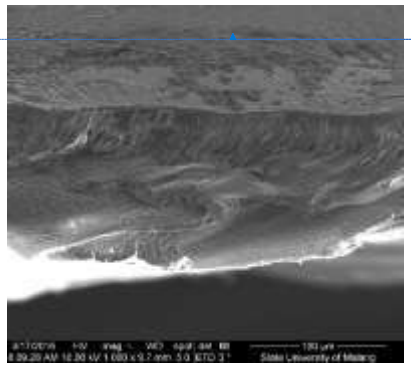

(2b)

Figure 5. Scanning Electron Microscope Images at magnification of 10.,000x: Clean clean Membranes membranes (1a- Surfacesurface), (2a- Crosscross Sectional sectional Structuresstructure) and Fouled fouled Membrane membrane after ultrafiltration of 30% CPO-Solvent solvent mixture(1b-Surfacesurface), (2b-Crosscross Sectional sectional Structuresructure)

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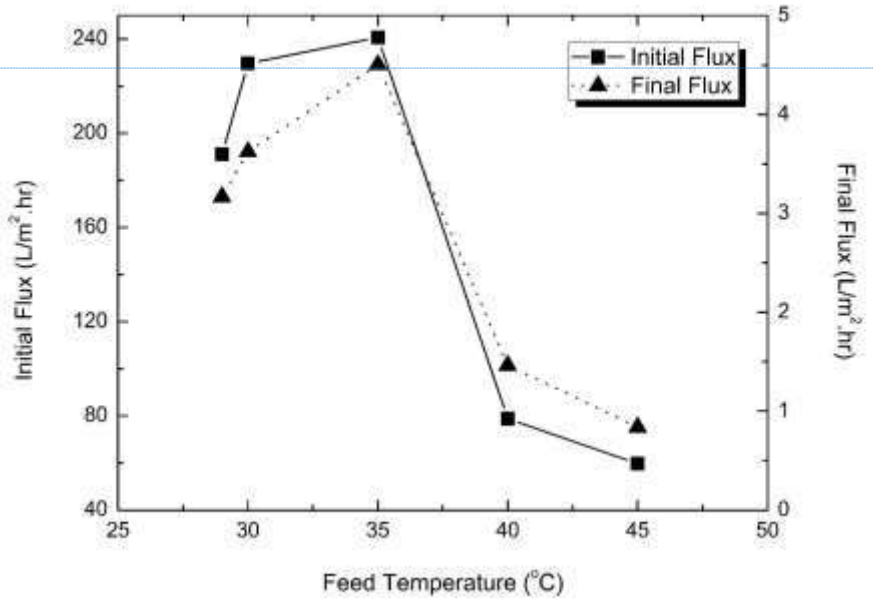

Figure 6~~. The eEffect of feed temperature on the initial flux (the first 10 minutes) and final flux at a pressure of 1 bar and CPO concentration of 30%~~.

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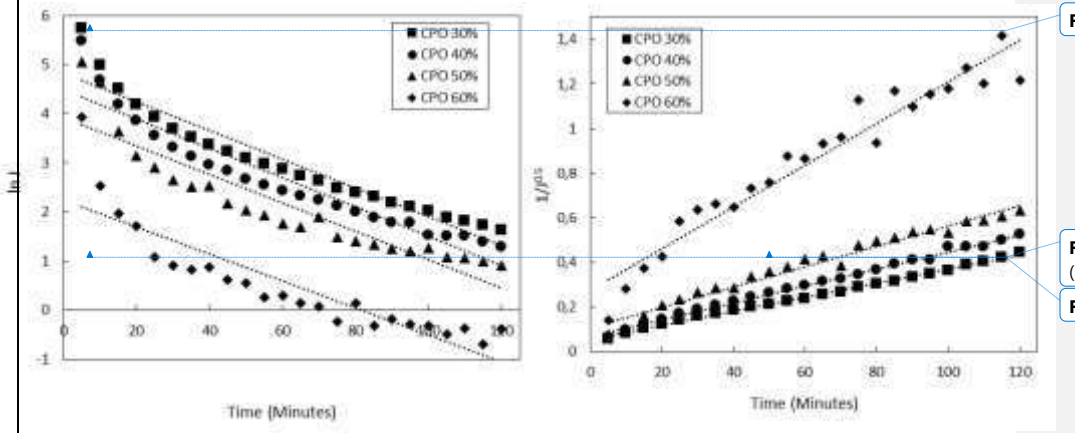
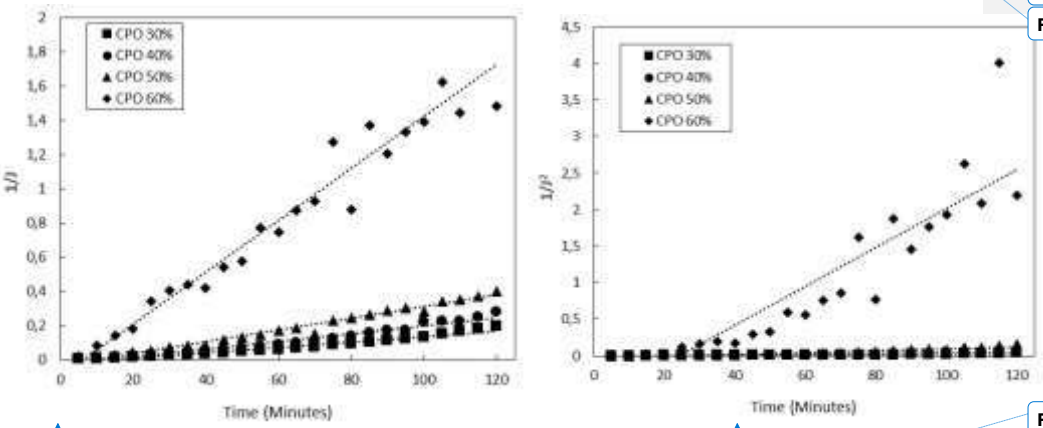


(a) (b)



(c) (d)

Figure 7 ~~Fitting of experimental data (feed temperature: 30°C, pressure: 1 bar) to Hermia's model: (a) complete blocking, (b) standard blocking, (c) intermediate blocking, and (d) cake/gel layer formation.~~

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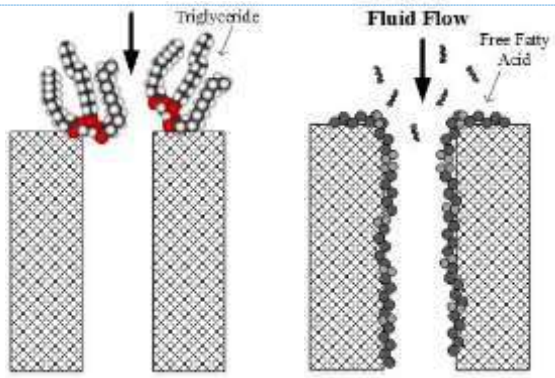

(a) (b)

Figure 8. Schematic illustration of (a) intermediate blocking and (b) standard blocking mechanisms in UF of the CPO-isopropanol mixture.

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Table 1 ~~Characteristic~~ Characteristics ~~of the Synthesized~~ synthesized ~~PES~~ ~~Membrane~~membrane

Parameter	
Rejection of 2 kDa PEG (R)	9.83 %
Rejection of 6 kDa PEG (R)	13.11 %
Rejection of 12 kDa PEG (R)	68.85 %
Rejection of 20 kDa PEG (R)	88.52 %
Rejection of 35 kDa PEG (R)	96.72 %
MWCO	25 kDa
Contact ~~Angle~~ angle (θ)	63.63°
Water ~~Permeability~~ permeability ($L_{h,w}$)	42.77 L ~~/m^2~~m^{-2} ~~-~~h^{-1}
Isopropanol ~~Permeability~~ permeability ($L_{h,Isp}$)	63.58 L ~~/m^2~~m^{-2} ~~-~~h^{-1}

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Table 2 ~~Specific Functional functional Groups groups as shown in FT-IR Spectra~~

Absorbance ~~p~~Peaks (cm^{-1})	Specific ~~f~~Functional ~~g~~Groups
1473.41 and 1560.62	Aromatic compounds (C-C stretching)
1219.01 and 1261.4	Aromatic ether compounds
849.2 and 862.2	Para substituted ~~Benzene~~benzene
1074.3, 1093.6 and 1114.8	-C-O-C- bonding
2872.01 and 2926.01	C-H asymmetric bonding
3375.43 and 3475.73	O-H alcohol bonding

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Table 3 ~~Rejection of Phospholipid~~ phospholipid ~~and Fatty~~ fatty ~~Acid~~ acid ~~at Various~~ various ~~CPO Concentration~~ concentrations ~~at pressure of 1 Bar~~ bar ~~and Feed~~ feed ~~Temperature~~ ~~temperature of 30°C~~

CPO c~~C~~oncentration	Phospholipid ~~Rejection~~ rejection (%)	Free ~~Fatty~~ fatty ~~Acid~~ acid ~~Rejection~~ rejection (%)
30 %	>99.21	16.13
40 %	92.93	12.93
50 %	37.52	9.09

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Table 4 ~~Rejection of Phospholipid phospholipid and Fatty fatty Acid acid at Various various Feed feed Temperature temperature at pressure of 1 bar and CPO Concentration concentration of 30 %~~

Feed c~~C~~oncentration	Phospholipid ~~Rejection~~ rejection (%)	Free ~~Fatty~~ fatty ~~Acid~~ acid ~~Rejection~~ rejection (%)
30 °C	>99.21	16.13
35 °C	86.60	7.17
40 °C	73.94	10.24

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Table 5 ~~R^2 values of the blocking mechanism based on Hermia's model.~~

	R^2			
	Complete ~~B~~blocking	**Intermediate ~~B~~blocking**	**Standard ~~B~~blocking**	**Cake/-Gel ~~F~~ormation**
CPO 30 %	0.9186	0.9512	0.9971	0.7755
CPO 40 %	0.9022	0.9618	0.9953	0.8053
CPO 50 %	0.8354	0.9811	0.9737	0.8769
CPO 60 %	0.7797	0.9432	0.9394	0.8052

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3 messages

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Ultrafiltration Membrane for Degumming of Crude Palm Oil-Isopropanol Mixture

N. Aryanti, [a,b,*] D. Hesti Wardhani,[a] and A. Nafiunisa[a]

[a] Department of Chemical Engineering, Diponegoro University

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Abstract

Ultrafiltration (UF) is a membrane technology that has been applied for crude palm oil (CPO) degumming. It is considered as an alternative for the conventional CPO degumming technology because of its lower energy consumption, no need for the addition of chemicals, and almost no loss of natural oil. In this research, we separated a CPO-isopropanol mixture via laboratory-made flat-sheet polyethersulfone (PES) UF. Flux profiles confirmed that the increase in the CPO concentration resulted in lower fluxes. However, increasing the temperature from 30 °C to 45 °C initially raised the flux, but it was further decreased when the feed temperature was raised from 40 °C to 45 °C. Using UF of the CPO-isopropanol mixture at crude oil concentrations of 30 % and 40 %, we were able to reject more than 99 % phospholipids and nearly 93 % phospholipids, respectively. However, the separation of free

fatty acids using this process was ineffective due to the small size of free fatty acids. Through the evaluation of the blocking mechanism in the Hermia model, it was proposed that the standard and intermediate blocking were the dominant mechanisms of filtration of CPO at a concentration of 30 and 40 %, and 50 and 60 %, respectively.

Keywords: crude palm oil, ultrafiltration, degumming

Introduction

Crude vegetable oil is a raw material used in the production of edible vegetable oil. Some examples of crude vegetable oils include crude palm oil (CPO), crude soybean oil, crude corn oil, crude coconut oil, crude sunflower oil, and crude castor oil[1]. Indonesia is one of the largest producers of CPO, followed by Malaysia, Thailand, Colombia, and Nigeria. Compared to other oilseed crops, palm oil produces more oil products[2]. Compared to other vegetable oils, it is preferable in many applications as it is substantially cost-effective[3]. CPO is widely used in various food and industrial products' manufacturing processes, such as ice cream, frying oils, shortening, cosmetics, toothpastes, and biodiesel[4]. CPO is extracted from the ripe mesocarp of the fruit of oil palm trees (*Elaeis guineensis*) through various methods, such as mechanical pressing followed by solid–liquid extraction[2].

The crude oil extracted from palm oil fruits is also rich in palmitic acid, β-carotene, and vitamin E, along with some undesirable compounds, such as phospholipids, free fatty acids (FFA), pigments, and proteins[5-6]. CPO is composed of a vast number of triglycerides (TAGs) and 6 % diglycerides (DAGs) that naturally consist of FFA[7]. Industrial regulations expect that high-quality oil must contain more than 95 % neutral TAGs and 0.5 % or less FFA; for some reason, the limit also decreases to less than 0.1 %[2,8].

Complex refining processes including degumming, neutralization, bleaching, and deodorization are performed to meet the desired requirement. The first step in the refining process is degumming, the function of which is to remove phospholipids and mucilaginous gums. Conventional degumming methods using water and acids possess numerous drawbacks due to the high energy consumption, oil loss, loss of nutrients, and requirement for large water quantities[9-10]. The membrane-based filtration process is a promising method for refining palm oil. Membrane filtration provides low energy consumption, without the addition of chemicals and with almost no loss of natural oil[11-12]. Previous studies on CPO refining using membrane filtration have been evaluated[3,13-17]. Arora *et al.*[3] evaluated the degumming of CPO and crude palm olein with a hexane solvent to remove phospholipids, Lovibond color value, carotenoids, major tocopherols and tocotrienols, and major fatty acids. Ong *et al.*[13] studied ultrafiltration (UF) of CPO degumming for the removal of phospholipids, carotenes, Lovibond color, FFAs, and volatile matter. Lai *et al.*[14] performed research on the deacidification of a model fatty system of CPO using various solvents and nanofiltration. On the other hand, polyvinylidene fluoride (PVDF) has been modified with polyvinyl alcohol (PVA) cross-linked as a UF membrane in the deacidification of CPO[15]. Deacidification of CPO using an aqueous NaOH solution in a hollow fiber membrane contactor was carried out by Purwasasmita *et al.*[16] Furthermore, a hexane solvent combined with a UF membrane has been applied to remove phospholipids from residual palm oil fibers[17].

Similar molecular weights of TAGs and phospholipids (about 900 and 700 Da, respectively) can interfere with their separation process using membrane technology. Phospholipids tend to form reverse micelles in nonpolar media like hexane or crude oil because of their amphiphilic properties[18,19]. This unique feature of phospholipid micelles increases their average molecular weight from 700 Da to around 20 kDa or even more[12], which is significantly different from TAGs. As a result, the UF membrane is able to separate the micelles from the

solvent–oil mixture, and the phospholipids are retained by the UF membrane[20]. However, the primary challenge in the use of membranes, especially UF, is the existence of a phenomenon called fouling. Fouling is an irreversible membrane change that is caused by specific physical and chemical interactions between the membrane and the various components present in the process flow. Membrane fouling is represented by a decrease in the permeate flux due to the effect of blocking on the surface as well as inside the membrane pores[21-22]. As it is essential to have a detailed investigation on fouling and there is no research investigating membrane fouling in the degumming of crude palm oil, this research is focused primarily on studying the flux decline as well as the fouling mechanism in the degumming of CPO by UF.

Fundamental studies on fouling mechanisms on UF membranes have been performed for coconut cream[23], organic compounds[24], whey models[25], and polyethylene glycol (PEG)[26]. In more detail, the fundamental studies focusing on the fouling mechanism in UF for oil degumming or separation of oil components are limited only for degumming corn oil[18-27], crude sunflower oil, and soybean oil[14]. This study placed emphasis on the fundamental and comprehensive analysis of the influence of oil solvents and micelles on fouling mechanism models. Specifically, this study addressed a novelty finding in the analysis of the fouling model and fouling mechanism in UF for degumming CPO.

Materials and methods

Materials

The main raw materials used in this experiment were CPO (Kalimantan, Indonesia) and isopropanol (Merck) as a solvent. The UF membrane was a laboratory-made polyethersulfone (PES) flat-sheet membrane. The PES material was Veradel PESU 3100P (Solvay, Singapore). The membrane was prepared via a non-solvent-induced phase separation method with PEG as the additive and N-methyl-2-pyrrolidone (NMP) as the solvent[28].

Membrane characterization

The membrane was characterized for its molecular weight cut-off (MWCO), contact angle, permeability, surface structure, and specific functional groups. The MWCO of the membrane represents the lowest molecular weight of solute (in Daltons), in which 90 % of the solute is rejected by the membrane. The MWCO value is evaluated to describe the pore size distribution and retention capabilities of membranes. In this work, solute rejection experiments were performed using PEG (from Sigma-Aldrich) as polymer solute with various molecular weights (MWs) of 2, 6, 12, 20 and 35kDa. The PEG solution was prepared in 1 wt.% concentration and then filtrated in a dead-end filtration cell. The permeate samples were analyzed using a digital handheld refractometer (PAL-91S, ATAGO, Japan). Plots of MW versus solute rejection were created, and then the MW corresponding to 90 % rejection was estimated as MWCO of the membrane. The hydrophobic/hydrophilic character of the membrane was determined by measuring the water-membrane contact angle (θ). The water-membrane contact angle values of the prepared membrane were measured using water contact angle meter (RACE contact angle meter, Japan) using deionized water as a probe liquid.

Membrane permeability was evaluated by determining the membrane flux of distilled water or isopropanol in the membrane module at various operating pressures (1–3 bar). The fluxes were calculated according to the sample volume (V), the sampling time (t), and the membrane surface area (A). The volumetric permeate flow rate (Q) was calculated by

$$Q = \frac{V}{t} \tag{1}$$

Further, the flux (J) was determined by:

$$J = \frac{1}{A} \cdot Q \tag{2}$$

The membrane's surface and the cross-sectional structure were characterized using scanning electron microscopy (SEM, FEI Type Inspect-S50). The specific functional groups of the membrane were determined using FTIR Spectroscopy (Prestige-21, Shimadzu, Japan).

Evaluation of UF Membrane performance for degumming of the CPO-isopropanol mixture

The UF performance was examined using laboratory-made cell filtration based on the total recycle model as illustrated in Fig. 1.

Figure 1 Schematic of ultrafiltration cell with total recycle operation

The cell filtration was equipped with a centrifugal pump (Kemflow, with nominal flow rate 1.0 LPM, maximum pump output of 7.58 bar, maximum inlet pressure of 4.14 bar) as the feed pump, gate valves, pressure gauge (JAKO, with maximum pressure of 10.34 bar) and a stainless steel ultrafiltration housing. The total recycle model involved returning the permeate and retentate flow back to the feed tank to maintain equivalent concentration during the process. All experimental runs were conducted at room temperature (29 ± 2 °C). Before starting the experiments, membranes were first compacted by filtering water through the membrane at a pressure of 1 bar for 60 min. For each run, a new circular membrane sheet with an effective area of 13.85 cm^2 was used.

A micellar solution was prepared by mixing CPO with isopropanol with ratios of CPO of 30 %, 40 %, 50 %, and 60 % weight of the solution. The filtration cell was operated at 1 bar for 120 min, and before returning it back to the feed tank, the permeate was collected every 5 min to determine the flux and concentration of phospholipids/fatty acids. The feed temperature

was varied—30 °C, 35 °C, 40 °C, and 45 °C—in order to investigate the effect of temperature on UF performance. The feed tank was equipped with a temperature regulator and a magnetic stirrer for homogenization of oil micelles. Membrane performance was evaluated in terms of permeate flux and phospholipid/FFA rejection. Permeate fluxes (*J*) were determined by weighing the volume of the permeate collected at 5-min intervals for 120 min and calculated using

$$J = \frac{W}{A \cdot t} \quad (3)$$

Where *W* represents the total weight of the permeate, *A* is the membrane area, and *t* is the time interval.

Rejection of phospholipids and FFAs was determined on the basis of the concentration of phospholipids/FFAs in the feed (C_f) and in the permeate (C_p). Rejection is calculated according to

$$R = \frac{C_f - C_p}{C_f} \quad (4)$$

Characterization of CPO and permeate

The specific characteristics of CPO and permeate included the phospholipid and FFA content. Phospholipids were expressed as total phosphorus and analyzed according to the AOAC Ca 12-55 method. Determination of FFA was performed via the acid-base titration method[14].

Blocking mechanism

The blocking mechanism of CPO-isopropanol UF was studied according to Hermia's model. This model has been previously applied for the evaluation of the fouling mechanism of

dye solution UF[28], konjac glucomannan separation[29], and UF of model dye wastewater[30]. Hermia's model describes the mechanism of membrane fouling on the basis of the blocking filtration law, consisting of complete pore blocking, standard pore blocking, and intermediate pore blocking and cake filtration. The blocking law filtration is expressed in terms of permeation time and filtration time, and was developed for dead-end filtration as shown in[31]:

$$\frac{\mathrm{d}^2 t}{\mathrm{d}V^2} = k\left(\frac{\mathrm{d}t}{\mathrm{d}V}\right)^n \tag{5}$$

where t is the filtration time, V is the permeate volume, k is a constant, and n is a value illustrating the different fouling mechanisms.

The values of n are described as follows: complete blocking with n = 2, intermediate blocking with n = 1, standard blocking with n = 1.5, and cake layer formation with n = 0. In the complete blocking model, it is assumed that each solute participated in blocking the entrance of the membrane pores completely. In intermediate blocking, it is assumed that every solute stays on the previously deposited solutes. Standard blocking considers the deposition of each solute on the internal pore wall. The cake layer formation occurs due to the accumulation of the solute on the membrane surface in a cake form[32]. Hermia's model was then linearized on the basis of the n value for each model by fitting equations (6) to (9) regarding the permeate flux versus time, as presented in the following.

For Complete Blocking (n = 2):

$$\ln J = \ln J_0 - k_c t \tag{6}$$

For Intermediate Blocking (n = 1):

$$\frac{1}{J} = \frac{1}{J_0} + k_i t \quad (7)$$

For Standard Blocking (n = 1.5):

$$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + k_s t \quad (8)$$

For Cake/Layer Formation (n = 0):

$$\frac{1}{J^2} = \frac{1}{J_0^2} + k_{cf} t \quad (9)$$

Here, k_c, k_i, k_s, and k_{cf} are constants for complete blocking, intermediate blocking, standard blocking, and cake layer formation, respectively.

Results and discussion

Membrane characteristics

Table 1 shows the characterization results of the synthesized membranes confirming PEG rejections, MWCO, contact angle, and permeabilities.

Table 1 Characteristics of the synthesized PES membrane

Details of the flux water and isopropanol flux profiles at various pressures for the UF membrane are presented in Fig. 2.

Figure 2 Flux profile of isopropanol and water at pressure of 1-3 bar

The figure shows an increase in water and isopropanol flux with the rise of pressure from 1 to 3 bar. According to the linearization regression ($y = mx$) of water and isopropanol flux in the figure, it was found that the water permeability and isopropanol permeability were 42.77 L m-

^{2} h^{-1} and 63.58 L m^{-2} h^{-1}, respectively. This is surprising, since water is predicted to have permeability higher than that of ethanol which is why water is the most polar solvent. This result is in contrast with de Meloet *et al.*[33], confirming that lower solvent polarity results in a decrease in permeation. In addition, the prepared PES membrane had the characteristics of hydrophilic membranes represented by the contact angle value as listed in Table 1, especially because of the addition of polyvinylpyrrolidone (PVP) and PEG[34]. With the hydrophilic characteristic of the PES membrane, water permeation is expected to be higher than that of isopropanol. Solvent characteristics, such as viscosity, surface tension, and polarity, as well as the molar volume of the solvent, have an effect on the transport of the solvent by the membrane[35-36]. According to the physicochemical characteristics of the solvent (viscosity and interfacial tension), the isopropanol flux should be below the water flux. However, this phenomenon was not observed in this research, presumably because there was a specific interaction between the membrane and the solvent. A similar result was observed by Araki *et al.*[37] The high permeability of isopropanol indicates that the conditioning process (immersing in isopropanol) created a less hydrophilic PES membrane. The alteration of the hydrophobic characteristic is caused by the transformation of the hydrophilic and hydrophobic sites of the membrane, resulting in the higher permeability of isopropanol. Water permeation is correlated to the hydrophilic characteristic (hydrogen bond formation) of the membrane. When an alcohol such as isopropanol is permeated, the hydrogen bond formation becomes less, contributing to a low water flux.

Specific functional groups

Specific functional groups of the membrane are shown in Fig. 3.

Figure 3 FT-IR Spectra of the membrane confirming specific functional groups

According to the figure, characteristics of the PES membrane are determined by peaks at 1492.9 and 1589.3 cm^{-1}. Moreover, the peaks of 1161.15 and 1172.7 cm^{-1} show a symmetric stretching sulfur SO_2. In more detail, Table 2 lists other specific functional groups of the membrane.

Table 2 Specific functional groups as shown in FT-IR spectra

Based on the table, the specific functional groups were matched with the chemical structure of main membrane materials. Beside the PES characteristic, the O-H bonding vibration, C-H asymmetric, C-C stretching in benzene ring and -C-O-C- bonding are representation of bonds in the polymer of PEG.

Permeate flux

The profile of the permeate flux showing flux versus time is presented in Fig. 4.

Figure 4 Permeate flux profile in the UF of the CPO-isopropanol mixture at various concentrations of CPO (feed temperature: 29 °C, transmembrane pressure: 1 bar)

The figure shows that there is a flux decline during the filtration of the solvent and CPO mixtures. A significant flux fall-off was observed during the first 5 min of filtration, followed by a flux reduction deceleration rate, and then finally the flux became steady. A three-step behavior was also perceived by Penha *et al.*[38] during the filtration of maracuja oil/*n*-hexane mixture. The initial flux decline is caused by a phenomenon called polarization concentration, whereas the following flux reduction is a result of membrane fouling. Comparable performances were reported for oil/hexane mixture permeation through the UF membrane using sunflower oil[39] as well as coconut oil, groundnut oil, mustard oil, sunflower oil, and rice bran oil [36-40]. In addition, it was reported that the flux reduction at the beginning of the

sunflower oil–*n*-hexane filtration was type of concentration polarization phenomenon and gel layer formation on the membrane surface[39]. Moreover, the flux drop at the end of the filtration was due to the deposition of a gel on the membrane surface[38,41,42]. The deposited layer is formed because of the phospholipids retained on the membrane surface and pores plugging[14,43].

Fig. 4 also confirms that the increase in oil concentration leads to a higher reduction in flux. This decrease takes place due to an increase in oil concentration, resulting in the increase in solution viscosity. With the rise of viscosity, a smaller flux is obtained since the permeability is influenced by the viscosity[35]. In addition, a lower flux is obtained as a result of polarized/gel layer formation. When the oil concentration is higher, the layer becomes larger and generates larger resistance to the flux permeation[33,36,41]. As elucidated by Kim *et al.*[41], convective solute transport to the membrane produces a sharp gradient of concentration inside the boundary layer. Because of diffusion, solute back-transport into the bulk takes place, and a close-packed arrangement of the solute is formed. As a consequence, no more solute can be accommodated, and the mobility of solutes is restricted.

Scanning electron microscopy images of the fouled membrane, as displayed in Fig. 5, confirm that a foulant layer on the membrane's surface is present.

Figure 5 SEM images at magnification of 10,000x: Clean membranes (1a- Surface), (2a-Cross-sectional structure) and fouled membrane after ultrafiltration of 30 % CPO-solvent mixture (1b-Surface), (2b-Cross-sectional structure)

Fig. 6 displays the effect of feed temperature on the initial and final permeate flux.

Figure 6 Effect of feed temperature on the initial and final flux at a pressure of 1 bar and CPO concentration of 30 %

The figure suggests that the increase in the mixture temperature from 29 to 35 °C had an effect on the higher flux permeate. This was expected due to the decrease in viscosity or the increase in phospholipid diffusion on the membrane pores. However, a further temperature increase (from 40 to 45 °C) led to a decrease in flux, but the reduction in viscosity had no effect on the flux. This result is close to that of Kim *et al.*[41], confirming that the operating temperature of 40 °C was suitable for the degumming of soybean extract; above the temperature of 40 °C, the flux decreased. A decline in flux is predicted because of the fouling on the membrane surface as a result of solid denaturation or gelatinization, as well as insoluble salts precipitation at a high temperature[44].

Phospholipid and FFA rejection

Membrane selectivity is represented as rejection, indicating the membrane's ability to reject or remove a feed compound. Micelles are formed when phospholipids are dispersed in water. The mixture of phospholipids in a nonpolar solvent such as isopropanol formed reverse micelles having an average molecular weight of 20,000 Daltons (10–200 nm)[44]. Based on the pore size, UF rejects compounds having a molecular weight in the range of 300–500,000 Daltons. Hence, in the phospholipids-isopropanol system, phospholipids are expected to be retained in the retentate, and the permeate comprises the oil and isopropanol. In contrast to phospholipids, the MWs of FFAs and TAGs are similar. TAGs and FFAs have a molecular weight of 800 Da and 300 Da, respectively[9]. Compared to the UF pore size, the separation of FFAs is challenging due to the low selectivity, and it results in a low rejection value. Rejection of phospholipids and FFAs at various CPO concentrations is displayed in Table 3.

Table 3 Rejection of phospholipid and fatty acids at various CPO concentrations at a pressure of 1 bar and feed temperature of 30 ºC

The table shows that rejection of phospholipids is significantly higher than that of fatty acids. This is noticeable since the molecular weight of micelle phospholipids is considerably greater than that of FFAs. The phospholipids' rejection is found to be greater than 99 % at a CPO concentration of 30 %, and slightly reduced to nearly 93 % with the increase in CPO concentration to 40 %. The reduction of phospholipid rejection becomes more obvious with the increase in CPO concentration to 50 %. In addition, a similar trend is shown when the feed temperature is raised. The rejection of both phospholipids and FFAs declines at higher temperatures from 30 °C to 40 °C, as presented in Table 4.

Table 4 Rejection of phospholipid and fatty acids at various feed temperatures at a pressure of 1 bar and CPO concentration of 30 %

Blocking mechanism by Hermia's model

In this research, Hermia's model was applied in order to evaluate the blocking mechanism during UF of the CPO-isopropanol mixture at various feed CPO concentrations. The fouling mechanism represented by the blocking mechanism is identified by fitting the experimental data into Hermia's linearized equation [equations (4) to (7)]. The fitting of experimental data to the four-type Hermia model is shown in Fig. 7, and the corresponding correlation coefficients (R^2) are listed in Table 5.

Figure 7 Fitting of experimental data (feed temperature: 30 °C, pressure: 1 bar) to Hermia's model: (a) complete blocking, (b) standard blocking, (c) intermediate blocking, and (d) cake/gel layer formation

Table 5 R^2 values of the blocking mechanism based on Hermia's model

According to the table, two dominant blocking mechanisms are found: standard blocking and intermediate blocking. At low concentrations of CPO (30 % and 40 %), the blocking mechanism is dominated by standard blocking. In contrast, at higher concentrations of CPO (50 % and 60 %), the intermediate blocking is the dominant mechanism. Standard blocking assumes that each solute is deposited into the internal pore wall. In intermediate blocking, it is proposed that every solute remains on the previously deposited solutes.

The proposed standard blocking and intermediate blocking mechanisms in UF of CPO-isopropanol are illustrated in Fig. 8.

Figure 8 Schematic illustration of (a) intermediate blocking and (b) standard blocking mechanisms in UF of the CPO-isopropanol mixture

According to Fig. 8(a), the large particles that accumulated on the membrane surface and blocked the membrane pores were TAGs. The large particles that formed at a high concentration of CPO were first presumed to be phospholipid-isopropanol micelles because of their large size and potential to block the pores. However, this assumption is in contradiction with phospholipid rejection. If the large particles were an agglomeration of phospholipid micelles, then rejection at high CPO concentrations should be greater. Hence, it can be assumed that, at high concentrations of CPO, not all phospholipids generate micelles with isopropanol. This confirms why phospholipid rejection at high concentrations of CPO was lower. Hence,

the larger particles that accumulated on the membrane surface were predicted to be other oil compounds such as TAGs.

In addition, Fig. 8(b) shows that, at low concentrations of CPO, the dominant fouling mechanism was standard blocking, representing small particles attached inside the membrane pore, and causing pore constriction (reduction in pore size). The compound that was possibly blocking the membrane pores was fatty acid, since fatty acids are smaller than phospholipid-isopropanol micelles. At low concentrations of CPO, a sufficient amount of phospholipid-isopropanol micelles was formed, with pore constriction providing high rejection of phospholipids. On the other hand, small molecules, such as fatty acids, can enter the membrane pores.

Conclusions

Phospholipids separation and FFAs removal in CPO have been performed using a PES UF membrane. In general, lower fluxes were obtained with the increase in CPO concentration. Raising the feed temperature from 30 °C to 40 °C resulted in a lower permeate flux, but further feed temperature increase to 45 °C decreased the permeate flux. The phospholipid rejection rate was in the range 93–99 %. However, the removal of fatty acids was unsuccessful. The decrease in flux due to membrane fouling was evaluated on the basis of Hermia's model, confirming that there were two dominant mechanisms observed: standard blocking and intermediate blocking.

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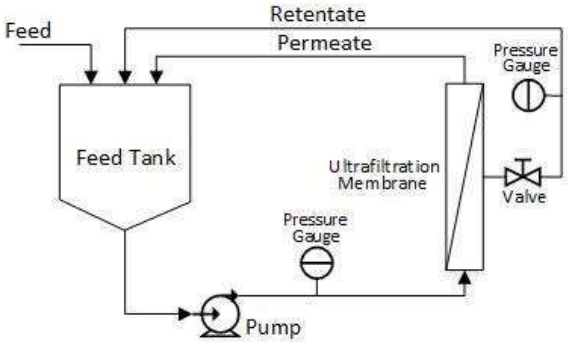
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Figure 1

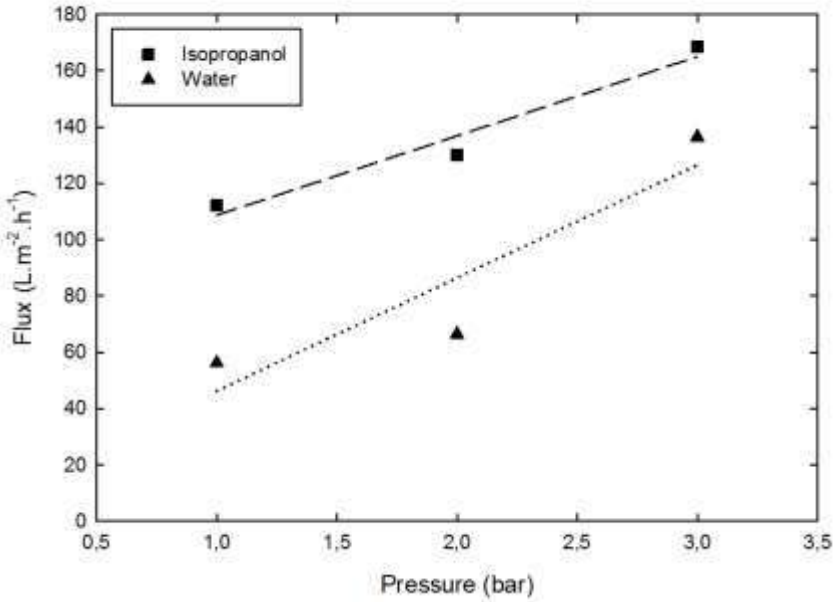

Figure 2

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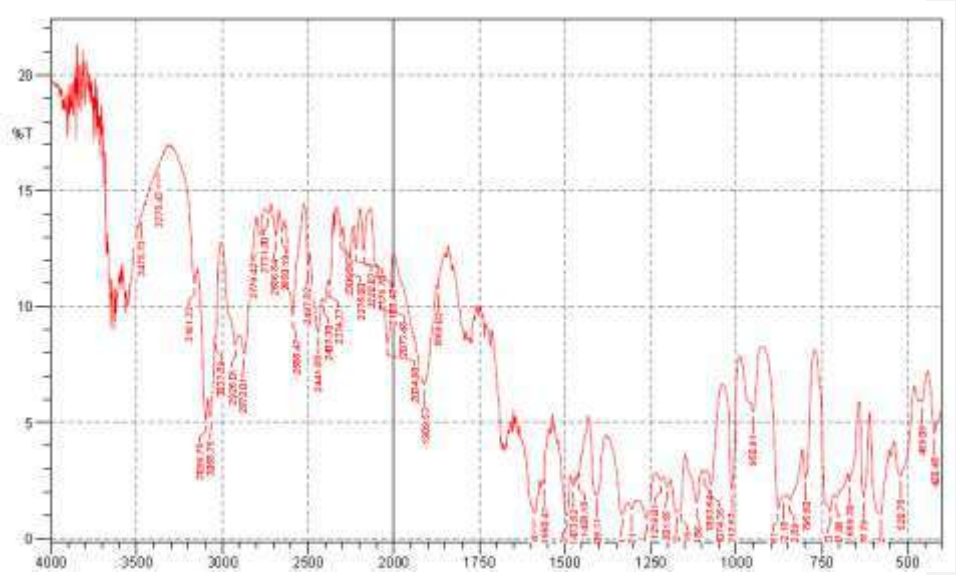
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Figure 3

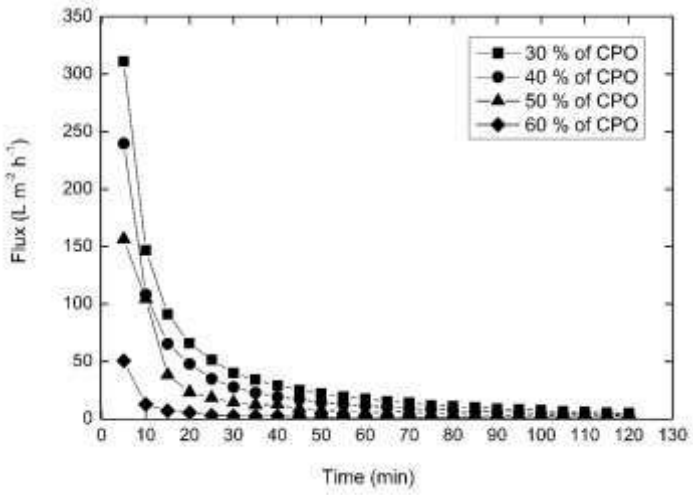

Figure 4

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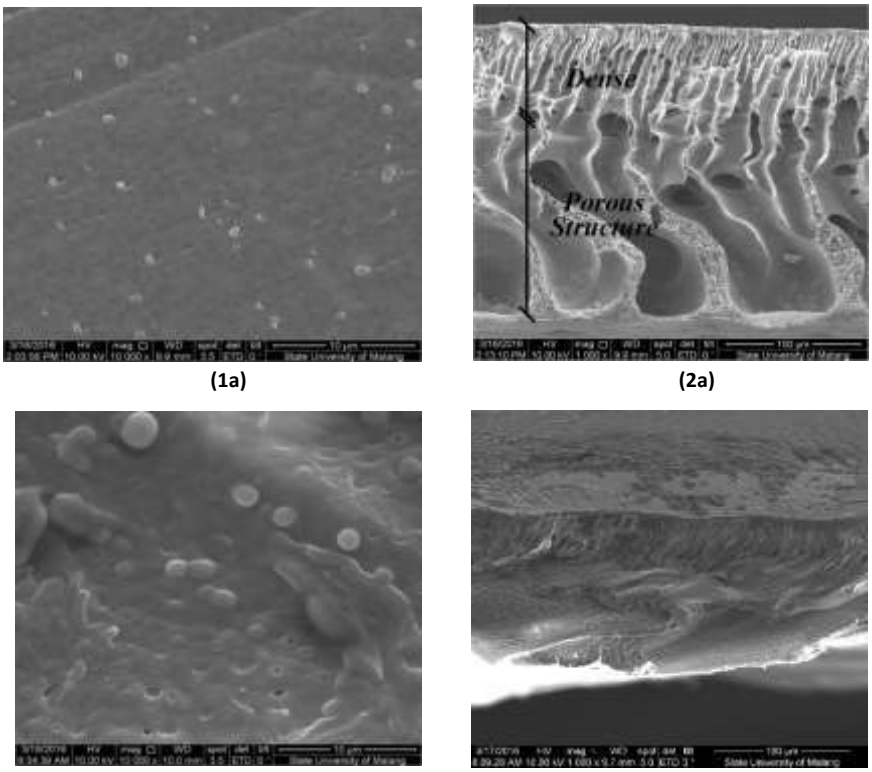

(1a) **(2a)**

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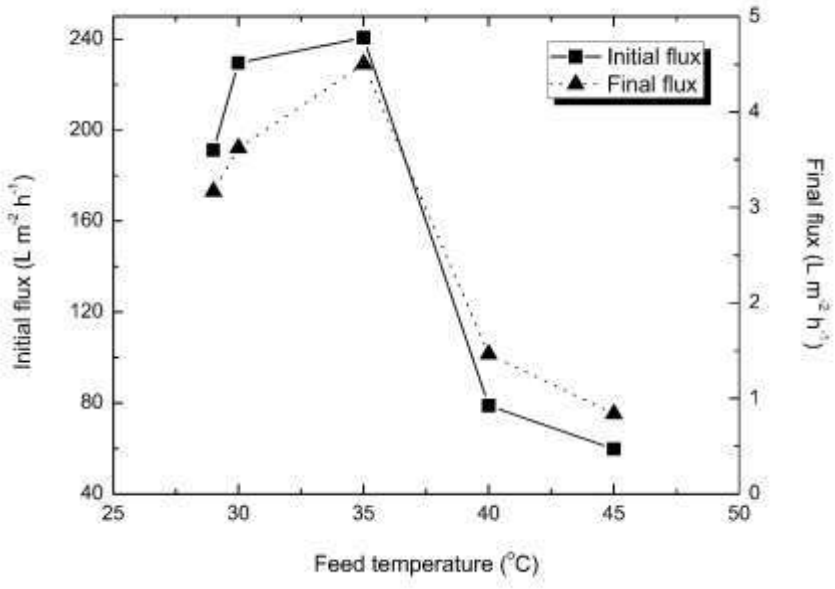
Figure 5



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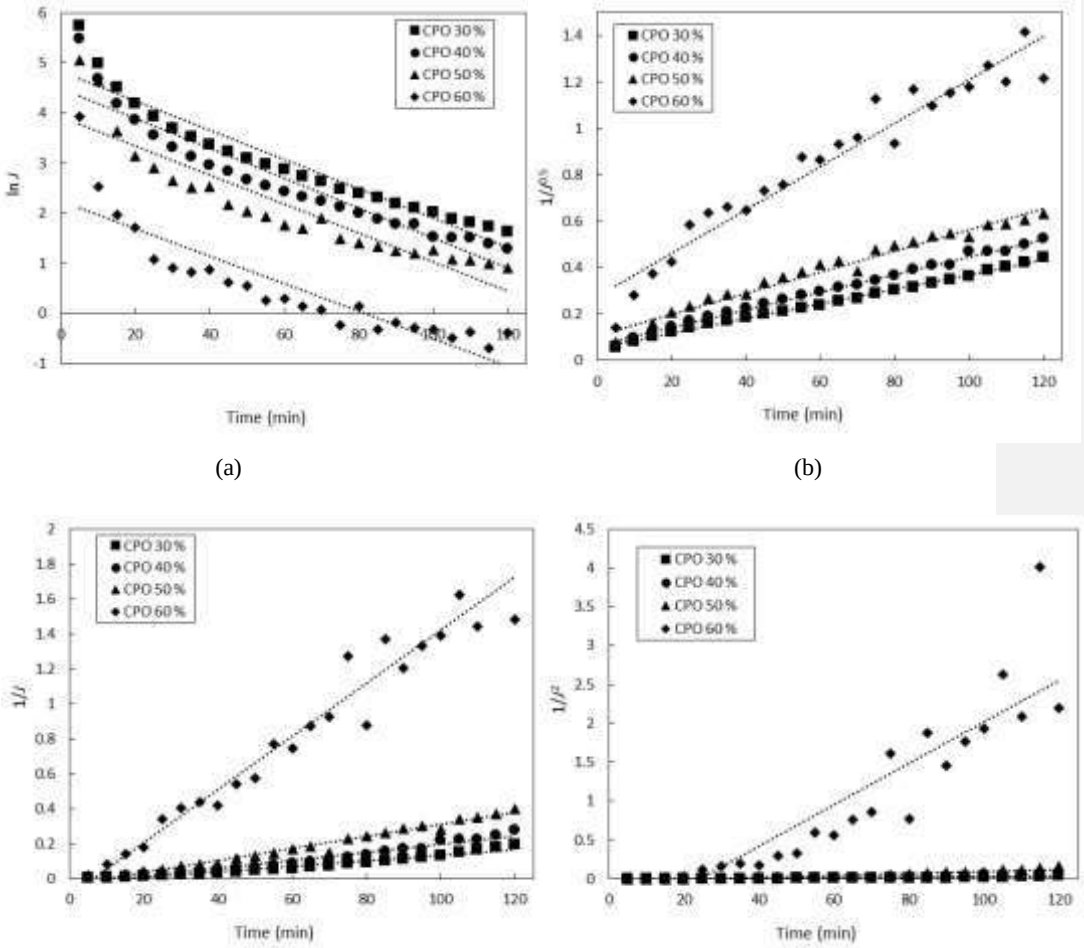

Figure 7

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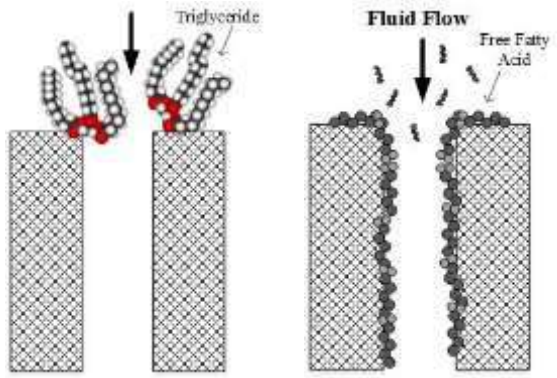

(a) (b)

Figure 8

Table 1

Parameter	
Rejection of 2 kDa PEG (R)	9.83 %
Rejection of 6 kDa PEG (R)	13.11 %
Rejection of 12 kDa PEG (R)	68.85 %
Rejection of 20 kDa PEG (R)	88.52 %
Rejection of 35 kDa PEG (R)	96.72 %
MWCO	25 kDa
Contact angle (θ)	63.63°
Water permeability ($L_{h,w}$)	42.77 L m^{-2} h^{-1}
Isopropanol permeability ($L_{h,Isp}$)	63.58 L m^{-2} h^{-1}

Table 2

Absorbance peaks (cm^{-1})	Specific functional groups
1473.41 and 1560.62	Aromatic compounds (C-C stretching)
1219.01 and 1261.4	Aromatic ether compounds
849.2 and 862.2	Para substituted benzene
1074.3, 1093.6 and 1114.8	-C-O-C- bonding
2872.01 and 2926.01	C-H asymmetric bonding
3375.43 and 3475.73	O-H alcohol bonding

Table 3

CPO concentration	Phospholipid rejection (%)	Free fatty acid rejection (%)
30 %	>99.21	16.13
40 %	92.93	12.93
50 %	37.52	9.09

Table 4

Feed concentration	Phospholipid rejection (%)	Free fatty acid rejection (%)
30 ˚C	>99.21	16.13
35 ˚C	86.60	7.17
40 ˚C	73.94	10.24

Table 5

	R^2			
	Complete blocking	**Intermediate blocking**	**Standard blocking**	**Cake/Gel formation**
CPO 30 %	0.9186	0.9512	0.9971	0.7755
CPO 40 %	0.9022	0.9618	0.9953	0.8053
CPO 50 %	0.8354	0.9811	0.9737	0.8769
CPO 60 %	0.7797	0.9432	0.9394	0.8052

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Ultrafiltration Membrane for Degumming of Crude Palm Oil-Isopropanol Mixture

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Ultrafiltration (UF) is a membrane technology that has been applied for crude palm oil (CPO) degumming. It is considered as an alternative for the conventional CPO degumming technology because of its lower energy consumption, no need for the addition of chemicals, and almost no loss of natural oil. In this research, we separated a CPO-isopropanol mixture via laboratory-made flat-sheet polyethersulfone (PES) UF. Flux profiles confirmed that the increase in the CPO concentration resulted in lower fluxes. However, increasing the temperature from 30 °C to 45 °C initially raised the flux, but it was further decreased when the feed temperature was raised from 40 °C to 45 °C. Using UF of the CPO-isopropanol mixture at crude oil concentrations of 30 % and 40 %, we were able to reject more than 99 % phospholipids and nearly 93 % phospholipids, respectively. However, the separation of free fatty acids using this process was ineffective due to the small size of free fatty acids. Through the evaluation of the blocking mechanism in the Hermia model, it was proposed that the standard and intermediate blocking were the dominant mechanisms of filtration of CPO at a concentration of 30 and 40 %, and 50 and 60 %, respectively.

Keywords:
crude palm oil, ultrafiltration, degumming

Introduction

Crude vegetable oil is a raw material used in the production of edible vegetable oil. Some examples of crude vegetable oils include crude palm oil (CPO), crude soybean oil, crude corn oil, crude coconut oil, crude sunflower oil, and crude castor oil[1]. Indonesia is one of the largest producers of CPO, followed by Malaysia, Thailand, Colombia, and Nigeria. Compared to other oilseed crops, palm oil produces more oil products[2]. Compared to other vegetable oils, it is preferable in many applications as it is substantially cost-effective[3]. CPO is widely used in various food and industrial products' manufacturing processes, such as ice cream, frying oils, shortening, cosmetics, toothpastes, and biodiesel[4]. CPO is extracted from the ripe mesocarp of the fruit of oil palm trees (*Elaeisguineensis*) through various methods, such as mechanical pressing followed by solid–liquid extraction[2].

The crude oil extracted from palm oil fruits is also rich in palmitic acid, β-carotene, and vitamin E, along with some undesirable compounds, such as phospholipids, free fatty acids (FFA), pigments, and proteins[5–6]. CPO is composed of a vast number of triglycerides (TAGs) and 6 % diglycerides (DAGs) that naturally consist of FFA[7]. Industrial regulations expect that high-quality oil must contain more than 95 % neutral TAGs and 0.5 % or less FFA; for some reason, the limit also decreases to less than 0.1 %[2,8].

Complex refining processes including degumming, neutralization, bleaching, and deodorization are performed to meet the desired requirement. The first step in the refining process is degumming, the function of which is to remove phospholipids and mucilaginous gums. Conventional degumming methods using water and acids possess numerous drawbacks due to the high energy consumption, oil loss, loss of nutrients, and requirement for large water quantities[9–10]. The membrane-based filtration process is a promising method for refining palm oil. Membrane filtration provides low energy consumption, without the addition of chemicals and with almost no loss of natural oil[11–12]. Previous studies on CPO refining using membrane filtration have been evaluated[3,13–17]. Arora *et al.*[3] evaluated the degumming of CPO and crude palm olein with a hexane solvent to remove phospholipids, Lovibond color value, carotenoids, major tocopherols and tocotrien-

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ols, and major fatty acids. Ong *et al.*[13] studied ultrafiltration (UF) of CPO degumming for the removal of phospholipids, carotenes, Lovibond color, FFAs, and volatile matter. Lai *et al.*[14] performed research on the deacidification of a model fatty system of CPO using various solvents and nanofiltration. On the other hand, polyvinylidene fluoride (PVDF) has been modified with polyvinyl alcohol (PVA) crosslinked as a UF membrane in the deacidification of CPO[15]. Deacidification of CPO using an aqueous NaOH solution in a hollow fiber membrane contactor was carried out by Purwasasmita*et al.*[16] Furthermore, a hexane solvent combined with a UF membrane has been applied to remove phospholipids from residual palm oil fibers[17].

Similar molecular weights of TAGs and phospholipids (about 900 and 700 Da, respectively) can interfere with their separation process using membrane technology. Phospholipids tend to form reverse micelles in nonpolar media like hexane or crude oil because of their amphiphilic properties[18,19]. This unique feature of phospholipid micelles increases their average molecular weight from 700 Da to around 20 kDa or even more[12], which is significantly different from TAGs. As a result, the UF membrane is able to separate the micelles from the solvent–oil mixture, and the phospholipids are retained by the UF membrane[20]. However, the primary challenge in the use of membranes, especially UF, is the existence of a phenomenon called fouling. Fouling is an irreversible membrane change that is caused by specific physical and chemical interactions between the membrane and the various components present in the process flow. Membrane fouling is represented by a decrease in the permeate flux due to the effect of blocking on the surface as well as inside the membrane pores[21–22]. As it is essential to have a detailed investigation on fouling and there is no research investigating membrane fouling in the degumming of crude palm oil, this research is focused primarily on studying the flux decline as well as the fouling mechanism in the degumming of CPO by UF.

Fundamental studies on fouling mechanisms on UF membranes have been performed for coconut cream[23], organic compounds[24], whey models[25], and polyethylene glycol (PEG)[26]. In more detail, the fundamental studies focusing on the fouling mechanism in UF for oil degumming or separation of oil components are limited only for degumming corn oil[18–27], crude sunflower oil, and soybean oil[14]. This study placed emphasis on the fundamental and comprehensive analysis of the influence of oil solvents and micelles on fouling mechanism models. Specifically, this study addressed a novelty finding in the analysis of the fouling model and fouling mechanism in UF for degumming CPO.

Materials and methods

Materials

The main raw materials used in this experiment were CPO (Kalimantan, Indonesia) and isopropanol (Merck) as a solvent. The UF membrane was a laboratory-made polyethersulfone (PES) flat-sheet membrane. The PES material was Veradel PESU 3100P (Solvay, Singapore). The membrane was prepared via a non-solvent-induced phase separation method with PEG as the additive and N-methyl-2-pyrrolidone (NMP) as the solvent[28].

Membrane characterization

The membrane was characterized for its molecular weight cut-off (MWCO), contact angle, permeability, surface structure, and specific functional groups. The MWCO of the membrane represents the lowest molecular weight of solute (in Daltons), in which 90 % of the solute is rejected by the membrane. The MWCO value is evaluated to describe the pore size distribution and retention capabilities of membranes. In this work, solute rejection experiments were performed using PEG (from Sigma-Aldrich) as polymer solute with various molecular weights (MWs) of 2, 6, 12, 20 and 35kDa. The PEG solution was prepared in 1 wt.% concentration and then filtrated in a dead-end filtration cell. The permeate samples were analyzed using a digital handheld refractometer (PAL-91S, ATAGO, Japan). Plots of MW versus solute rejection were created, and then the MW corresponding to 90 % rejection was estimated as MWCO of the membrane. The hydrophobic/hydrophilic character of the membrane was determined by measuring the water-membrane contact angle (q). The water-membrane contact angle values of the prepared membrane were measured using water contact angle meter (RACE contact angle meter, Japan) using deionized water as a probe liquid.

Membrane permeability was evaluated by determining the membrane flux of distilled water or isopropanol in the membrane module at various operating pressures (1–3 bar). The fluxes were calculated according to the sample volume (V), the sampling time (t), and the membrane surface area (A). The volumetric permeate flow rate (Q) was calculated by

$$Q = \frac{V}{t} \tag{1}$$

Further, the flux (J) was determined by:

$$J = \frac{1}{A} \cdot Q \tag{2}$$

The membrane's surface and the cross-sectional structure were characterized using scanning electron microscopy (SEM, FEI Type Inspect-S50). The specific functional groups of the membrane were determined using FTIR Spectroscopy (Prestige-21, Shimadzu, Japan).

Evaluation of UF membrane performance for degumming of the CPO-isopropanol mixture

The UF performance was examined using laboratory-made cell filtration based on the total recycle model as illustrated in Fig. 1.

The cell filtration was equipped with a centrifugal pump (Kemflow, with nominal flow rate 1.0 LPM, maximum pump output of 7.58 bar, maximum inlet pressure of 4.14 bar) as the feed pump, gate valves, pressure gauge (JAKO, with maximum pressure of 10.34 bar) and a stainless steel ultrafiltration housing. The total recycle model involved returning the permeate and retentate flow back to the feed tank to maintain equivalent concentration during the process. All experimental runs were conducted at room temperature (29 ± 2 °C). Before starting the experiments, membranes were first compacted by filtering water through the membrane at a pressure of 1 bar for 60 min. For each run, a new circular membrane sheet with an effective area of 13.85 cm^2 was used.

A micellar solution was prepared by mixing CPO with isopropanol with ratios of CPO of 30 %, 40 %, 50 %, and 60 % weight of the solution. The filtration cell was operated at 1 bar for 120 min, and before returning it back to the feed tank, the permeate was collected every 5 min to determine the flux and concentration of phospholipids/fatty acids. The feed temperature was varied –30 °C, 35 °C, 40 °C, and 45 °C – in order to investigate the effect of temperature on UF performance. The feed tank was equipped with a temperature regulator and a magnetic stirrer for homogenization of oil micelles. Membrane performance was evaluated in terms of permeate flux and phospholipid/FFA rejection. Permeate fluxes (J) were determined by weighing the volume of the permeate collected at 5-min intervals for 120 min and calculated using

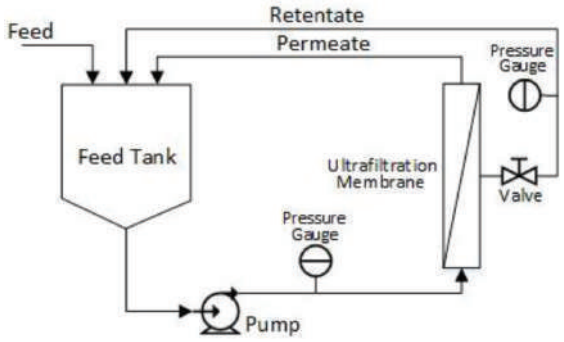


Fig. 1 – *Schematic of ultrafiltration cell with total recycle operation*

$$J = \frac{W}{A \cdot t} \tag{3}$$

Where W represents the total weight of the permeate, A is the membrane area, and t is the time interval.

Rejection of phospholipids and FFAs was determined on the basis of the concentration of phospholipids/FFAs in the feed (C_f) and in the permeate (C_p). Rejection is calculated according to

$$R = \frac{C_f - C_p}{C_f} \tag{4}$$

Characterization of CPO and permeate

The specific characteristics of CPO and permeate included the phospholipid and FFA content. Phospholipids were expressed as total phosphorus and analyzed according to the AOAC Ca 12–55 method. Determination of FFA was performed via the acid-base titration method[14].

Blocking mechanism

The blocking mechanism of CPO-isopropanol UF was studied according to Hermia's model. This model has been previously applied for the evaluation of the fouling mechanism of dye solution UF[28], konjacglucomannanseparation[29], and UF of model dye wastewater[30]. Hermia's model describes the mechanism of membrane fouling on the basis of the blocking filtration law, consisting of complete pore blocking, standard pore blocking, and intermediate pore blocking and cake filtration. The blocking law filtration is expressed in terms of permeation time and filtration time, and was developed for dead-end filtration as shown in[31]:

$$\frac{\mathrm{d}^2 t}{\mathrm{d}V^2} = k\left(\frac{\mathrm{d}t}{\mathrm{d}V}\right)^n \tag{5}$$

where t is the filtration time, V is the permeate volume, k is a constant, and n is a value illustrating the different fouling mechanisms.

The values of n are described as follows: complete blocking with n = 2, intermediate blocking with n = 1, standard blocking with n = 1.5, and cake layer formation with n = 0. In the complete blocking model, it is assumed that each solute participated in blocking the entrance of the membrane pores completely. In intermediate blocking, it is assumed that every solute stays on the previously deposited solutes. Standard blocking considers the deposition

of each solute on the internal pore wall. The cake layer formation occurs due to the accumulation of the solute on the membrane surface in a cake form[32]. Hermia's model was then linearized on the basis of the *n* value for each model by fitting equations (6) to (9) regarding the permeate flux versus time, as presented in the following.

For Complete Blocking (n = 2):

$$\ln J = \ln J_0 - k_c t \tag{6}$$

For Intermediate Blocking (n = 1):

$$\frac{1}{J} = \frac{1}{J_0} + k_i t \tag{7}$$

For Standard Blocking (n = 1.5):

$$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + k_s t \tag{8}$$

For Cake/Layer Formation (n = 0):

$$\frac{1}{J^2} = \frac{1}{J_0^2} + k_{cf} t \tag{9}$$

Here, k_c, k_i, k_s, and k_{cf} are constants for complete blocking, intermediate blocking, standard blocking, and cake layer formation, respectively.

Results and discussion

Membrane characteristics

Table 1 shows the characterization results of the synthesized membranes confirming PEG rejections, MWCO, contact angle, and permeabilities.

Details of the fluxwater and isopropanol flux profiles at various pressures for the UF membrane are presented in Fig. 2.

Table 1 – *Characteristics of the synthesized PES membrane*

Parameter	
Rejection of 2 kDa PEG (R)	9.83 %
Rejection of 6 kDa PEG (R)	13.11 %
Rejection of 12 kDa PEG (R)	68.85 %
Rejection of 20 kDa PEG (R)	88.52 %
Rejection of 35 kDa PEG (R)	96.72 %
MWCO	25 kDa
Contact angle (q)	63.63°
Water permeability ($L_{h,\,w}$)	42.77 L m^{-2} h^{-1}
Isopropanol permeability ($L_{h,\,Isp}$)	63.58 L m^{-2} h^{-1}

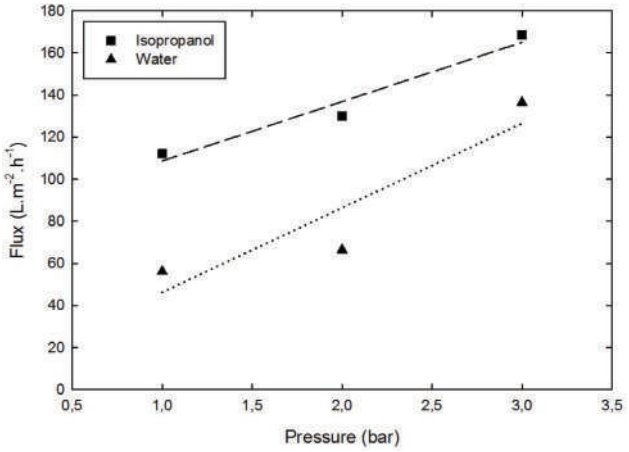


Fig. 2 – *Flux profile of isopropanol and water at pressure of 1–3 bar*

The figure shows an increase in water and isopropanol flux with the rise of pressure from 1 to 3 bar. According to the linearization regression (y = mx) of water and isopropanol flux in the figure, it was found that the water permeability and isopropanol permeability were 42.77 L m^{-2} h^{-1}and 63.58 L m^{-2} h^{-1}, respectively. This is surprising, since water is predicted to have permeability higher than that of ethanol which is whywater is the most polar solvent. This result is in contrast with de Meloet*et al.*[33], confirming that lower solvent polarity results in a decrease in permeation. In addition, the prepared PES membrane had the characteristics of hydrophilic membranes represented by the contact angle value as listed in Table 1, especially because of the addition of polyvinylpyrrolidone (PVP) and PEG[34]. With the hydrophilic characteristic of the PES membrane, water permeation is expected to be higher than that of isopropanol. Solvent characteristics, such as viscosity, surface tension, and polarity, as well as the molar volume of the solvent, have an effect on the transport of the solvent by the membrane[35–36]. According to the physicochemical characteristics of the solvent (viscosity and interfacial tension), the isopropanol flux should be below the water flux. However, this phenomenon was not observed in this research, presumably because there wasa specific interaction between the membrane and the solvent. A similar result was observed by Araki *et al.*[37] The high permeability of isopropanol indicates that the conditioning process (immersing in isopropanol) created a less hydrophilic PES membrane. The alteration of the hydrophobic characteristic is caused by the transformation of the hydrophilic and hydrophobic sites of the membrane, resulting in the higher permeability of isopropanol. Water permeation is correlated to the hydrophilic characteristic (hydrogen bond formation) of the membrane. When an alcohol such as isopropanol is permeated, the hydrogen bond formation becomes less, contributing to a low water flux.

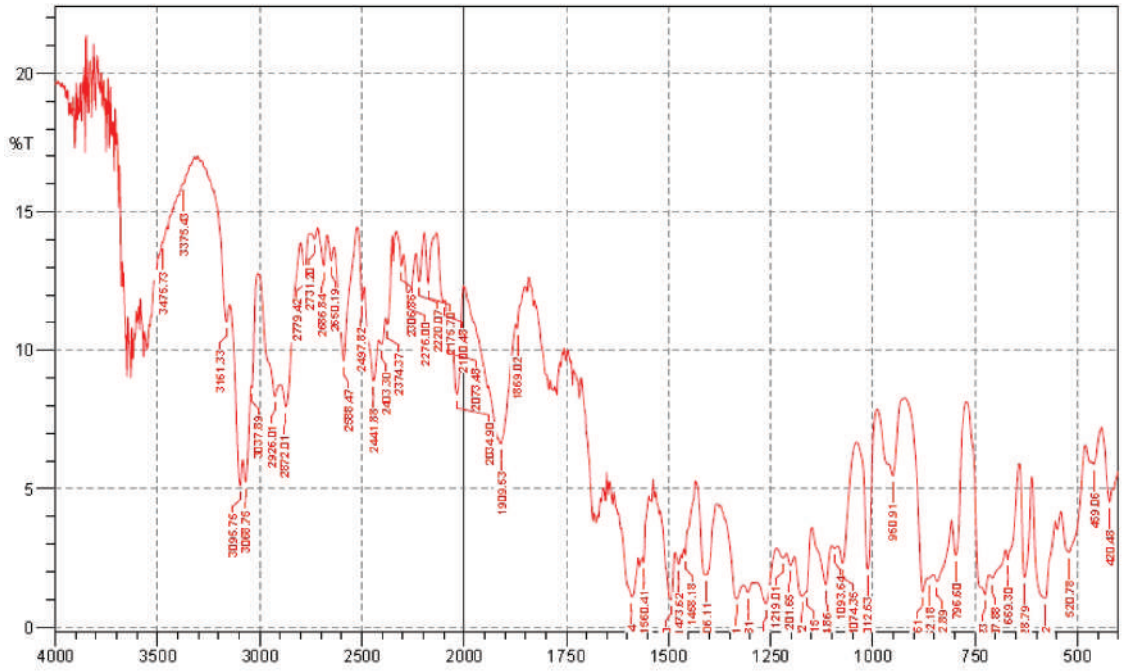


Fig. 3 – *FT-IR Spectra of the membrane confirming specific functional groups*

Specific functional groups

Specific functional groups of the membrane are shown in Fig. 3.

According to the figure, characteristics of the PES membrane are determined by peaks at 1492.9 and 1589.3 cm^{-1}. Moreover, the peaks of 1161.15 and 1172.7 cm^{-1} show a symmetric stretching sulfur SO_2. In more detail, Table 2 lists otherspecific functional groups of the membrane.

Based on the table, the specific functional groups were matched with the chemical structure of main membrane materials. Beside the PES characteristic, the O-H bonding vibration, C-H asymmetric, C-C stretching in benzene ring and -C-O-C- bonding arerepresentation of bonds in the polymer of PEG.

Permeate flux

The profile of the permeate flux showing flux versus time is presented in Fig. 4.

The figure shows that there is a flux decline during the filtration of the solvent and CPO mixtures. A significant flux fall-off was observed during the first 5 min of filtration, followed by a flux reduction deceleration rate, and then finally the flux became steady. A three-step behavior was also perceived by Penha *et al.*[38] during the filtration of maracuja oil/*n*-hexane mixture. The initial flux decline is caused by a phenomenon called polarization concentration, whereas the following flux reduction is a result of membrane fouling. Comparable performances were reported for oil/hexane mixture per-

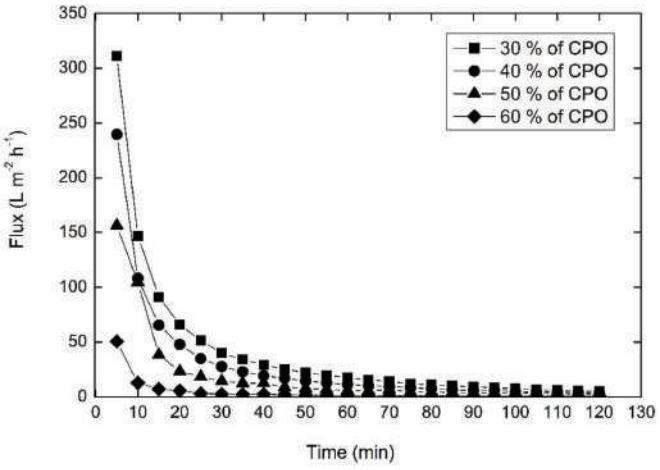
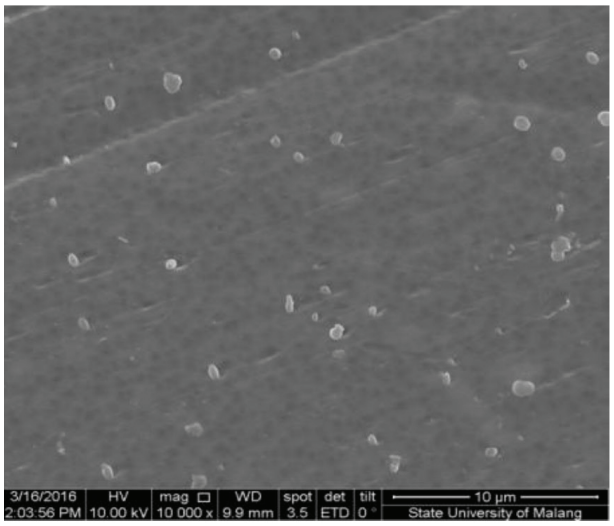


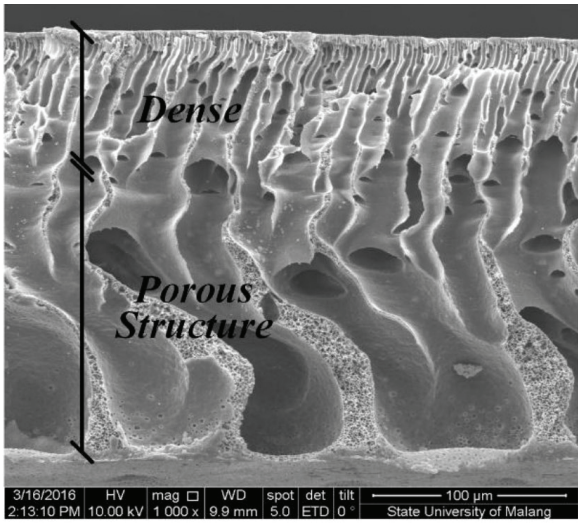
Fig. 4 – *Permeate flux profile in the UF of the CPO-isopropanol mixture at various concentrations of CPO (feed temperature: 29 °C, transmembrane pressure: 1 bar)*

Table 2 – *Specific functional groups as shown in FT-IR spectra*

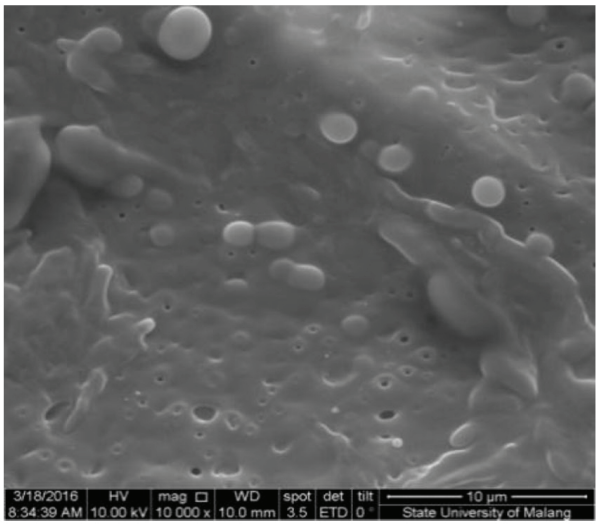
Absorbance peaks (cm^{-1})	Specific functional groups
1473.41 and 1560.62	Aromatic compounds (C-C stretching)
1219.01 and 1261.4	Aromatic ether compounds
849.2 and 862.2	Para substituted benzene
1074.3, 1093.6 and 1114.8	-C-O-C- bonding
2872.01 and 2926.01	C-H asymmetric bonding
3375.43 and 3475.73	O-H alcohol bonding



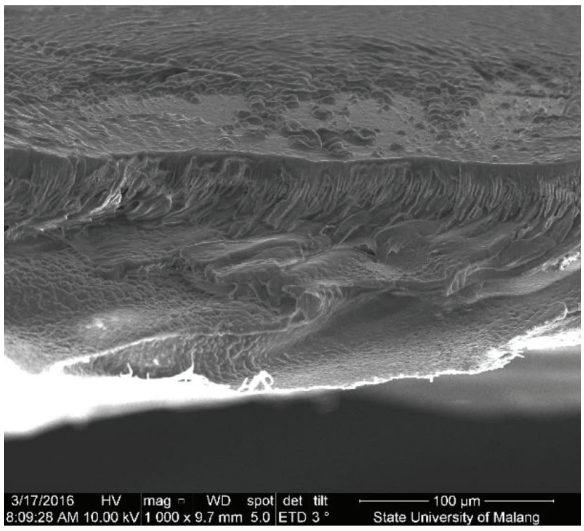
(1a)



(2a)



(1b)



(2b)

Fig. 5 – *SEM images at magnification of 10,000x: Clean membranes (1a- Surface), (2a- Cross-sectional structure) and fouled membrane after ultrafiltration of 30 % CPO-solvent mixture (1b-Surface), (2b-Cross-sectional structure)*

meation through the UF membrane using sunflower oil[39] as well as coconut oil, groundnut oil, mustard oil, sunflower oil, and rice bran oil [36–40]. In addition, it was reported that the flux reduction at the beginning of the sunflower oil–*n*-hexane filtration was type of concentration polarization phenomenon and gel layer formation on the membrane surface[39]. Moreover, the flux drop at the end of the filtration was due to the deposition of a gel on the membrane surface[38,41,42]. The deposited layer is formed because of the phospholipids retained on the membrane surface and pores plugging[14,43].

Fig. 4 also confirms that the increase in oil concentration leads to a higher reduction in flux. This decrease takes place due to an increase in oil concentration, resulting in the increase insolution viscosity. With the rise of viscosity, a smaller flux is obtained since the permeability is influenced by the viscosity[35]. In addition, a lower flux is obtained as a result of polarized/gel layer formation. When the oil concentration is higher, the layer becomes larger and generates larger resistance to the flux permeation[33,36,41]. As elucidated by Kim *et al.*[41], convective solute transport to the membrane produces a sharp gradient of concentration inside the boundary layer. Because of diffusion, solute back-transport into the bulk takes place, and a close-packed arrangement of the solute is formed. As a consequence, no more solute can be accommodated, and the mobility of solutes is restricted.

Scanning electron microscopy images of the fouled membrane, as displayed in Fig. 5, confirm that a foulant layer on the membrane's surface is present.

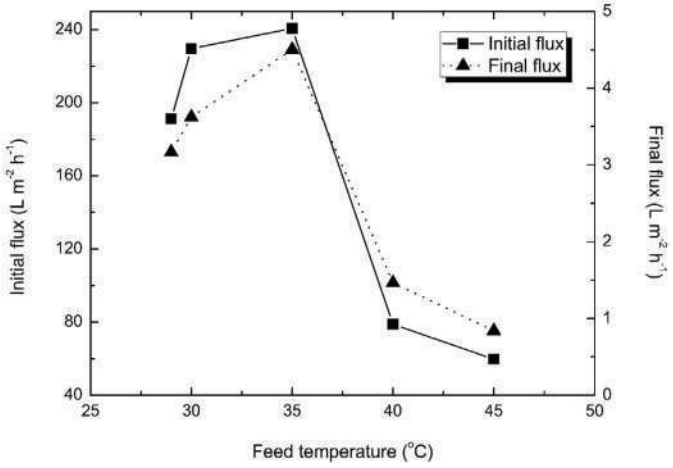


Fig. 6 – *Effect of feed temperature on the initial and final flux at a pressure of 1 bar and CPO concentration of 30 %*

Fig. 6 displays the effect of feed temperature on the initial and final permeate flux.

The figure suggests that theincreasein the mixture temperature from 29 to 35 °C hadan effect on the higher flux permeate. This was expected due to the decrease in viscosity or the increase in phospholipid diffusion on the membrane pores. However, a further temperature increase (from 40 to 45 °C) led to a decrease in flux, but the reduction in viscosity had no effect on the flux. This result is close to that of Kim *et al.*[41], confirming that the operating temperature of 40 °C was suitable for the degumming of soybean extract; above the temperature of 40 °C, the flux decreased. A decline in flux is predicted because of the fouling on the membrane surface as a result of solid denaturation or gelatinization, as well as insoluble salts precipitation at a high temperature[44].

Phospholipid and FFA rejection

Membrane selectivity is represented as rejection, indicating the membrane's ability to reject or remove a feed compound. Micelles are formed when phospholipids are dispersed in water. The mixture of phospholipids in a nonpolar solvent such as isopropanol formed reverse micelles having an average molecular weight of 20,000 Daltons (10–200 nm)[44]. Based on the pore size, UF rejects compounds having a molecular weight in the range of 300–500,000 Daltons. Hence, in the phospholipids-isopropanol system, phospholipids are expected to be retained in the retentate, and the permeate comprises the oil and isopropanol. In contrast to phospholipids, the MWs of FFAs and TAGs are similar. TAGs and FFAs have a molecular weight of 800 Da and 300 Da, respectively[9]. Compared to the UF pore size, the separation of FFAs is challenging due to the low selectivity, and it results in a low rejection value. Rejection of phospholipids and FFAs at various CPO concentrations is displayed in Table 3.

Table 3 – *Rejection of phospholipid and fatty acids at various CPO concentrations at a pressure of 1 bar and feed temperature of 30 °C*

CPO concentration	Phospholipid rejection (%)	Free fatty acid rejection (%)
30 %	>99.21	16.13
40 %	92.93	12.93
50 %	37.52	9.09

Table 4 – *Rejection of phospholipid and fatty acids at various feed temperatures atapressure of 1 bar and CPO concentration of 30 %*

Feed concentration	Phospholipid rejection (%)	Free fatty acid rejection (%)
30 °C	>99.21	16.13
35 °C	86.60	7.17
40 °C	73.94	10.24

The table shows that rejection of phospholipids is significantly higher than that of fatty acids. This is noticeable since the molecular weight of micelle phospholipids is considerably greater than that of FFAs. The phospholipids' rejection is found to be greater than 99 % at a CPO concentration of 30 %, and slightly reduced to nearly 93 % with the increase in CPO concentration to 40 %. The reduction of phospholipid rejection becomes more obvious with the increase in CPO concentration to 50 %. In addition, a similar trend is shown when the feed temperature is raised. The rejection of both phospholipids and FFAs declines at higher temperatures from 30 °C to 40 °C, as presented in Table 4.

Blocking mechanism by Hermia's model

In this research, Hermia's model was applied in order to evaluate the blocking mechanism during UF of the CPO-isopropanol mixture at various feed CPO concentrations. The fouling mechanism represented by the blocking mechanism is identified by fitting the experimental data into Hermia's linearized equation [equations (4) to (7)]. The fitting of experimental data to the four-type Hermia model is shown in Fig. 7, and the corresponding correlation coefficients (R^2) are listed in Table 5.

According to the table, two dominant blocking mechanisms are found: standard blocking and intermediate blocking. At low concentrations of CPO (30 % and 40 %), the blocking mechanism is dominated by standard blocking. In contrast, at higher concentrations of CPO (50 % and 60 %), the intermediate blocking is the dominant mechanism. Standard blocking assumes that each solute is deposited into the internal pore wall. In intermediate blocking,

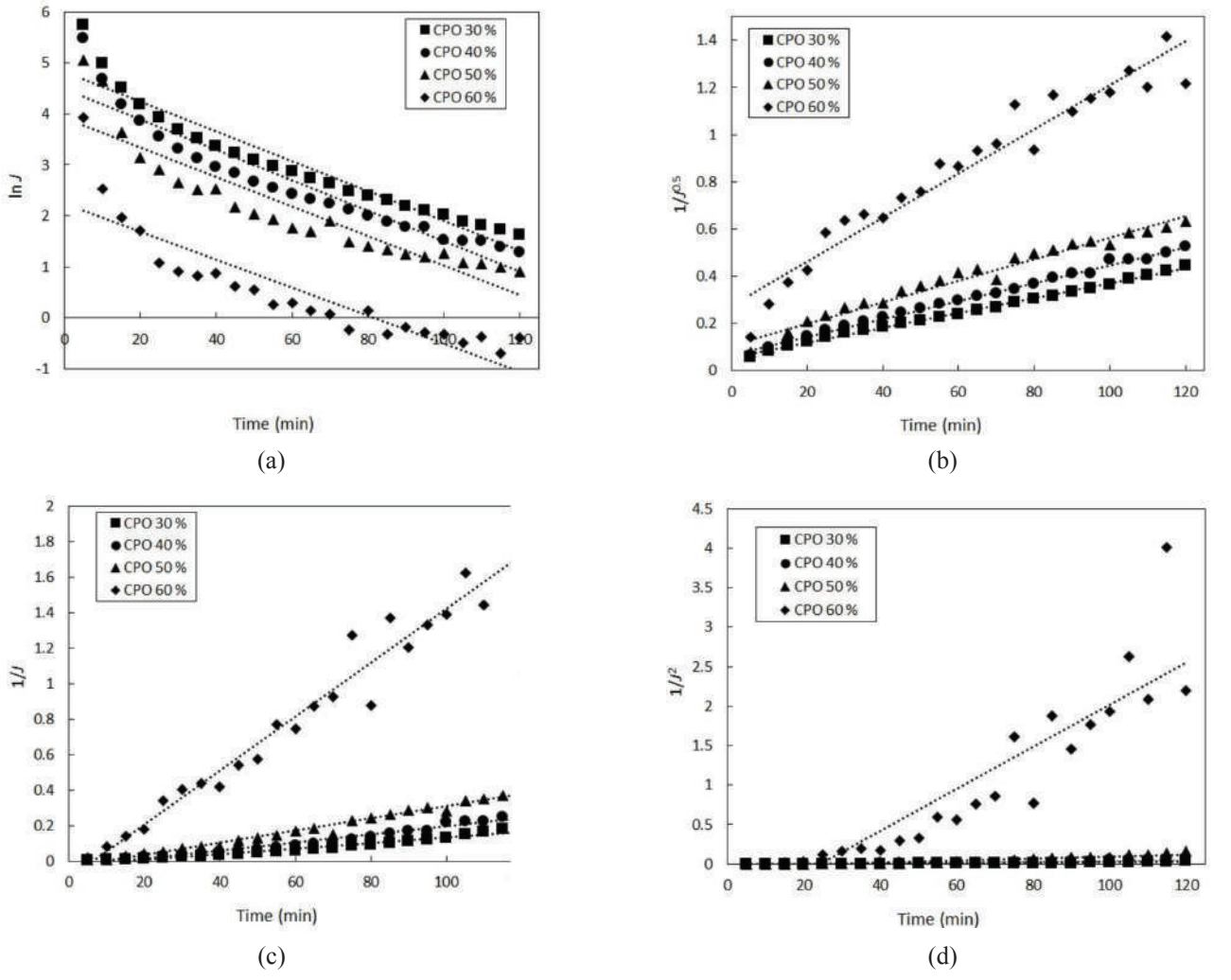


Fig. 7 – *Fitting of experimental data (feed temperature: 30 °C, pressure: 1 bar) to Hermia's model: (a) complete blocking, (b) standard blocking, (c) intermediate blocking, and (d) cake/gel layer formation*

Table 5 – *R^2 values of the blocking mechanism based on Hermia's model*

	R^2			
	Complete blocking	Intermediate blocking	Standard blocking	Cake/Gel formation
CPO 30 %	0.9186	0.9512	0.9971	0.7755
CPO 40 %	0.9022	0.9618	0.9953	0.8053
CPO 50 %	0.8354	0.9811	0.9737	0.8769
CPO 60 %	0.7797	0.9432	0.9394	0.8052

it is proposed that every solute remains on the previously deposited solutes.

The proposed standard blocking and intermediate blocking mechanisms in UF of CPO-isopropanol are illustrated in Fig. 8.

According to Fig. 8(a), the large particles that accumulated on the membrane surface and blocked the membrane pores were TAGs. The large particles that formed at a high concentration of CPO were first presumed to be phospholipid-isopropanol micelles because of their large size and potential to block the pores. However, this assumption is in contradiction with phospholipid rejection. If the large particles were an agglomeration of phospholipid micelles, then rejection at high CPO concentrations should be greater. Hence, it can be assumed that, at high concentrations of CPO, not all phospholipids generate micelles with isopropanol. This confirms why phospholipid rejection at high concentrations of CPO was lower. Hence, the larger particles that accumulated on the membrane surface were predicted to be other oil compounds such as TAGs.

In addition, Fig. 8(b) shows that, at low concentrations of CPO, the dominant fouling mechanism was standard blocking, representing small particles attached inside the membrane pore, and causing pore constriction (reductionin pore size). The compound that was possibly blocking the membrane pores was fattyacid, since fatty acids are smaller than phospholipid-isopropanol micelles. At

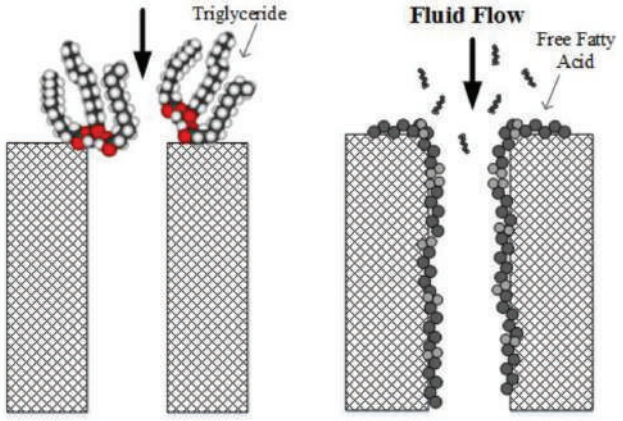


Fig. 8 – *Schematic illustration of (a) intermediate blocking and (b) standard blocking mechanisms in UF of the CPO-isopropanol mixture*

low concentrations of CPO, a sufficient amount of phospholipid-isopropanol micelles was formed, with pore constriction providing high rejection of phospholipids. On the other hand, small molecules, such as fatty acids, can enter the membrane pores.

Conclusions

Phospholipids separation and FFAs removal in CPO have been performed using a PES UF membrane. In general, lower fluxes were obtained with the increase in CPO concentration. Raising the feed temperature from 30 °C to 40 °C resulted in a lower permeate flux, but further feed temperature increase to 45 °C decreased the permeate flux. The phospholipid rejection rate was in the range 93–99 %. However, the removal of fatty acids was unsuccessful. The decrease in flux due to membrane fouling was evaluated on the basis of Hermia's model, confirming that there were two dominant mechanisms observed: standard blocking and intermediate blocking.

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corrected text.: Contact angle (θ)

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page: 303 line: 12 (1st column)

present text: otherspecific
corrected text.: other specific

---

page: 303 line: 19 (1st column)

present text: arerepresentation
corrected text.: are representation

---

page: 305 line: 8 (1st column)
present text: theincreasein
corrected text.: the increase in

---

page: 305 line: 9 (1st column)
present text: hadan
corrected text.: had an

---

page: 306 line: 1, Fig.7:

Position of Fig 7a should be lowered and hence not cover the line/border in the header

No right border of Fig 7.c

---

page: 306 line: 19 (2nd colum)

present text: reductionin

corrected text.: reduction in

---

page: 306 line: 21 (2nd colum)

present text: fattyacid

corrected text.: fatty acid

---

page: 307 line: 29 (Acknowledgements)

present text: *LuhAstla Diva Savitri and AsihMustika Sari*

corrected text.: Luh Astla Diva Savitri and Asih Mustika Sari

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page: 307 line: 31 (Acknowledgements)

present text: *NAacknowledges*

corrected text.: NA acknowledges

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page: 307 line: 35 (Acknowledgements)

present text: *The research was funded by the Fundamental Research Grant in 2017.*

corrected text.: The research was funded by the Fundamental Research Grant.

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page: 307 line: 27 (2nd column, Referrence no 8)

present text: FoodTechnology

corrected text.: Food Technology

---

page: 308 line: 44 (Reference no 27)

present text: Wibisono, Y., Nugroho, W. A., Chung, T.-W.

corrected text (in Italic).: *Wibisono, Y., Nugroho, W. A., Chung, T.-W.*

---

page: 308 line: 46 (Reference no 27)

present text : 9

corrected text : **9**

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page: 308 line: 48, Reference no 28

present text: Aryanti, N., Sandria, F. K. I., Putriadi, R. H., Wardhani, D. H.

corrected text (in Italic).: *Aryanti, N., Sandria, F. K. I., Putriadi, R. H., Wardhani, D. H.*

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page: 308 line: 51, Reference no 28

present text : 21(3)

corrected text: **21(3)**

---

page: 308 line: 53, Reference no 29

present text: Aryanti, N., Wardhani, D. H., Supandi, S.

corrected text (in Italic).: *Aryanti, N., Wardhani, D. H., Supandi, S.*

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page: 308 line: 56, Reference no 29

present text : 17(2)

corrected text: **17(2)**

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page: 308 line: 57, Reference no 30

present text: Aryanti, N., Sandria, F. K. I., Wardhani, D. H.

corrected text.(in Italic): *Aryanti, N., Sandria, F. K. I., Wardhani, D. H.*

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page: 308 line: 60, Reference no 30

present text : 23

corrected text: **23**

---

page: 308 line: 62, Reference no 31

present text: Hermia, J.

corrected text.(in Italic): *Hermia, J.*

---

page: 308 line: 62, Reference no 31

present text : 160

corrected text: **160**

Tamara
[Quoted text hidden]

---

tamara.jurina@pbf.hr <tamara.jurina@pbf.hr> Wed, Sep 26, 2018 at 1:47 PM
To: Nita Aryanti <nita.aryanti@che.undip.ac.id>

Dear Nita,

I have a question regarding Table 4: In the column "Feed concentration" you are mentioning temperatures (30, 35, 40 oC). Unit for concentration is not Degree of Celsius. Maybe you will need to rename column (perhaps "Temperature"). You were following phospholipid rejection and Free fatty acid rejection at one concentration (CPO concentration of 30 %) but at three different temperatures.
This column is a little bit confusing.

Please respond ASAP.
Thank you very much in advance.
Sincerely,

Tamara Jurina
[Quoted text hidden]

Nita Aryanti <nita.aryanti@che.undip.ac.id> Wed, Sep 26, 2018 at 7:16 PM
To: tamara.jurina@pbf.hr

Dear Tamara,
Thank you for the correction..
Yes. You are right..The first column in Table 4 should be "Feed temperature" or just "Temperature" not Feed concentration.
I also found that there was a typo on the title of Table 4. It was written atapressure..it should be changed as "at a pressure"
And also do you think that it will be better if "Feed concentration" is written on the top row of first column and remove border left border on Table 5, so the visual representation of the table is similar with others.

Many thanks.

Regards,
Nita
[Quoted text hidden]

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tamara.jurina@pbf.hr <tamara.jurina@pbf.hr> Thu, Sep 27, 2018 at 7:00 PM
To: Nita Aryanti <nita.aryanti@che.undip.ac.id>

Dear Nita,

I have done corrections regarding Table 4: Instead of Feed concentration I put Temperature and separated atapressure.

Regarding Table 5, I added Feed concentration as a "name" of the first row snd deleted border on the right side of the table (in the "uuper" part where R2 is written).
It seems to me now that Table 5 is similar with other.
Sincerely,

Tamara
[Quoted text hidden]

Nita Aryanti <nita.aryanti@che.undip.ac.id> Fri, Sep 28, 2018 at 10:50 AM
To: tamara.jurina@pbf.hr

Dear Tamara,

Many thanks for the correction.

Regards,
Nita

Nita Aryanti, Ph.D.
Department of Chemical Engineering, Diponegoro University
Kampus UNDIP Tembalang, Semarang, Indonesia
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AUN Accreditated

[Quoted text hidden]