Evaluation of Ultrafiltration Performance for Phospholipid Separation

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Abstract. Ultrafiltration membrane for degumming of crude palm oil has been applied as an alternative method since the membrane process required less procedure than the conventional degumming. This research focused on the examination of ultrafiltration performance for phospholipid separation from model crude palm oil degumming. Specifically, profile flux and rejection, as well as blocking mechanism, were investigated. Feed consisting of Refined Crude Palm Oil – Isopropanol – Lecithin mixtures were represented as crude palm oil degumming. Lecithin was denoted a phospholipid component, and the concentrations of lecithin in feed were varied to 0.1%, 0.2%, and 0.3%. The concentration of phospholipid was determined as phosphor content. At the concentration of lecithin in feed representing phospholipid concentration of 8.45 mg/kg, 8.45 mg/kg, 24.87 mg/kg and 57.58 mg/kg, respectively. Flux profiles confirmed that there was a flux decline during filtration. In addition, the lecithin concentrations do not significantly effect on further flux decline. Rejection characteristic and phospholipid concentration in the permeate showed that the phospholipid rejections by ultrafiltration were in the range of 23 - 79.5% representing permeate’s phospholipid concentration of 1.73 - 44.25 mg/kg. Evaluation of fouling mechanism by Hermia’s blocking model confirmed that the standard blocking is the dominant mechanism in the ultrafiltration of lecithin mixture.

1. Introduction
Application of membrane technology for edible oil refining process has been performed and is able to eliminate undesired components [1-4]. Ultrafiltration combined with solvents such as n-hexane has been known as the widest application degumming technology based on membrane method [5-8]. Phospholipid separation from edible oil by ultrafiltration membrane can be performed by one stage of the process through the separation of phospholipid and solvent micelle. The phospholipid forms a micelle having a molecular weight about 20,000 Da and a molecular size approximately of 20-200 nm. The ultrafiltration membrane separates the micelle from the solvent-oil mixture, and the phospholipid is retained by the ultrafiltration membrane [9]. However, the main challenge in the application of membranes especially ultrafiltration is the phenomena called fouling. Fouling is an irreversible membrane change caused by specific physical and / or chemical interactions between the membrane and the various components present in the process flow. Membrane fouling can be identified by the permeate flux decreased due to the effect of blocking on the surface as well as inside the membrane pore [10].
Fundamental studies of fouling mechanisms on the ultrafiltration membranes have been performed, for example for ultrafiltration of coconut cream [11], organic compounds [12], whey models [13] and...
Polyethylene Glycol [14]. Study of fouling mechanism on ultrafiltration for oil degumming or separation of oil components are limited only for degumming of crude sunflower and soybean oil [6] and POME [10].

Separation of phospholipid and triacylglycerol could not be performed based on different sizes because they have almost similar size (900 Da). However, due to a specific characteristic of phospholipid as an amphiphilic molecule forming a micelle with a solvent, then it is possible to be separated by the ultrafiltration membrane. The oil components (fatty acids and phospholipids) and the solvents in the degumming process have complex effect in the formation of fouling. Fouling can be formed by fatty acid components of the oil structure and phospholipids. In addition, the micelle in the solvent-oil system has a specific effect on the formation of fouling. The micelles have an affinity with other polar components and the wetting properties (hydrophilicity and hydrophobicity) of the membrane. Furthermore, the formed micelle is also capable of binding other impurities and contributes to the formation of the membrane fouling. The phospholipid amphiphilic molecule can be strongly adsorbed on the membrane and allows changes in the fouling properties of reversible fouling to irreversible fouling. As a consequence, the solvent-oil ultrafiltration phenomenon is complex and have specific properties. This due to the characteristic of separation is determined not only by the particle size of phospholipids and fatty acids alone. Therefore, the analysis of the fouling mechanism in the ultrafiltration membrane for degumming crude palm oil (CPO) should be studied comprehensively. In order to understand the fouling mechanism and dominant foulant, the study was performed by ultrafiltration of CPO model comprising a mixture of Refined CPO-Solvent-Lecithin.

2. Materials and method

2.1. Materials

For preparing feed solution, a mixture of Refined Crude Palm Oil (CPO) from Indofood, isopropanol (Multi Kimia Raya, Semarang) and Lecithin (Indrasari, Semarang) were used. Polyethersulphone (PES), PolyEthylene Glycol (PEG) and N-Methyl Pyrrolidone (NMP) were materials for membrane preparation. The PES material was Veradel3100P from Solvay.

2.2. Methods

2.2.1. Membrane preparations

In this research, flat sheet ultrafiltration membranes were used. The membranes were prepared by a non-solvent induced phase separation method [15]. PolyEthylene Glycol (PEG) was the additive and N-Methyl Pyrrolidone (NMP) was the solvent.

2.2.2. Ultrafiltration Cell

Experimental works were carried out by a laboratory-scale Ultrafiltration cell. Schematic diagram of the Ultrafiltration Cell is illustrated in Figure 1.
Figure 1. Schematic Illustration of Ultrafiltration Cell System.

All experimental runs were performed at room temperature (29 ± 2°C). In the first step, membranes were compacted by filtering water through the membrane at a pressure of 1 bar for 30 minutes. For every run, a new circular membrane sheet with an area of 13.85 cm² was applied. The feed comprising a mixture solution of Refined CPO, isopropanol, and Lecithin at a certain concentration. In this study, the concentrations of Lecithin were varied (0.1%, 0.2% and 0.3% w/w). The ultrafiltration was operated by filtering feed solution at a temperature about 24 - 25°C and 1 bar operating pressure. Permeate fluxes (J) were determined by measuring the volume of permeate collected at 5-minute intervals for 120 minutes and calculated by using equation (1).

$$J = \frac{Q}{(A \cdot t)}$$  \hspace{1cm} (1)

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

The filtrations were conducted at total recycle mode where both permeate and retentate were recycled back to the feed tank to maintain same concentration. After each flux determination, the collected permeate was returned to the feed tank. After 120 minute operation, a permeate of 10 ml was collected and analysed.

2.2.3. Membrane Rejection
The filtration efficiency of phospholipid removal from the feed solution was calculated based on the rejection of phospholipid. The rejection (R) was calculated by equation (2).

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100$$  \hspace{1cm} (2)

where $C_p$ and $C_f$ are a concentration of phospholipid in the permeate and the feed, respectively. The concentration of phospholipid was determined based on phosphor content by AOAC 1999 method.

2.2.4. Blocking Mechanism
Blocking mechanism of CPO degumming model ultrafiltration was studied based on Hermia’s model. This model has been previously applied for fouling mechanism evaluation of konjac glucomannan separation [16], ultrafiltration of batik wastewater [17] and ultrafiltration of dye solution [18].
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) [19]:

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

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 follow: 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 [20]. 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 ($n = 2$):

$$\ln J = \ln J_0 - k_c t$$

(4)

For Intermediate Blocking ($n = 1$):

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

(5)

For Standard Blocking ($n = 1.5$):

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

(6)

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

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

(7)

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

3.1. Effect of lecithin concentration

The performance of the ultrafiltration membrane at various lecithin concentration in the term of flux profile is presented in Figure 2.

The figure shows flux decline over the time during ultrafiltration then reach the constant flux. The flux decline was more pronounced at the end of filtration than at the beginning of filtration. This was due to gel deposited on the membrane surface [6, 21,22]. The gel layer was formed as a result of concentration polarisation caused by concentration gradient at boundary layer on the membrane surface. The gradient was denoted due to solute accumulation retained by the membrane. The gel layer was a part of the polarisation layer of the concentration from the micelle (phospholipid) and arose when the critical solubility is reached [23]. In addition, the retention of phospholipid agglomeration in the membrane pores had a contribution to the increase of deposited layer on the membrane surface and pore clogging [24].

Scanning Electron Microscope images of fouled membrane as displayed in Figure 3 confirmed that there was a foulant layer on the membrane surface. It was predicted that the foulant layer comprised oil and lecithin (phospholipid). Lecithin is categorised as lipid-containing phosphatidylcholine and other types of lipid. As a phospholipid, lecithin has characteristic of the amphiphilic molecule and hence it was likely to have interaction with the typically hydrophilic Polyethersulphone membrane. Moreover, the phospholipid could form reverse micelles with the isopropanol that contribute to the fouling layer formation [24].
3.2. Rejection of phospholipid

A rejection indicates membrane selectivity in rejecting or removing a compound in the feed. Phospholipids are compounds that form micelle when dispersed in water. In a non-polar solvent such as isopropanol, the phospholipids forms reverse micelles having the average molecular weight of 20,000 daltons (10-200 nm) [23]. Ultrafiltration can reject compound with a molecular weight in the range of 300-500,000 Dalton. Hence, in this case, the phospholipid was expected could be retained in the retentate and the oil and isopropanol were produced in the permeate. Figure 4a and 4b display rejection of phospholipid and concentration of phospholipid in the permeate, respectively.
The figure presents that the higher phospholipid concentration, the lower of the rejection. The rejection indicates that performance of the membrane in the term of phospholipid rejection is poor (in the range of 25-80%). Membrane rejection was unpredictable, and the performance depended on the specific solvents. There was the possibility of strong solvent and membrane polymer interaction causing a membrane swelling and affect the membrane pores contraction. Phospholipids have molecular weight approximately 700 Da. When the phospholipids mixed with the solvents, they generated micelles having a size approximately 20.000 Da and hence rejected by the membrane [7].

3.3. Blocking mechanism by Hermia’s model

Hermia’s model was applied in order to understand the membrane fouling during ultrafiltration of Refined CPO-Isopropanol-Lecithin. By fitting the experimental data into the Hermia’s linearized equation (equation (4) to equation (7)), mechanism prevailing the fouling was identified. Figure 5 showed the fitting experimental data to four types of Hermia’s model. Table 1 showed all the corresponding correlation coefficients ($R^2$), and the bold maximal $R^2$ value indicating the best fitting model.

| Blocking Mechanism | Lecithin 0.1% $R^2$ | Lecithin 0.2% $R^2$ | Lecithin 0.3% $R^2$ |
|--------------------|---------------------|---------------------|---------------------|
| Complete Blocking  | 0.9236              | 0.8891              | 0.9272              |
| Intermediate Blocking | 0.9591              | 0.9642              | 0.9934              |
| Standard Blocking  | 0.9983              | 0.9909              | 0.9965              |
| Gel/Cake Formation | 0.9945              | 0.9862              | 0.9923              |

According to Table 1, it was confirmed that ultrafiltration of Refined CPO-Isopropanol-Lecithin mixture at all lecithin concentrations was fit with the Standard Blocking model. In this model, it was predicted that there was deposition of solutes to the internal pore wall. This finding indicated that solutes were penetrating inside the membrane pore and deposited on the internal wall. When the solutes were deposited inside the pores, the size of the solutes was smaller than the membrane pores. It was predicted that the droplet of CPO plays a role in standard blocking. Moreover, it was possible that the PES membrane have hydrophobic characteristic and hence the standard blocking was taken place.
Comparing to Figure 3 illustrating SEM of membrane surface shows that there was foulant deposited on the membrane surface. It was analysed that the standard blocking mechanism occurred in the initial filtration. Further, at the end of filtration, the mechanism was cake/gel formation [25].

![Graphs](image)

Figure 5. Fitting of experimental data to Hermia’s model: (a) complete blocking (b) intermediate blocking (c) standard blocking (d) cake/gel layer formation

4. Conclusion

An ultrafiltration cell with flat sheet ultrafiltration membrane was performed for phospholipids separation of the Refined CPO-Isopropanol-Lecithin mixture. The ultrafiltration membranes were laboratory-made membrane produced through a non-solvent induced phase separation method. The membranes were prepared based on Polyethersulphone (PES) material with the N-Methyl Pyrrolidone (NMP) and Poly Ethylene Glycol (PEG) as the solvent and additive, respectively. Feed consisting of Refined CPO – Isopropanol – Lecithin mixtures were represented as crude palm oil degumming. Lecithin was denoted a phospholipid component, and the concentrations of lecithin in feed were varied to 0.1%, 0.2%, and 0.3%. The concentration of phospholipid was determined as phosphor content. At
the concentration of lecithin in feed representing phospholipid concentration of 8.45 mg/kg, 8.45 mg/kg, 24.87 mg/kg and 57.58 mg/kg, respectively. Analysis of blocking mechanism was studied based on Hermia’s blocking model. Flux profiles confirmed that there was a flux decline during filtration. In addition, the lecithin concentrations do not significantly affect on further flux decline. Rejection characteristic and phospholipid concentration in the permeate showed that the phospholipid rejections by ultrafiltration were in the range of 23-79.5% representing permeate’s phospholipid concentration of 1.73 - 44.25 mg/kg. Analysis of fouling mechanism based on the highest $R^2$ value confirms that the standard blocking is the dominant mechanism in the ultrafiltration of lecithin mixture.

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