Ultrafiltration of oil-in-water emulsion stabilized with surfactants

N Aryanti¹, I N Widiast¹, H Susanto¹
¹Membrane Research Centre (MeR-C), Department of Chemical Engineering, Diponegoro University, Semarang, Indonesia
E-mail: nita.aryanti@che.undip.ac.id

Abstract. Application of ultrafiltration membrane in the separation of oil-in-water emulsion has a consequence of fouling formation and relate to significantly flux reduction. Filtration of oil-in-water emulsions is challenging since both oil and surfactant have interaction with the membranes. In addition, there is a possibility of droplet deformation to enter the membrane pores. This research was focused on the effect of surfactant type on the ultrafiltration performance. Models of oil-in-water emulsion consisted of crude oil, diesel oil and lubricant oil as dispersed phase and mixture of distilled water with the addition of 0.1% of Tween 80 or Alkyl Benzene Sulfonate as the continuous phase. Flat-sheet Polyethersulfone having 10 kDa molecular weight cut-off was selected as the membrane. The result showed that there were fluxes decline during 2 hours of operation in ultrafiltration of oil-in-water emulsion stabilized with a non-ionic surfactant (Tween 80). On the other hand, when oil-in-water emulsion was stabilized with anionic surfactant (Alkyl Benzene Sulfonate), the fluxes were relatively constant during 2 hours filtration. The COD rejection was in the range of 98-97%, 94-96% and 90-94% for oil types of crude oil, diesel oil and lubricant oil respectively. Total oil content rejection was found as 98-99% for both crude oil and lubricant oil and 98-97% for the diesel oil. Based on Scanning Electron Microscopy, images of the membrane after filtration of oil-in-water emulsion stabilized with Tween 80 showed foulant deposit which was predicted as oil and surfactant. However, when filtering oil-in-water stabilized surfactant only less deposit on the membrane surface was observed.

1. Introduction
Ultrafiltration membranes for the treatment of oil-in-water emulsion wastes have been widely applied and were capable of producing discharge having the characteristic that meets the maximum allowable standard limits [1-6]. However, the main challenge in the application of ultrafiltration membranes was the occurrence of a phenomenon called fouling. Fouling is irreversible membrane changes caused by specific physical and/or chemical interactions between membranes and various components in the process flow. Fundamental studies of fouling mechanisms on ultrafiltration caused by oil droplet have been carried out such as gel polarization models [7], fouling resistance [8], modelling of flux reduction permeate [9], complete blocking model [10], cake deposition fouling model [11], based on threshold flux [12]. The oil component and the volatile nature of the oil-water emulsion, as well as type of surfactant in the oil-in-water emulsion, have a consequence on more complex influence on fouling formation.

Structure of the water-oil emulsion has specific characteristics where the hydrophobic part of the surfactant adsorbed on the oil droplets and the hydrophilic part of the surfactant is attached to the
water phase. In addition, there are free surfactants in the water phase. Both surfactants and oil droplets have an effect in the ultrafiltration of oil-in-water emulsions. Oil droplets have the ability to deform and enter the membrane pore. This cause the oil droplets to pass through the membrane pore even though the membrane has a smaller pore diameter than the droplet diameter [13]. In addition, amphiphilic surfactants can be adsorbed strongly on the membrane and allow changes in fouling properties from reversible fouling to irreversible fouling. This complex system causes the phenomenon of ultrafiltration of oil-water emulsions to have specific properties because the separation characteristics are not only determined by particle size (emulsion).

This study focused on the evaluation of membrane performance for ultrafiltration of oil-in-water emulsions stabilized surfactants. In more specific, as oil phases were crude oil, lubricant oil and diesel oil. Those type of oil represented oil component that was usually found in produced water or petroleum refinery wastes. To investigate the effect of surfactant, two types of surfactant comprising non-ionic and anionic surfactant were selected. Several researchers have published the effect of surfactant on ultrafiltration performance [14-16]. However, the use of Tween 80 and Alkyl Benzene Sulfonate as a surfactant in ultrafiltration of crude oil/lubricant oil/diesel oil-in-water emulsion system was not found.

2. Materials and Method

2.1. Materials

Oil-in-water emulsion feed was prepared by dispersing oil phase in continuous phase through a homogenizer (Manual Ultra Trax Homogenizer) at a rotation speed of 21.200 rpm for 2 minutes. The concentration of oil (dispersed phase) was 20 mg/L, and as the continuous phase was a mixture of distilled water with surfactant at concentration of 0.1%. Crude oil, lubricant oil dan diesel oil from Pertamina were used as oil/dispersed phase. Two types of surfactant are selected, those were a nonionic surfactant of Tween 80 (Sigma) and an anionic surfactant of Alkyl Benzene Sulphonate (ABS) from Sigma Flat-sheet membrane of Polyethersulphone (PES) from NADIR Filtration, Germany having MWCO of 10 kDa was used as ultrafiltration membrane. Membrane surface morphology was examined by using Scanning Electron Microscope/SEM (FEI type Inspex-550) at a specific magnification. The SEM images of the new/clean membrane are presented in Figure 1.

![SEM images of new/clean membrane](image_url)  
Figure 1. SEM images of new/clean membrane: (a) Membrane Surface at a magnification of 15.000, (b) Cross-sectional Structure at a magnification of 1.000
2.2. Method

Ultrafiltration of oil-in-water emulsions was conducted in a laboratory scale test cell. The ultrafiltration apparatus comprises a feed tank, a pump, a pressure indicator and a stainless steel cell with a schematic diagram as illustrated in Figure 2.

![Figure 2. Schematic Illustration of Ultrafiltration Cell](image)

Ultrafiltration runs were conducted at room temperature (27 ± 2°C). Before starting the experiments, membranes were first compacted by filtering distilled water through the membrane at a pressure of 2 bars for 1 h. For each experimental runs, a new circular membranes sheet having a membrane area of 13.85 cm² was used. After the compaction process, distilled water was filtered through the membrane and initial water flux (J₀) was then measured. The initial water fluxes (J₀) were obtained by measuring the weight of permeate water collected at the specific recorded time. For ultrafiltration of oil-in-water emulsion, feed tank was filled with oil-in-water emulsion, and the ultrafiltration cell was operated with the same procedure as filtering distilled water.

2.3. Analysis

The permeate fluxes (J) were determined by analytically weighing the permeate collected at every 5 minutes intervals for 120 minutes. The membrane fluxes or permeate fluxes (J) were then calculated by dividing the volume of permeate (Q) by effective membrane area (A) and the sampling time (t) as defined in equation (1):

$$J = \frac{Q}{A \cdot t}$$

where: J: flux (L/ m².h), Q: volume (L), A: membrane area (m²) and t: time interval (h).

In order to maintain the same concentration, the filtrations were carried out using total recycle mode where both permeate, and retentate was recycled to the feed tank. Hence, after each flux determination, the collected permeate was returned back to the feed tank. Further, normalized fluxes (J₀) were obtained by dividing fluxes (J) with initial water fluxes (J₀).

The efficiency of filtration for oil-in-water emulsion was evaluated through the total oil content and Chemical Oxygen Demand (COD) rejection. The rejection (R) defined as rejection percentage was calculated by equation (2).

$$R = \left(1 - \frac{C_p}{C_r}\right) \times 100$$
where $C_p$ and $C_f$ are total oil content or COD value in the permeate and in the feed, respectively. COD was measured by COD Meter (HANA HI 839800). The total oil content was determined by Gas Chromatography.

3. Result and Discussion

3.1. Profile Flux

Figure 3 presents profile flux for ultrafiltration of oil-in-water emulsion with Tween 20 as surfactant.

The figure shows that after a 5-minute ultrafiltration process, the normalized fluxes tend to decrease. At the beginning of ultrafiltration process, a deposit of solutes on the membrane surface is possibly not formed. Along with the filtration times, more particles are retained on the membrane surface, forming a gel layer and eventually creates a cake layer. Solid deposition on the membrane surface has an effect on the significantly flux decrease. However, with the increase of filtration time, transfer of solutes on the membrane surface relatively is reduced. Further, compression of cake layer that has been formed gives a gradual decrease of flux at a later stage. After twenty minutes of operation, a relatively less flux decrease is reached indicating the thickness of the cake layer is constant. Average flux for crude oil emulsion, lubricating emulsion and diesel oil emulsion were found as 5.29 L/m² h (at $J_0 = 16.87$ L/m².h), 97 L/m² h (at $J_0 = 16.06$ L/m². h) and 4.27 L/m² h (at $J_0 = 11.32$ L/m². h), respectively. According to the figure, it is confirmed that crude oil emulsion has the lowest flux value, while the flux of diesel oil emulsion is the greatest. This is presumably due to the size of oil droplets in the emulsion system. Cumming et al. [17] reported that the value of permeate flux is influenced by the size of emulsion droplets. In filtering oil-in-water emulsion by ultrafiltration, droplet size distribution has an effect on deformation and transfer of oil droplet both on the membrane surface and membrane pores. It is predicted that the size of crude oil droplets was the smallest compared to other oil droplets. Stability of oil-in-water emulsion is effected by droplet size. Droplet having bigger size is less stable compared to those with small size. Unstable droplets are easier to
break, forming an oil phase and the oil phase are retained on the membrane surface. On the other hand, stable droplets have possibility to deform and enter to the membrane pores.

In addition, membrane hydrophilicity is also an important factor in successfully filtering the oil [18]. As surfactant is given as emulsifier, the availability of surfactant has a significant effect on membrane performance for emulsion separation. The presence of surfactants also influences the decrease in membrane fluxes [19, 20]. The decrease in flux due to the presence of surfactants was caused by the polarization of concentrations due to retained micelles in the membrane [21,22] and adsorption of surfactant molecules in the membrane pores [22]. In our research, Tween 20 was a non-ionic surfactant, and the PES membrane was a hydrophilic membrane. According to Jonsson and Jonsson [23], it was elucidated that the decrease in flux due to nonionic surfactant on hydrophilic membranes was caused by polarization of the concentration generated by micelles that are stuck on the membrane, absorption due to hydrophilic interactions between hydrophilic membranes and hydrophilic parts of surfactants and capillary condensation (hydrophobic solute at the membrane matrix). For Tween 80, the hydrophilic part is polyethoxylated sorbitan, and the hydrophobic part is oleic acid. Mechanism of adsorption of a nonionic surfactant on the membrane pore is illustrated in Figure 4.

![Figure 4](https://example.com/figure4.png)  
**Figure 4.** Schematic image of non-ionic surfactant adsorption on the membrane pore. B-b2 layer illustrates hydrophobic parts of surfactant and b-b2 represents a hydrophilic layer. The image is modified from [19].

When there was a decrease in flux due to nonionic surfactant internal adsorption, it was assumed that the hydrophobic part of the surfactant was adsorbed to the pore wall and the hydrophilic head group toward the centre of the membrane pore [19].

Normalized flux profile in ultrafiltration of oil-in-water emulsion with ABS as surfactant is depicted in Figure 5.

![Figure 5](https://example.com/figure5.png)  
**Figure 5.** Normalized Profile Flux for Ultrafiltration of oil-in-water emulsion with ABS as surfactant at various oil type
The figure demonstrates relatively stable fluxes during filtration indicating unusual trend compared to Figure 2. Average flux for filtration of crude oil emulsion, lubricant oil emulsion and diesel oil emulsion are $1.07 \text{ L/m}^2\cdot\text{h}$ (at $J_0 = 53.8 \text{ L/m}^2\cdot\text{h}$), $1.07 \text{ L/m}^2\cdot\text{h}$ (at $J_0 = 58.4 \text{ L/m}^2\cdot\text{h}$) and $1.1 \text{ L/m}^2\cdot\text{h}$ ($J_0 = 71.5 \text{ L/m}^2\cdot\text{h}$). The stable fluxes confirm that fouling formation is minimized. In the usage of Tween 80 as surfactant with its non-ionic characteristic, emulsion stabilization is based on the steric hindrance mechanism. The mechanism of stabilization takes place where the hydrophobic part of the surfactant is attached to the oil phase, while the hydrophilic part is attached to the water phase. On the contrary, ABS is an anionic (negatively charged) surfactant. The emulsion stabilization mechanism refers to the electrostatic repulsion mechanism. In this mechanism, droplets are covered by a chain of the charged group, and the droplet surface brings a positive or negative charge. Stabilization of emulsion by steric hindrance and electrostatic repulsion is presented in Figure 6.

![Diagram showing emulsion stabilization mechanisms](image)

**Figure 6.** Schematic of emulsion stabilization mechanism (a) Steric Hindrance, (b) Electrostatic Repulsion

On the other hand, the PES membrane is generally neutral. However, measurements based on zeta potential indicated that most PES membrane surfaces have a negative charge [24, 25]. A negatively charged membrane surface and the negative charged of ABS surfactants result in the formation of highly negatively charged layers on the surface of oil droplets. Hence, the electrostatic repulsion mechanism is high enough to produce emulsions that are more stable and smaller in size [26]. The use of anionic surfactants in the oil-in-water emulsion has the possibility on the adsorption of the hydrophilic portion of the surfactant on the hydrophobic surface of the membrane. However, the adsorption of the hydrophilic part that in the anionic surfactants was less compared to the hydrophilic part adsorption in nonionic surfactants [19]. In this study, a similar surfactant concentration of 0.1% was used. For Tween 80 surfactants, the concentration exceeded Critical Micelle Concentration (CMC) of Tween 80 (CMC=0.0016% w/v), and as a result, aggregation of surfactant namely micelle is formed. These micelles also influenced the formation of fouling. In contrast, for ABS surfactant, the concentration relatively has the same value with the CMC of ABS (CMC= 0.1 g/L) confirming that the micelles as represented in Figure 7 are not formed.

![Diagram showing various micelle types](image)

**Figure 7.** Illustration of various micelle types: (a) spherical micelle (b) rod-shape micelle (c) lamellar micelle
3.2. **Rejection**

Rejection of total oil content and COD for ultrafiltration on oil-in-water emulsion using Tween 80 and ABS as surfactant are listed in Table 1 and Table 2, respectively.

### Table 1. The concentration of COD and Total Oil Content at feed and permeate at various oil type emulsion using Tween 80 as surfactant

| Emulsion Type | COD Concentration (mg/L) | Rejection (%) | Total Oil Content (mg/L) | Rejection (%) |
|---------------|--------------------------|---------------|--------------------------|---------------|
|               | Feed | Permeate | Feed | Permeate |
| Crude oil     | 1850 | 143      | 92   | 200  | 0.01 | 99 |
| Lubricant oil | 3900 | 228      | 94   | 200  | 1.27 | 99 |
| Diesel oil    | 2400 | 230      | 90   | 200  | 2.43 | 98 |

### Table 2. The concentration of COD and Total Oil Content at feed and permeate at various oil type emulsion using ABS surfactant

| Emulsion Type | COD Concentration (mg/L) | Rejection (%) | Total Oil Content (mg/L) | Rejection (%) |
|---------------|--------------------------|---------------|--------------------------|---------------|
|               | Feed | Permeate | Feed | Permeate |
| Crude oil     | 2050 | 54       | 97   | 200  | 0.14 | 99 |
| Lubricant oil | 4132 | 150      | 96   | 200  | 0.14 | 99 |
| Diesel oil    | 2575 | 155      | 94   | 200  | 5.97 | 97 |

In ultrafiltration of oil-water emulsion, oil droplets passing through the membrane are able to change shape (deform) and give pressure to the membrane pore. Deformation of oil droplet that passed through the membrane pores has an influence on the total efficiency of the separation process since the oil droplets can contaminate the permeate. Rejection of oil is determined by the ability of oil deformation and the ability of the oil to flow through the membrane pore. Inside the membrane pore, the oil flows according to the permeating speed and the rejection is not determined by the hydrodynamic strength of the droplets [17]. The penetration of oil through the membrane depends on the level of oil droplets on the membrane surface. Larger oil droplets on the membrane surface contributed to greater oil penetration [27].

3.3. **Fouling Analysis**

SEM images of the fouled membrane after ultrafiltration of oil-in-water emulsion using Tween 80 and ABS as surfactants are presented in Figure 8 and Figure 9, respectively.
Figure 8. SEM images of membrane surface after ultrafiltration of oil-in-water emulsion: (a) crude oil emulsion (b) lubricants oil emulsion (c) diesel oil emulsion, with Tween 80 as surfactant (magnification of 15.000)

According to the figure, it can be seen that there is significant view of the membrane surface compared to Figure 1. Some solute is observed to deposit on the membrane surface, indicating a fouling membrane. In ultrafiltration of emulsion stabilized non-ionic surfactant, both oil and surfactant have the possibility as foulant on the membrane surface. Foulant due to surfactant was due to the polarization of the concentration generated by micelles that are stuck on the membrane, absorption due to hydrophilic interactions between hydrophilic membranes and hydrophilic parts of surfactants. In addition, the figure shows that membrane (a) has less fouling on its surface compared to the membrane (b) and membrane (c). It is presumably due to the smaller emulsion size of the crude oil emulsion. When the emulsion has a lower droplet size, it is assumed that the droplets can enter into interspace of surfactant hydrophobic parts or inside the membrane pores. As a result, foulant observed on the membrane surface is emulsion droplets covered with a surfactant. On the other hand, images of the membrane (b) and membrane (c) show some deposits of oil on the top of surfactant layers.

Figure 9 represents SEM images of the membrane after ultrafiltration of oil-in-water stabilized with anionic surfactant (ABS).
Figure 9. SEM images of membrane surface after ultrafiltration of oil-in-water emulsion: (a) crude oil emulsion (b) lubricants oil emulsion (c) diesel oil emulsion, with ABS as surfactant (magnification of 10,000)

Compared to Figure 8, Figure 9 shows less solute deposited on the membrane surface, confirming there is no membrane fouling. These images support the result of profile flux in which the profile remains constant during ultrafiltration of oil-in-water stabilized with an anionic surfactant. Some solute deposit on the membrane surface is presumably oil droplets, and no surfactant deposit is observed. Theoretically, only a small amount of surfactant deposited on the membrane surface since no micelle is formed and only less of the hydrophilic part of the anionic surfactants adsorbed on the membrane surface.

4. Conclusions
Normalized flux profile for ultrafiltration membrane of oil-water-emulsion stabilized with surfactant presented that fluxes of an oil-in-water emulsion stabilized with Tween 80 surfactant tends to decrease with the increase of filtration time. In contrast, when ABS was selected as surfactant, the normalized flux profile confirmed relatively constant fluxes during filtration. In this research, rejection of COD and total oil content were found in the range of 90-98% and 97-99% for COD rejection and total oil content rejection, respectively. Scanning Electron Microscopy images of the membrane after filtration of an oil-in-water emulsion stabilized with Tween 80 showed that there was foulant deposit which was predicted as oil and surfactant. On the other hand, when filtering oil-in-water stabilized surfactant only less deposit on the membrane surface was observed.
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