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Fouling Reduction by Ozone-Enhanced Backwashing Process in Ultrafiltration of Petroleum-Based Oil in Water Emulsion

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Abstract. Ultrafiltration membrane has been successfully applied for oily waste water treatment. However, one significant drawback of membrane technology is fouling which is responsible for permeate flux decline as well as reducing membrane performance. One method commonly used to reduce fouling is a backwashing process. The backwashing is carried out by a push of reversed flow from permeate side to the feed side of a membrane to remove fouling on the membrane pore and release fouling layer on the external side. However, for adsorptive fouling, the backwashing process was not effective. On the other hand, Ozone demonstrated great performance for reducing organics fouling. Hence this research was focused on backwashing process with ozone for removing fouling due to ultrafiltration of petroleum based oil emulsion. Gasoline and diesel oil were selected as dispersed phase, while as continuous phase was water added with Tween 80 as a surfactant. This research found that the Ozone backwashing was effective to improve flux recovery. In ultrafiltration of gasoline emulsion, the flux recovery after Ozone backwashing was in the range of 42-74%. For ultrafiltration of diesel oil emulsion, the permeate flux recovery was about 35-84%. In addition, foulant deposition was proposed and predicting that foulant deposition for ultrafiltration of gasoline-in-water emulsion was surfactant as the top layer and the oil was underneath the surfactant. On the other hand, for ultrafiltration of diesel oil-in-water emulsion, the oil was predicted as a top layer above the surfactant foulant.

INTRODUCTION

Oily wastewater is usually generated as a waste product in the metal processing industry, petroleum refinery, and offshore oil exploration. The wastewater can be found in the form of free-floating oil, unstable oil in water emulsion and stable oil in water emulsion [1]. The oil component of emulsion is a mixture of hydrocarbons comprising benzene, toluene, ethylbenzene and xylene (BTEX), naphthalene, phenanthrene, dibenzothiophene (NPD), polyaromatic hydrocarbons (PAHs) and phenol. Those substances are characterized as lethal (deadly) and sublethal (inhibit the growth, reproduction, and other physiological processes) on aquatic ecosystems. [2-4]. In the petroleum refinery, about 0,4-1,6 oily wastewater was generated for every oil production [5]. Oily wastewater from petroleum refinery having Chemical Oxygen Demand (COD) value of 850-1020 mg/L, the oil content of 100-300 mg/L on water desalter and up to 5000 mg/L in the bottom of the tank [4]. Those COD value and oil content of oil wastewater do not meet with the Government Regulation in Indonesia, where the maximum oil content and COD value for oily wastewater from petroleum refinery were 20 mg/L and 160 mg/L, respectively. Several methods to remove oil impurities were applied including treatment by electrochemical, membrane filtration, biological treatment, adsorption, flotation and chemical coagulation [6].

In membrane filtration, ultrafiltration has been applied for treatment of oil in water emulsion wastewater, for example, refinery wastewater [7], industrial oily wastewater [8] and oily waste effluent from copper cable factory [9]. Furthermore, the ultrafiltration membranes have successfully been applied for separation of oil in water [6]. However, the main drawback in ultrafiltration application is fouling which is related to reducing of membrane performance.

Some methods of fouling control and membrane cleaning in ultrafiltration membrane have been applied [10-13]. In general, fouling control is classified as physical method such as backwashing, backflushing, rotating and ultrasonic and chemical method (by acid washing, caustic washing, enzymatic washing and dispersant use) [14]. Backwashing is carried out by a push of reversed flow from permeate side to the feed side of a membrane. The reversed flow removes the foulant on membrane pores and releases fouling layer on the external side [14]. Nevertheless, the physical method is not able to eliminate fouling caused by adsorption. On the other hand, the chemical method is capable of removing adsorptive fouling, but it has a negative effect on the environment due to by-product formation. On the other hand, Ozone has been examined for reducing membrane fouling caused by ibuprofen, Bezafibrate, Amoxicillin and Sulfamethoxazole [15], accumulation of organic particles on water treatment [16], trihalomethanes [17] and phenol/tannic [18]. In oil waste water treatment, ozone has been applied for reducing the concentration of Benzene, Toluene, Xylene in oil waste [19]. As a matter of fact, Ozone was able to reduce membrane fouling, this research was aimed to investigate a combined Ozone and backwashing process for fouling reduction. Special emphasis is focused on reducing fouling in ultrafiltration of petroleum-based oil in water emulsion.

MATERIALS AND METHODS

Materials

Oil in water emulsions were prepared at oil concentration of 200 mg/L. The oil or dispersed phase was gasoline and diesel oil obtained from a local petrol station. A mixture of Tween 80 (Sigma) at concentration of 0,1% (v/v) and water was the continuous phase. Oil in water emulsion obtained by using IKA Homogenizer at a rotation speed of 21,200 rpm for 2 minutes. Ultrafiltration membrane was a Polyethersulphone (PES) membrane (NADIR Filtration, Germany) having MWCO of 10 kDa. Membrane surface morphology was examined by using Scanning Electron Microscope (FEI type Inspek-550) at a specific magnification.

Ultrafiltration

Ultrafiltration experiments were conducted in a laboratory scale test cell. The ultrafiltration apparatus comprises a feed tank, a pump, a pressure indicator and stainless steel cell. Schematic diagram of ultrafiltration is shown in Fig.1.

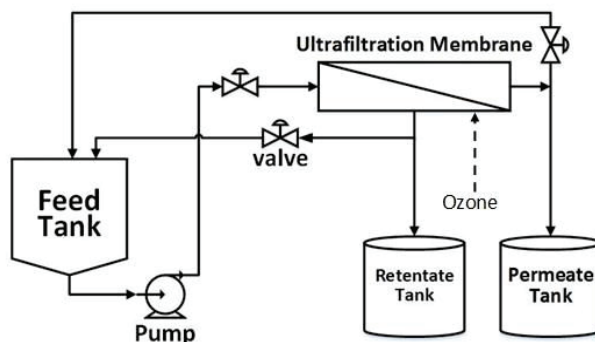


FIGURE 1. Schematic illustration of Ultrafiltration Apparatus

All ultrafiltration runs were conducted at room temperature ($28 \pm 2^\circ\text{C}$). Before starting the experiments, membranes were first compacted by filtering water through the membrane at pressure of 3 bars for 0.5 hr. For each experimental runs, a new circular membranes sheet having membrane area of 13.85 cm^2 was used. After the compaction process, distilled water was filtered through the membrane and initial water flux (J_0) was then measured. The initial water fluxes (J_0) were obtained by measuring the weight of permeate water collected at specific recorded time. Subsequently, the apparatus was operated for ultrafiltration of oil in water emulsion. 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):

$$J = \frac{Q}{(A \times t)} \quad (1)$$

Where: J : flux ($\text{L}/\text{m}^2 \cdot \text{hr}$), Q : volume (L), A : membrane area (m^2) and t : time interval (hr).

In order to maintain same concentration, the filtrations were carried out using total recycle mode where both permeate and retentate were recycled to the feed tank. Hence, after each flux determination, the collected permeate was returned back to feed tank. Further, normalized fluxes are obtained by dividing fluxes (J) with initial water fluxes (J_0).

Ozone Backwashing

In backwashing operation, Ozone was generated by Ozonizer (Krisbow) was injected. The ozone generator was equipped with a flowmeter for determining Ozone flow rate. Ozone concentration was tested by using HI38054 Ozone Test Kit.

RESULT AND DISCUSSION

Flux Profiles

The variation of permeate flux as a function of operational time for ultrafiltration of Gasoline and Diesel oil emulsions were shown in Fig. 2. Ozone backwashing was applied at filtration time of 60 minutes for specific Ozone flow rate and backwashing time.

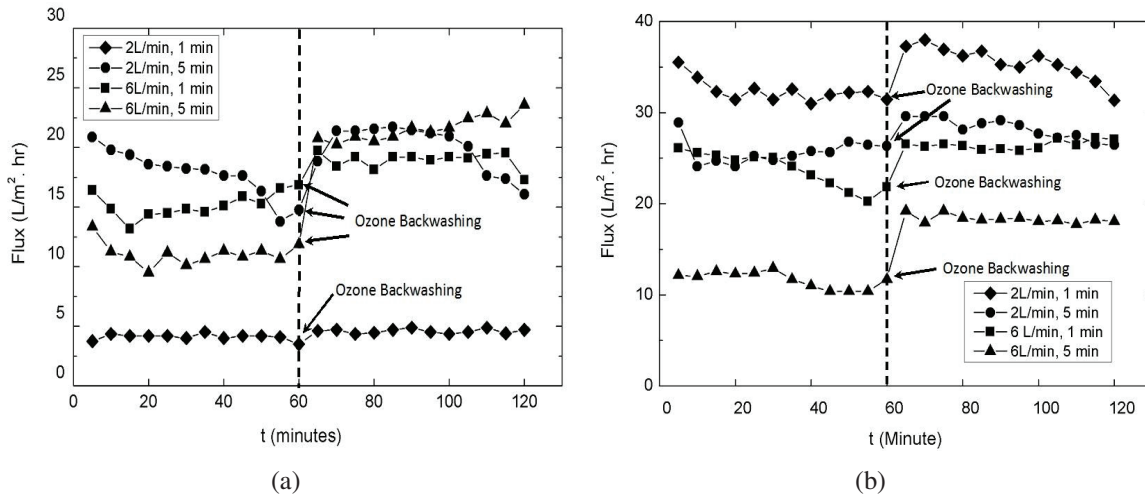


FIGURE 2. Permeate flux profile of Ultrafiltration of Gasoline emulsion (a) and Diesel oil emulsion (b) at various Ozone flow rate and backwashing time.

Figure 2 illustrates the permeate fluxes of gasoline and diesel oil ultrafiltration decline during filtration. The flux declines were generally found in membrane filtration due to the accumulation of foulant on the membrane surface or membrane pore blocking. Based on Fig. 2, it was displayed that the permeate flux of gasoline ultrafiltration was dropped about 40-50% from its initial fluxes in the first 20 minutes. A similar result was found for diesel oil ultrafiltration, there was a decline of permeate fluxes about 50-70% from its initial flux in the first 20 minutes. After the ozone backwashing was applied, there was an increase of permeate fluxes. Ozone backwashing effects were shown at fluxes after 60 minutes as backwashing point. In general, the ozone backwashing improved the permeate flux for all ozone flow rate and backwashing time. However, the result was more pronounced at higher Ozone flow rate and backwashing time (6L/min for 5 minutes). In more detail, the normalized fluxes as well as flux increases after backwashing process were listed in Table 1 and Table 2 for ultrafiltration of Gasoline and Diesel oil emulsion, respectively.

TABLE 1. Normalized Flux (J/J_0) and effect of Ozone backwash on flux increase in ultrafiltration of gasoline emulsion.

Ozone Flowrate (L/min)	Backwash Time (minutes)	Ozone Concentration (mg/L)	Normalized Flux (J/J_0)		% Flux Increase before and after Ozone backwash
			Before Ozone Backwash (t=60 minute)	After Ozone Backwash (t=120 minute)	
2	1	0,1	0,47	0,63	32
2	5	0,2	0,33	0,36	28
6	1	0,15	0,37	0,48	50
6	5	0,3	0,43	0,84	75

TABLE 2. Normalized Flux (J/J_0) and effect of Ozone backwash on flux increase in ultrafiltration of diesel oil emulsion.

Ozone Flowrate (L/min)	Backwash Time (minutes)	Ozone Concentration (mg/L)	Normalized Flux (J/J_0)		% Flux Increase before and after Ozone backwash
			Before Ozone Backwash (t=60 minute)	After Ozone Backwash (t=120 minute)	
2	1	0,1	0,30	0,30	19
2	5	0,2	0,32	0,33	12
6	1	0,15	0,31	0,38	22
6	5	0,3	0,51	0,79	64

Table 1 and Table 2 support the finding as presented in Fig. 1 and Fig. 2, respectively. After the Ozone backwashing (at times of 65 minutes) there was permeate flux increase approximately 28 – 75% and 12-64% of their previous fluxes (at the time of 60 minutes) for gasoline and diesel oil ultrafiltration, respectively. Comparing the flux after backwashing time (at the time of 65 minutes) with the initial flux (J_0) resulted in flux recovery of 42-74% and 35-84% for ultrafiltration of gasoline emulsion and diesel oil emulsion, respectively. The higher permeate fluxes after ozone backwashing indicating a reduction of membrane fouling as a result of ozone reaction with the organic compound (oil and surfactant) deposited on the membrane surface. Ozone reaction not only removed deposited layer on the membrane surface but also broke down large molecules and particles [17]. Oxidation by ozone was influenced by several factors such as ozone concentration, reaction time, reaction temperature and pH [20]. Table 1 and Table 2 confirmed that the highest flux recovery was found at Ozone flowrate of 6 L/minutes at backwashing time of 5 minutes. Ozone is an oxidation agent having the ability to change the structure and composition of petroleum and decomposed some organic compounds into CO_2 and H_2O [20]. Ozone reacts with alkene contained compound and break up its double bond of a carbonic atom into new stable molecules such as ketone and aldehydes as well as unstable molecules such as hydrogen peroxide and OH radical [21]. Moreover, it was confirmed that ozone was able to lower concentration of organic petroleum compound [19].

Membrane Characteristic after Ultrafiltration

Scanning Electron Microscopy images of fouled membranes after ultrafiltration of gasoline and diesel oil is displayed in Fig. 3 and Fig. 4, respectively.

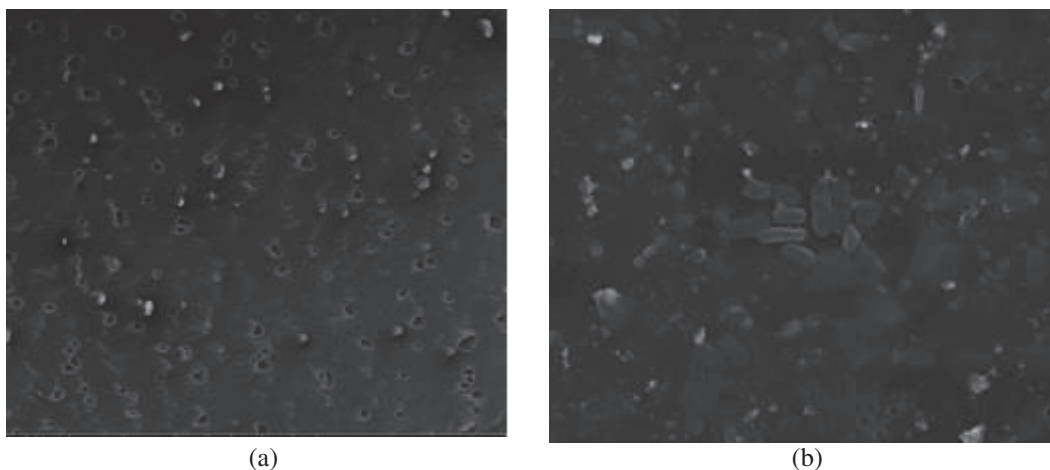


FIGURE 3. Scanning Electron Microscopy (SEM) images of membrane surface at a magnification of 10,000x: (a) After ultrafiltration of gasoline emulsion without Ozone backwashing (b) After ultrafiltration of gasoline emulsion with ozone backwash Ozone flow rate was 6L/min, backwashing time was 5 minutes.

Figure 3 (a) shows that the fouled membrane due to gasoline emulsion feed without ozone backwashing representing 'sealed' and dense foulant on the membrane surface. On the other hand, as displayed in Fig. 3 (b), after Ozone backwashing the deposited foulant on the membrane surface, was diminished and deposited particles and gel-like foulant previously covered by dense foulant became visible.

Figure 4 presents the images of fouled membrane after ultrafiltration of diesel oil emulsion without Ozone backwashing (Fig. 4a) and with Ozone backwashing (Fig. 4b).

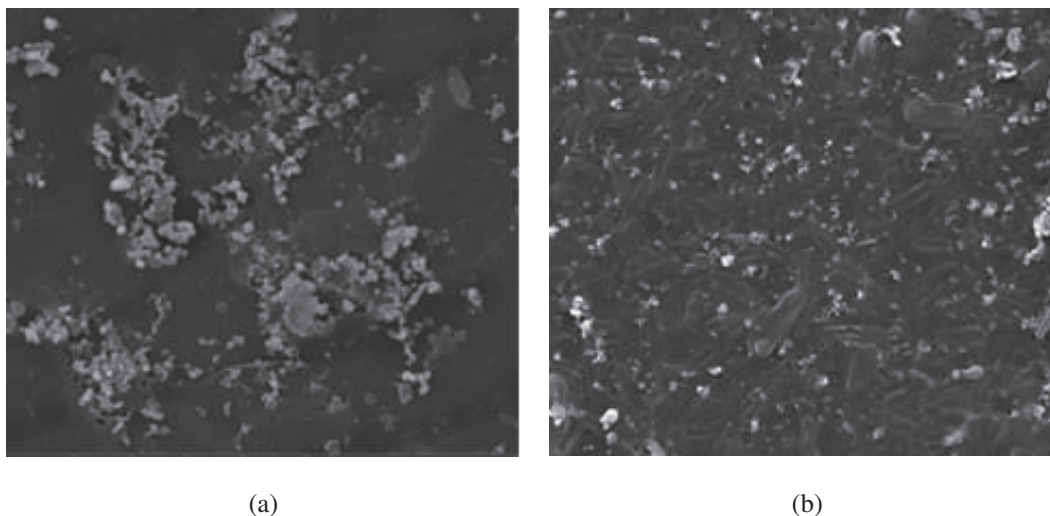


FIGURE 4. Scanning Electron Microscopy (SEM) images of membrane surface at a magnification of 10,000x: (a) After ultrafiltration of diesel oil emulsion without ozone backwashing (b) After ultrafiltration of diesel oil emulsion with ozone backwash Ozone flow rate was 6L/min, backwashing time was 5 minutes.

Figure 5a illustrates the fouled membrane without Ozone backwash indicating some large particles deposited on the membrane surface. When the Ozone backwashing was employed, there was a break up of those large particles into smaller particles. By reducing the particle-deposited size, a gel-like structure was noticeable. Both Fig. 3 and Fig. 4 clearly confirmed that the Ozone backwash has the ability to reduce membrane fouling.

Foulant Deposition

According to SEM images in Fig. 3 and Fig. 4, foulant deposition on the membrane surface was proposed. In this research, the feed was gasoline or diesel emulsion stabilized with a surfactant. Ultrafiltration of emulsion (consisting of oil droplets in their continuous phase) has different characteristic compared to ultrafiltration of general solution. Firstly, fouling by oil droplets take place by deposition of droplets on the membrane surface or pore blocking by droplets deformation inside the membrane pores [22]. Secondly, the surfactant also having a contribution for flux reduction due to polarization concentration [23-25], or adsorption of surfactant molecules on the membrane pores [24,26-27]. Hence, the foulant in ultrafiltration of gasoline and diesel oil emulsion comprise oil and surfactant. In ultrafiltration of gasoline emulsion, oil was probably blocking the membrane pores or deposited on the membrane surface followed by gel formation of surfactant deposited on the membrane surface as illustrated in Fig. 5 (a). On the contrary, for ultrafiltration of diesel oil emulsion, deposition of surfactant on the membrane surface was first contributed, then followed by the oil deposition on the membrane surface (see Fig. 5 (b) for illustration).

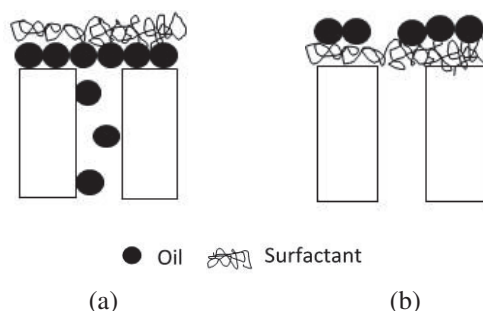


FIGURE 5. Illustration of foulant deposition (a) Ultrafiltration of gasoline emulsion (b) Ultrafiltration of diesel oil emulsion

Consequently, when the Ozone backwashing was applied, it has a function to diminish gel layer due to surfactant foulant in ultrafiltration of gasoline emulsion. Conversely, in ultrafiltration of diesel oil emulsion, the Ozone backwashing resulted in a reduction of oil deposition foulant.

CONCLUSION

Ozone backwashing process has been investigated in ultrafiltration of petroleum based oil in water emulsion. Permeate flux profiles confirmed that there was a decrease of permeate flux to about 40-50% and 50-70% from its initial flux for gasoline-in-water emulsion and diesel oil-in-water emulsion, respectively. When the Ozone backwashing was applied, permeate flux recovery in ultrafiltration of gasoline emulsion was in the range of 42-74%. For ultrafiltration of diesel oil emulsion, permeate flux recovery was about 35-84%. Scanning electron microscopy images verified that Ozone was able to remove the first layer of foulant on the membrane surface. In addition, foulant deposition was proposed, illustrating that the foulant deposition for ultrafiltration of gasoline emulsion was surfactant foulant in the top layer while for ultrafiltration of diesel oil foulant, the oil foulant was predicted exist on the top layer.

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