Effect of Backwash Ozone In Ultrafiltration System For the Separation of Waste of Water-oil Emulsion

Indah Prihatiningtyas D.S[1], Nita Aryanti[2], Diyono Ikhsan[3]
Magister Teknik Kimia Universitas Diponegoro Jl. H. Prof. Sudarto, SH, Tembalang Semarang 50239
Telp 024-7460058 Fax. 024-7480675

Abstract— *Membrane technology, in particular ultrafiltration is an effective technology to separate oil from water. In the oil-water emulsion, foulant in the form of oil and surfactants will affect the performance of the membrane due to fouling caused. One method to reduce fouling and keeping the permeation flux is by ozonation. This study aimed to assess the performance of the membrane by knowing the profile of membrane flux and rejection, knowing analyze membrane fouling membrane morphology. In a study using 10 kDa PES ultrafiltration membranes, the feed is crude oil emulsion with a concentration of 200 mg / L and surfactant (Tween 80) at a concentration of 0.1%. Ultrafiltration operation time is 1 hours at a pressure of 1 bar, flux determined was 15,21 L /* m^2*.hour, COD rejection was 92% and the oil rejection 99,%. From the results of SEM shows that the membrane pore is blocked by surfactant foulant, after ozone backwash flow rate 6 L / min and a 5-minute backwash, flux recovery of 8%. From this study that the ozone backwash does not significantly affect the flux recovery.*

Keywords- *membrane, ultrafiltration, emulsion, fouling, backwash ozone*

I. INTRODUCTION

Waste containing oil emulsion derived from various industrial processes such as metal industry, automotive industry, transport, food, petrochemical and petroleum refineries [1,2]. In the petroleum refinery oily wastes generated are very dangerous because they contain compounds benzene, toluene, ethylbenzene and xylene (BTEX), naphtalena, phenanthrene, dibenzothiophena (NPD), polyaromatic hydrocarbons (PAHs) and phenols [3]. The resulting oily wastes containing petroleum oil refineries 100-300 mg / L in water desalter and up to 5000 mg / L in the bottom of the tank, COD levels up to 600 mg / L [4], while the corresponding effluent concentration limits of waste water quality standards specify that oil and grease concentration maximum of 25 mg / L with levels of COD 200 mg / L.

The main kinds of oily wastewater are free floating oil, unstable oil/water (O/W) emulsion and stable O/W emulsion. Unstable water-oil emulsion droplet size larger than 50 µm [5], while the droplet size less than 10 µm is an oil-water emulsion stable. Waste treatment for water oil emulsion have done include addition of coagulant and acid and heating to break down the oil-water emulsion, the oil-water is separated by the principle of gravity and using an oxidation process [6,7,8], but it still produces sludge which includes hazardous waste. Membrane technology, particularly microfiltration and ultrafiltration, quickly recognized as an effective technology to separate oil from water because this technology can produce pure water with consistent quality and also this technology can process oil-in-water emulsions with particle diameter less than 5 microns, which can not be processed with the hydrocyclone [9].

The main challenge in membrane technology is the fouling, because adsoprsi and accumulation of oil and other components on the surface of the membrane. Membrane fouling is generally characterized as a reduction of flux, due to blocking of pores, concentration polarization and cake. In general, fouling control methods can be grouped into two: physically (backwashing, backflushing, rotating, ultrasonic) and chemical (acid washing, caustic washing, enzymatic washing, the use of dispersant) [10,11]. Physical methods are not able to eliminate the fouling that occurs through a mechanism adsobsi while chemical methods allow the production of waste or residue that may cause environmental pollution.

We tried using ozone to keep the high permeation flux and reduce fouling in the system (UF) ultrafiltration. Ozone is one of the most powerful oxidizing reagent with the advantage that oxidized products are usually lessfouling substances than the parent compounds. Ozone, in particular has many of the oxidizing properties desirable for use in water treatment: is readily available, soluble in water, and generally leaves to less-toxic substances, ozone can react with solutes either by direct oxidation (pH < 6), in which molecular ozone reacts at electron-rich sites of the organic compounds, or by an indirect pathway (pH > 6), whereby hydroxyl radicals resulting from the decomposition of ozone serve as the oxidants through chain reactions, ozonation does not leave by-products that need to be removed[12.13]. Ozone is used to reduce membrane fouling caused by

Ibuprofen (IB), Bezafibrate (BZ), Amoxicillin (AM) and Sulfamethoxazole (SMX) [14], organic compounds [15], the results of disinfectants such as trihalomethanes [16], phenolic / tannic [17].

The purpose of this study to assess the performance of the membrane by knowing the profile flux and rejection membranes, membrane fouling analyzed by knowing the membrane morphology.

II. EXPERIMENTAL

II.1 Preparation of Emulsion

O/W emulsion was prepared by adding 200 mg crude oil and 0,1% of Tween-80 to 1 L distillated water, then stirring for 2 min at the rate of 21.200 rpm by homoginezier Ika Turac Basic. *R* is retention defined as follows :

$$R = \left(1 - \frac{C_p}{C_f}\right) x100\%$$

Where C_f and C_p are the oil concentration of the feed and the permeat, respectively, expressed by chemical oxygen demand (COD).

II.2 Membrane Characterization

Pure water flux J_0 was determined in a cross-flow UF apparatus under different transmembrane pressures. The permeat flux was the average values for the first 5 min, and the result is listed in Table 1.

Table 1 Properties of membrane

TMP/Bar	$J_0(L.m^{-2}.h^{-1})$
1	56,66
2	80,61
3	103,02

II.3 Membrane Filtration System

The ozone-membrane filtration system used in these experiments is illustrated in Fig.1. Plate and frame PES (From NADIR, Germany) membranes with a molecular weight cut-of 10 kD, asymmetric membrane, an area of 0,00138 m^2 were used in the system.

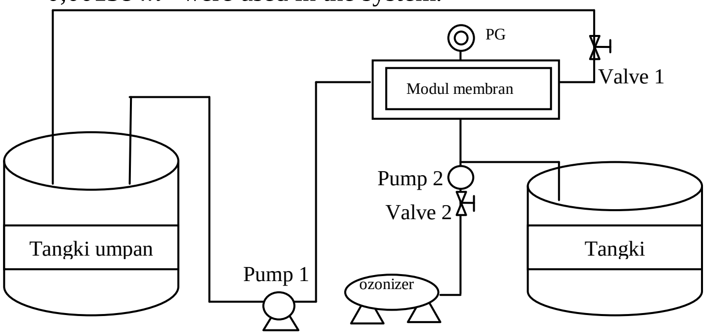

Fig.II.1 Schematic diagram of experimental apparatus for backwash ozone experiments

After the membrane had been placed in the membrane module , distilled water was circulated for about 30 min at 3 bar pressure. Pure water flux J_0 was determined. Valve 1 allowed for adjustment of transmembrane pressure. Ultrafiltration system is run at a constant pressure of 1 bar. The feed emulsion of crude oil are generated by centrifugal pump 1 and was fed into the membrane module. The flux through membrane was measured by weighting the permeat and timing the collection period (5 min). After running 60 minutes of crude oil emulsions, ozone (from the ozone generator) was injected into the system through the pump 2. Ozone was injected at a rate of 6 L/min for 5 minutes then emulsified crude oil feed run again in the ultrafiltration system. Three types of flux measurements were performed : i). Initial flux, ii) before backwash ozone, iii) after backwash ozone. Permeat flux was recorded as a function of time, both permeate and retentate sample were analyzed for oil contents and COD.

III. RESULT AND DISCUSSION

III.1 Membrane Permeability

The performance of membrane separation process can be generally expressed by membrane permeability and selectivity. Membrane permeability indicates the ability of membrane to pass the water[18]. This research used flux of pure water as parameter, which is 56,66 L/m^2.hour.

III.2 Rejection

The ultrafiltration effectively caused the oil concentration to decrease, both with or without ozonation. The membrane shows more than 99% oil rejection within the initial oil concentration 200 ppm, and COD rejection was 92% from 1850 mg/L.

III.3 Characteristic of Flux Degradation

This research uses crude oil emulsion with oil content 200 ppm as feed. As shown in Fig.III.1, there is flux degradation while the filtration process.

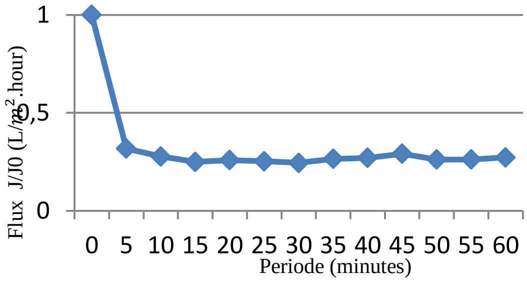

Fig.III.1 Flux profile of crude oil emulsion

In Fig. III.1 shows that flux of the crude oil emulsion decrease in every period, in the first 5 minutes, flux determined was 17,98 L/m^2 and in the last 60 minutes the flux of crude oil emulsion was calculated 15,45 L/m^2. This flux degradation caused by fouling in the membrane surface. Membrane fouling occure through one or more of the following mechanism : i) accumulation of solute and gradual irreversible changes in the polarized layer such as cake formation, ii) surface adsorption: deposition of solutes, iii) adsorption : deposition of solute within membrane[19].

III.4 SEM images

The images of the surface of membrane before using for filtration examined by SEM are shown in Fig.III.2. The surface and the pores of a new membrane sample were clear. However, in case of fouled membranes after 60 minutes filtration crude oil emulsion, the membrane surface was covered by foulant layer and most of the pores were clogged (Fig.III.3).

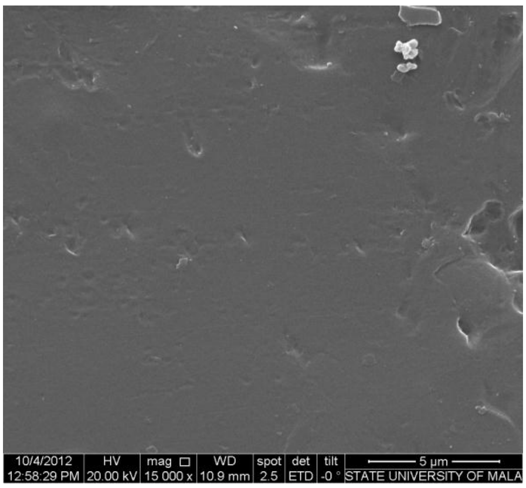

Fig.III.2 SEM of new membrane (magnification of 15000)

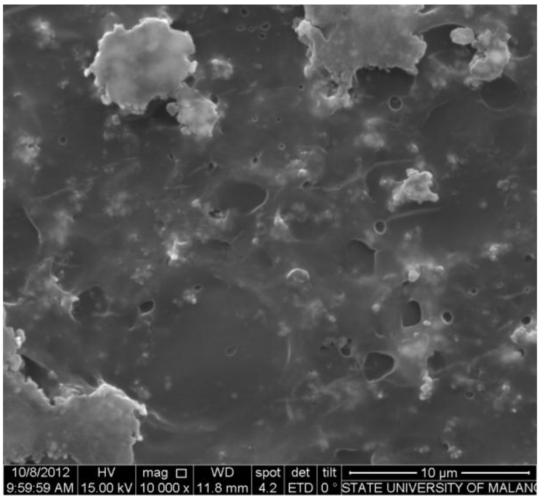

Fig.III.3 SEM of fouled membrane (magnification of 10000)

Membrane pore blockage can be caused by foulant in the form of oil or surfactant. A surfactant usually consists of a hydrophilic headgroup to which one or two hydrocarbon chains are connected. There are many examples of surfactants decreasing the membrane flux. The flux reduction has in some cases been explained by concentration polarization caused by retained micelles[20,21].The nonionic surfactant (Tween-80) was the only surfactant that reduced the flux of the hydrophilic PES membrane. The flux decrease of the PES membranes may have at least three explanations: (1) concentration polarization caused by retained micelles; (2) adsorption due to hydrophobic interactions (the adsorption begins at a higher concentration than for the hydrophobic membranes owing to the hydrophilic of the PES membranes); (3) adsorption due to hydrophilic interactions (example : between the hydrophilic membrane and the hydrophilic polyethylene oxide segments)

III.5 Effect of Permeate of Flux by Ozonization

Fig. III.4 shows the effect on the permeate flux, before and after ozonation. The permeate flux decreased sharply after 5 min, then decrease gradually to about 10% of the initial permeate flux, which was 18,58 L/m^2 after backwash ozone. It was observed that the permeate flux decreased slowly the first 5 min after backwash ozone,as oxidation destroyed some of the solutes that had been adsorbed onto the inner pore membrane.

Flux recovery after backwash ozone was 8%. Fouling on the strength of adhesion of the particles on the membrane surface can be divided into reversible fouling and irreversible fouling. Reversible fouling can be removed with a strong shear force or backwashing. The establishment of a strong matrix of fouling layer solute premises during continuous filtration will produce reversible fouling layer becomes irreversible fouling layer. Irreversible fouling is generally caused due to the inherent strength of particles that can not be removed by washing the physical[22].

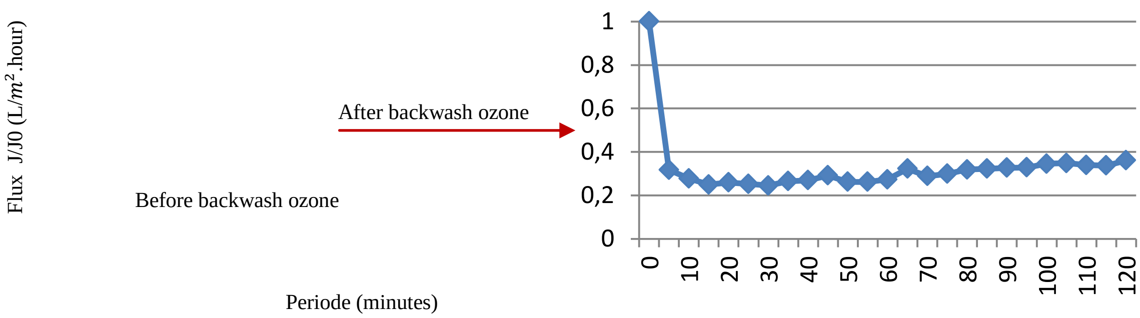

Fig.III.4 Effects on the permeate flux before and after backwash ozone

IV. CONCLUSIONS

Experiments were conducted to investigate the effect of backwash ozone to reduce membrane fouling in crude oil emulsion separation. Results from all experimental runs revealed that:

1. The PES membrane shows more than 99% oil rejection within the initial oil concentration 200 ppm, and COD rejection was 92% from 1850 mg/L.
2. Flux of the crude oil emulsion decrease in every period. This flux degradation caused by fouling in the membrane surface. Membrane fouling occure through one or more of the following mechanism : i) accumulation of solute and gradual irreversible changes in the polarized layer such as cake formation, ii) surface adsorption: deposition of solutes, iii) adsorption : deposition of solute within membrane.
3. The nonionic surfactant (Tween-80) was the only surfactant that reduced the flux of the hydrophilic PES membrane. The flux decrease of the PES membranes may have at least three explanations: (1) concentration polarization caused by retained micelles; (2) adsorption due to hydrophobic interactions (3) adsorption due to hydrophilic interactions.
4. The permeate flux decreased sharply after 5 min, then decrease gradually to about 10% of the initial permeate flux, flux recovery was 8% after backwash ozone. From this study that the ozone backwash does not significantly affect the flux recovery.

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