Performance of cellulose acetate membrane with different additives for palm oil mill effluent (POME) liquid waste treatment

N A S Aprilia\textsuperscript{1,3}, Fauzi\textsuperscript{1}, N Azmi\textsuperscript{1} and N Najwan\textsuperscript{1} and A Amin\textsuperscript{2}

\textsuperscript{1} Department of Chemical Engineering, Faculty of Engineering, Universitas of Syiah Kuala, Darussalam, Banda Aceh, 23111, Indonesia
\textsuperscript{2} Department of Mechanical Engineering, University of Abulyatama, Lampoh Keude, Banda Aceh, Indonesia.

E-mail: sriaprilia@unsyiah.ac.id

Abstract. Performance of cellulose acetate membrane for treatment of POME liquid has studied with different additives. Cellulose acetate membranes were prepared with different additive ie formamide and polyethylene glycol and used acetone as solvent. The function of formamide and polyethylene glycol (PEG) is to increase the porosity of the membrane surface. Performance of the membrane were included SEM, FT-IR and coefficient permeability. Membrane performance has been performed for percent rejection of total suspended solid (TSS) and turbidity of POME liquid waste. Cellulose acetate with formamide shows an increased percentage of rejection in removing TSS and turbidity than cellulose acetate with PEG.

1. Introduction

Indonesia still used aerobic siystem for processing liquid waste of palm oil industry. Liquid waste is channeled to the collection unit (fatpit) in the form of a trench and then flowed into the collecting oil (oil quote pool) for the oil to be taken and the temperature drop. After that liquid waste is fed into the aerobic treatment pond. The system is very simple and cheap. But this system has a disadvantage: the land used must be wide, when using a closed system can produce greenhouse gases such as methane and carbon dioxide. Processing this system is not economical because once processed, the waste directly discharged into the water channel.

One of the technologies selected for POME's liquid waste treatment is ultrafiltration membrane technology. This technology does not require a lot of energy and large land. The ultrafiltration membrane is an asymmetric membrane, in which the dense top layer of pore and the lower layer has larger pores which have good mechanical strength. Aprilia (2011) [1] stated that the most important goal in membrane technology is to control the membrane structure that will affect membrane performance. The formation of...
asymmetric membrane pores are influenced by several factors, including the use of solvents, non-solvents and additives. A very serious problem in the membrane process is fouling, because the adsorption of the solute on the membrane surface will clog the membrane pores (pore bloking).

Some literature has studied blending a polymer with hydrophilic materials or changed additives. This is considered to be an attractive and simple method to modify the membrane properties in order to minimize fouling. Aryani et al (2016) [2] has used PEG400 and acetone as additives on polysulfone membranes. They investigated that the used PEG400 and acetone in polysulfone membrane will increase the hydrophylicity and in a lower fouling will increasing the resistance of organic matter during up to five hours of peat water filtration. To reduce fouling in the membrane system, it is need to add additives as anti fouling. The addition of additives in membrane hydrophobicity such as in polysulfone, polyether sulfone, polypropylene, polyethylene can be fabricated by increasing the outer surface porosity and removing the inner skin layer during spinning process. Moreover, despite depending on the property of the membrane material, it can also be adjusted by the membrane pore size [3].

The objective of the research was to treat the POME by using performance of cellulose acetate membrane with additive PEG and acetone in removing TSS and turbidity. The characterization of the membrane include SEM, FT-IR and permeability coefficients.

2. Experimental procedure and methodology

2.1. Materials
The type of polymer that has been used in this experiment are cellulose acetate supply by Sigma-Alderich, acetone as solvent, PEG and formamide as additives. As liquid waste was used the POME from PT Surya Panen Subur II Kabupaten Nagan Raya, Aceh Province.

2.2. Membrane preparation
Membrane preparation was carried out by phase inversion method. The cellulose acetate was dissolved into the acetone and then mixed with the additives PEG and formamide at room temperature. The solution was stirred for 8 hours and save in the refrigerator for 2-3 hours until no bubbles were observed. Then, the cellulose acetate solution was casted on a flat glass plate and immediately immersed in a destilled water bath as coagulant. Then the membrane followed by annealing process, and then immersion in hot distillate water (70°C) for 20 minutes. The variations of casting cellulose acetate solution used in this experiment are shown in Table 1.

| Membrane code | Composition of cellulose acetate solution |
|---------------|------------------------------------------|
|               | Cellulose acetate | Acetone | PEG (%) | Formamide |
| CA-1          | 15              | 85      | 5       | -         |
| CA-2          | 15              | 75      | -       | 10        |

2.3. Characterization of membrane

2.3.1. SEM. The prepared membrane was characterized by scanning electron microscopy (SEM) to obtain visual information of the top surface structure and geometric pore. Surface of the membrane sample was cuted to 0.5 x 0.5 cm and then the sample is attached to the sample plate (brass disk) and deposited with gold using a sputter coater. Then, the sample was imaged using a scanning electron microscope (low vacuum) with a magnification of 5000 times
2.3.2. **FT-IR.** Analysis of Fourier Transform Infrared Spectroscopy (FT-IR) Spectrometer employed to characterize the membrane in absorption spectra which provide information about the surface organic structure. The analysis was used by using a FT-IR spectroscopy (Shimadzu FT-IR Spectrometer). The sample cut into 1 x 1 cm then was put into the Nicolet Avatar FT-IR Spectrometer. Spectra were recorded in the range 4000-400cm⁻¹.

2.3.3. **Coefficient permeability membrane.** Permeability is carried out by permeation experiments with pure water. The membrane flux is obtained from each pressure difference. Membrane permeability was obtained from the graphical slope between pressure and flux.

2.4. **Test the performance of membrane**

The membrane performance test was performed by passing the POME liquid through the ultrafiltration module at a pressure of 2 bar. POME liquid waste was performed before membrane process, by filtering out suspended particles. The membrane rejection was calculated based on TSS and turbidity.

3. **Result and Discussion**

3.1. **Characterization of the membrane**

3.1.1. **Effect of additives at SEM analysis.** Surface structure of the membrane blending with PEG and formamide (CA-1 and CA-2) has investigated by SEM in Figure 1. The CA-1 membrane (Figure 1A) provides a uniform pore structure and spread more evenly on the surface compared to the CA-2 membrane (Figure 1B). Membrane CA-2 the structure surface more smooth. This suggests that PEG have a major effect on the formation of pores rather than formamide.

The addition different additives into membranes influence the pores formation in the membranes structure [2]. Ramos-Olmos et al. (2008) [4] also employed that the different additives will increase the voids size. The SEM images indicated that the membranes have asymmetrical structure with a skin layer at the top, intermediate layer and a bottom layer [4]. The different additives displayed improved characteristics of the membranes such as porosity optimum, large pore size and thin membrane thickness coupled with finger-like structure extended from both inner and outer layers of the membrane [5]. All of condition could be observed by SEM cross section of the membranes. But the cross section images does not imply in this study.

![Figure 1. SEM images of the cellulose membrane with additives on the surface membranes (A) PEG and (B) formamide.](image)

Additives in the membrane will provide large pores compared to membranes without additives. This is
shown that adding PEG as an additive will increase membrane pore, while maintaining membrane resistance to external factors [6]. Rosnelly (2012) [6] has implied that high flux on the membrane with the addition of PEG compared to the membrane without PEG. The higher concentration of PEG, the larger pore size form of the membrane. This is because the addition of PEG is homogeneous into the polymer and the solvent. In the process of immersion into PEG coagulation tubs will also diffuse into non-solvent. The more PEG that dissolves into water the larger of pore size is generated and the PEG additive is scattered on the membrane surface and also increases the porosity of the membrane [7].

3.1.2. Effect of additives at FT-IR analysis. FT-IR spectroscopy is used to highlight differences in the functional groups effect of additives PEG and formamida. The effect of different additives on cellulose acetate membrane is used to determine the compounds present in the membrane. The effect of additives on the structure membrane can be seen in Figure 2.

![Figure 2. FT-IR spectra of cellulose acetate membranes with formamide and PEG.](image)

The presence of carbonyl groups in Figure 2 shows that cellulose acetate and acetone in the membrane (Figure 2. A and B). In Figure 2A with a wavelength of 3483.44 cm\(^{-1}\) representing the absorption of the wavelength contains the OH functional group. In the presence of the group identifies (-OH) the presence of PEG additives on the cellulose membrane. In Figure 2B there is a C-N amide group at wavelength 1180-11360 cm\(^{-1}\). In the presence of CN-amide on the FTIR spectrum identifying the presence of a formamide additive contained in the membrane.

3.1.3. Coefficient permeability membranes. The permeability coefficient (Lp) is the membrane's ability to pass water (aquadest) on the basis of pressure increase [1], where flux is determined by passing aquadest under operating pressure conditions. Lp of the membrane is obtained from the graph slope to the operating pressure [8]. Table 2 show the result of Lp.

| Type of membrane | Lp (L/m\(^2\).h.bar) | Flux (L/m\(^3\).h) |
|------------------|----------------------|-------------------|
| CA-1             | 17.95                | 23.32             |
| CA-2             | 9.21                 | 19.40             |
Base on permeability of the membrane (Lp), ultrafiltration membrane has a Lp range of 10-50 L/m².h.bar. and the nanofiltration membrane has a Lp range 1.4-12 L/m².h.bar. From Table 2, type of membrane CA-1 with additives PEG in range ultrafiltration membrane but of CA-2 with additive formamide in range nanofiltration membrane.

From the flux it is also known that the CA-1 membrane with PEG additive has a higher flux value than the CA-2 membrane with formamide additives. The second flux value of the membrane can be seen in Table 5. The flux value on the CA-1 membrane is higher than of CA-2. This indicates that the surface pore size is larger [9]. Increased pores result in the flow of water more easily pass through the membrane. Aprilia et al (2013) [10] mentions that membranes with a dense pore structure will have greater mass transfer resistance, so water permeability becomes smaller.

3.2. Performance of the membranes in POME treatment
Flux is one of parameter that is measured in deriving parameters on POME. Table 3 show the fluxes of the two membranes. Flux membrane CA-1 larger than membrane CA-2. The effect of PEG additives on cellulose acetate membranes provides a larger pore size than that of formamide additives in membrane.

| Membrane Type | Flux (L/m².h) |
|---------------|--------------|
| CA-1          | 8.30         |
| CA-2          | 7.55         |

The result of research on membrane performance as an additive influence on decreasing parameter of POME such as turbidity and total suspended solid (TSS) has been done. Turbidity is a parameter used to indicate the level turbidity of a waste. In this research, the value of POME turbidity before separation is 4.85 NTU. After the separation process of POME turbidity is successively CA-1 and CA-2 membranes are 3.28 and 2.62 NTU. The rejection calculation obtained turbidity rejection value as in Table 4. From the Table 6 showed that CA-1 membrane capacity gave a greater percentage of yield than the CA-2 membrane.

| Type of membrane | Percent of rejection (%) |
|------------------|--------------------------|
|                  | Turbidity    | TSS         |
| CA-1             | 59.79        | 38.46       |
| CA-2             | 63.09        | 53.85       |

From the membrane characterization results, the CA-2 membrane has more dense pores, and the ability to pass permeate is better than the CA-1 membrane. So the percent of rejection for TSS and turbidity on the CA-2 membrane is greater than that of the CA-1 membrane. According to Sofyana et al (2011) [11]. The value of rejection is inversely proportional to the value of flux obtained. The higher the value of flux, the value of rejection obtained will be lower. This is because the larger the POME flowing through the membrane, the resistance on the membrane surface becomes smaller.

4. Conclusion
Based on the results of the study can be concluded that SEM analysis shows the additive variation on the
cellulose acetate membrane makes the membrane have different pore structure. The addition of PEG additive makes the distribution and pore size of the membrane more evenly compared to the additive of formamide. The CA-1 membrane provides good membrane performance over the CA-2 membrane in terms of flux and the CA-2 membrane performs better than the CA-1 membrane in terms of TSS and turbidity injection percent of POME. Cellulose acetate membrane with PEG additive is better than formamide additives.

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