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# INCREASING SEPARATION PERFORMANCE OF PES`MEMBRANE VIA COMBINATION OF POLYMER COMPOSITION AND UV IRRADIATION FOR PRODUCED WATER TREATMENT

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## ABSTRACT

Produced water is generated in large quantities from oil processing and petroleum. Before being discharged into the environment, produced water need a pre-treatment. In this research will be produced ultrathin membrane nanofiltration with polyethersulfone polymer materials for produced water treatment. Specifically, the objectives of this research are to produce ultrathin nanofiltration membrane to investigate the effect of polymer concentration and Ultra violet irradiation toward the surface structure and polyether sulfone membrane activity for the produce water treatment. Membrane is produced by phase inversion method with composition of polyether sulfone used 15, 17 and 19 %wt, respectively. This research of production of the polyethersulfone membrane for produced water treatment is conducted by varying the UV irradiation time 10 until 300 seconds. The membrane performance will be investigated using dead end filtration cell with the flux and rejection parameters. The membrane characterization will be done using SEM and FTIR analysis. Product analysis is done to determine the turbidity, TDS, COD, $Ca^{2+}$, $S^{2-}$ and oil content in the produced water before and after membrane separation. PES membrane with a concentration of 19 wt% performed the best rejection rate. UV irradiated membrane flux tends to rise due to the influence of UV light that makes the better pore structure of the cavity so that the membrane flux becomes high.

**Keywords:** cellulose acetate, membrane, polyethylene glycol, phase inversion method, ultra violet.

## INTRODUCTION

Produced water is ground water as waste in the production process of crude oil. A large volume of produced water is usually produced as by product during recovery of natural gas and crude oil from offshore and onshore production operations. Produced water out along with oil is taken to the surface by bringing a variety of compounds that are harmful. Existing content in produced water include COD, grease, oil, dissolved sulfide, ammonia, total phenol dan TDS (Alzahrani *et al*., 2013a). Due to their toxic nature and effects on the environment, the proper management of produced water is becoming major issue for the public and regulators due to high volume generated and the disposal practices of many gas and oil companies.

Some conventional methods require more chemicals and produce sludge which needs complex handling processes. (Weschenfelder *et al*., 2015; Zhang *et al*., 2013; Ahmadun *et al*., 2009). A membrane is one of water treatment technology with filtration based method. Membrane capable of separating specific chemical components, can operate at low temperatures, continuous, low energy consumption, indestructive technology for treated feed and environmental friendly (Motta *et al.,* 2014; Mondal and Wickramasinghe 2008). Membrane is a selective obstacle between two phases. The membranes have different thicknesses, there are thick and some are thin and there is a homogeneous and there is also a heterogeneous. Membrane serves to separate material by size and shape of the molecule, hold the components of the feed which has a size larger than the membrane pores and missed components that have a smaller size (Alzahrani *et al*., 2013b). Produced water treatment using membrane separation method is expected to reduce the contaminant content effectively.

Membrane stability and good membrane performance are important factor in the membrane application. Polyethersulfone (PES) offers an excellent mechanical strength and thermal stability during membrane treatment operation (Baker, 2004). The optimum conditions are affected by the performance of membrane permeability and selectivity of chemical compounds, the greater permeability and selectivity of the membrane increase the performance of the membrane (Macedonio *et al*., 2014; Cakmack *et al*., 2008 and Kirk *et al*., 1996). However, current conditions are selectivity or rejection on the separation membrane is inversely proportional to the permeability or flow rate products. The efforts to create membrane material with high permeability and selectivity are the main objective of the current study. All of the membrane properties are dependent on dope solution (polymer concentration, solvent), casting temperature, solvent evaporation rate, thickness of cast solution, and post treatment (Bargeman and Smolders, 1986).

In this study, PES membranes with different concentration of polymer are fabricated using inversion phase technique and the membrane films are also subjected under UV irradiation. The combination of PES concentration variation and UV irradiation are expected to produce the membrane materials with more resistant to fouling characteristic. The performances of membrane in terms of permeate flux and contaminant rejections are investigated.

## EXPERIMENTAL

### Materials selection

The materials used in this research are polyether sulfone (PES), n-methyl-2-pyrrolidone (NMP) and original produced water. Polyethersulfone was supplied by Solvay Advanced Material (USA). The polymers were dried in a vacuum oven at 120 $^{o}$C overnight before dope preparation; N-methyl-pyrrolidinone (NMP) from Merck was used as the solvent due to its low toxicity.

### Fabrication of polyether sulfone membranes

In this study, homogenous dope solution consists of polyether sulfone (PES) of 15, 17 and 19 wt% concentration was dissolved in mixture of N-methyl-2pirrolydone (NMP). The dope solution was agitated with a stirrer at least 24 hours to ensure complete dissolution of the polymer. After all of the materials mix completely, the dope solution allowed to stand for 24 hours to remove bubbles. Casting membranes using phase inversion method that is by casting membrane on glass plate, and then in some membranes were irradiated with UV rays and then put into the coagulation bath for one hour followed in different coagulation bath for 24 hours and then the membrane was dried for 48 hours (Wenten, 1999; Mulder, 1996).

### Characterization of polyether sulfone membrane

### Permeation test

Produced water flux measurements by using dead end filtration system. The filter paper and membrane placed with effective area 12.57 cm$^2$ was placed in the cell filtration. 5 liters distilled water was filled in feed tank in a cell filtration and sealed, the compaction process was conducted for 30-45 minutes. After the compacting process, distilled water in a filtration cell was replaced with original produced water feed, produced water flux measurement by measuring the volume of produced water that can be accommodated during a certain time interval with intervals 15 minutes. Flux was calculated by the ratio of permeate volume per unit area of membrane per unit time as shown in equation (1). Rejection coefficient determination was calculated by determining the concentration of pollutant present in produced water before and after treatment process using membrane as shown in equation (2).

$$J = \frac{V}{A.t} \tag{1}$$

$$R = \left(1 - \frac{C_P}{C_F}\right) x\, 100\% \tag{2}$$

The test of membrane performance begins with an analysis of turbidity. The analyzes were performed by turbidimeter, turbidimeter will analyze the value of NTU turbidimeter (Nefelometrik Turbidity Unit) produced water before and after passing through the membrane. The next analysis is the analysis of TDS of the produced water before and after passing through the membrane. The basic principle of measurement is the produced water which as homogeneous that has been filtered with a glass fiber filter paper, the filtrate is collected in a cup and evaporated at a temperature of 180$^0$C ± 2$^0$C and weighed to obtain a constant weight. The increase in weight of the cup is proportional to the weight of total dissolved solids (TDS). And then analysis of $Ca^{2+}$ with materials used for analysis of $Ca^{2+}$ ions are the indicator Mureksid (C8H8N6O6), indicator Eriochrome Black T (EBT = $C_20H_{12}N_3NaO_7S$), 1 N NaOH, pH 10 buffer solution, the standard solution of calcium carbonate ($CaCO_3$ 0.01M ), disodium ethylenediamine tetra acetate dihydrate ($Na_2EDTA_2H_2O$ = $C_{10}H_{14}N_2Na_2O_{8}.{}_2H_2O$) 0.01 M, KCN powder and distilled water. First, take 50 mL of sample and add 2 ml of 1 N NaOH solution until range of pH 12-13. For test turbidity, add 1mL to 2 ml of 10% KCN solution. Add the tip of a spatula or equal to 30 mg - 50 mg murexid indicator. Titration with a standard solution of 0.01 M $Na_2EDTA$ until the color changes from pink to purple. Record the volume of standard solution $Na_2EDTA$ used and calculated $Ca^{2+}$ content using the equation below:

$$Ca\ (mg/L) = \frac{V_{titrant}\ x\ M_{EDTA}\ x\ BM_{Ca}\ x\ 1000}{V\ samples}$$

Other parameter is $S^{2-}$ ion analysis with iodometri prinsiple. The materials used for the analysis of $S^{2-}$ ion are 0.1N KI solution, a solution of 1 N $Na_2S_2O_3$, indicators amylum, $K_2Cr_2O_7$ solution 0.01 N $NH_4OH$ and $H_2SO_4$ solution, concentrated HCl solution and distilled water. Acidity test on the sampel was performed first, $NH_4OH$ and $H_2SO_4$ were used to maintain the pH of solution. 10 mL sample was prepared for titration; add 12 ml of 0.1 N KI solutions. Titration was performed using $Na_2S_2O_3$ as titrant and the end of titration was indicated by the color change of solution become colorless, amilum indicator was used to confirm the presence of remaining iodine. The required titrant is used to calculate $S^{2-}$ contents by using the equations below:

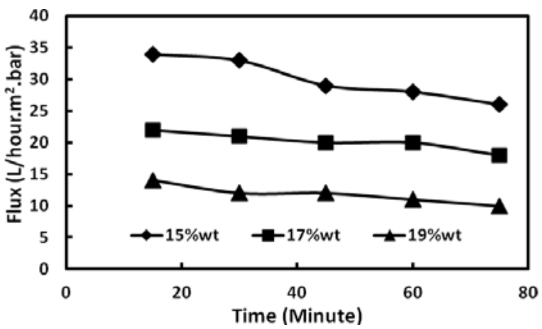
$$S^{2-} = (V.\ N)\ Na_2S_2O_3.\ BM\ S.\ \frac{1000}{V\ sample}$$

The permeate water flux and rejection rate result from the performance test were discussed to investigate the effect of polymer concentration of polyethersulfone and UV irradiation on the membrane surface during casting to the performance membrane for produced water treatment.

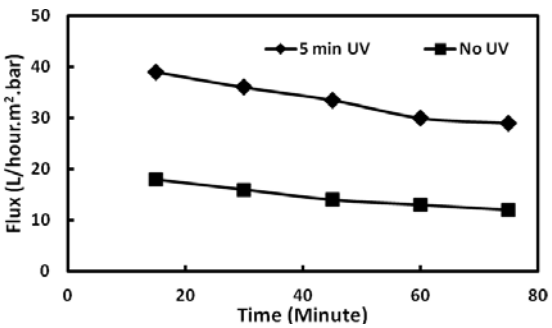
## RESULTS AND DISCUSSIONS

### Effect of PES concentration and UV irradiation to flux of the membrane

Performance of polyethersulfone membrane is determined by membrane flux profile. Flux of the prepared membrane is measured by dead end filtration device to obtain flow rate membrane permeate per unit area per unit time.




(a)




(b)

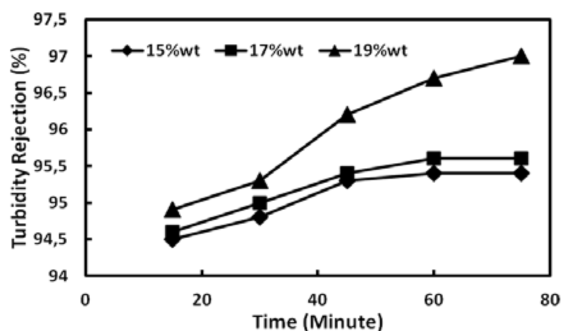
**Figure-1.** (a) Effect of PES concentration to flux value of produced water (b) effect of Irradiation UV rays to flux value of produced water.

Figure-1 (a) shows the PES membranes with varying concentrations. Flux value of membrane decreases during the time. So that the increasing time causes decreasing of flux value. This is because more long the time of operation, more fouling which occurs at the membrane. This fouling will be increased, and will pile up at the pores of the membrane, which makes the membrane becomes more severe and resulted the lower number of permeate produced. Because the permeate flux is proportional to the volume of the permeate at a certain time, so that the decreasing of volume permeate causes the decreasing of flux (Chen *et al.*, 2009). Can be seen in the Figure-1 (a) that the membrane with a concentration of 19wt% PES has the smallest value of flux and the membrane with a concentration of 15wt% PES has the highest value of flux. This is because the principle of filtration mechanisms, there are sifting or screening process based on particle size that will pass. The results show that more high the concentration of PES, will smaller the flux obtained. This is because of the higher concentration of PES, will be decreasing the pore size of the membrane surface. Because the amount of solvent released into the coagulation solution during the process of coagulation are decrease (Ahmad, 2005). Small pores causes the flow past the membrane will be slower and also the flux value of the membrane.

From Figure-1 (b) can be seen a different phenomenon occurs at the membrane which irradiated UV rays for 5 minutes, the membrane flux are increase than the membrane flux without UV irradiation. UV irradiation makes the membrane pores become macrovoid. Although the pores of the membrane are closer, the pore structure of the membrane is better so so the filtrate can be flow faster and obtained a higher flux. This phenomenon also occurs in the earlier study (Nur et al., 2013) that the membrane which irradiated with UV rays has the decrease of flux, but at a certain exposure time will increase as an impact of UV radiation flux.

**Effect of PES concentration and UV irradiation on the membrane rejection**

One that determines the performance of a membrane is the percent of rejection. It is necessary to do test rejection used the permeate results from produced water filtration.

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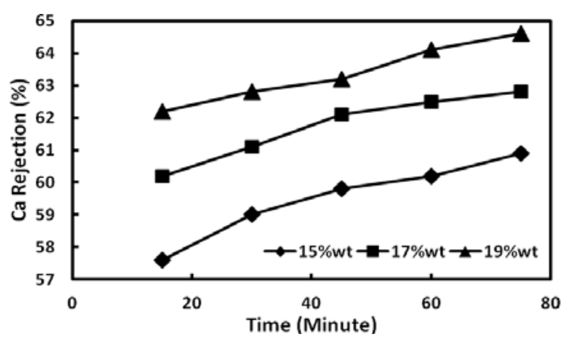


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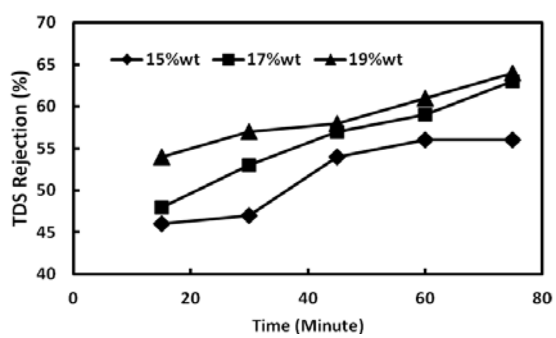


(c)

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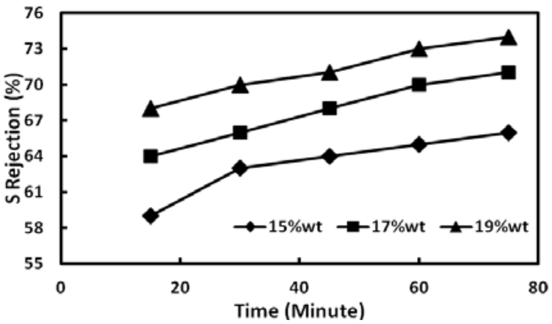


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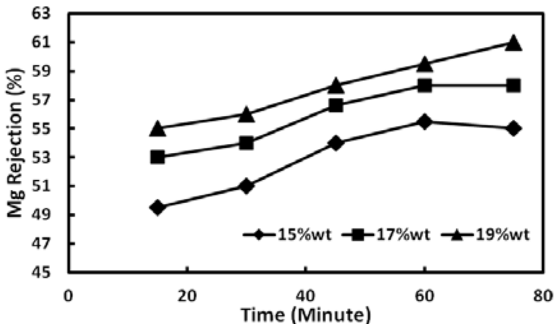
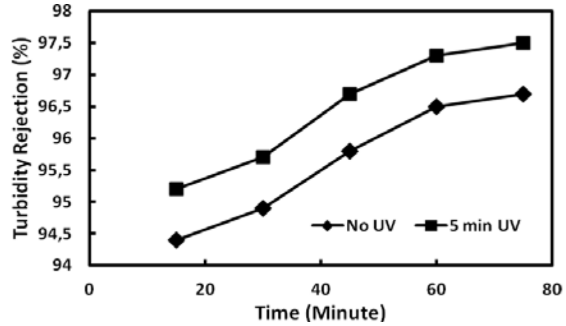


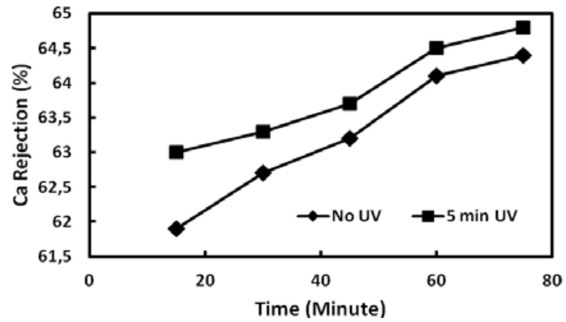

(e)

**Figure-2.** The effect of PEG concentration to percent rejection of the produced water (a). Percent rejection of turbidity (b). Percent rejection of TDS (c). Percent rejection of $Ca^{2+}$ (d). Percent rejection of $S^{2-}$ (e). Percent rejection of $Mg^{2+}$.

Based on Figure-2 (a) - (e) membrane with PES concentration 19wt% has the highest percent rejection, while the PES membrane with a concentration of 15wt% has the smallest percent rejection. This shows that the higher the concentration of PES in the dope solution, the percent rejection membranes of the produced water will be higher too. As has been explained previously that the membrane pore size formed will be smaller when the higher concentration of PES in dope solution. Pore size of the membrane that forms made contaminants such as TDS, $Ca^{2+}$, $M^{2+}$ and $S^{2-}$ restrained. And for turbidity apart because the pores are small, PES membrane is a hydrophobic membrane so that turbidity which comes from oil from produced water will be attached to the membrane and the membrane turns into yellow. Figure-2 (c) - (e) shows that the rejection of $Ca^{2+}$ ion rejection higher than the ion rejection of $Mg^{2+}$ and ion rejection of $Mg^{2+}$ higher than $S^{2-}$. The difference between the ions is proportional to the size of molecules. From the three ions, $Ca^{2+}$ ions have the biggest molecular size with a radius 190 pm so $Ca^{2+}$ have the highest rejection. For ion $Mg^{2+}$ and $S^{2-}$ in sequence has a size of molecules with a radius of 145 and 88 pm.




(a)

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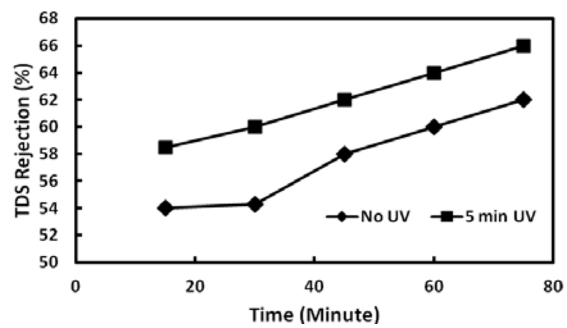


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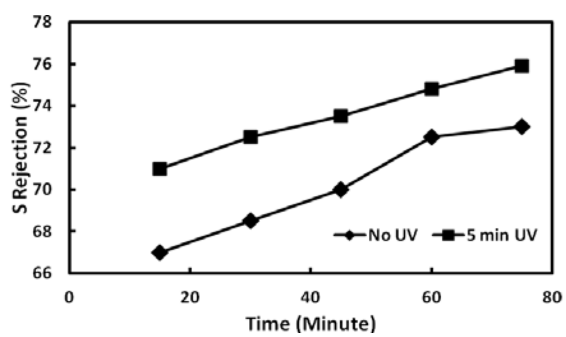


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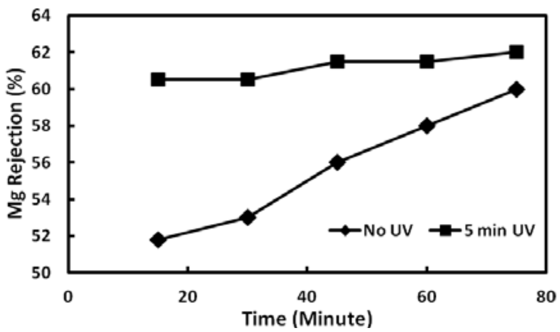


(e)

**Figure-3.** The Effect of UV Irradiation to Percent Rejection of the produced water (a). Percent rejection of turbidity (b). Percent rejection of TDS (c). Percent rejection of $Ca^{2+}$ ion (c). Percent rejection of $S^{2-}$ ion (e) Percent rejection of $Mg^{2+}$.

To determine the effect of UV irradiation exposure the time of the rejection of the membrane, in this research, manufactured 19wt% PES membrane with UV irradiation and without UV irradiation. The membrane was applied to the produced water filtration and the percent rejection for TDS, turbidity, ion $S^{2-}$, $Ca^{2+}$ ions and $Mg^{2+}$ ions will be calculated. Based on Figure-3 (a) - (e), membrane with UV irradiation provides higher rejection than the membrane without UV irradiation. This indicates that the PES membrane rejection increased with UV irradiation. Irradiation causes chain scission and crosslinking processes more perfect so that percent of rejection membrane against contaminants are increase (Ravikumar *et al*., 2015; Kaeselev *et al*., 2002). In addition to the effects of UV irradiation, there are the effects of evaporation; evaporation will lead to more dense pores so percent of the rejection will increase.

## CONCLUSIONS

Ultra thin polyether sulfone (PES) membrane produced by the method of inverse phase, where the concentration of PES and UV radiation effect on the formation of membrane pores. The larger the concentration of PES in the membrane causes the smaller the pore size on the surface of the membrane so that the membrane rejection higher and the flux is lower. PES membrane with a concentration of 19wt% performed the best rejection rate. UV irradiated membrane flux tends to rise due to the influence of UV light that makes the better pore structure of the cavity so that the membrane flux becomes high. PES membrane rejection intensified with the process of UV irradiation, because UV radiation causes chain scission and crosslinking processes more perfect that rejection membrane against contaminants increasing. Besides the pressure applied to the membrane by UV irradiation, lower pressure and relatively stable there is no increase where it shows fouling not affect in this separation process and in the presence of UV radiation can prevent fouling.

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