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Research Article
Surface Modification and Performance Enhancement of Polyethersulfone (PES) Membrane Using Combination of Ultra Violet Irradiation and Thermal Annealing for Produced Water Treatment

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Abstract
Background: Produced water is waste water from crude oil production process. A large volume of water is produced during operation as a by-product. This volume is expected to increase from maturing conventional oil and gas fields. Due to its hazardous contents, produced water needs to be treated before disposing to the environment or being utilized. **Materials and Methods:** The membrane was prepared by casting a stable and homogeny dope solution containing 19% weight polyether sulfone and 81% weight n-methyl-2-pyrrolidone using dry/wet phase inversion technique. The performance of the membrane was investigated as effects of set of variables: UV irradiation (10, 25 and 300 sec), annealing temperature (150 and 180°C) and annealing time (10, 25 and 60 sec). Permeation test was used to investigate flux and rejection, SEM analysis was used to observe the morphology of the membrane and FTIR analysis was employed to investigate the functional group contained in the membrane. **Results:** Flat sheet PES membranes were successfully fabricated via dry/wet phase inversion technique. Subjecting the membrane under UV irradiation for 300 sec showed the highest flux of 38 L h^{-1} m^{-2} bar^{-1}. The annealing treatment to the membrane at 180°C for 10 sec performed the highest rejection efficiency of 76% as S^{2-} rejection, 70% as TDS rejection and 65% as Ca^{2+} rejection. Cross-sectional SEM images showed the asymmetric and finger-like structure, the surface images showed no voids could be observed. The FTIR spectra analysis showed the formation of hydrophilic functional group as an effect of UV irradiation on the membrane surface. **Conclusion:** The PES membrane was successfully modified using UV irradiation and thermal annealing treatment. The UV irradiation on the membrane for 300 sec and thermal annealing at 180°C for 10 sec significantly increased the flux and rejection.

Key words: Polyethersulfone membrane, produced water, UV irradiation, thermal annealing

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Produced water is waste water from crude oil production process. Produced water is generated along with oil from the reservoir and contains much of dangerous pollutants such as organic compounds, salt, sulfide and heavy metals. Over the economic life of producing field, the volume of produced water can be more than 10 times the volume of hydrocarbon produced. This volume is expected to increase with age conventional oil and gas fields. Produced water contains high concentration of minerals and emulsified oil in water. Therefore, before being disposed of, it should be given some treatments properly so that the produced water is appropriate with quality standard for disposal or utilization purposes[1]. Produced water can be used for oil well water injection to enhance oil production. The utilization of produced water as oil well water injection could maintain the pressure of reservoir during crude oil production process[2]. The benefits of using this method are it keeps the environment clean and it can reduce the hazardous contaminant that can affect human health, plants and the others. There are many pre-treatment methods that can be used such as air flotation, hydrocyclone, coalescer bed and filtration. Conventional waste water treatment technologies such as air floatation, hydrocyclone and coalescer bed normally cannot meet the high purity requirement for oil well water injection quality standard. Filtration technology is one of other alternative technologies that can be developed because it has many advantages[2].

Membrane based separation technology is one of many water treatment technologies. Membrane capable to separate chemical components specifically, mild operating condition, continuously, energy saving, the process is not destructive for the separated components and low negative impact on the environment. The membrane is a selective obstacle between two phases. The membrane separates material based on molecule size and shape, sustain the component from the feed that is having a larger size than membrane pores and release the component that is having a smaller size. Nano filtration membranes have nano-scale pore size, between 0.5-2 nm, therefore, it can be used to filter out dissolved solids with low molecular weight effectively. An asymmetric membrane is one of membrane types which is often applied in water treatment because of a higher flux of an asymmetric membrane. The flux resulting from an asymmetric membrane is higher than symmetric membrane due to a dense layer of the asymmetric membrane surface.

The polymer-based membrane was chosen for water treatment instead of metal oxide/ceramic based membrane due to the asymmetric structure of the polymeric membrane[3]. Several polymers which are widely used as membrane material such as cellulose acetate, polyacrylonitrile, polysulfone, polyethersulfone, polyamide, polyetherimide and polyvinyldeneflouride. Polyethersulfone (PES) is a membrane material that is often used, because it has good characteristics, resistant to chemicals, robust, tolerant of high temperatures and has a high dimensional stability for use as a membrane under various conditions.

The current condition, membrane separation for water treatment still have some weaknesses such as rejection decreasing along with flux increasing and fouling. Several methods were studied in previous studies to improve the performance of the membrane. Chemical treatment, polymer blending, UV photo-grafting and cross-linking were conducted to enhance membrane performance in terms of permeability and selectivity[4,5]. Zhuang[6] have prepared thermal annealed PPO-silica mixed matrix membrane, they stated that thermal annealing treatment at a temperature close to the polymer glass transition (Tg) induced the polymeric chain re-crystallize to form smaller pores size, thus significantly improved the selectivity of the membrane. Konruang[7] studied the surface modification of polysulfone membrane by UV irradiation, they stated that the result based on FTIR analysis showed the formations of polar functional groups such as hydroxyl and carbonyl groups. Consequently, the surface of asymmetric polysulfone membranes was changed from slightly hydrophobic to hydrophilic by UV irradiation leading to the enhancement of the water flux. Similar studies have been reported by Abu Seman *et al*.[8] and Homayoonfal *et al*.[9] that UV irradiation on the membrane surface enhanced water flux of membrane. However, the proposed methods still have high deposition of foulant on the surface of the membrane that caused lower productivity. Therefore, the present study proposes an alternative preparation of asymmetric polyethersulfone membrane by introducing the membrane under ultraviolet irradiation as the pre-treatment surface of the membrane and thermal annealing as post-treatment of membrane surface to increase separation performance of asymmetric polyethersulfone membrane for oil field produced water treatment. Based on the previous study, there is no documentation about the combination treatment of ultraviolet irradiation and thermal annealing to modify the surface of polyethersulfone membrane. The combination of irradiation and thermal annealing was expected to improve the membrane structure so that it enhances membrane performance for produced water treatment and improves the anti-fouling performance.

MATERIALS AND METHODS

Materials selection: Polyethersulfone was supplied by Solvay Advanced Material (USA). The polymers were dried in a vacuum oven at 120°C overnight before dope preparation; N-methyl-pyrrolidinone (NMP) from Merck was used as the solvent due to its low toxicity. Produced water was taken at PT. Pertamina Jatibarang as samples.

Fabrication of polyethersulfone membranes: Asymmetric polyethersulfone (PES) membrane was produced with a dope solution containing of PES as much as 19% weight and n-methyl-2-pyrrolidone (NMP) as a solvent. Membranes are casted using dry/wet phase inversion method. This method was done by casting the membrane on the glass plate using a casting knife. To investigate the effect of UV irradiation, before being put into the coagulation bath, the membrane films on the glass plate were irradiated with UV rays for 10 sec and 5 min, subsequently the membrane films was immersed into the coagulation bath containing distilled water and they were left for 24 h in distilled water. The membrane was then dried at ambient temperature for 24 h. Furthermore, to examine the effect of post treatment, such as temperature and heating time, the membranes were heated in an oven at temperature of 150 and 180°C for 10 sec. To determine the effect of heating time, the membranes were heated for 10, 25 and 60 sec.

Characterization of polyethersulfone membrane permeation test: Flux value was determined by dead-end filtration cell. The schematic diagram of dead-end filtration cell was depicted in Fig. 1. Polyethersulfone (PES) membrane with effective area of 12,57 cm^2 was mounted inside of dead-end filtration cell and reinforced by a piece of fine cloth. Before permeability test, the membrane was compacted with aquadest for 30-45 min with constant pressure 3.5 bar gauge, hence the polymer chains could arrange themselves. After that, aquadest in the feed tank was replaced by produced water. Produced water fluxes values were obtained by measuring the permeate volume every 15 min. Flux value was calculated using the Eq. 1. Determination of membrane permeability was performed by determining the concentration of Total Dissolved Solid (TDS), turbidity, S^{2-}, Ca^{2+} and Mg^{2+}. Determination of produced water TDS was performed using a TDS meter, the analysis of produced water turbidity was determined by turbidimeter, while the determination of S^{2-}, Ca^{2+} and Mg^{2+} ions were using substitution and hardness titration. The rejection percentage was determined by measuring the concentration of feed and permeate water:

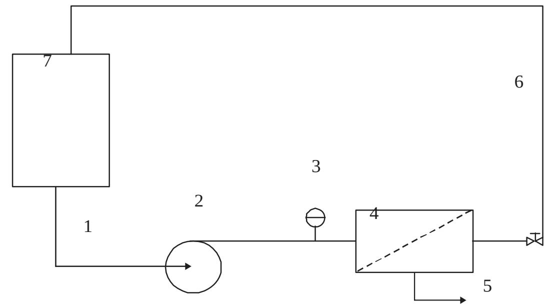

Fig. 1: Dead-end filtration cell, 1: Feed stream, 2: Feed pump, 3: Pressure gauge, 4: Membrane module, 5: Permeate, 6: Retentate and 7: Feed tank

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

Where:

J = Flux (L m^{-2} h^{-1} bar^{-1})
V = Volume of permeate (L)
A = Membrane surface area (m^2)
T = Time (h)
P = Pressure (bar)

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{2}$$

Where:

R = Membrane rejection coefficient (%)
C_p = Solute concentration in permeate
C_f = Solute concentration in feed

Scanning Electron Microscopy (SEM): Membrane characterization with Scanning Electron Microscopy (SEM) was used to determine the cross-sectional and surface morphology of the membrane. The membrane samples were cleaned with filter paper, then fractured in liquid nitrogen and coated with a gold layer by sputtering. The SEM analysis was done in Mineral and Advanced Material Laboratory, Central Laboratory of Science and Mathematic Faculty, State University of Malang, Indonesia.

Fourier Transform-Infrared Spectroscopy (FT-IR): Characterization membrane using FTIR is used to determine the functional groups of the membrane product. The FT-IR analysis was done in Mineral and Advanced Material Laboratory, Central Laboratory of Science and Mathematic Faculty, State University of Malang, Indonesia.

RESULTS AND DISCUSSION

Produced water used in this experiment is a byproduct of oil refinery activities such as three phase separation, dehydration and hydrocarbon stabilization. A large volume of water was obtained from those activities. Produced water contains high concentration of mineral salts and oil, the initial characteristic of the produced water used in this experiment was shown in Table 1.

Based on Table 1, the initial concentration of mineral salts in produced water is much higher than waste water quality standard that may be discharged into the environment. Due to its hazardous content in the produced water, it needs to be treated before being disposed.

Effect of ultraviolet on the flux of PES membrane for produced water treatment: Ultraviolet (UV) is electromagnetic radiation with a wavelength from 10-400 nm, shorter than visible light but longer than x-rays. The UV carries high photon energy which the radiation can cause chemical reaction. Polymers which are subjected to UV exposure will change their structure. Polymer alteration of the membrane will affect to the separation performance. The effect of UV irradiation on the PES membrane flux in treating produced water was presented in Fig. 2.

Based on Fig. 2, membrane flux which is UV irradiated for 10 sec is lower compared to membrane flux without UV irradiated. The same phenomenon was also occurred for membrane with UV irradiation for 25 sec, respectively. There is no possibility of any special effect in UV irradiation time for 10 and 25 sec, there is the only effect from evaporation, so it will make the flux decreasing compared to membrane without UV irradiation. This could be due to the time lag between the membrane after being casted and before being put into a coagulation bath (delayed mixing) which caused the formation of the non-porous membrane[10]. When the solvent is evaporated, polymer solution which is still in liquid phase moves to fill the pores producing a membrane with dense structure.

The different phenomenon occurs to UV-irradiated membrane for 300 sec. The membrane flux is higher than the membrane flux without UV irradiation and the membrane flux with 10 and 25 sec UV irradiation. High flux occurs because of UV irradiation that makes membrane pores become larger. Although membrane becomes denser, the pores structure getting better so the water can quickly through the membrane thus the flux UV irradiated membrane is higher than membrane without UV irradiation. The pores structure of membrane that has been UV irradiated can be seen in Fig. 3. This phenomenon also occurs in the earlier study[7,11], the results showed that UV irradiated membrane flux kept decreasing at the initial stage but at a certain exposure time will increase the membrane flux.

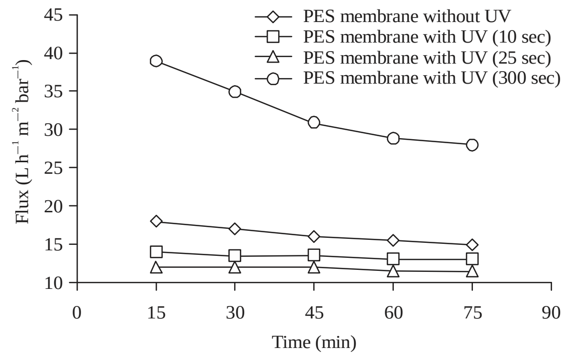

Fig. 2: Effect of UV irradiation on the membrane flux

Table 1: Characterization of produced water

Parameters	Analysis result
TDS (mg L^{-1})	6500
Turbidity (NTU)	80.6
Sulfide (mg L^{-1})	1536
Ca^{2+} (mg L^{-1})	2834
Mg^{2+} (mg L^{-1})	267
COD (mg L^{-1})	150.82
Oil content (mg L^{-1})	0.15

Table 2: Rejection rate of the UV irradiated PES membrane

	Rejection (%)				
Membrane	TDS	Turbidity	Sulfide	Ca^{2+}	Mg^{2+}
PES membrane without UV irradiation	57.88	95.59	70.09	63.22	56.35
PES membrane with UV irradiation (300 sec)	62.50	96.39	73.45	63.94	62.11

Effect of ultraviolet on the rejection of PES membrane for produced water treatment: Rejection is an important parameter of the membrane performance which indicates the selectivity of the membrane. Membrane rejection ability depends on membrane structure. Table 2 shows that rejection of each ion has the same tendency that the percent of rejection with 300 sec UV irradiation is significantly higher than membrane rejection without UV irradiation. This happens due to the effect of UV irradiation that makes membrane become denser so it can preclude more contaminants through to the quarter. The UV irradiation causes chain scission and cross-linking[12]. Cross-linking and chain scission caused the membrane with single polymer chain bind to other bonds producing a membrane with denser structure. Some earlier works[8,9,13] revealed the effect of UV-assisted surface modification of the polymeric membrane, at the specific time the UV irradiation decreased the membrane pores size slightly but for longer UV irradiation pores sizes become larger.

Figure 3 shows that the pressure applied to the membrane without UV irradiation tends to increase during the filtration process. Meanwhile, membrane with UV irradiation has lower pressure and relatively stable where it indicates that fouling is not so influential in the process of this produced water treatment filtration.

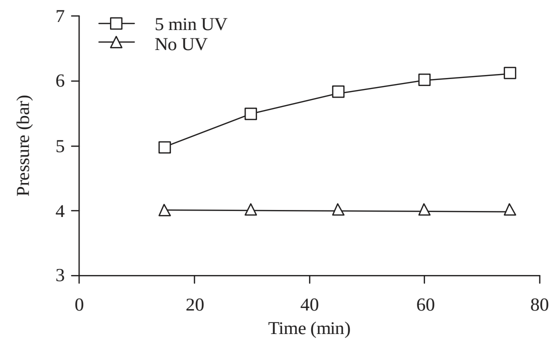

Fig. 3: Operation pressure of produced water treatment with UV irradiation membrane

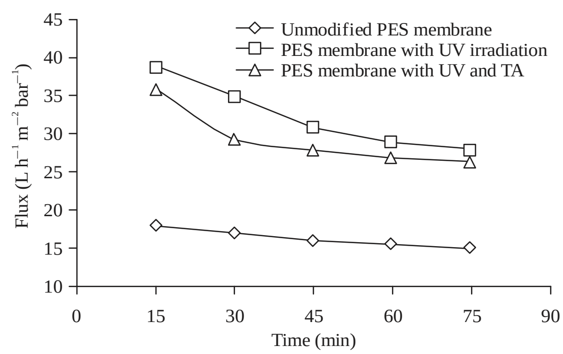

Fig. 4: Effect of combination treatment on the membrane flux

Effect of combination treatments of thermal annealing and UV Irradiation to enhance separation performance of PES membrane: In this study, the effect of combination UV irradiation and thermal annealing on the PES membrane performance for produced water treatment was investigated. To obtain the information about the effect of thermal annealing and UV irradiation on PES membrane performance, the investigation was conducted by comparing the results of the analyzed performance of PES membrane without thermal annealing with UV irradiation (control variable) and the results of the analyzed performance of PES membrane with thermal annealing and UV irradiation (independent variable). Thermal annealing was carried out at 180°C for 10 sec before the membrane was applied for produced water treatment.

The performance of PES membranes is represented by two parameters that are the generated flux value and membrane rejection of TDS, turbidity, sulfide, Mg and Ca. The flux of the UV irradiated and thermal annealed PES membrane compared to the UV-irradiated PES membrane and unmodified PES membrane is shown in Fig. 4.

Based on Fig. 4, PES membrane flux with thermal annealing is lower than PES membrane flux without thermal annealing but higher than unmodified PES membrane. The thermal annealing on membrane causes adjustment of the polymer structure on the membrane surface and makes the membrane become more stable. Pores structure on membrane surface adjusts the thermodynamic equilibrium that has changed as a result of the heat given[14]. The polymer chain structure adjustment led to changes in membrane morphology. Thermal annealing at 180°C approaching the polymer PES glass transition temperature (Tg = 220°C) thus the thermal treatment induces the polymer chain re-crystallize[15]. Heating that approached the glass transition temperature will cause the PES breaking the bonds between polymer molecules into rubbery so that the membrane has a denser skin layer structure.

The results confirmed the previous study that was conducted by Kusworo *et al*.[16]. Thermal annealing will cause adjustment on polymer chain structure at the membrane surface. Pores structure at membrane surface adjusting thermodynamic equilibrium that changed because the heat was given. The denser pores decreasing membrane flux that obtained. The higher temperature applied to the membrane on thermal annealing, the membrane pores will be more compact that the flux that obtained getting lower[16].

Justification about PES membrane performance must be observed through two parameters, flux of the membrane and the rejection. The rejection rate of UV irradiated and thermal annealed PES membrane compared to the unmodified PES membrane was shown in Table 3.

Table 3 shows the value of TDS, turbidity, S, Mg and Ca rejection rate performed by UV-irradiated and thermal annealed PES membrane are higher than unmodified PES membrane. This is due to pores on the membrane surface is

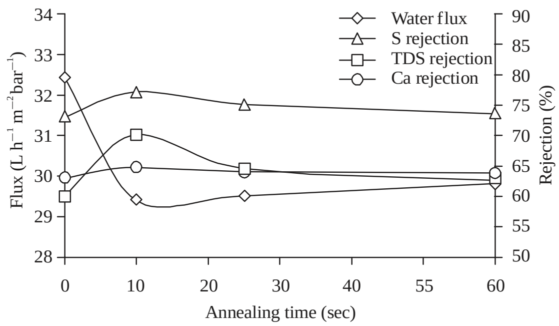

Fig. 5: Effect of thermal annealing time on the membrane performance

Table 3: Rejection rate of the UV irradiated and thermal annealed PES membrane

	Rejection (%)				
Membrane	TDS	Turbidity	Sulfide	Ca^{2+}	Mg^{2+}
PES membrane without UV irradiation	57.88	95.59	70.09	63.22	56.35
PES membrane with UV irradiation	62.50	96.39	73.45	63.94	62.11
PES membrane with UV and thermal annealing	70.09	97.50	78.25	64.84	69.27

narrowed due to thermal annealing treatment in a membrane. Thermal annealing causes membrane structure rearrangements that change the structure of membrane morphology. Higher annealing temperatures will cause denser and stable pore[17]. A membrane with a pore size that is denser and stable gives better filtering effect so that the levels of TDS, turbidity, S, Mg and Ca in the permeate are lower[18].

Effect of annealing time on PES membrane flux and rejection: Figure 5 shows that the annealing time affects the flux and rejection where rejection rate increased from 0 sec annealing time to 10 sec annealing time. This is due to the membrane pores are narrowed due to thermal annealing treatment. Thermal annealing treatment causes the rearrangement of molecules of the membrane becomes more dense and stable. Denser and stable pores provide higher rejection rate of solute contaminant. The rejection reduced in 25 sec annealing time and 1 min annealing time.

The similar result has been obtained by the Li *et al.*[19] on the separation of NaCl by the membrane where the longer annealing time will be obtained flux tends to decrease but the separation rate increased to 10 min annealing.

Morphology of polyethersulfone (PES) membrane with Scanning Electron Microscopy (SEM): Scanning Electron Microscopy (SEM) analysis can be used to observe morphology

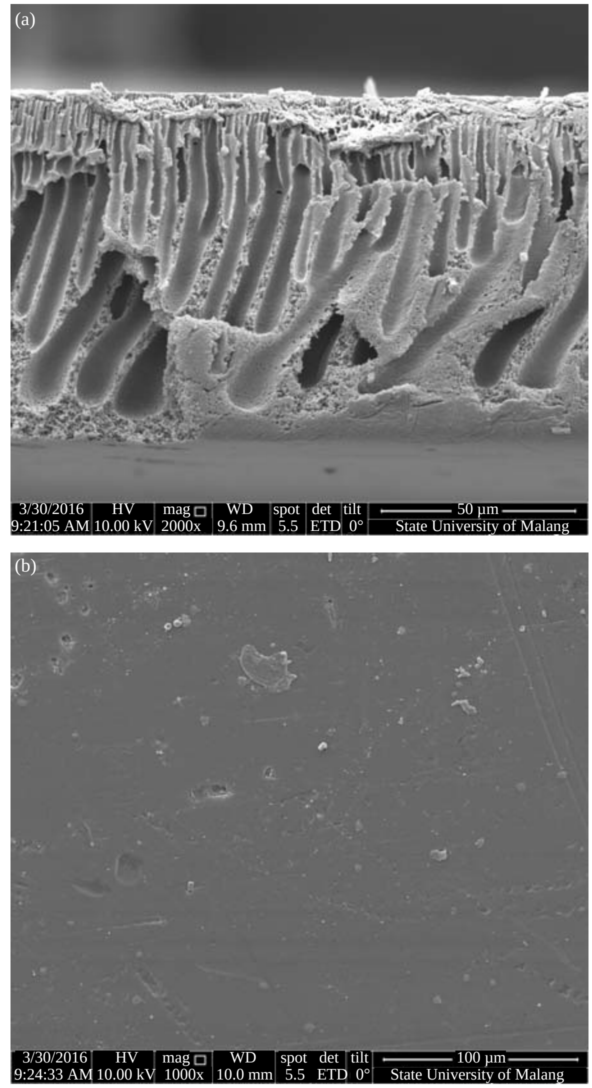

Fig. 6(a-b): SEM images of membrane morphology (a) Cross-section and (b) Surface section

structure of the membrane. The analysis results are surface section images and cross-sectional images of the PES membrane. In this study, SEM analysis was conducted to investigate formed morphology structure. The PES membrane with 19% weight of PES concentration, 5 min UV irradiation and 10 sec thermal annealed at 180°C is analyzed.

The viscosity of the dope solution and difference in the solubility parameter between solvent and non-solvent are the two main factors that determine membrane structure. The asymmetric structure of PES membrane was shown in Fig. 6a. Macro-voids of sponge-like and finger-like support in the sub-layer are formed due to the resistance of the polymer concentration for the exchange of solvent and non-solvent. Furthermore, the dense sponge-like structure in the top-layer occurs when the dope solution has high viscosity.

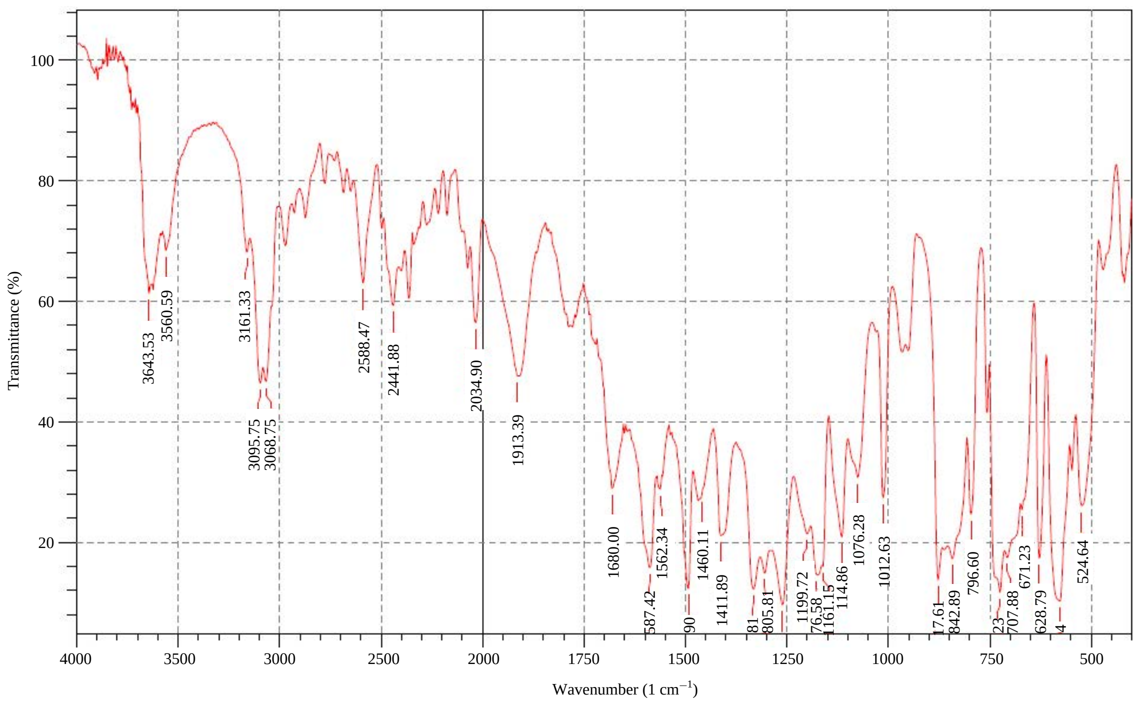

Fig. 7: FTIR result of PES membrane 19% weight, 5 min UV, 10 sec thermal annealing

Figure 6 shows the cross-sectional and surface sectional morphology of the membrane at the magnification of 1000. No pores could be observed on membrane surface at this magnification. Nevertheless, some macro-voids are found on the surface of the membrane, the formation of this macro-voids are due to the rapidly evaporation of solvent from the outermost surface of the membrane during polymer casting[20,21]. The formation of macro-voids must be prevented by directly dipped into the coagulation bath after casting the polymer film. This is confirmed that evaporation and dissolution rate of the solvent could affect the membrane structure and pores.

Functional group analysis using fourier transform infrared spectrometer (FTIR): Figure 7 shows the FTIR spectra of the modified membrane by UV irradiation for 5 min and thermal annealing for 10 sec at 180°C. The PES membrane consists of carbonyl (C=O) groups showed a strong peak at 1690-1760 cm^{-1} which respect to ester functional group.

The bands at 1500-1600 belong to the vibration of aromatic (C=C) in PES molecule. Amine/amide (N-H) functional group and hydroxyl functional group also appear on the FTIR spectra at 3300-3500 and 3600 cm^{-1}, respectively after the membrane was subjected to UV irradiation. The appearance of the peaks around 3600 and 1760 cm^{-1} by UV irradiation indicates that the carbons in methyl group and benzene ring of PES were attacked and oxidized by UV ray to form hydroxyl (-OH) group and carbonyl (C=O) group. Carbonyl and hydroxyl were polar functional groups which resulting in an increase of the hydrophilic property of the membrane. The hydrophilic property of the membrane was a factor of the high flux of the PES membrane. The similar result was also reported by Konruang *et al.*[7] that UV irradiation to the polysulfone membrane leads to form hydroxyl and carbonyl groups due to oxidation of methyl group in polysulfone molecule. While thermal annealing treatment didn't affect the molecular structure of the polymer, it induces the polymer re-arranged the chain to be more crystalline[22].

Stability test on PES membrane performance: Stability test of the membrane needs to be tested before applying the membrane in large scale produced water treatment. Membrane stability test performed by applying the membrane to the produced water for 8 h and then seen the value of flux and rejection in intervals of 15 min.

Figure 8 shows that the PES membrane either by heating or not the membrane flux decreases. Membrane flux value is inversely proportional to the time function, the increasing stability over the operating time of 8 h, the flux of a membrane tends to decrease. The flux of the membrane with thermal annealing at a temperature of 180°C lower than the flux of the untreated membrane. In terms of rejection rate can

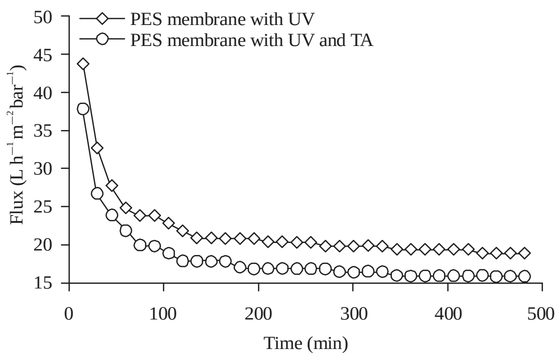

Fig. 8: Modified PES membrane stability in term of flux

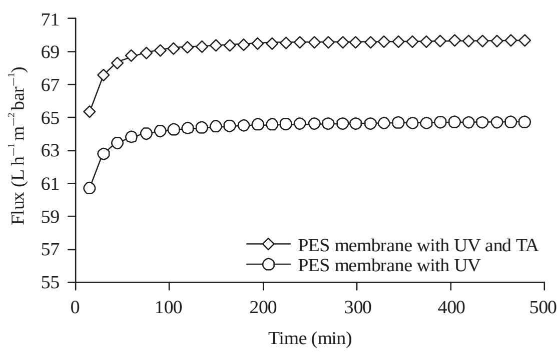

Fig. 9: Modified PES membrane stability in term of Ca rejection

be seen in Fig. 9, the PES membrane with thermal treatment has higher rejection rate of Ca^{2+}, it indicates that modification of the membrane using combination treatment improves the performance significantly. The modified membrane has good stability as shown in Fig. 9, whereby at 50 min of operation the rejection rate achieved steady condition.

Heating membrane at 180°C temperature approaching the glass transition temperature of the PES polymer (Tg = 220°C). Heat treatment approaching the glass transition temperature will cause the PES breaking the bonds between the polymer molecules become more tightly so that the membrane has a dense structure of the skin layer thicker. The results obtained are consistent with results of previous studies[23-25]. Heat treatment or annealing will cause structural adjustment of polymer chains on the surface of the membrane. Pores structure on the surface of membrane adjusts with the thermodynamic equilibrium which has changed due to the heat was given. The polymer chain structure adjustment led to changes in membrane morphology. As a result, the formed pores became more stable and denser[6,26]. A denser pore gives the lower membrane flux. At the higher annealing temperature applied to the membrane, the membrane pores will be denser so that the obtained flux was becoming lower. The decreasing flux continues until steady state was reached.

CONCLUSION

The PES membrane was successfully modified using UV irradiation and thermal annealing treatment. The UV irradiation on the membrane for 5 min increased the flux and rejection. Longer annealing time affects rejection where the rejection rate increased from 0-10 sec annealing time but then decreased at the time of over than 25 sec annealing time. Based on experiments on UV irradiation and thermal annealing on the membrane, it obtained with the best combination of UV irradiation for 5 min and thermal annealing at a temperature of 180°C for 10 sec.

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