

Effect of combination dope composition and evaporation time on the separation performance of cellulose acetate membrane for demak brackish water treatment

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Abstract. The coastal areas in Indonesia often have a problem of clean water lack, because the water is classified as brackish water. Therefore, this research investigated the fabrication of CA membranes using phase inversion method for brackish water treatment. Investigation was conducted to study the effect of combination dope composition and evaporation time on separation performance and morphology of the membrane. Membrane was fabricated by dry-wet phase inversion technique with variation of polymer concentration 17, 18 and 20 wt% in the total solid and evaporation time of 5, 10 and 15 seconds, respectively. The asymmetric membranes were characterized by permeability test through rejection and flux measurements using brackish water as feed. The experimental results from SEM images analysis showed that all the membranes have a thin small porous layer and thicker sub-structure of larger porous layer formed asymmetric membrane. Moreover, the greater polymer concentration is resulting smaller pore size and smaller membrane porosity. The longer evaporation time was also resulted in denser membrane active layer. The best membrane performance was observed at the composition of 20 wt% CA polymer, 1 wt % polyethylene glycol with the solvent evaporation time of 15 seconds.

1. Introduction

Membrane separation could be defined as a selective barrier between two phases. The advantages of membrane based separation are continuous process, energy efficient, modular, can be operated under mild condition, membrane properties are adjustable, without any required additives. With aforementioned benefits of membrane usage, the application of membrane become more extensive such as desalination of saline water, sea water and brackish water, the concentration and separation in industrial waste water (waste water treatment), sterilization and purification of potable water, gas separation, biomedical technology [1]. Research about membrane which focuses on conditioning of membrane production is still interesting. Many factors in fabrication process variables affect the characteristic, morphology, and separation properties of membrane. By combining several various parameters allows obtaining tailor-made membranes that are specific to a particular separation purposes.

Polymeric membrane with asymmetric structure is mostly applied in water and waste water treatment. Permeate water flux that is resulted by asymmetric membrane is higher than symmetric membrane. This is due to the dense layer of membrane is thinner than symmetric membrane. The asymmetric membrane consisting sub-layers structure with different thickness.

The upper skin layer has a thickness approximately 0.1-0.5 μm and 50 to 100 μm thickness of other layer. The top layer of asymmetric membrane acts as a filter medium, while the sub-layer or intermediate layer contributes as a supporting medium of the top skin layer. Hence, the asymmetric structured membranes are suitable for water treatment [2]. The membrane performance parameters were defined by the value of permeate flux and pollutant rejection efficiency. The higher permeate water flux and rejection efficiency indicates that the membrane has an excellent separation performance. However, the conditions encountered is an effort to improve membrane flux will be lowering the membrane rejection.

The membrane performance was affected by several factors such as the dope composition, solvent evaporation time, solvent type, additive type and concentration, and shear rate [3]. In the research reported by another researcher [4-9] concluded that the dope composition was affected the performance of asymmetric membrane. They stated that the greater polymer concentration, membrane pore size and porosity will decrease. This will obtained smaller flux, while rejection increased. Evaporation time of solvent is an important factor that affected the membrane properties. The variation of evaporation time resulted the different membrane morphology and separation properties. Bhongsuwan et al. [2] prepared a nanofiltration

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membranes with different solvent evaporation time where the membrane was evaporated in 40 seconds the rejection of tannin increased up to 21.68% and the permeate flux decreased up to 69.78%. The significant decline of permeate flux of nanofiltration membrane solvent evaporation for a while, it indicates that the evaporation time of solvent is an important factor in membrane production. Longer evaporation time will result membrane with a smaller pore size and increase the thickness of the active layer membrane. This morphology causes smaller membrane flux, while rejection will increase. These results have been confirmed with previous researchers [10-11]. Therefore, for further investigation needs to be conducted to obtain the optimum evaporation time which produces an excellent membrane separation performance.

In this study of asymmetric CA membrane fabrication, acetone is commonly used as a solvent in dope preparation [3-5]. CA was selected as polymer material because CA capable to form a thin active layer of asymmetric structure and dissolved solid can be retained in the support layer of membrane as well as chemical tolerant and resistant to foulant deposition. Therefore, the stability of membrane and separation performance are the important factors for membrane application in water treatment. Furthermore, the main purpose of this research is to study the effect of dope composition and evaporation time to enhance the performance of nanofiltration CA membrane for treating Demak brackish water.

2. Experimental Details

2.1. Materials

Cellulose acetate (CA) was used as membrane material and was purchased from MKR Chemicals Indonesia, 99.75% acetone was supplied by Mallinckrodt Chemicals, Polyethylene glycol with molecular weight 4000 g/mole was supplied by Merck, and original brackish water sample was obtained from Demak.

2.2. Fabrication of asymmetric CA

Asymmetric CA membrane was fabricated by preparation of dope polymer solution consists of 17, 18 and 20 wt-% CAs, acetone, distilled water and Polyethylene glycol as an additive with concentration of 1 wt-%. The stable and homogeneous CA solution was prepared according to the following procedure; an appropriate amount of CA polymers were dissolved into the acetone and constantly stirred for 6 hours subsequently add an appropriate amount of polyethylene glycol. The solution was continuously mixed with a suitable stirrer for 6 hours to ensure complete dissolution of the polymer. A desired amount of distilled water was added to the homogenous solution. This dope solution was constantly agitated at high speed for at least 12 hours. After all the ingredients dissolved completely, then the dope solution allowed for 1 hour in order to remove air trapped. The membrane was casted using the

technique of dry-wet phase inversion on a glass plate via a casting knife and allowed to correspond with the variation of evaporation time 5, 10 and 15 seconds. The membrane then was immersed into a coagulation bath containing distilled water in coagulation tank for 24 h at ambient temperature ($30 \pm 2^\circ\text{C}$). The experimental brackish water treatment with membranes was performed using a dead-end nanofiltration system. Flux and rejection is periodically measured to obtain the profile of permselectivity performance of each membrane.

2.3. Characterization of Asymmetric CA membranes

Permeate water flux and rejection were measured via dead-end filtration. An appropriate effective area of CA membrane was mounted into membrane cell. Before performing experimental test using original samples, the membrane was compacted using distilled water for 30-45 minutes. After the membrane being compacted, the distilled water was replaced with original brackish water. The permeate volume was measured periodically every 5 minutes. Rejection was determined by performing the analysis of pollutant such as TDS, Ca^{2+} , Mg^{2+} , and turbidity of feed and permeate water. TDS was measured using TDSmeter, Ca and Mg ions were analyzed using complexometry conventional titrimetry. Schematic diagram of dead-end filtration was illustrated in Figure 1. The flux was determined by evaluating the equation as stated in equation 1 [12]:

$$J = \text{Vol} / (\text{P.A.}\tau)$$

(1)

$$J = \text{Flux (L.bar}^{-1}\text{m}^{-2}\text{.h}^{-1}\text{)}$$

$$P = \text{Pressure, bar}$$

$$\tau = \text{Time (hour)}$$

$$\text{Vol} = \text{Volume of Permeate water (Liter)}$$

$$A = \text{Membrane effective Surface Area (m}^2\text{)}$$

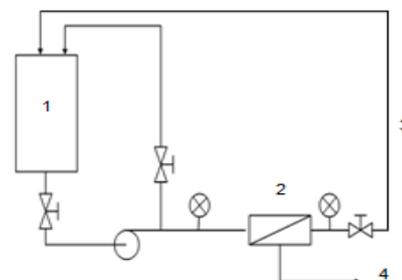


Fig. 1. Filtration cell dead-end type 1. Feed; 2. Membrane cell; 3. Retentate stream; 4 Permeate stream

The observation of asymmetric structure of membrane was performed using Scanning Electron Microscope (SEM). Membrane samples were prepared by fracturing in liquid nitrogen. The prepared membranes were mounted on an aluminium disk with a double surface tape and then the sample holder was placed and evacuated in a sputter-coater with gold. The

chemical structure alteration as an effect of several variation of treatments in membrane preparation was analyzed using FTIR (Fourier Transform Infrared). The IR absorption spectra were scanned in a range from 4000 to 500 cm^{-1} with a spectral resolution of 8 cm^{-1} and averaged over 16 scans.

3. Results and discussions

3.1. Effect of Dope Composition on the Performance of CA Membrane

In this study the variation of dope composition by varying the polymer concentration in dope solution. Effect of dope composition on the performance of CA membrane at different evaporation time is shown in Figure 2. Figure 2 indicated that the higher CA concentration, the flux was decreased. This phenomenon was occurred on all evaporation time. The decrease of flux was caused by lowering of membrane porosity with increasing polymer concentration. Increased of polymer concentration will be lead to the increasing number of polymer concentration at the membrane interface. This phenomenon indicated that the volume fraction of polymer was increased; hence, it has a smaller porosity. The results were in agreement with the previous study [13]. In the solid-liquid phase separation, increasing the polymer concentration will increase the density, whereas it will also reduce porosity. Polymer concentrations had a major impact on the bulk porosity and structure of the membrane. The decreasing porosity was occurred primarily in bulk porosity membrane. This is reinforced by the fact that the increase of polymer concentration was decreased the internal pore size [9].

Increasing polymer concentrations of membranes was also formed a membrane with thicker active layer. Therefore, the productivity was decreased. Increasing polymer concentration in solution will increase viscosity of dope solution. As a consequence, the interaction between the solvent and the polymer becomes more powerful, interaction between non-solvent and polymer becomes larger, thus reducing the ability of solvent to dissolve the polymer. This will accelerate the aggregation of polymer molecules on the surface to form a closer bond. The increase in viscosity will also prevent the diffusion exchange between solvent and non-solvent in the sub-layer, it makes the precipitation rate becomes slower. The rapid phase separation at the surface and slow in the sub-layer will produce asymmetric membrane with dense and thick layer [6].

Both porosity and membrane thickness decreased with increasing CA concentration. The increasing of concentration will strengthen the thermodynamic instability of dope solution, so de-mixing in this solution can be done with less amount of non-solvent. The increased viscosity of the solution due to the increased concentration will result in decreased diffusivity between the non-solvent and solvent on the system during the solidification process of dope solution. Greater use of CA makes precipitation process stops after a long time and will form a denser and thin membrane [8].

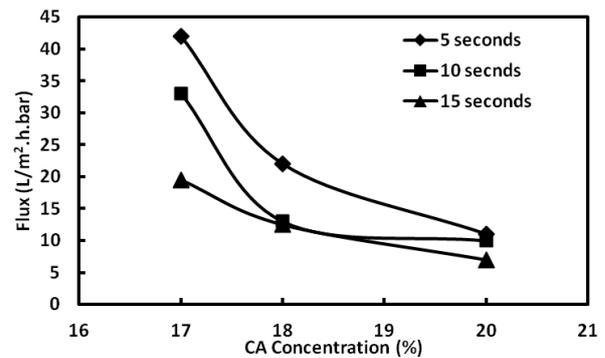


Fig. 2. The effect of polymer concentration on membrane Flux with different evaporation time

3.2. Effect Dope Composition on the rejection of CA membrane

Effect of dope composition on CA membrane rejection rate at different evaporation time was presented in Figure 3. Figure 3 showed that increasing of polymer concentration was increased the rejection. This phenomenon was occurred on all evaporation time. The increase of rejection is due to higher CA concentrations inversely with decreasing flux. As discuss in section 3.1, the increase in the polymer concentration induced the formation of fine membrane pores and was also reduced the thickness of the membrane and resulted the membrane active layer will thicken. Therefore, the membrane was able passed the water, but not able to get through dissolved solids larger than the pore size. Thick active layer allows more dissolved solids are retained on the membrane section. Thus, the smaller of pore size and the thickness of active layers, gave more dissolved solids rejected, where it shows the selectivity of the membrane is great [13].

3.3. Effect of Solvent Evaporation Time on the Performance of CA membrane

Effect of solvent evaporation time on the performance of CA membrane at different polymer concentrations is shown in Figure 4. As shown in Figure 4, the increasing of evaporation time was decreased the flux. The decreasing of flux was due to longer of evaporation time caused during the evaporation process, the molecular solvent was swapped places with air molecules. Empty space left by the solvent will be occupied by air molecules. The longer of evaporation time, the closure of space by air molecule getting larger. Moreover, the membrane with smaller pore size was formed, as a result flux was decreased.

Basically, the evaporation in membrane manufacturing aims to create a more selective membrane. This is because during evaporation of solvent, the polymer concentration in the surface layer increased which will form a dense surface. Moreover, this layer will inhibit the speed of solvent exchange with non-solvent through a membrane sub-layer during coagulation processes and produced a smaller pore size

and ultimately will reduce the flux [11]. That the longer of evaporation time can also increase the active layer thickness of the membrane.

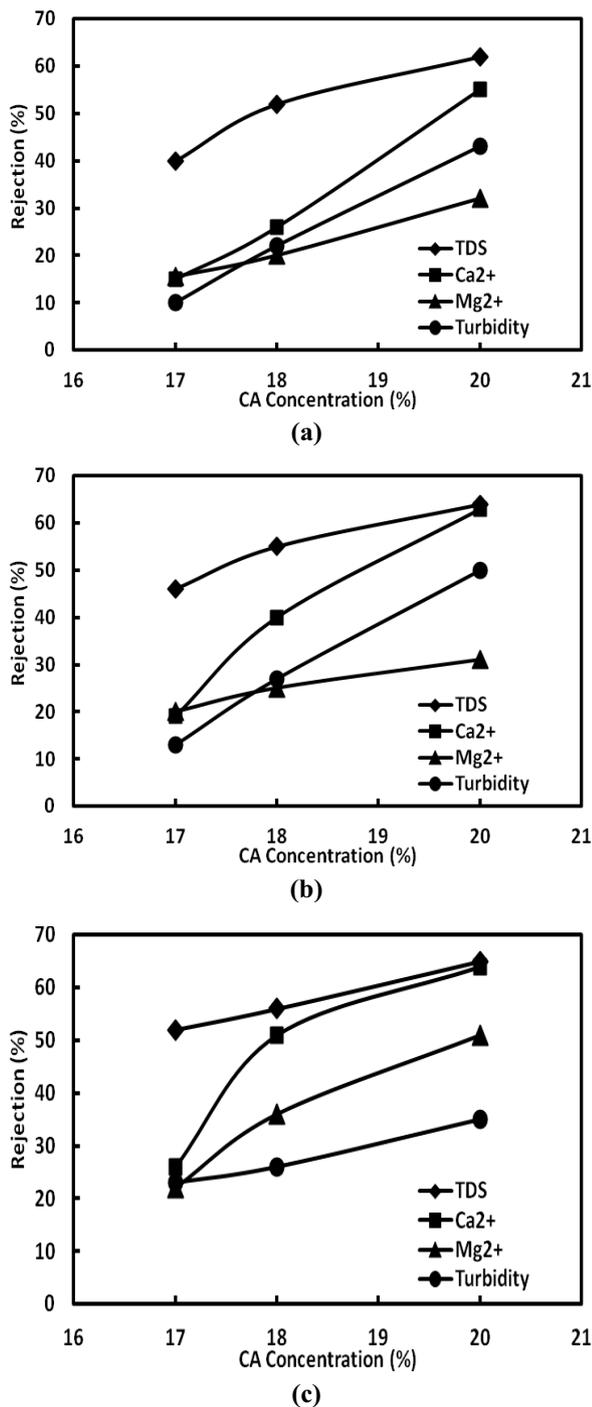


Fig. 3. Dope Composition effect on the rejection at different evaporation time: (a) 5 seconds; (b) 10 seconds; (c) 15 seconds

The outer part of the membrane will experience phase separation during evaporation process. Evaporation before immersion in bath coagulation gave a huge impact on the thickness of the active layer membrane. This process is called dry/wet phase separation that occurred during the formation of a very thin layer. Increased evaporation time make a thicker active layer membrane [10].

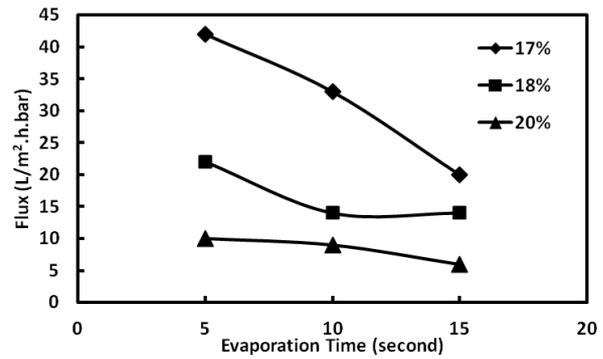


Fig. 4. The evaporation time effect on flux of membrane at different polymer concentration

3.4. Effect of evaporation time on the rejection of CA membrane

Effect of evaporation time on CA membrane rejection at different polymer concentrations is shown in Figure 5. As shown in Figure 5, increasing solvent evaporation time was resulted in the greater rejection. This phenomenon was occurred at all concentrations of CA. The increase in rejection was also occurred in all types of rejection. The increase in rejection due to higher evaporation time is inversely proportional to the decrease in flux. As discussed earlier, the longer evaporation time will reduce membrane pore size and thicken membrane active layer. Membrane is only able to get through water and dissolved solids that are smaller than the pore size of the membrane. Thick active layer allows more dissolved solids to be retained on the layer. Thus, the smaller of pore size and the thickness of the active layer membrane, will result in more dissolved solids are left behind that indicates great membrane selectivity[13].

3.5. Effect of dope composition on the morphology of CA membrane

Surface morphology and the appearance of cross section CA membranes can be determined through analysis using SEM (Scanning Electron Microscopy). SEM analysis results the effect of the polymer concentration of membranes is shown in Figure 6. From Figure 6, it can be seen that both membranes have an asymmetric porous structure and visible difference. At the appearance of the membrane surface with a magnification of 2500 times, the membrane b (20% CA) has a smaller pore size. While on the cross-section with a CA membrane has a 20% has smaller internal porosity than membrane with 17% CA.

This confirms a phenomenon that occurs in flux and rejection, as has been reviewed previously. Similar results were also obtained by Van de Witte et al. [20], which states the increase of polymer concentration will increase the thickness of the upper layers, lower porosity and pore inter-connectivity of membrane, resulting formation of macrovoid will be reduced.

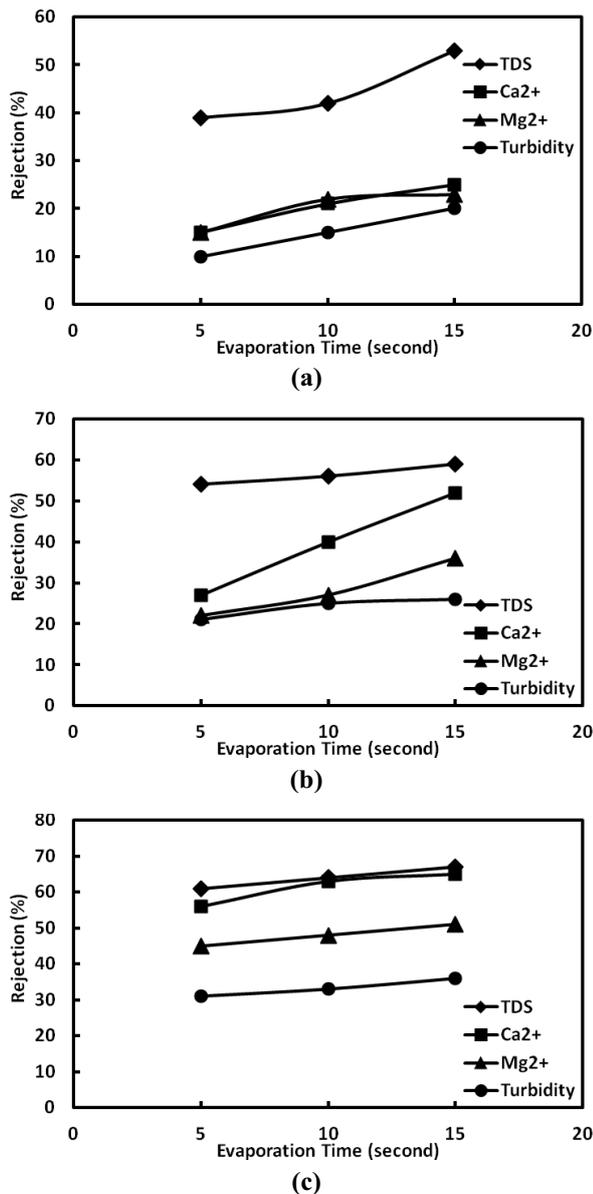


Fig. 5. Evaporation time effect on Membrane Rejection on Different Polymer Concentration: (a) 17 wt%; (b) 18 wt%; (c) 20 wt%

In Figure 6 seems to have a larger pore size. This is due to the dope solution has a lower viscosity. After the solidification of the polymer phase, low viscosity will result in the formation of pores quickly. Internal pore rapid growth led to the formation of larger pore size. With the decrease in the polymer concentration, the overall porosity increases [16].

3.6. Effect of evaporation time on the morphology of CA membrane

Effect of evaporation time at 20% polymer concentration on the membrane morphology is shown in Figure 7. From Figure 7, it can be observed that the membranes also have an asymmetric porous structure. At the appearance of the membrane surface with a magnification of 2500 times, the membrane b (evaporation time 15 seconds) has more dense surface and smaller pores. Whereas the membrane crosses

section with evaporation time of 15 seconds has internal porosity of membrane smaller than the 5 seconds evaporation time. This confirms a phenomenon that occurs in flux and rejection, as has been reviewed previously. Similar results were reported by See-Toh et al. [18], which states that the shorter time evaporation will increase the size of the gap (pores) in the membrane. Moreover, Muliawati [14] states the longer of time evaporation indicates that the delayed of demixing process also longer, so that membranes produce are more dense.

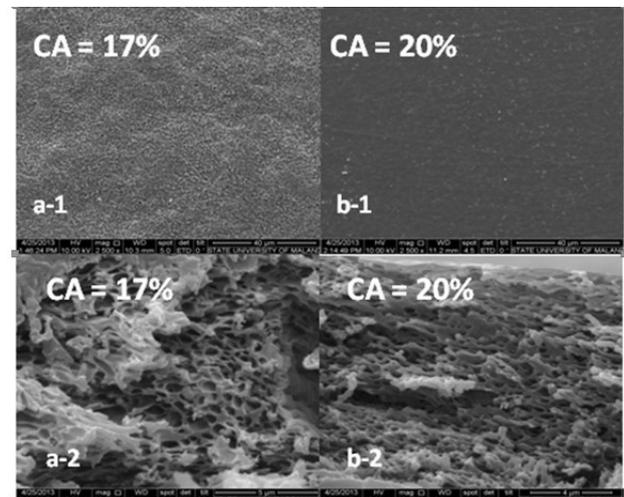


Fig. 6. Morphology of CA Membrane : a) 17% CA, 1% PEG, 1% aquadest, 15 seconds evaporation time; b) 20% CA, 1% PEG, 1% aquadest, 15 second evaporation time; 1) surface; 2) cross section

However, the longer of evaporation time (> 30 seconds) will make the membrane pore size becomes larger. It is because there are two influencing factors during membrane exposure, i.e the evaporation of solvent and water absorption in the dope solution. When the evaporation time is less than 30 seconds, the solvent evaporation has bigger influence because the short time absorption is very small.

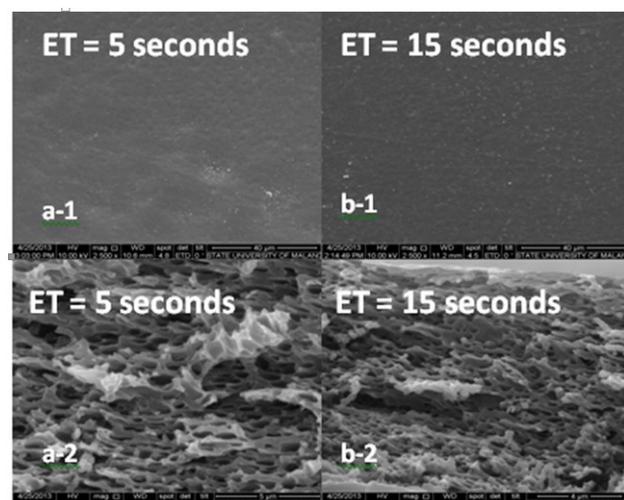


Fig. 7. Morphology of CA Membrane : (a) 20% CA, 1% PEG, 1% aquadest, 5 seconds evaporation time; (b) 20% CA, 1% PEG, 1% aquadest, 15 seconds evaporation time; 1) surface; 2) cross section

At the evaporation time of 1-2 minutes, the effect of solvent evaporation is almost balanced by the effects of water absorption, so that the pore size in the range appears at this time. However, more than 2 minutes evaporation will cause the water absorption become a major factor during the evaporation process, so it will form a membrane with a larger pore size [11].

4. Conclusion

Based on the experimental results of this research can be concluded that in this study, the concentration of polymer is very influential. The higher polymer concentration, the flux will decline, while rejection increased. This is because the increase in concentration will minimize membrane pore size. Results of SEM analysis showed that the high concentration of CA will produce asymmetric membranes with smaller pore size and porosity. Evaporation time also affects the membrane performance. The longer evaporation time, smaller flux will be obtained and rejection will increased. This is because the longer evaporation time will cause the decrease of membrane pore size. SEM analysis showed the longer evaporation time will produce increasingly dense membrane. The best membrane was achieved with a composition of 20 wt % of CA, 1 wt % of PEG, 1 wt % aquadest and the evaporation time of 15 seconds with the performance in term of flux as large as $6.08 \text{ L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$, TDS rejection value of 66.99 %, rejection Ca^{2+} ions 64.71%, Mg^{2+} ion rejection 37.10%, and 53.28% turbidity rejection, respectively.

References

- [1] R.W. Baker, *Membrane Technology and Applications*, 2nd ed. (John Wiley & Sons, Ltd., 2004)
- [2] D. Bhongsuwan and T.J. Bhongsuwan, *Nat. Sci.* **42**, 311-317. (2008)
- [3] A.F. Ismail, A.R. Hasan, and B.C. Ng, *J. Sci. Technol.*, **24**, 878-889. (2002)
- [4] T.D. Kusworo, Budiyono, J. Supriyadi and D.C. Hakika, *J. of Wast. Res.* **4**, 1. (2014)
- [5] T.D. Kusworo, Budiyono, A.I. Wibowo, G.D. Harjanto, A.D. Yudisthira and F.B. Iswanto, *J. App. Sci., Eng. and Tech.* (2014).
- [6] M.I. Mustaffar, A.F. Ismail, and R.M. Illias, *Study on the Effect of Polymer Concentration on Hollow Fiber Ultrafiltration Membrane performance and Morphology*, University Teknologi Malaysia. (2004)
- [7] A. Sofyan, and N. Pocut, *Desalination of Brackish water using nanofiltration Membrane*, (Thesis) Syiah Kuala University. (2007).
- [8] E. Saljoughi, M. Sadzadeh, and T.J. Mohammadi, *Mem. Sci.* **326**, 627-634. (2009)
- [9] A. Akbari and R.J. Yegani, *Mem. Sci.* **1**, 100-107. (2012)
- [10] I. Soroko, M. Markowski, F. Spill, and A.J. Livingston, *Mem. Sci.* **381**, 163-171. (2011)
- [11] L. Gao, B. Tang, and P.J. Wu, *Mem. Sci.* **326**, 168-177. (2009)
- [12] M.S.F. Dasilva, *Disertation. Polyamide and Polyetherimide Organic Solvent Nanofiltration Membranes*, (Disertation) University Of Nova De Lisboa. (2007)
- [13] M. Mulder, *Basic Principles of Membrane Technology. 2nd edition.* (Kluwer Academic Publisher, Netherland, 1996)
- [14] E.C. Muliawati, *Fabrication and characterization of Nanofiltration Membrane for Water Treatment*, (Thesis) Diponegoro University. (2012)
- [15] L. Amand, and C.J. Tullin, *The Theory Behind FTIR Analysis*. (The Centre of Combustion Science and Technology, Lund University, 1999)
- [16] J.C. Jansen, M. Macchione, C. Oliviero, R. Mendichi, G.A. Ranieri, and E. Drioli, *Polymer* **46**, 11366-11379. (2005)
- [17] K. Scott, K. and R. Hughes, *Industrial Membrane Separation Technology*. (Blackie Academic and Professional, London, 1996)
- [18] Y.H. See-Toh, F.C. Ferreira, and A.G.J. Livingston, *Mem. Sci.* **299**, 236-250. (2007)
- [19] R.U. Somantri, *Pengaruh Penambahan Formamide dan Lama Penguapan Pelarut (Aseton) terhadap Membran Selulosa Asetat*. (Bogor Agricultural Institute, Bogor, 2003)
- [20] P. Van de Witte, P.J. Dijkstra, J.W.A. van de Berg, and J.J. Feijen, *Mem. Sci.* **117**, 1-31. (1997)