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Studies of thermal annealing and dope composition on the enhancement of separation performance cellulose acetate membrane for brackish water treatment from Jepara

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Abstract - Membrane is an alternative technology of water treatment with filtration principle that is being widely developed and used for water treatment. The main objective of this study was to make an asymmetric membrane using cellulose acetate polymer and study the effect of additive and annealing treatment on the morphology structure and performance of cellulose acetate membranes in brackish water treatment. Asymmetric membranes for brackish water treatment were casted using a casting machine process from dope solutions containing cellulose acetates and acetone as a solvent. Membranes was prepared by phase inversion method with variation of polyethylene glycol (PEG) concentration of 1 and 5 wt% and with thermal annealing at 60 ^oC in 10 seconds and without thermal annealing behavior. Membrane characterization consists of calculation of membrane flux and rejection with brackish water as a feed from Jepara. The research concluded that asymmetric cellulose acetate membrane can be made by dry/wet phase inversion method. The more added concentration of PEG will be resulted the larger pore of membrane. Meanwhile the higher temperature and the longer time of annealing treatment, the skin layer of membrane become denser. Membrane with the composition of 18 wt% cellulose acetate, 5 wt% PEG, 1 wt% distilled water, with heat treatment at temperature of 60 ^oC for 10 seconds is obtained optimal performance.

Keywords - Asymmetric membrane, PEG, Cellulose Acetate, Annealing, Brackish Water

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1. Introduction

Membrane is a thin layer, a barrier between the two phases that are semipermeable, and serves as a selective separation media based on the coefficient of diffusivity, electrical charge, and the difference in solubility [1-2]. Membrane technology is the latest technology in water treatment because of its strategic, related to the process, separation, purification and concentration. This technology also uses more efficient in energy because it doesn't use high operating temperature. Membrane technology uses modular equipment so easy to scale-up. Its classified in a clean technology because its relatively no waste and the process can be merged with other separation process [3]. Asymmetric membrane is one type of membrane that the most widely applied in water treatment process. Flux resulted from performance of asymmetric membrane is higher than symmetric membrane because its dense layer is thinner than symmetric membrane. Asymmetric membrane with a pore size of porous membranes having the outer skin layer with a thickness of 0.1 to 0.5 μm and below the top layer there is another layer with a thickness of approximately 50-100 μm. The upper layer of the asymmetric porous membrane serves as a filter, while the bottom layer serves as a buffer medium of the upper layer. Therefore, the asymmetric membranes are widely used in water treatment applications [4].

In the study of making asymmetric membranes, aceton solution is commonly used as a solvent with a cellulose acetate as a polymer [5,6]. Cellulose acetate was chosen as the polymer component due to the cellulose acetate can form an asymmetric structure with a very thin active layer and the dissolved material can withstand the rough on the support layer, as well as chlorine tolerant and resistant to the occurrence of precipitation [7-8]. Therefore, as mentioned above, membrane stability and high performance become one of the important factors for the application of membranes. Therefore, the main objective of this study is to investigate the effect of PEG as aditif in the dope solution and thermal annealeing on the performance cellulose acetate membrane for Jepara brackish watertreatment.

2. Material and Method

Materials used in the making of membranes are cellulose acetate from MKR Chemicals, 99.75% acetone from Mallinckrodt Chemicals, distilled water, PEG 4000 and brackish water from Jepara. In this study, the dope solution consists of 18 wt % cellulose acetates, acetone, distilled water and PEG as additives with various concentration of 1% wt and 5% wt.The homogeneous dope solutions were prepared according to the following procedure; the cellulose acetate polymers were dispersed in to the solvent and stirred for 6 hours followed by the addition of a desired amount of PEG. The dope solution was agitated with a stirrer at least 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 than agitated at high speed for at least 12 hours. After all the ingredients mix completely fit variable, then the dope solution allowed to stand for 1 hour to remove bubbles. Casting membrane using the method of phase inversion that is scored on a glass plate using a casting knife and allowed to correspond with the time variation of evaporation and then dipped into a coagulation bath containing distilled water in place for 1 day at room temperature. Defect on the membrane surface were repaired by a thermal annealing method. Asymmetric membranes module after the air drying were dried in an oven at 60 °C in 10 seconds was also carried out. After the treatment the membranes were cooled down slowly to room temperature. To determine the thermal annealing treatment of the membranes that others do not thermal annealing too. The treated membrane after being subjected to different heat treatment methods were tested using a dead-end nanofiltration testing system. Subsequently membrane filtration cell is cut to size for the characterization of the flux and rejection. Brackish water flux values was measured by measuring the volume of brackish water every 1 hour. Determination of membrane rejection was performed by determining the concentration of total disolved solid (TDS), Ca^{2+}, Mg^{2+}, and brackish water turbidity before and after passing through the membrane. Determination of brackish water TDS was performed using a TDS meter, the analysis of brackish water turbidity was determined by turbidimeter, while the determination of Ca^{2+} and Mg^{2+}ion is using substitution and hardness titration. The flux was calculated using the equation as stated by Dasilva [9]:

$$J = V/(A.t.p) \quad \ldots\ldots (1)$$

Where, J is the flux ($L.m^{-2}.h^{-1}$ bar^{-1}), V is the permeate volume (liter), A is the membrane surface area (m^2), t is the time and p is the pressure (bar).

3. Results and Discussion

3.1. Effect of PEG on the membrane performance.

From the data presented in Figure 1 shows that the more PEG is added to the dope solution, so that the greater the flux membranes to be obtained. The increase is due to the pore membrane flux which formed the greater. The addition of PEG concentration of 5% wt on dope solution affect the pore formation, membrane pore formed by the more or greater with the addition of PEG concentration. PEG as an additive not only acts as a pore-forming agent or multiply the number of pores, but also led to an adjustment movement of molecules in the formation of cellulose acetate membranes. This is because PEG is a hydrophilic additive, so that an increase in the concentration of PEG would lead to the formation of larger macrovoid the pore structure of the membrane [10]. As a result, the larger the pore size of the membrane will increase the value of the flux in the membrane, so that the value of the flux in the membrane with a concentration of 1% wt PEG has a more stable performance is indicated by the small flux during the filtration process in progress.

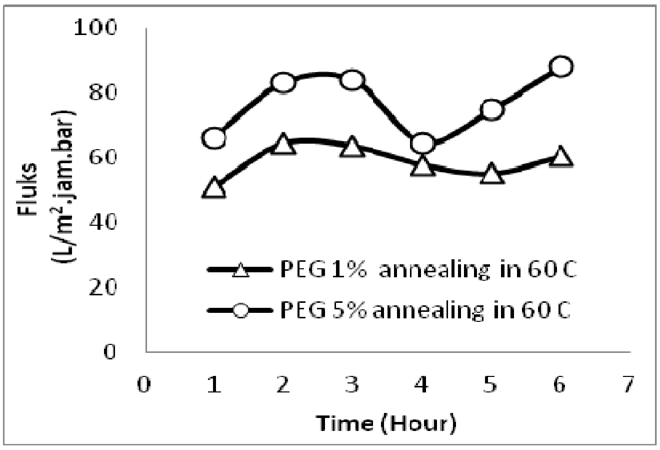

Figure 1: The effect addition of PEG on the rejection of Ca^{2+} and Mg^{2+}

Based on Figure 2, it can be seen that greater the concentration of PEG membrane rejection values for $Ca^{2+}$and Mg^{2+} decreases. Membrane with a concentration of 1 wt% PEG resulted in rejection values greater than the membranes with PEG concentration of 5 wt%. This is because the more the concentration of PEG is added to the dope solution will increase the pores or pore size formed greater. PEG serves as a porogen (pore-forming) which is soluble in water so that the PEG molecules diffuse into the coagulation bath containing water and leave pores in the matrix of cellulose acetate [11]. As a result, the greater the concentration of PEG is added, will form macrovoid greater in the membrane, the greater porosity and pore size of the membrane will cause a lot of monovalent who escaped and are not filtered as it passes through the membrane so that the value of rejection is getting smaller which causes membrane's ability to filter the Ca^{2+} and Mg^{2+} is reduced. At least the concentration of

PEG is added to improve the performance of the membranes in filtering the solids, especially Ca^{2+} and Mg^{2+}.

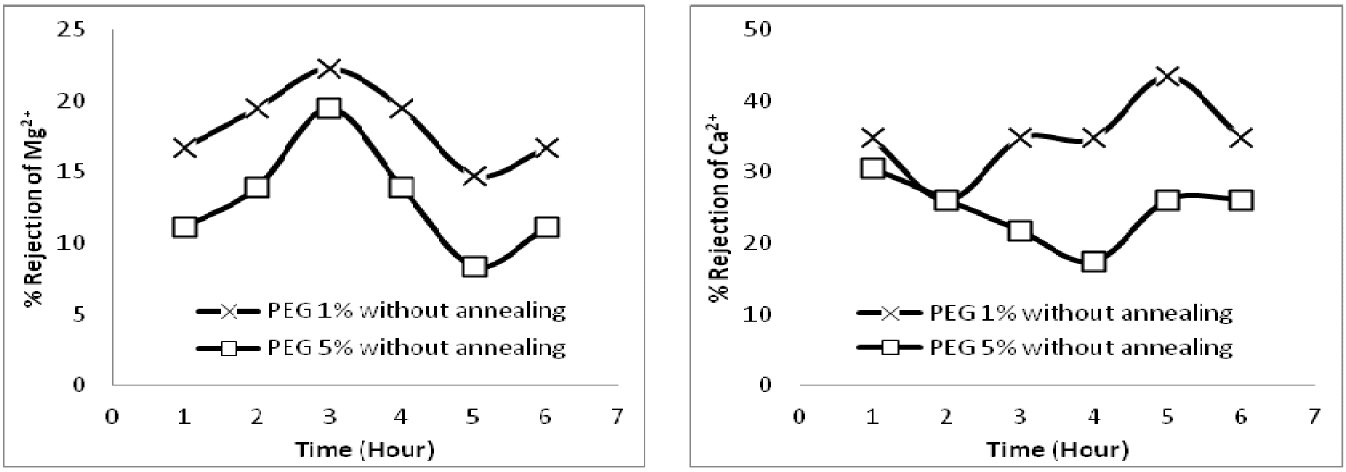

Figure 2: Effect of PEG addition on the rejection of Ca^{2+} and Mg^{2+}

3. 2. The Effect of Thermal Annealing On Membrane Stability

In this research we used four variations of the membrane, the membrane 1 with a concentration of 1 wt% PEG and without annealing, membrane 2 with a concentration of 5 wt% PEG and without annealing, the membrane 3 with 1 wt% PEG concentration and annealing temperature of 60° C, and the membrane 4 with 5 wt% PEG concentration and annealing temperature of 60°C.

In accordance with Figure 3, illustrated by a comparison of membrane flux values without annealing and with annealing at 60 ° C on each source (Jepara, Semarang and Demak). Judging from the overall value of the flux at each source, flux values by using a membrane with a temperature of 60 ° C annealing tends to produce a more stable flux values and smaller compared to the membrane without the use of thermal annealing. The existence of this thermal annealing will improve the performance of the membrane because the setting causes the molecules so that a more stable membrane during the filtration process. The higher the annealing temperature and the longer the thermal annealing time on the membrane. The membrane surface layer will experience shrinking so that the membrane becomes more tightly pore [12]. As a result of narrowing of the pore membrane is then lowers the value of the membrane flux.

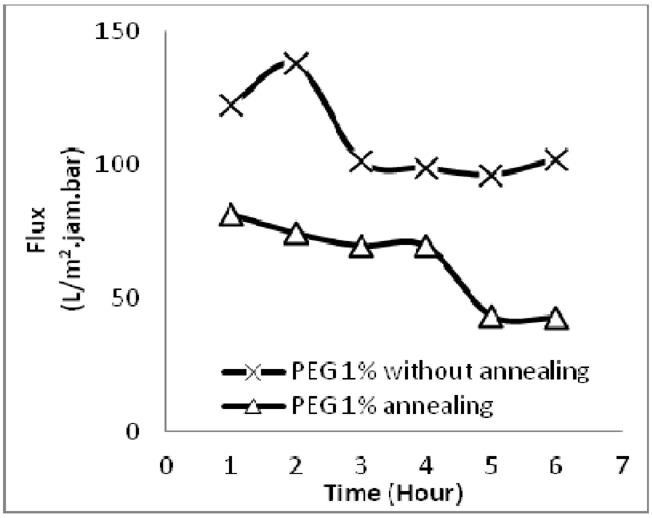

Figure 3: The effect of annealing on the stability of membrane

In accordance with Figure 4, discussed the value of rejection Ca^{2+} and Mg^{2+} in the ratio of membrane without annealing and with annealing at 60 ° C each source (Jepara, Semarang and Demak). In terms of overall value at each source rejection, rejection values of Ca^{2+} and Mg^{2+} by using a membrane with a temperature of 60 ° C thermal annealing tends to produce a more stable value and rejection larger than the membrane without using thermal annealing. The existence of this thermal annealing will improve the performance of the membrane for causing the settings so that the membrane molecules are more stable. The higher the temperature the longer the annealing and thermal annealing of the membrane, the membrane surface layer will experience shrinking so that the membrane becomes more tightly pore [13]. As a result of narrowing of the pore membrane is then increase the value of the membrane rejection affects the membrane performance.

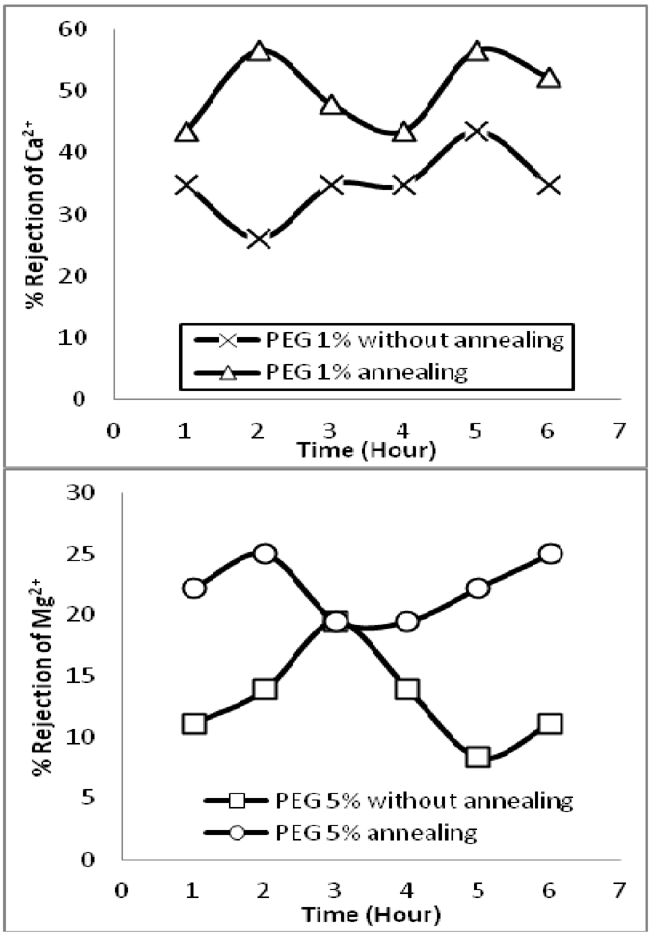

Figure 4: The effect of annealing on the rejection of Ca^{2+} and Mg^{2+}

4. Conclusion

Based on research it can be concluded that the asymmetric cellulose acetate membranes can be produced by the method of dry / wet phase inversion. In this research, the concentration of additives and annealing are factors that affect performance in the membrane and the membrane stability, where the concentration of PEG effect on membrane pore formation. The greater of concentration of PEG is added resulting in the greater pore size. Thus the greater value of flux and rejection values are getting smaller. To improve the performance and stability of the membrane is carried out by annealing the resulting membrane. Thermal annealing given to the effect on the formation of pores of the membrane, where the greater warming temperatures cause the smaller the pore size, so the smaller the flux values while values the greater rejection. The smaller the value of flux and rejection are the greater value indicates that the membrane performance is good and stable.

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