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The Influence of Cellulose Acetate Concentration for Ultrafiltration Membranes

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Abstract: Separation process using a membrane is a common method used in many fields. The objective of this research is to find out the influence of polymer concentration on the physical properties and performance of cellulose acetate as an ultrafiltration membrane. The cellulose acetate membrane is made by phase inversion technique. This technique is carried at by dissolving cellulose acetate in a range of concentration (18%, 19%, 20%, 21%, and 22%) in the solvent (acetone/DMSO = 15%/60%) and DMP as additives (3% mL). Then the mixtures homogenized and added PEG400 for 10% of cellulose acetate concentration (% w/w), strired ± 12 hours left in place until the buble disappeared. Then the dope solution is printed the glass plate, evaporated for 3 minutes, and immersed in a coagulation bath containing 5% acetone. The results suggest that the greater the concentration of cellulose acetate membrane increase the number density while the swelling degree decrease. The performance of the membrane showed that the greater concentration of cellulose acetate will water of flux the membrane decrease and rejection coefficient increase. Cellulose acetate membrane by varying the concentration of 21% and 22% included in the classification of ultrafiltration membranes for rejection coefficient value (90,37% and 91,43%) 90% may rejection by a membrane.

Keywords: Cellulose acetate, Flux, immersion, Rejection coefficient, Ultrafiltration.

INTRODUCTION

One of the currently developing ultrafiltration membrane materials is cellulose acetate membrane. The advantages of cellulose acetate as a membrane material are that it is easy to produce and its raw materials are renewable sources. The disadvantages of cellulose acetate membranes are that they are very sensitive to pH (limited by pH between 2 and 8), biodegradable so they are very susceptible to microbes in nature [1], and only compatible with a few plasticizers [2]. Cellulose acetate for ultrafiltration membranes (MWCO (molecular weight cut off) 10^4-10^8 kDa) can be made using the phase inversion method. Phase inversion has advantages including being easy to do in membrane manufacturing, pore formation can be regulated and controlled with phase inversion technique parameters and can be used on various types of polymers [3].

Poly(ethylene glycol) (PEG) is a membrane pore former and increases membrane flux. [4] has studied the effect of PEG4000 on the characteristics of cellulose acetate membranes with a PEG dope solution composition of 11%, 12% CA and 77% acetone producing an ultrafiltration membrane with an MWCO of 69 kDa. While [5] has studied the effect of PEG weight variation with PEG200 producing a dialysis membrane.

One of the parameters that affect the formation of membrane structure with phase inversion technique is polymer concentration. The variation of cellulose acetate concentration used in this study was 18% - 22% with the addition of PEG400 (10% concentration of cellulose acetate concentration) and evaporation time of 3 minutes and coagulation tank composition of 5% acetone. This composition was chosen based on the composition that was done [5] with MWCO 100-200 kDa and [6] with MWCO 39.2 kDa. This study aims to determine the effect of polymer concentration on the physical properties and performance of cellulose acetate ultrafiltration membranes.

EXPERIMENTAL

The equipment used for the membrane manufacturing process is a membrane printing tool (glass plate and neon lamp), electrical tape, and coagulation tank. Additional equipment consists of a magnetic stirrer, glassware, analytical balance, flat module ultrafiltration tool dead-end system, and Spectronic 21D spectrophotometer.

The materials used include: cellulose acetate brand sigma aldrich (BM = 30 kDa), dimethyl phthalate (Merck; M = 194.19 g / mol; ρ = 1.19 g / mL, pa), acetone (Bratako; ρ = 0.79 g / mL, pa), dimethyl sulfoxide (DMSO) (Merck);, PEG400 [poly (ethylene glycol), MW 400 kDa ρ = 1.444 g / mL] distilled water, dextran (100-200 ka) sigma aldrich, phenol 5% and H_2SO_4 (Schuchardt).

Preparation of Membran

The preparation of this cellulose acetate membrane used the phase inversion method. Cellulose acetate with 18%-22% by weight was dissolved in a mixture of 9.1 mL of solvent (acetone/DMSO = 15%/60%) + 0.3 mL (3%) DMP and stirred with a magnetic stirrer until the solution was homogeneous. Then PEG400 10% of the weight of cellulose acetate was added. The homogeneous polymer solution was then left to stand until there were no air bubbles. The polymer solution that did not contain air bubbles was printed on a glass plate whose edges had been given tape to adjust the thickness of the membrane and pressed evenly over the entire surface of the glass using a neon lamp until a cellulose acetate film was formed. Then the membrane was evaporated by leaving it in the open air with an evaporation time of 3 minutes and dipped in a 5% acetone coagulation bath [6].

Cellulose Acetate Membrane Characterization

The membrane characterization includes physical tests, namely density tests and swelling degree tests, as well as performance tests including flux and rejection.

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The flux measured is water flux and rejection is % rejection (rejection coefficient) 90% can be rejected by the membrane using 100-200 kDa dextran.

RESULT AND DISCUSSION

Membran Selulosa Asetat

The process of forming cellulose acetate membrane begins with cellulose acetate in powder form (Figure 4a) with a concentration of 18% -22% dissolved in a mixture of solvents (acetone / DMSO = 15% / 60%) and added DMP (3%), stirred for ± 12 hours until homogeneous. The homogeneous membrane is added with PEG 10% of the weight of cellulose acetate then printed on a glass plate and for 3 minutes is then inserted into the coagulation tank (5% acetone) until the membrane separates itself from the glass plate. This is due to the interaction between the solvent and non-solvent, before water as a non-solvent pushes the solvent in the polymer (dope solution) it will attract the acetone in the water first until the solvent slowly leaves the membrane and the solidification process occurs [7]. The physical form of the cellulose acetate membrane is shown in Figure 1.

Figure 1. Cellulose acetate before (a) and after the manufacturing process (b)

Physical Characteristics of Cellulose Acetate Membranes

Figure 2 shows the density value and degree of swelling at various polymer concentrations. The density value will increase with the increase in concentration. The increase in polymer concentration will form tight pores and can also be small in size. As mentioned by [1] decreasing polymer concentration can enlarge the pores. This phenomenon is related to the degree of swelling of the membrane. A polymer concentration of 22% has a high membrane density value, conversely the degree of swelling is low. While at a concentration of 18% the membrane density is low and the degree of swelling is high. A high density value indicates that the pores in the membrane are tight so that water molecules are difficult to enter the membrane so that few water molecules are bound to the membrane. Likewise, on a membrane with a low density, the pores in the membrane are large so that water can easily enter (absorb) into the membrane and form hydrogen bonds that are strong enough with the membrane.

The presence of evaporation time and coagulation tank composition also affect the density value. The density value will be greater with the presence of 3 minutes evaporation time and 5% acetone coagulation tank. This is possible because when the solvent is evaporated, the polymer solution that is still formed liquid moves to fill the pores so that it produces pores that are denser than without solvent evaporation, resulting in a membrane with a dense structure. The presence of a 5% acetone coagulation tank composition will also produce a dense membrane because of delayed demixing. The concentration of 18% (without 3 minutes evaporation and 5% acetone coagulation tank) has a smaller density value (0.343 g / cm^3) compared to 18% (0.368 g / cm^3). The density value of 18% (without 3 minutes evaporation and 5% acetone coagulation tank) is smaller, meaning that the pores formed are larger and more numerous compared to the concentration of 18% with evaporation time and 5% acetone coagulation tank. The tendency of the degree of swelling is inversely proportional to the density value because of the evaporation time of 3 minutes and the composition of the coagulation tank of 5% acetone so that the pores formed have a high density level and water molecules have difficulty in diffusing into the membrane.

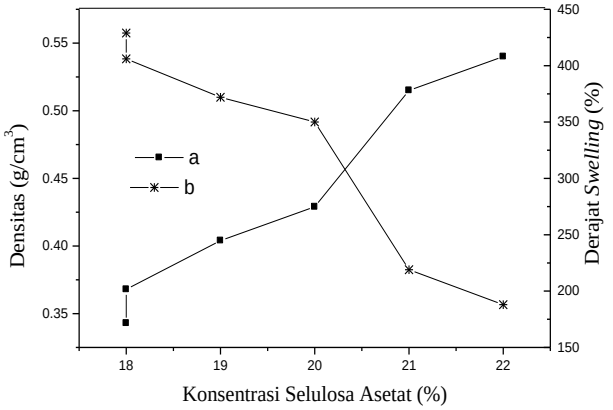

Figure 2. Physical properties curve of membrane for variations in cellulose acetate concentration (a) density (b) degree of swelling

Figure 3. Shows the effect of adding PEG as a pore former. The largest density value (0 mL) even though the concentration is the same (18%). This is because the pores formed are tight because there is no PEG added. When PEG has been added to the dope solution, then the membrane is dipped into the coagulation tank, PEG will leave the matrix in the membrane so that it forms pores and increases the pores [8]. While the density value added 10% of the polymer weight (0.15 mL) the density value is greater than the addition of PEG (0.9 mL) this is because the amount of PEG added is different. The amount of PEG added is greater, namely 10% of the amount of dope solution. So that more pores are formed. The matrix on the membrane left by PEG when the membrane is inserted into the coagulation tank will form pores. So that the level of pore formation becomes large. This also affects the swelling properties of the membrane. The highest swelling degree value is (0.9 mL) this is because the addition of more PEG compared to (0.15 mL). The density value is large so that the swelling degree value is low (0 mL PEG) meaning that the water molecules are slightly bound in the membrane. The swelling degree is also influenced by the level of density.

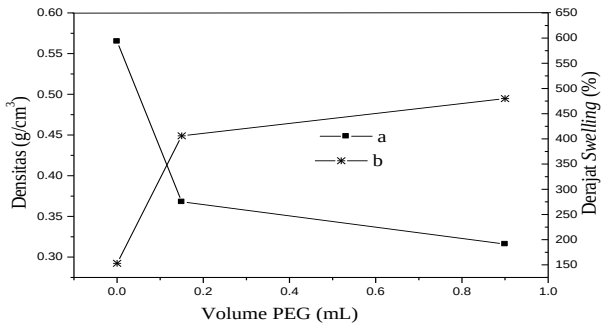

Figure 3. Physical properties curve of membrane on the effect of PEG addition (a) density (b) degree of swelling

Performances of Cellulose Acetate Membranes

Membrane performance can be indicated by the value of water flux, permeability coefficient and rejection coefficient. The flux value indicates the value of the permeate flow rate to pass through the membrane and the rejection coefficient describes the ability of the membrane to retain solute molecules, where this rejection coefficient is a measure of membrane selectivity. The first stage to determine membrane performance is to determine the compaction time of the membrane to be tested. The purpose of determining the compaction time is to obtain a constant flux value and compaction time at a given operational pressure of 2 bar. Compaction is a mechanical deformation process in the polymer matrix that makes up the membrane, aimed at rearranging the newly formed membrane pores, due to pressure and other treatments that affect the membrane pores. Compaction is carried out until a constant flux is obtained, where the membrane no longer experiences mechanical deformation.

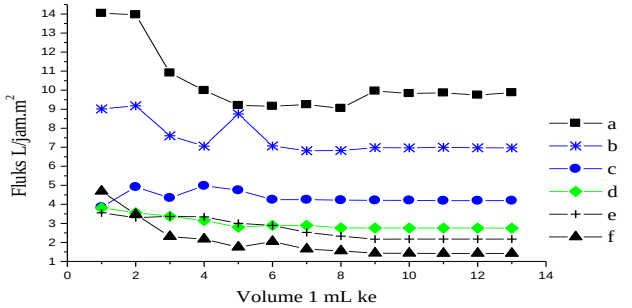

Figure 4. Effect of Concentration on Cellulose Acetate Membrane Compaction (a) 18% CA (non-evaporation time 3 minutes & coagulation tank 5% acetone) (b) 18% CA (c) 19% CA (d) 20% CA (e) 21% CA (f) 22% CA

The compaction results on the membrane with varying polymer concentrations are shown in Figure 4, which shows that the trend of the CA membrane compaction time curve to achieve constant flux will decrease with increasing polymer concentration. Large concentrations tend to have denser pore sizes, so the ability of water to pass through the membrane will also be more difficult and the membrane pores will also be more organized. Evaporation time and coagulation tank composition also affect the membrane compaction time value. Long evaporation tends to reduce the compaction time to achieve constant flux. The test value of physical properties with an evaporation time of 3 minutes and a coagulation tank composition of 5% acetone will produce a membrane that has denser pores.

The addition of PEG also affects the membrane compaction time. Figure 5 shows the membrane compaction time to achieve constant flux. The largest compaction time (0.9 mL) compared to the others is because the PEG added is greater.

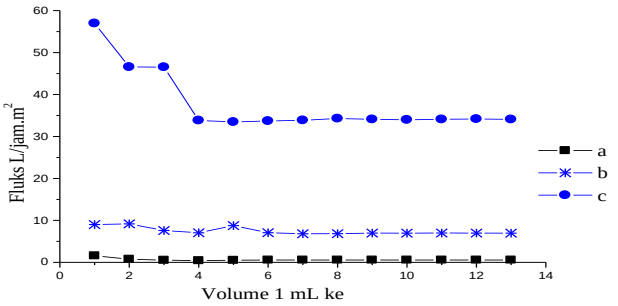

Figure 5. Effect of PEG on cellulose acetate membrane compaction (a) 0 mL (b) 0.15 mL (c) 0.9 mL.

After compaction of the membrane, the flux value on the CA membrane is determined according to the variation of polymer concentration. Water flux or permeation rate is one of the parameters that determine membrane performance. Determination of water flux is obtained by measuring the volume of water that passes through each unit of membrane surface area per unit of time.

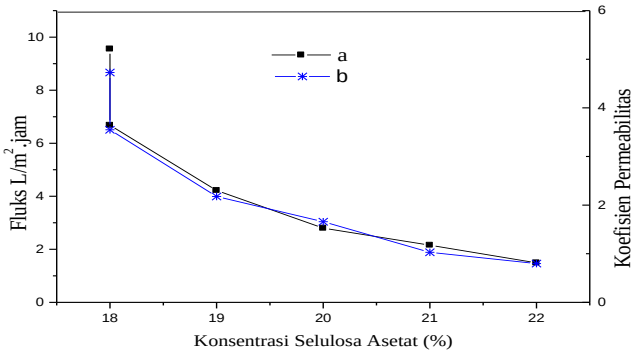

Figure 6. Effect of cellulose acetate concentration on water flux and membrane permeability coefficient (a) flux (b) permeability coefficient.

The increase in polymer concentration causes the viscosity of the solution to increase. As a result, the polymer-solvent will be difficult to interact so that the rate of solvent-polymer exchange with water is slow, and the pores of the membrane formed become tight so that it can reduce the water flux value. The permeability coefficient (figure 6) of the membrane can be obtained by measuring the water flux value. This water flux is one of the parameters that determines membrane performance. The membrane permeability coefficient decreases with increasing polymer concentration. Based on these results, it is known that the largest membrane permeability coefficient value is in the 18% membrane, because the membrane has large pores so that more water molecules can pass through the membrane. While the membrane with a polymer concentration variation of 22% has the lowest permeability coefficient value because the membrane has tight pores so that water molecules are more difficult to pass through the membrane. This permeability coefficient value is directly proportional to the water flux value

(Figure 6).

The evaporation time of 3 minutes and the composition of the coagulation tank of 5% acetone also affect the water flux value and the membrane permeability coefficient. Before water as a non-solvent pushes the solvent in the polymer (dope solution), there is an interaction between the solvent in the polymer and the solvent in the coagulation tank so that the slow solidification process in the polymer solution is called delayed demixing. The evaporation time of 3 minutes makes the pores of the membrane that are formed tend to be tight. This is because during evaporation the solvent tends to evaporate first before forming pores in the membrane matrix. That process finally forms tight pores (the water flux value and its permeability coefficient also decrease).

Figure 7 shows the effect of PEG addition on the water flux value and membrane permeability coefficient. The membrane with the addition of 0.9 mL PEG has a greater water flux value than 0.15 mL and 0 mL. This is due to the addition of more PEG, which is 10% of the amount of dope solution. The pores formed are more numerous and larger.

The function of PEG is to form pores in the membrane, allowing water molecules to enter the pores of the membrane. The membrane without PEG added (0 mL) has a small permeability coefficient. This indicates that the membrane permeability coefficient is related to the size of the pores of a membrane that is formed. The smaller or denser the membrane pores, the lower the water flux value. The lower the water flux value, the lower the permeability coefficient. Likewise, the larger the pores of a membrane, the higher the water flux value and the higher the permeability coefficient.

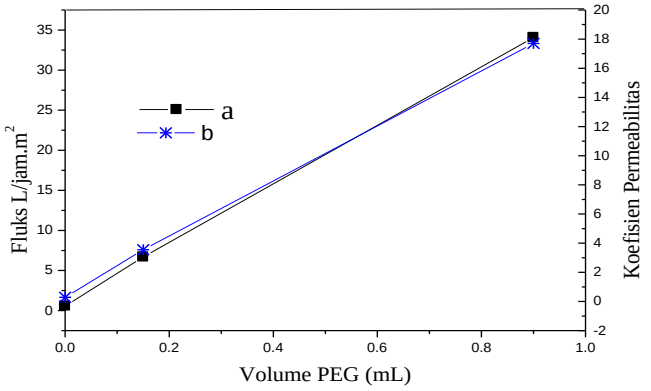

Figure 7. Effect of PEG addition on the permeability coefficient and water flux values of cellulose acetate membrane (a) flux (b) permeability coefficient

The rejection coefficient is a measure of membrane selectivity. A 100-200 kDa dextran solution was used as the test solution. The selection of this test solution was due to the use of ultrafiltration membranes to separate macromolecules from a solution. The first stage to determine the rejection coefficient is to determine the maximum wavelength absorbed by dextran. The results of the optimum wavelength scanning is obtained a wavelength of 483 nm.

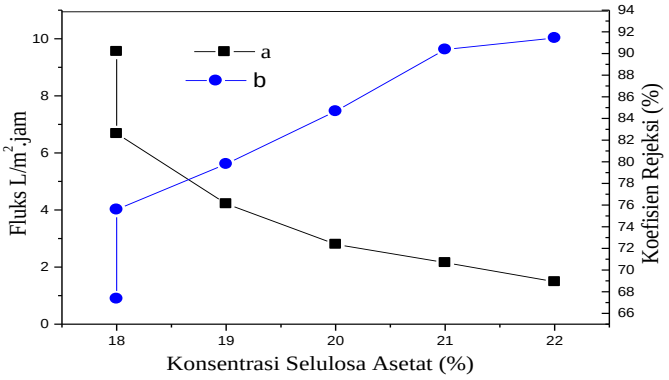

Figure 8. Rejection coefficient curve and water flux of CA membrane at various concentrations (a) flux (b) rejection coefficient

Figure 8 shows that the variation of polymer concentration will also affect the rejection coefficient value of a membrane. The higher the polymer concentration, the higher the rejection coefficient of a membrane. This phenomenon occurs because with the increase in polymer concentration, the pores of the membrane formed will be denser so that the water flux decreases and the molecules retained by the membrane increase. There are 2 membrane concentrations that are included in the selectivity measure of the ultrafiltration membrane in this study where the rejection coefficient of the membrane is above 90%, namely the CA membrane at a concentration of 21% with a rejection coefficient value of 91.15% and the CA membrane at a concentration of 22% which is 92.18%.

Evaporation time of 3 minutes and coagulation tank composition of 5% acetone affect the value of membrane rejection coefficient. Increasing solvent evaporation time can increase the rejection coefficient. This phenomenon occurs because with increasing evaporation time and the presence of acetone in the coagulation tank, the pores of the membrane formed are increasingly dense (water flux decreases) so that more molecules are retained by the membrane.

Figure 9 shows the effect of PEG on the rejection coefficient and water flux values. The rejection coefficient is the largest (94.42%) at 0 mL PEG, this is because there is no addition of PEG that can form pores. So that the water flux decreases and more molecules are retained.

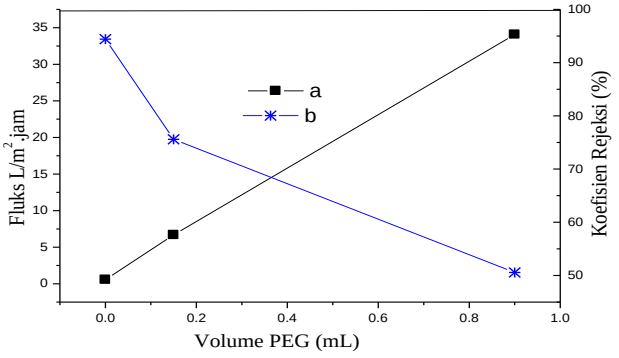

Figure 9. Effect of PEG on the rejection coefficient and water flux of cellulose acetate membrane (a) flux (b) rejection coefficient

CONCLUSION

The concentration of cellulose acetate polymer greatly affects the characteristics of the membrane, namely the greater the concentration, the higher the density of the membrane and the lower the degree of swelling. The greater the concentration of the polymer affects its performance, the lower the water flux test and the higher the dextran rejection coefficient. The concentration variation in this study that has a rejection coefficient value (90% can be exjected) is the membrane at a concentration of 21% and 22%.

REFERENCES

[1] R. Baker, Membrane Technology and Applications [2nd ed]. England: Interscience Publisher a Devision of John Wiley & Son, 2004.

[2] J. T. Jung, H. H. Wang, J. F. Kim, S. M. Jeon, S. H. Park, W. H. Lee, S. J. Moon, E. Drioli, and Y. M. Le, "Microfiber aligned hollow fiber membranes from immiscible polymer solutions by phase inversion," *Journal of Membrane Science*, vol. 617, p. 118654, 2021.

[3] L. Ren, J. Chen, Q. Lu, J. Han, and H. Wu, "Anti-biofouling nanofiltration membrane constructed by in-situ photo-grafting bactericidal and hydrophilic polymers," *Journal of Membrane Science*, vol. 617, no. 1, p. 118658, 2021

[4] A. Idris and K. L. Yet, "The effect of different molecular weight peg additives on cellulose acetate asymmetric dialysis membrane performance," *Jurnal of membrane science*. vol. 280, no. 1-2, pp. 920-927, 2006.

[5] L. Kartika, Pemisahan Surfaktan Anionik Sodium Dodesil Sulfat (SDS) dengan menggunakan Membran Ultrafiltrasi Selulosa Asetat (CA). Skripsi. Jember. Universitas Jember, 2010.

[6] A. Wibowo, Studi Kinerja Membran Ultrafiltrasi Berbasis Selulosa Asetat untuk Klarifikasi Sari Buah Naga. Skripsi. Jember: Universitas Jember, 2008.

[7] F. Mark, J. Ketta, and D. F. Othmer, Encyclopia of Chemical Tehnology. Second Edition. Vol 4. New York: Interscience Publisher a Devision of John Wiley & Son, Inc. p 632 and 657, 1968.

[8] V. Vatanpour, M. E. Pasaoglu, H. Barzegar, O. O. Teber, R. Kaya, M. Bastug, A. Khataee, and I. Koyuncu, "Cellulose acetate in fabrication of polymeric membranes: A review," *Chemosphere*, vol. 295, no. 5, p. 133914, 2022.