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Synthesis and Characterization of Cellulose Acetate Membrane from Cassava Peel for Microfiltration

A. Ma'ruf†, E. Puspawiningtiyas, D. N. Afifah and E. Diaz
Chemical Engineering Department, Universitas Muhammadiyah, Purwokerto Jl., K. H. Ahmad Dahlan, Dukuh Waluh, Kembaran, Purwokerto 53182, Indonesia
†Corresponding author: A. Ma'ruf; anwarump@yahoo.com

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ABSTRACT

Cassava peel is a waste product from cassava starch or modified cassava flour (mocaf) production. It is currently not utilized optimally. Cassava peel is a lignocellulosic material that can be used as a source of cellulose. Acetylation of cassava peel cellulose was successfully done using acetic anhydride with glacial acetic acid and sulfuric acid as catalysts. The content of acetyl is 49.54%, and the degree of substitution (DS) is 3.69. The percentage of acetyl of more than 43% and the DS of 3.69 show that the cellulose acetate obtained is categorized as cellulose triacetate. The CA–PEG membrane has a pore range of 1- 4 µm depending on the molecular weight of PEG. The coefficients of rejection of the CA-PEG membrane range from 95.99% to 98.88%. The CA-PEG membrane is effective as a microfiltration membrane.

INTRODUCTION

Cassava peel, a byproduct of cassava starch or modified cassava flour (mocaf) production, is currently underutilized. Cassava peel contains lignin, cellulose, and hemicellulose. The percentages of lignin, cellulose, and hemicellulose are 10.88%, 14.17%, and 23.40%, respectively (Pondja et al. 2018). The content of cellulose and hemicellulose in cassava peel has great potential as a raw material for making cellulose acetate (Rosa et al. 2020, Maryana et al. 2020). Furthermore, cellulose acetate can be used as a raw material for the synthesis of cellulose acetate membranes.

Membrane technology is a technology that has bright prospects. Membrane technology is currently widely used in various processes such as filtration, waste treatment, desalination, and chemical reactions (Roy & Ragunath 2018). Cellulose acetate membranes can be used in various fields of application. Cellulose acetate membranes have the potential to be developed due to the abundant and renewable availability of raw materials. Perera et al. (2014) produced thin film composite (TFC) reverse osmosis membranes from cellulose acetate onto an ultrafiltration membrane support. Cellulose acetate used was commercial acetate (CA, 30 kDa molecular weight, and 39.8 wt% acetyl content). Serbanescu et al. (2020) modified the commercial cellulose acetate membrane for Gd (III) separation. The modification of commercial CA membranes used aminopropyl triethoxy silane (APTES) immobilization and glutaraldehyde (GA) linkages to the amino groups of APTES, followed by the immobilization of calmagite. Djayanti et al. (2019) synthesized cellulose acetate membrane from cotton spinning waste. The acetylation of cotton spinning waste cellulose used acetic acid for activation and sulfuric acid as a catalyst.

The utilization of cellulose from cassava peel as the material of a cellulose acetate membrane is still rare. This research aims to produce and characterize the cellulose acetate membrane from cassava peel. The production of cellulose acetate membrane involves several stages: delignification of cassava peel, acetylation of cellulose, and cellulose acetate membrane production. The performance of the cellulose acetate membrane produced was evaluated for the microfiltration process.

MATERIALS AND METHODS

Materials

Cassava peel was obtained from PT. Rumah Mocaf Indonesia, Banjarnegara district, Indonesia. Hydrogen peroxide, sodium hydroxide, sulfuric acid, glacial acetic acid, acetic anhydride, polyvinyl alcohol (PVA), and polyethylene glycol (PEG) were obtained from Merck. Demineralized water was produced by Elva-Veolia Technology. Synthetic

limewater as wastewater was obtained from the Chemical Engineering Department Laboratory.

Preparation of Cassava Peel

The cassava peel was separated from the outer skin, then cut and washed using clean water. The cut cassava peel was dried in the sun for 1 day and then dried in an oven at 80°C for 2 hours. The dry cassava skin was then mashed and sieved using a 60-80 mesh. The sifted cassava peel fiber was dried again using an oven until it reached a constant weight at 80°C.

Delignification

Delignification of cassava peel was conducted by alkaline hydrogen peroxide (Ma'ruf et al. 2017). The weight of 20 grams of cassava peel fiber was delignified using a 1.5% alkaline hydrogen peroxide solution with a ratio of 1:9 b/v at 100°C for 3 hours. The delignification process was carried out at a pH of 11.5, and the reaction pH was adjusted using a sodium hydroxide solution.

Bleaching

The delignified cassava fiber was then added to 180 mL of a 3% hydrogen peroxide solution, heated using a hot plate, and stirred using a magnetic stirrer for 2 hours. The cassava fiber was then filtered, washed until it reached a neutral pH, and dried in an oven at 80°C.

Acetylation

The acetylation of cassava peel cellulose uses glacial acetic acid and sulfuric acid as catalysts. The volume of 97 mL of glacial acetic acid was mixed with 1.6 mL of 95% sulfuric acid in a beaker glass and stirred until homogeneous. Prepare as much as 5 g of cassava cellulose (after the bleaching process), then add a mixture of the acetic acid glacial and sulfuric acid solution, stir, and heat in a water bath at a temperature of 55°C for 1 hour. After that, add the mixture to the acetic anhydride solution in a weight-to-acetic-anhydride ratio of 1:2 (w/v) and stir at 55°C for 2 hours. The mixture was then put into a certain amount of water to form a precipitate. The precipitate obtained was then washed until neutral and dried at 70°C in an incubator oven for 24 hours. The cellulose acetate obtained was then analyzed to determine the acetyl content and degree of substitution (DS) to determine the type of cellulose acetate produced.

Cellulose Acetate Membrane Production

PVA solution preparation: Polyvinyl alcohol (PVA) was weighed at 10 g and then dissolved in 10 mL of 1 M nitric acid and 190 mL of distilled water using an Erlenmeyer glass. The mixture was stirred using a magnetic stirrer for 2 hours at 80°C. PVA was used as an adhesive agent between cellulose acetate powders to form a dense cellulose acetate membrane.

CA-PEG solution preparation: The CA–PEG solution was made from cellulose acetate (CA) and polyethylene glycol (PEG) with acetone as solvent. The amounts of 1 g of CA and 1 g of PEG (with various variations of PEG molecular weight: PEG 400, PEG 600, and PEG 4000) were weighed and then dissolved in 8.5 mL of acetone solution in the Erlenmeyer glass. The mixed solution was then stirred using a magnetic stirrer for 8 hours until all of the cellulose acetate dissolved in the acetone. After a homogeneous solution, the Erlenmeyer was opened for 3 hours so that the acetone evaporated.

Membrane synthesis: The CA-PEG solution was then added to 15 mL of PVA solution and stirred for 24 hours using a magnetic stirrer. The homogeneous dope solution was then cast using a Petri dish glass. Then, the dope solution was dried for 8 hours at 80°C in the oven.

Characterization of Cellulose Acetate Membrane

The characteristics of the cellulose acetate membrane were determined using the Fourier transform infrared (FTIR) spectrophotometer to analyze the functional groups and a scanning electron microscope (SEM) to analyze the morphology of the membrane.

Performance Test of Cellulose Acetate Membrane

Permeability test: The permeability test of the membrane was conducted by passing pure water through it. The pure water was flowed using a pump to the surface of the membrane at constant pressure. the volume. The volume of water that passed through the membrane was weighed. The permeability of the membrane can be calculated using Equation (1).

$$L_P = \frac{V}{A.t.\Delta P} \quad \ldots(1)$$

Where L_P is permeability ($L.m^{-2}.h^{-1}.bar^{-1}$), V is the volume (L), A is the surface area of the membrane (m^2), and ΔP is transmembrane pressure (bar).

Ultrafiltration test: The microfiltration test can be explained in Fig. 1. The limewater, as synthetic wastewater, was inserted into the feed tank (1). The laundry wastewater was then pumped to the surface of the membrane (3) using a pump (2). The pressure was set by the valve (4). The pressure can be measured by the pressure gauge (5). The permeate was collected in the Erlenmeyer (6) and weighed using a balance (7). The flux of the membrane was calculated by Equation (2).

$$J = \frac{V}{A.t.} \quad \ldots(2)$$

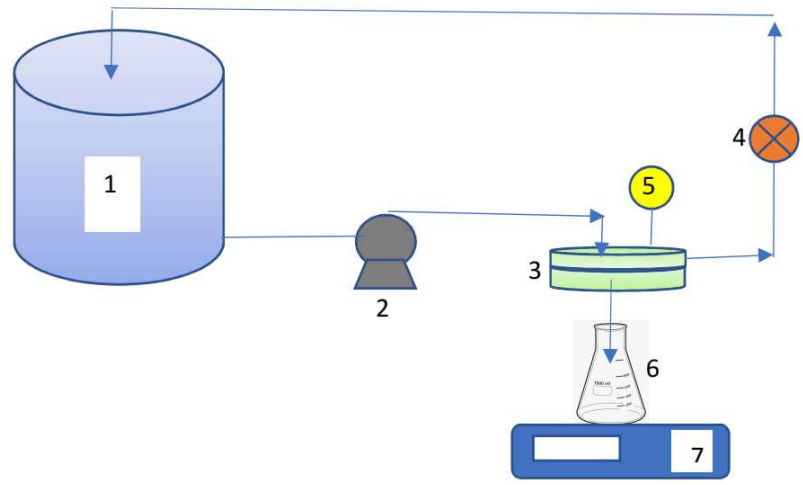

Fig. 1: Equipment set for microfiltration.

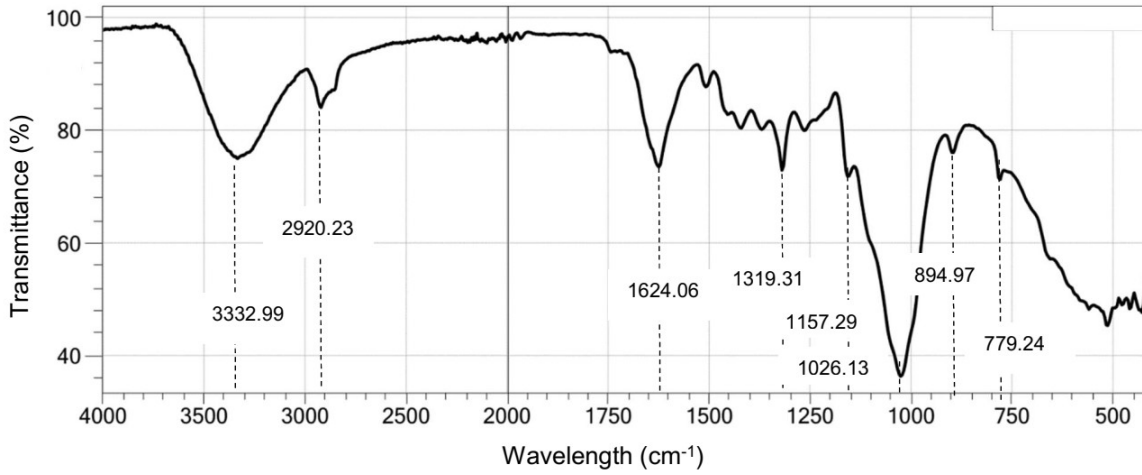

Fig. 2: FTIR spectra of cassava peel cellulose.

RESULTS AND DISCUSSION

The Characteristics of Cellulose and Cellulose Acetate from Cassava Peel

Cassava peel is a lignocellulosic material. The three main components are cellulose, hemicellulose, and lignin. The proximate analysis of cassava peel was done using the Chesson-Data method (Ma'ruf et al. 2017). Table 1 shows the approximate analysis of cassava peel. To use the cellulose from cassava peel, delignification of the peel must be conducted. Delignification of cassava peel was done by alkaline hydrogen peroxide. Delignification of cassava peel using alkaline hydrogen peroxide effectively removes the lignin. The analysis shows that almost 89.5% of the lignin was removed.

The FTIR spectra of cassava peel cellulose are shown in Fig. 2. The wave number range of 3660-2900 cm^{-1} is characteristic of the stretching vibration of O-H and C-H bonds in polysaccharides (Hospodarova et al. 2018). The special characteristics of lignin, the guaiacyl (G) unit (at 1269 cm^{-1}) are not found in this FTIR spectra, and the syringyl (S) unit (at 1326 cm^{-1}) is found but has a low intensity. The peak of 1624 cm^{-1} corresponds to the vibration of water

Table 1: The proximate analysis of cassava peel.

Component	Weight percentage
Cellulose	33.33
Hemicellulose	18.57
Lignin	19.00
Water	29.10

molecules absorbed in cellulose. The peaks at 1369.46, 1319.31, 1026.13, and 894.97 cm^{-1} belong to stretching and bending vibrations of -CH_2 and -CH, -OH, and C-O bonds in cellulose, respectively.

Acetylation of cassava peel cellulose was done using acetic acid glacial activation and acetic anhydride acetylation with sulfuric acid as a catalyst. The acetylation process requires a cellulose/acetic anhydride ratio of 1:2 (w/v), a temperature of 40 °C, and a reaction time of 3 hours. The analysis of acetyl in cellulose acetate obtained shows that the content of acetyl is 49.54%. While the degree of substitution (DS) is 3.69. The percentage of acetyl of more than 43% and DS of 3.69 show that the cellulose acetate obtained is categorized as cellulose triacetate (Djuned et al. 2014). Fig. 3 shows the reaction of cellulose with acetic anhydride.

The Characteristics of Cellulose Acetate Membrane

The CA-PEG membrane was synthesized using acetone as a solvent. The method of membrane synthesis is phase inversion. The ratio of CA to PEG is 1:1 (w/w). Fig. 4b shows the membrane obtained from cellulose acetate obtained from cassava peel. Fig. 5 shows the FTIR spectra of the cellulose acetate and CA-PEG membranes. There are two main peaks in the difference between cellulose acetate and CA-PEG membranes, indicating the existence of PEG. The peak of 948.98 cm^{-1} shows stretching of C–O and 840.96 cm^{-1} shows rocking vibration of the -CH_2- groups in the PEG (Chirea et al. 2011).

The Morphology of Cellulose Acetate Membrane

Fig. 6 shows the morphology of the CA-PEG membrane, (a) using PEG 600 as an additive and (b) using PEG 4000 as an additive. The pores of the membrane are not symmetric, with a range of pores between 2–4 µm and 1–2 µm for PEG 600 and PEG 4000, respectively. It can be seen that the higher weight membrane obtained was more compact. The pores of the membrane are still larger compared with commercial polymeric membranes for microfiltration (polyvinylidene fluoride (PVDF) membrane, 0.22 µm) (Nourbakhsh et al. 2014).

Performance of CA-PEG Membrane

Permeability test: Table 2 shows the permeability of the CA–PEG membrane obtained. At a higher molecular weight of PEG, the permeability of the membrane will decrease, while the membrane resistance will increase. The permeability of the CA–PEG membrane was found to be higher than the permeability of the polyether imide membrane (100 kDa) (Pertile et al. 2018).

Microfiltration performance: The performance test of CA

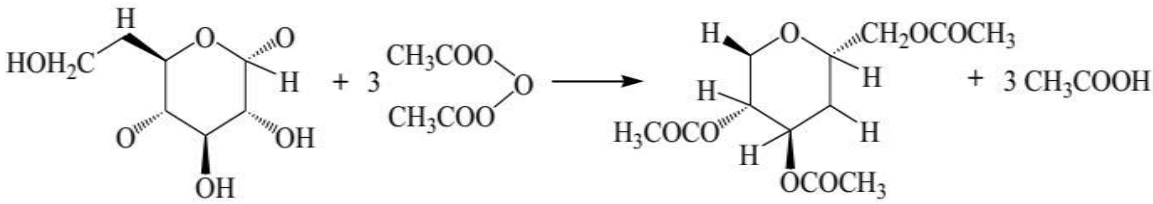

Fig. 3: The reaction of acetylation of cellulose.

Fig. 4: (a) Cellulose acetate obtained from cassava peel cellulose; (b) CA-PEG membrane.

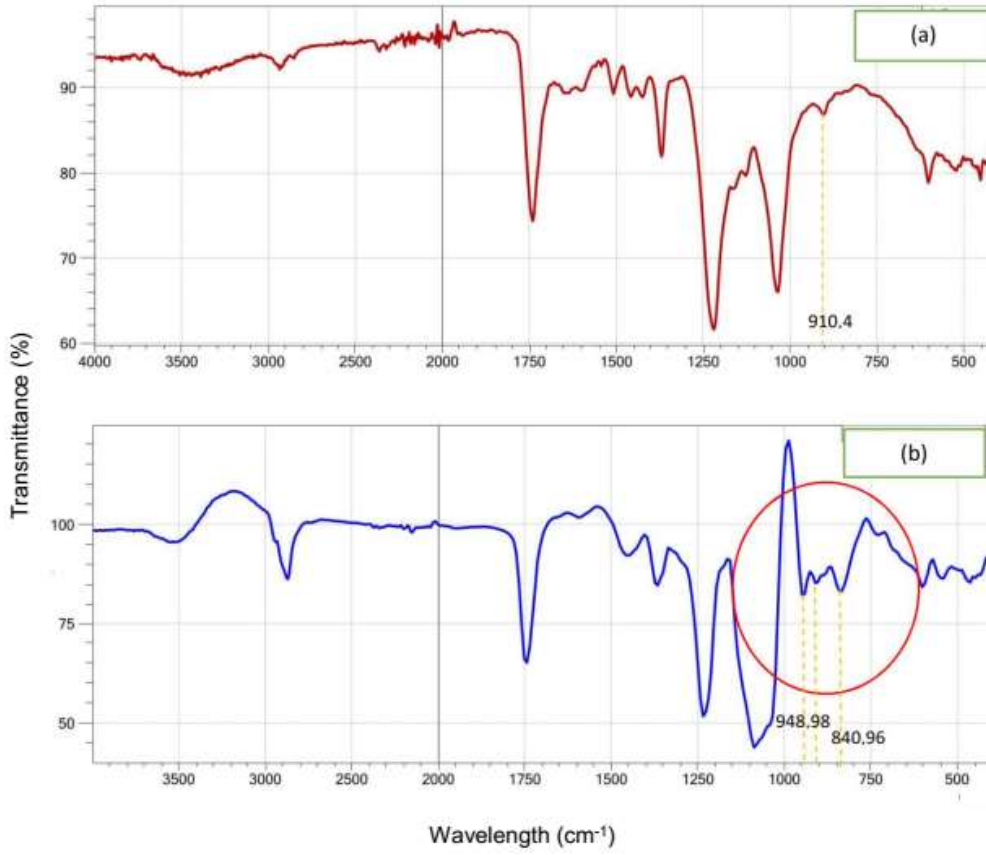

Fig. 5: FTIR spectra: (a) cellulose acetate; (b) CA-PEG membrane.

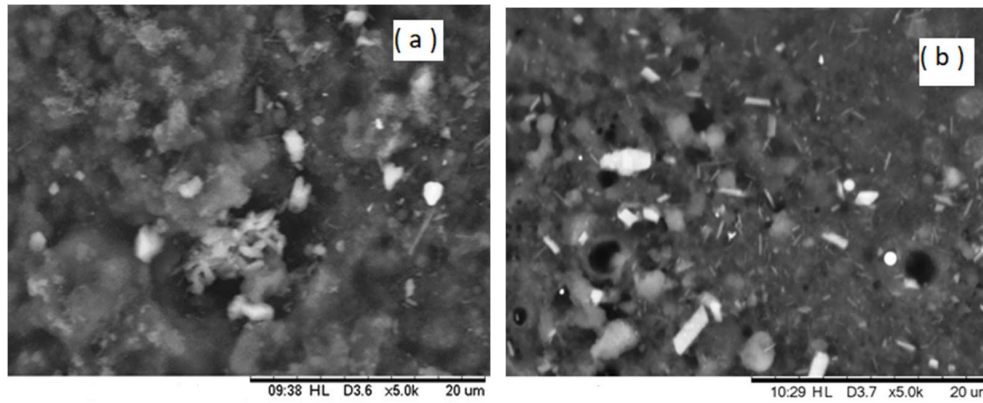

Fig. 6: Morphology of the CA-PEG membrane: (a) PEG 600; (B) PEG 4000.

Table 2: Permeability and membrane resistance of CA-PEG membrane.

Membrane	Permeability ($L.m^{-2}.h^{-1}.bar^{-1}$)	Membrane Resistance ($m.kg^{-1}$)
CA-PEG 400	1.83×10^3	19.688×10^6
CA-PEG 600	1.29×10^3	27.891×10^6
CA-PEG 4000	1.06×10^3	34.066×10^6

membranes was conducted for the microfiltration of synthetic wastewater of limewater. The initial turbidity of limewater is 672 NTU. Fig. 7 shows the flux of the membrane during the microfiltration process. Table 3 shows the rejection coefficient of the membrane. The range of rejection coefficient of 95.99% - 98.99% indicates that the membrane is effective as a microfiltration membrane.

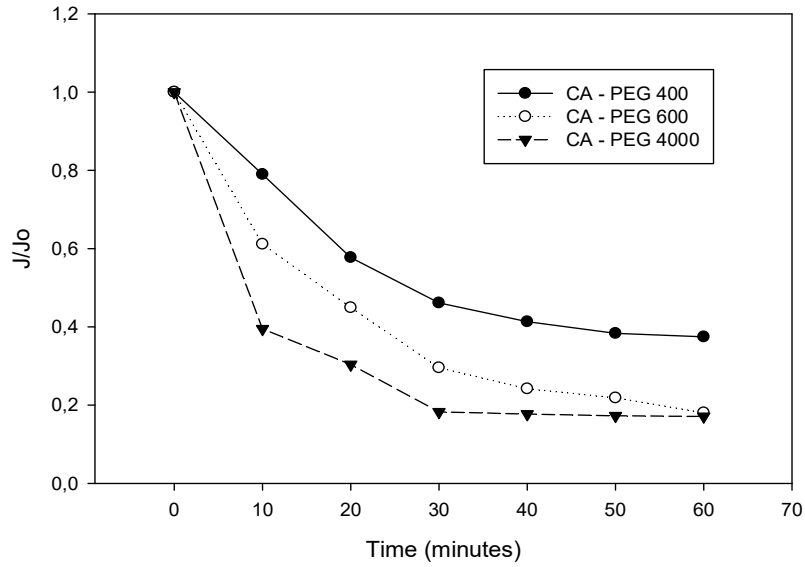

Fig. 7: Flux of the membrane during microfiltration.

Table 3: Rejection coefficient of microfiltration.

PEG	Rejection Coefficient (%)
PEG 400	95.99
PEG 600	98.38
PEG 4000	98.88

CONCLUSION

Cassava peel is a lignocellulosic material that can be used as a source of cellulose. Acetylation of cassava peel cellulose was successfully done using acetic anhydride with glacial acetic acid and sulfuric acid as catalysts. The content of acetyl is 49.54%, and the degree of substitution (DS) is 3.69. The percentage of acetyl of more than 43% and DS of 3.69 show that the cellulose acetate obtained is categorized as cellulose triacetate. The CA–PEG membrane has a pore range of 1-4 μm depending on the molecular weight of PEG. The coefficients of rejection of the CA-PEG membrane range from 95.99% to 98.88%. The CA-PEG membrane is effective as a microfiltration membrane.

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