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ORIGINAL RESEARCH

PRODUCTION OF CELLULOSE ACETATE MEMBRANE FROM COCOA (*THEOBROMA CACAO L*) SHELL MODIFIED POLYETHYLENE GLICOL FOR PB METAL ION FILTRATION

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Abstract. In this study, a modified polyethylene glycol-modified cellulose acetate membrane was made. Cellulose acetate was synthesized from cocoa husk waste (*Theobroma cacao L*) with several steps, namely isolation of alpha-cellulose from cocoa husk waste, synthesis of cellulose acetate from alpha cellulose, preparation of 10% cellulose acetate membrane with the addition of polyethylene glycol 0, 5, 10, 15, 20 & 25%. From the results of the research, it was found that the FT-IR analysis of cellulose from cocoa shells showed an absorption peak at wave numbers between 3400 – 3500 cm^{-1} which indicated the presence of O-H stretch groups. At wave numbers 2800-2900 cm^{-1} indicates C-H stretching, then it can be seen at wave numbers 1160 cm^{-1} indicates C-O-C stretching, and at 1035-1060 cm^{-1} indicates C-O stretching. In the fingerprint area, we found absorption peaks at wave numbers around 1300 cm^{-1} which indicated the presence of C-H bending, and around 1400 cm^{-1} indicating the presence of CH_2 bending. The cellulose acetate obtained is white and smooth compared to alpha-cellulose. At the membrane preparation stage, the results of the insoluble cellulose acetate & PEG using acetone as a solvent. So it is necessary to do a solubility test and find a suitable solvent to form a polyethylene glycol-modified cellulose acetate membrane for Pb metal ion filtration.

Keywords: membranes, alpha-cellulose, cellulose acetate, polyethylene glycol, cacao

1. INTRODUCTION

Cellulose acetate was one of the first polymer membrane materials used specifically for solution separation. Cellulose acetate membranes have good strength, are hydrophilic, have high flux values and relatively low costs, so they have been widely used for Reserve Osmosis (RO) separation, ultrafiltration (UF), microfiltration and gas separation [1].

In previous studies, cellulose acetate membranes had been prepared from cocoa shell waste (*Theobroma cacao L*). Cellulose acetate was prepared in

several stages, namely isolation of α-cellulose from cocoa shell (*Theobroma cacao L*) and isolation of α-cellulose into cellulose acetate. The high content of cellulose, hemicellulose, and lignin in cocoa (*Theobroma cacao L*) can be converted into useful products and materials. The advantages of using cellulose acetate are that it can be produced at a low cost, adsorption selective, soluble in most solvents (especially organic solvents), hydrophilic, and renewable sources. Cellulose acetate is also widely used for the adsorption process or adsorption of metal ions or industrial waste due to its good absorption properties [2].

In the previous research, the research results were obtained where in the first stage, α-cellulose was obtained from cocoa shell (*Theobroma cacao L.*) which was white in color and had a functional group analysis structure close to the standard α-cellulose structure. The cellulose acetate obtained was followed by the preparation stage of the cellulose acetate membrane. The results showed that the cellulose acetate membrane obtained had mechanical properties that were very weak and easily destroyed, making it difficult to proceed to the testing phase using cell membranes. To be able to make cellulose acetate membranes with strong mechanical properties it is necessary to add additives. Additives commonly used for the manufacture of cellulose acetate membranes include Polyethylene Glycol (PEG), Polyvinyl Chloride (PVC), Dioctyl phthalate, and others. Thaiyibah 2016 [3] conducted research on the manufacture and characterization of cellulose acetate-PVC membranes from water hyacinth (Eichhornia crassipes) for the adsorption of Cu(II) metal. In this study, isolating cellulose from water hyacinth through soxhletation, delignification, and bleaching extraction processes, then continued with the synthesis of acetylation. To observe the concentration of doped Cu(II) metal ions bound by the membrane, an Atomic Absorption Spectrophotometer (AAS) analysis was carried out, by looking at changes in absorbance in dopant solutions. So that the optimum composition of the cellulose acetate-PVC membrane can be known.

Additives are added to improve the properties of the membrane, plasticizers so that the resulting membrane is not easily brittle and stiff. One of the additives and plasticizers that are often used is polyethylene glycol (PEG). PEG has the properties of non-toxic, biocompatible, and hydrophilic, has high flexibility, antifoaming agent, and antifouling. The addition of PEG to the membrane can produce membranes with smaller and more regular pores and can increase membrane flux [4]

This research is a follow-up study where previously the cellulose acetate membrane from cocoa shell (*Theobroma cacao L.)* was found to have weak mechanical properties. Therefore it is hoped that the addition of polyethylene glycol can improve the mechanical properties of the cellulose acetate membrane and can increase the flux value in the Pb(II) feed solution.

2. METHODOLOGY

1Materials and Equipment

The using materials in the research were cocoa shell waste (*Theobroma Cacao L*), Na_2SO_3, NaOH, H_2O_2, nitric acid p.a, glacial acetic acid p.a, sulfuric acid, acetic anhydride, distilled water, acetone, chloroform, polyethylene glycol, and Pb(II) metal.

The using tools in the research were stirred membrane cell, 42 Whatman paper, pH meter, a universal pH

indicator, a hotplate, a gas cylinder, an analytical balance, an oven, a 100 mesh sieve, a magnetic stirrer, stainless steel rod, 25 x 30 cm glass, thick tape, bowl coagulation, regulators, nitrogen gas cylinders, stopwatches, FT-IR and glassware.

2Reseach Methods

2.1Cellulose Isolation from Cocoa Shell (Theobroma Cacao L)

Samples of the cocoa shell (*Theobroma Cacao L*) were soaked using sodium bisulfite ($NaHSO_3$), then the cocoa shells were air-dried and cut into small pieces. 150 grams of chocolate peel pieces were taken, added 1 liter of 3.5% (v/v) HNO_3 and 10 mg $NaNO_2$, then heated at 90^{o}C for 2 hours. The mixture was filtered and the dregs obtained were washed until the pH was neutral. The neutral dregs were added to 750 ml of 2% (w/v) NaOH and 2% (w/v) Na_2SO_3 in a 1:1 ratio at 50^{o}C for 1 hour. Filter and dregs washed until neutral pH. Then bleaching was carried out with 250 ml of 1.75% NaOCl solution at 70 °C for 30 minutes. Filter and dregs washed until the filtrate is neutral. Bleaching the α-cellulose from the sample with 500 ml of 17.5% NaOH solution at 80°C for 30 minutes. Filter and wash until the filtrate is neutral. Continue bleaching with 10% H_2O_2 at 60°C . Dry in the oven at 60°C. Store in a desiccator.

2.2 Synthesis of Cellulose Acetate from α-Cellulose from Cocoa Shell (Theobroma Cacao L)

10 grams of cellulose which had been mashed with a blender was then put into a three neck flask which was assembled with a hotplate magnetic stirrer, then dissolved with 250 mL of glacial acetic acid and stirred for 3 hours. Then 75 ml of anhydrous acetic acid and 3 drops of concentrated sulfuric acid catalyst were added at 25°C for 2.5 hours. After that, 10 ml of distilled water and 25 ml of glacial acetic acid were added to the solution and left for 30 minutes. Add sodium acetate as much as 5 grams to the solution and wait for the process for 5 minutes. Then wash with tap water to get rid of acetic acid odor, then soak in methanol for 10 minutes. Then filtered and dried in the oven at 50°C and crushed and sifted. The obtained cellulose acetate was characterized by Fourier Transform Infrared Spectroscopy (FT-IR).

2.3 Production of Cellulose Acetate Membrane with PEG Additive

The membrane is made from cellulose acetate obtained from cocoa shell waste (*Theobroma Cacao L*). Cellulose acetate membranes were prepared by precipitation immersion phase inversion method with the following procedure : Dissolve 10% (w/w) cellulose acetate in acetone, add PEG plasticizer with variation 0; 10; 15; 20; 25% (w/w) then leave for 24 hours. This solution is then stirred with a magnetic stirrer until homogeneous. This solution is called a dope solution. Prior to the printing process, the dope solution was allowed to stand for 30 minutes to remove the air bubbles contained in it. The dope solution was poured onto a glass plate that had been smeared with chloroform and then leveled with a stainless steel rod to form a thin layer and left for 7 minutes. The thin layer was immersed in a water coagulation bath for 10 minutes until the membrane was released. Then characterized by Fourier Transform Infrared Spectroscopy (FTIR), the pore surface morphology of the membrane with a Scanning Electron Microscope (SEM).

3. RESULTS AND DISCUSSION

1 *Isolation of α-Cellulose from Cocoa Shell (Theobroma cacao L.)*

In this research, α-cellulose was isolated from cocoa shell *(Theobroma cacao L*.). This isolation stage is based

on previous research (Riani, Pevi 2019) where the initial stage of the research was the preparation of cocoa shell powder by drying and smoothing the cocoa shell.

Figure 1. dry cocoa shell

The dried cocoa peel sample was soaked in 2% NaOH for 24 hours, then filtered and a blackish-brown solution was obtained. Samples were washed with distilled water until neutral, dried, and blended until smooth. The next stage is the pretreatment stage, namely by adding 3.5% HNO_3 to the sample, then heating it at 90°C for 2 hours. After that, it was filtered and the dregs were washed until the filtrate was neutral. Swelling by solvents occurred at this pretreatment stage so that the cellulose structure was stretched from hemicellulose and lignin which were still tight, damaging the crystal structure of cellulose and increasing the volume of the material [5]. As a result, the pore volume of the cocoa shell fiber will become larger. The next step was delignification using 2% (w/v) NaOH and 2% (w/v) Na_2SO_3 with a ratio of 1:1 at 50°C for 1 hour. The results obtained were filtered and the dregs were washed until the pH was neutral. The research was continued to the cellulose purification stage by adding 17.5% (w/v) NaOH solution at 50°C for 60 minutes, then filtering until the filtrate was neutral. The purpose of the delignification process is to remove the lignin in the cocoa shell powder fibers. The results of lignin degradation were indicated by a change in the color of the solution to dark brown.

The final step in the isolation of α-cellulose is the bleaching process by adding 10% (v/v) H_2O_2 at 60°C for 15 minutes. The results obtained were dried in an oven at 60°C and stored in a desiccator. The bleaching process aims for a bleaching process where degradation of the remaining lignin occurs. The results of α-cellulose obtained can be seen in Figure 2 below.

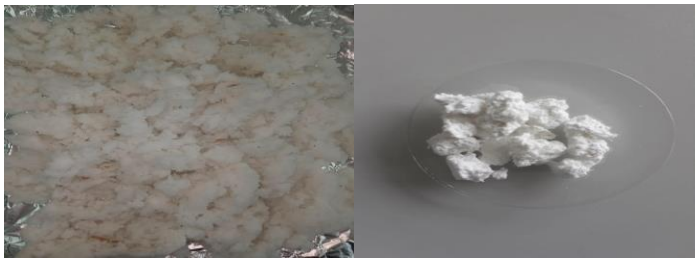

Figure 2. α-cellulose from cocoa shell (*Thebroma cacao L.*)

In Figure 2 we can see the α-cellulose powder from cocoa shell (*Thebroma cacao L.*) is white and dry. This α-cellulose is still in rough form and can then be processed into cellulose acetate.

α-cellulose from cocoa shell (*Thebroma cacao L.*) was then tested using FT-IR. FT-IR analysis data of α-cellulose from cocoa shell (*Thebroma cacao L.*) can be seen in Figure 3 below:

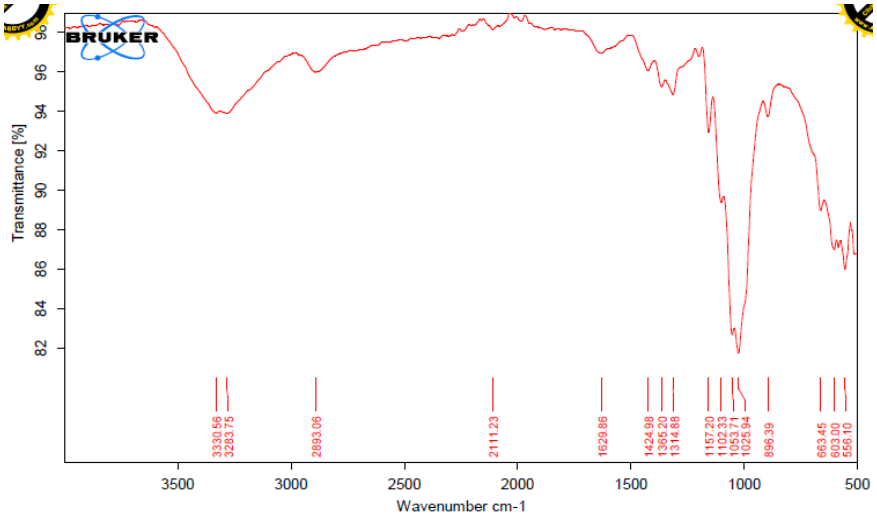

Figure 3. FT-IR analysis of α-cellulose from cocoa shell (*Thebroma cacao L.*)

From the results of FT-IR analysis of α-cellulose from cocoa shell (*Thebroma cacao L.*) it can be seen that there are absorption peaks at wave numbers between 3400 – 3500 cm^{-1} indicating the presence of O-H stretch groups. At wave numbers 2800-2900 cm^{-1} it shows C-H stretching, then it can be seen at wave numbers 1160 cm^{-1} it indicates C-O-C stretching, and at 1035-1060 cm^{-1} it shows C-O stretching. In the fingerprint area, absorption peaks were found at wave numbers around 1300 cm^{-1} indicating the presence of C-H bending, and around 1400 cm^{-1} indicating the presence of CH_2 bending.

Table 1 below shows the identification of α-cellulose from cocoa shell (*Thebroma cacao L.)*

Table1. IR spectrum absorption bands on α-cellulose from cocoa shell (*Thebroma cacao L.)*

wavelength (cm^{-1})	Identification
3330	O-H *strecthing*
2893	C-H *stretching*
1157	C-O-C *stretching*
1035-1060	C-O *stretching*
1365	C-H bending
1424	CH_2 bending

2. Preparation of Cellulose Acetate (SA) Membrane from Cocoa Peel (Theobroma cacao L.)

Research on cellulose acetate (SA) membranes from cocoa shells (*Theobroma cacao L.*) has been done before [2]. The method used was a phase inversion technique with acetone as a solvent (density 0.79 gr/ml) and as a non-aqueous solution.

The homogeneous solution that is formed will be printed into thin sheets and coagulated into a non-solvent, namely distilled water. During the immersion process in the coagulation bath, the acetone solvent will diffuse out of the membrane to form an active layer with small pores on the top surface of the membrane. This technique is called the submerged precipitation phase inversion technique. This technique makes it possible to obtain a tight and porous membrane [6].

The results of previous studies showed that the cellulose acetate (SA) membrane from cocoa shell (*Theobroma cacao L.)* with the organic solvent acetone showed that the membrane formed was very thin and had very weak mechanical properties [2]

Based on this research, the membrane modification was carried out by adding Polyethylene Glycol 1000 as an additive when making the membrane. From the research results that have been obtained, a 10% cellulose acetate (SA) membrane without the addition of PEG obtained a membrane that was brittle and easily separated from the glass plate. We can see the 10% SA membrane obtained in Figure 4 below.

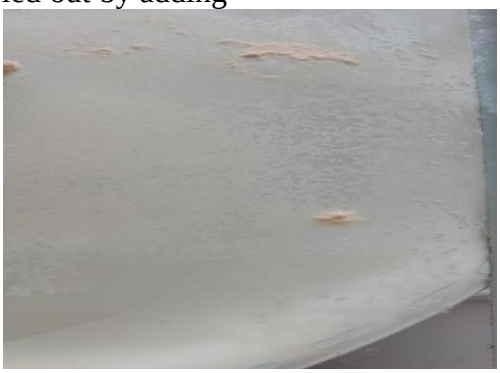

Figure 4. Cellulose acetate (SA) membrane 10% from cocoa shell (*Theobroma cacao L*.)

At the time of casting the membrane on the glass plate formed a very thin layer. The glass plate is immersed in the coagulation bath so that the membrane formed is easily separated and the acetone as the solvent will diffuse into the aquadest. However, from the results obtained, the membrane formed is very thin, making it difficult to form and damage. To strengthen the cellulose acetate (SA) membrane from cocoa shell (*Theobroma cacao L*.) mechanically, we can later use additives or plasticizers to strengthen the membrane. Membranes that are added with additives or plasticizers are able to strengthen the membrane structure so that it can be used to operate on membrane cells [2].

Acetone solvent has not been able to dissolve cellulose acetate with the addition of 5%, 10%, 15%, 20% and 25% PEG. To assist the dissolution process, sonication is carried out before stirring using a magnetic stirrer. Sonication is a material modification method by utilizing ultrasonic waves. The use of sonication can cause changes in the average molecular mass of the viscosity in the presence of viscosity degradation due to the administration of ultrasonic waves [7].

Therefore, for further research, a suitable solvent replacement can be carried out to dissolve cellulose acetate & PEG so that it can form PEG-modified cellulose acetate membranes for Pb metal ion filtration.

4. ACKNOWLEDGMENT

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5. REFERENCE

Bai, Haolong,. Zhou,Yitong,. Wang, Xuan,. Zhang, Liping. 2012. *The Permeability and Mechanical Properties of Cellulose Acetate*

Membranes Blended with Polyethilene Glycol 600 for Treatment of Municipal Sewage. Procedia Enviromental Science 16. The 7th International Conference on Waste Management and Technology. Journal of Membrane Science. 2012 ; 346-351

Riani,Pevi dkk., 2019., *Pembuatan dan Karakterisasi Membran Selulosa Asetat dari Limbah Kulit Kakao (Theobroma cacao L.) dengan Metode Inversi Fasa untuk Adsorpsi Logam Timbal*. Andalas Civil Engineering (ACE) Conference. Universitas Andalas. Padang

Thaiyibah, Nazaratun, *et al.*, 2016. *Pembuatan dan Karakterisasi Membran Selulosa Asetat-PVC dari Enceng Gondok (Eichornia crassipes) untuk Adsorpsi Logam Tembaga (II)*. Jurnal Kimia Mulawarman Vol.14 No.1 November 2016. Univ. Mulawarman, Samarinda

Husni, Dina Apriana Putri, *et al*, 2018. *Pembuatan Membran Selulosa Asetat dari Selulosa Pelepah Pohon Pisang*. Kovalen, 4(1):41-52, April 2018. Jurnal Riset Kimia. Palu. 2018

Lismeri, Lia.2016. *Sintesis Selulosa Asetat dari Limbah Ubi Kayu*. Jurnal Rekayasa Kimia & Lingkungan Vol 11 No. 2 : Hal 82 – 91 Bandar Lampung

Mulder,Marcel., 1991. *Basic Principles of Membrane Technology*. Kluwer Academic Publisher. London.

Anugraini,Annisa ., Syahbanu,Intan., Amalya Melati, Husna., 2018. *Pengaruh Waktu Sonikasi Terhadap Karakteristik Selulosa Asetat Hasil Sintesisndari Sabut Pinang*., Jurnal Kimia Khatulistiwa Tahun 2018, 7(3) ; 18-26. Pontianak