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Cellulose Isolation from Tropical Water Hyacinth for Membrane Preparation

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Abstract

The presence of water hyacinth (*Eichhornia crassipes*) as an aquatic plant in many lakes or other basins causes many conservation problems. Many efforts have been devoted to overcome these problems such as by utilization of water hyacinth for energy production, for water treatment, etc. In this research, cellulose was isolated from water hyacinth and further used for membrane preparation. Cellulose isolation was performed by extraction followed by acetylation resulting cellulose diacetate. The membranes were prepared by phase separation methods. The resulting membranes were then characterized by measuring water flux and surface chemistry (by FTIR). In addition, the membranes were examined for filtering humic acid solution as a model of surface water. The results show that cellulose can be isolated from water hyacinth and can further be processed into cellulose diacetate with the yield of 5,6 %. The membrane preparation shows that the concentration of polymer and evaporation time influence the performance of the membrane, where the greater concentration of the cellulose polymer and the longer of the evaporation time results in the denser and the smaller membrane pores.

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Keywords: tropical water hyacinth, cellulose, membrane preparation, humic acid filtration

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1. Introduction

Water hyacinth *(Eichhornia crassipes)* is a floating plant species that live in water. Rapid breeding led to water hyacinth plant has turned into a weed in some areas in Indonesian waters such as in many lakes or other basins. Water hyacinth is called the world's worst aquatic weed due to its ability to rapidly cover whole waterways. The growth of water hyacinth within 6 months reaches 125 tonnes wet weight in the area of 1 ha [1]. It forms dense, impenetrable mats over the water surface, and other specific impacts such as blocking irrigation channels and rivers, restricting livestock access to water, destroying natural wetlands, eliminating native aquatic plants, reducing infiltration of sunlight, changing the temperature, pH and oxygen levels of water, reducing gas exchange at the water surface, increasing water loss through transpiration (greater than evaporation from an open water body), altering the habitats of aquatic organisms, restricting recreational use of waterways, reducing aesthetic values of waterways, reducing water quality from decomposing plants, destroying fences, roads and other infrastructure when large floating rafts become mobile during flood events, and destroying pastures and crops when large floating rafts settle over paddocks after flood events [2].

Rawa Pening (with the area of 2,670 hectares), a lake located in Semarang district, Central Java has problems caused by water hyacinth. It was found that lake sedimentation rate due to the presence of water hyacinth reaches 778.93 tons/year. As a result the water volume decreased 29.34% over the last 22 years [3]. Therefore, the problems due to water hyacinth are very important to be overcome. *Eichhornia crassipes* is an excellent source of biomass as bioenergy raw material. Gasification of one ton dry matter by air and steam at high temperatures (800°C) gives approximately 1,100 m^3 natural gas (143 Btu/cuft) containing 16.6% H_2, 4.8% methane, 21.7% CO, 4.1% CO_2, and 52.8% N. Nevertheless, the high moisture content of water hyacinth, causing high handling cost, tends to limit commercial ventures [4]. In traditional process water hyacinths are used to make furniture, handbags, rope, art paper [5], bioethanol production and particle board [6].

High cellulose content in water hyacinth (i.e. 25 % cellulose, 33 % hemicellulose, and 10 % lignin) has potential to be used as raw material for cellulose base polymers, which have a higher economic value compared the existing use. In previous studies, Thiripura and Ramesh [7] have isolated cellulose from water hyacinth. On the other hand, production of cellulose base polimers using another biomas material also has done (Santoso) [8]. Saljoughi et al. [9] conducted a study on the effect of pretreatment variables on the morphology structure and flux of asymmetric membrane prepared from cellulose acetate. The result showed that the polymer concentration variations affect the membrane performance. Several previous membrane studies more focused on the process of membrane preparation, while the analysis of alternative materials that have economic value has not been done. Therefore, th purpose of this study is to investigate the potential of water hyacinth for the preparation of cellulose base polymers. Further, the resulted cellulose base polymers are used for membrane preparation. The effects of process condition in membrane manufacturing on membrane performance for surface water filtration are presented.

2. Materials and Methodes

2. 1. Materials

Water hyacinth in dry fiber form was obtained from the Rawa Pening lake. Toluene 99.9%, ethanol 99.8%, , acetone 99.8 %, $(CH3CO)_2O$ (acetic anhydride) 98,5 % and PEG (polyethylene glycol) were purchased from Merck, Germany. While cellulose acetate was taken from Aldrich, Germany.

2.2. Methods

2.2.1. Cellulose isolation

Water hyacinth fibers were extracted using mixed toluene/ethanol solvent with ratio of 2: 1 for 3 hours at 115 ^{0}C. Furthermore, bleaching process using NaClO 3% for 2 hours at 80 ^{0}C was performed. Then, hemicellulose was removed by hydrolysis using NaOH 1% at 60 ^{0}C for 2 hours. The second bleaching was performed to remove the remaining lignin through cooking process using NaClO 1% and stirred at 75 ^{0}C for 3 hours. The last stage was

hydrolysis using HCl 5% as catalyst for 6 hours at 65^{0}C. The sample was filtered and the obtained solid was washed with distilled water until free of acid.

2. 2.2. Cellulose product acetylation

Cellulose acetylation was conducted using the following processes: initially 10 g of cellulose from fiber stalks of water hyacinth and 24 ml glacial acetic acid were mixed and stirred at 40 ^{0}C for 1 hour. Furthermore, 0,1 ml sulfuric acid and 60 ml glacial acetic acid were added, and stirred again for 45 minutes at the same temperature. The mixture was cooled to 18 ^{o}C and then 27 ml acetic anhydride was added. Thereafter, 1 ml sulfuric acid and 60 ml glacial acetic acid were added to the mixture, and acetylation time of 3 hours at a temperature of 40 ^{o}C. Furthermore 67% acetic acid was added to the mixture at 40 ^{o}C for hydrolysis process as long as 15 hours at room temperature. After doing acetylation and hydrolysis, cellulose acetate was precipitated by adding distilled water drop by drop and stirred to obtain powder precipitate. The resulted powder precipitate was washed and dried in an oven at 50 ^{o}C.

2.2.3. Preparation of Cellulose Acetate Membranes

Cellulose diacetate solutions with concentration of 13-15 % were prepared using aceton as solvent then stirred for 3 hours until all the cellulose acetate dissolved. Polyethylene glycole (5%) was added drop by drop. The homogenous polymer solution was left without stirring until no bubbles were observed. The polymer solution was cast with a thickness of 200 m using a steel casting knife on a glass substrate, then left in free air contact with time varies ie 0, 5, 10 and 15 seconds. Thereafter, the proto-membrane was solidified by inserting into a coagulation bath containing water for 1 day at room temperature. The resulting membranes were washed to remove excess solvent [10].

2.2.4. Membrane Characterization

2.2.4.1. Flux and rejection test

The resulted membranes were examined for filtration of humic acid solution as a model of surface water. Firstly, compaction process was done by filtering pure water at a pressure of 0,5 atm. After the compaction process, distilled water in a filtration cell is replaced with 25 ppm humic acid solution. The filtration was performed at a pressure of 0.5 atm. Flux measurement was performed by measuring the volume of solution that can be accumulated for 120 minutes with an interval of 10 min. Flux value was measured by calculating volume ratio of permeate per unit membrane area per unit time. While the rejection rate was obtained by measuring the concentration of the solution before and after passing through the membrane by using spectrophotometer and turbidimeter.

2.2.4.2. FTIR (Fourier Transform Infra Red)

The chemical characteristic of water hyacinth, cellulose and membranes was investigated by using a Shimadzu FTIR spectrophotometer. There IR Spectra were then compared with commercial cellulose acetate.

3. Result and Discussion

3.1. Isolation of cellulose from water hyacinth

Isolation of cellulose for hyacinth was performed by exctraction, bleaching and alkaline hydrolysis respectively. During extraction the mass of hyacinth was reduced about 44% of initial mass. As reported by Thiripura and Ramesh [7] extraction process could remove extractive compounds contained in the stalks of water hyacinth except lignin, cellulose and hemicellulose. The resulted product from extraction had brown color (Fig. 1a), indicating other impurities such as lignin and hemicellulose in the fiber have not been removed yet. Bleaching process using NaOCl could further removed lignin by breaking ether bond and increased the whitness degree of fibers (Fig 1b). Alkaline hydrolysis was performed by cutting the chain to separate hemicellulose from the main chain, namely cellulose (Fig. 1c). In addition, reaction with NaOH solution will also cause degradation of lignin molecules due to the termination of aryl-ether bonds, carbon-carbon, aryl-aryl and alkali-alkali [7]. Second bleaching and hydrolisis processes were performed to remove the remaining lignin and hemicellulose.

From Fig.2 it can be observed that the results of the IR spectrum of water hyacinth displays peaks at a wavelength of 1734.08 cm^{-1}, which indicates the presence of acetyl and ester in carboxyl group chain of the acid p-koumeril as well

(a) (b) (c)

Fig 1. Isolation process result (a) after extraction(b) after bleaching (c) hydrolisis

as indicating the presence of lignin and hemicellulose. This result is in agreement with previous work presented by Thiripura and Ramesh [7]. There are also peaks at a wavelength of 1519 cm^{-1}, which indicates the presence of the C=C group on the aromatic ring of lignin. Hemicellulose is seen from the presence of the peak at a wavelength of 1622.20 cm^{-1}. All three groups showed the presence of impurities in the form of hemicellulose and lignin. The IR spectrum of cellulose shows that some peaks have been lost due to the purification process that has been carried out. On the other hand, the results of the IR spectrum of cellulose maintained peaks at a wavelength of 3404 cm^{-1} and 2920 cm^{-1} which indicates the presence of C-H and O-H groups, where both groups are the main functional groups of cellulose. The resulted spectrum shows that impurities contained in the water hyacinth has been removed. Then the high purity cellulose was produced.

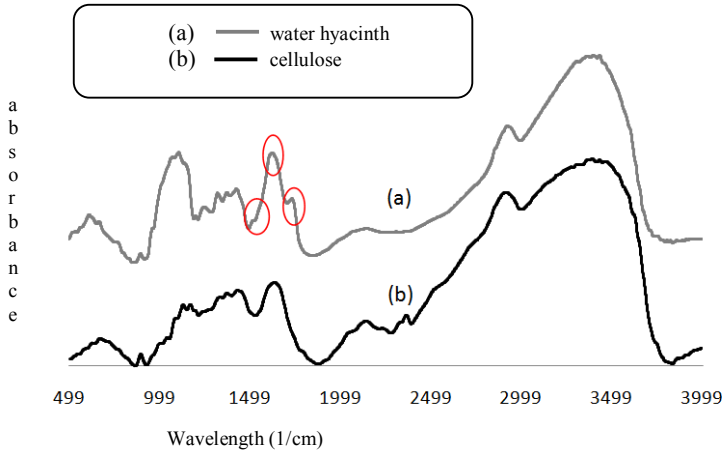

Fig. 2. IR spectrum of water hyacinth and cellulose from water hyacinth

3.2. Cellulose Acetylation

Cellulose acetylation process produced white solid cellulose diacetate (CA). To determine the functional group changes after acetylation, the acetylation products were tested using FTIR instrument. Based on Fig. 3, it can be seen that the results of the IR spectrum of cellulose diacetate has a significant difference compared with the results of the IR spectrum of cellulose. In the IR spectrum of cellulose diacetate results appear sharp peaks at wavelength of 1730.15 cm^{-1} and 1247.94 cm^{-1} which indicates the presence of carbonyl group C=O and C-O ester group. This result suggests that cellulose acetylation process has successfully performed. A comparative analysis between the functional groups of the resulted CA and commercial CA was also performed (Fig. 4). The result shows that the IR spectrum of the the resulted CA and commercial CA are similar indicating that isolation and acetilation have been well performed. Overall, each 100 grams of dried water hyacinth produced 5.6 grams cellulose diacetate. Thus, the yield obtained in the manufacture of cellulose diacetate from water hyacinth is about 5.6%.

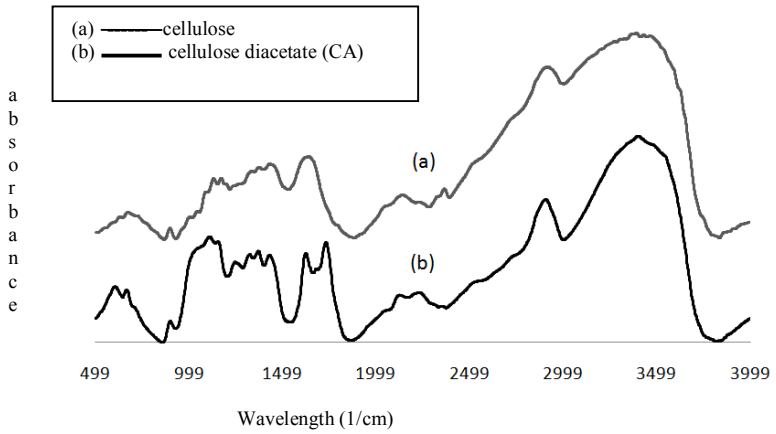

Fig. 3. IR spectrum of cellulose and cellulose diacetate (CA)

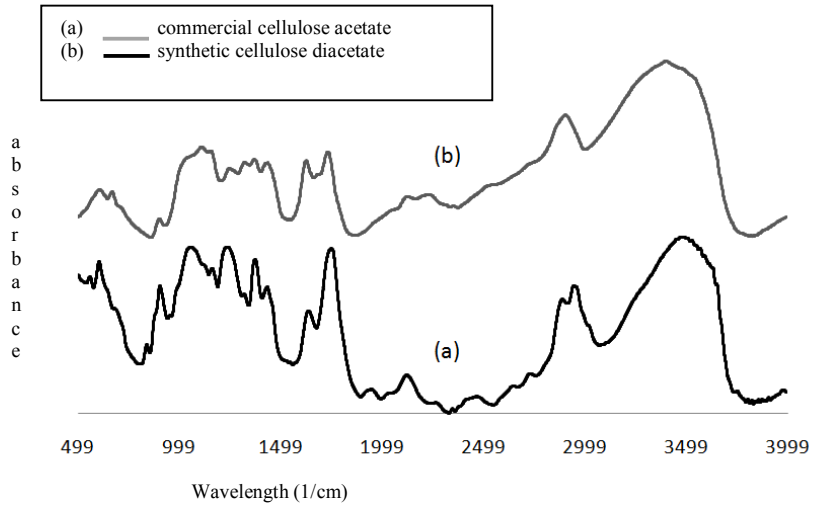

Fig. 4. IR spectrum of synthetic cellulose diacetate and commercial cellulose diacetate

3.3. Membrane Preparation

3.3.1. Effect of evaporation time on flux and rejection

In this work, the effect of evaporation time on flux and rejection was investigated. Humic acid solution was used during rejection experiment. The results are presented in Fig. 5 and Table 1. It can be seen that flux decreases with increasing time of evaporation, because the longer evaporation time will cause the membrane pore size becomes smaller due to increasing polimer concentration on the top layer of membrane. The interaction of solvent exchange with the ambient air is smaller than interaction between the solvent exchange and non solvent [11, 12]. Moreover, the top layer will inhibit the exchange rate between residual solvent and non solvent through the membrane surface during immersion process in the coagulation bath. However, the membrane with smaller pores size have higher rejection towards humic acid. In general, the results show that a trade off between flux and rejection was found and this is in a good agreement with previous results which reported membrane preparation using non CA polymers. Good membranes should have high both flux and rejection [13, 14]. In this context, the best membrane was obtained

from the result of casting process with 10 seconds evaporation time.

3.3.2. Effect of polymer concentration on flux and rejection

The effect of CA concentration on flux and rejection was investigated. The increase in polymer concentration decreases flux on the one hand and increases rejection on the other hand. This phenomenon can be explained by the higher concentration of cellulose acetate the higher number of polymer molecules per unit volume; consequently the number of solvent molecules which will be replaced by non-solvent into the pore decreases [15]. In addition, the increase in polymer concentration also strengthens the thermodynamic stability of the solution to be formed into films. Thereby, the membrane pore sizes resulted from a higher polymer concentration should be narrower. Figure 5 presents measurement data with the variation of evaporation time and polymer concentration.

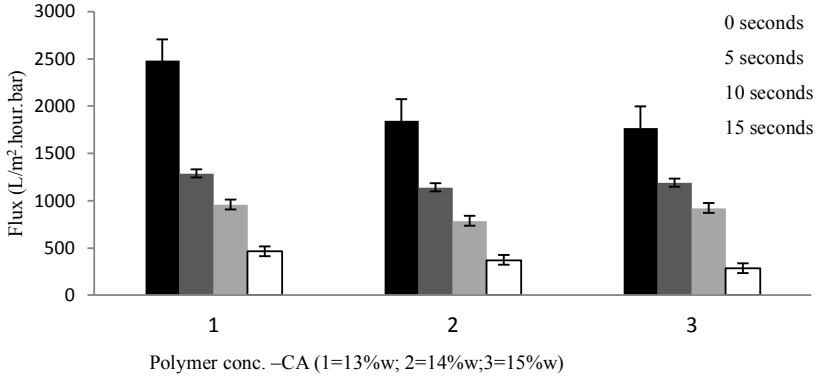

Fig.5. Membrane flux vs concentration of CA with variation of evaporation time (pressure 0.5 atm)

3.4. Membrane Rejection Measurement

Table 1. Membrane Rejection on each membrane composition and evaporation time

Polimer Concentration (w/w)	Evaporation Time (seconds)	Rejection (%)	
		NTU	Humic Acid
13	0	44.10	42.31
	5	46.28	45.15
	10	49.81	45.69
	15	50.55	48.59
14	0	55.52	50.70
	5	58.53	51.24
	10	58.81	56.28
	15	59.10	57.38
15	0	60.09	58.95
	5	65.73	63.15
	10	66.62	64.28
	15	68.62	67.50

3.5. FTIR Analysis

To determine the functional groups present in the membrane, the membranes were analyzed using FTIR

spectrophotometer (Fig. 6). Based on the test results of FTIR analysis can be seen that all membranes have a C=O group, CH_3 and -COOH as shown with wavelengths contained in Table 2. Overall no difference in chemical structure is observed for the membrane s prepared with different evaporation time, meaning that evaporation did not change the chemical structure of resulted membrane.

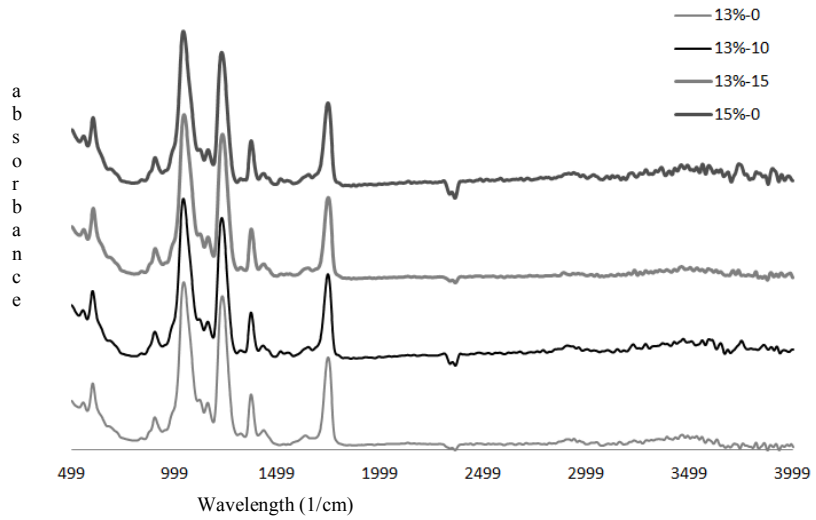

Fig. 6. IR Spectrum of CA membrane with variation of concentration and evaporation time

Table 2. Functional Group of IR Spectrum CA membrane

No	Functional group	Wavelength (cm^{-1})			
		13% - 0 second	13% - 10 seconds	13% - 15 seconds	15% - 0 seconds
1	C=O	1744.69	1743.72	1744.69	1743.72
2	CH_3	1371.45	1370.48	1370.48	1370.48
3	-COOH	1231.60	1229.67	1231.60	1227.74

4. Conclusion

Celloluse has been successfully isolated from water hyacinth and can further be processed into cellulose diacetate (CA). The yield obtained for preparation of CA from hyacinth was 5.6%. The resulted CA has similar chemical structure with commercial CA. The resulted CA was used to prepare membranes. Polymer concentration and time of evaporation affects on flux and rejection have been investigated. The higher evaporation time, the lower flux and the higher rejection were resulted. The higher CA concentration, the lower flux and the higher rejection were resulted. CA concentration of 15% and evaporation time of 10 seconds are the best operating conditions used in the manufacture of the membrane with a flux value of 460.54 L/m2.hours and the rejection coefficient of 64.28%.

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