Polymeric Membrane Made of Cellulose Isolated from Tropical Water Hyacinth Blended with Chitosan

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Abstract. In Indonesia, membrane application is limited by the use of high cost imported membranes. Therefore, efforts to produce membrane using local materials are very important to be performed. Cellulose and chitosan are two materials, which their availability in Indonesia is abundant. In this work, cellulose acetate (CA) has been successfully produced from tropical water hyacinth via isolation and acetylation processes. By using FTIR, a comparative analysis of functional groups between the resulted CA and commercial CA was also investigated. The result shows that the IR spectra of the resulted CA and commercial CA are similar. The produced CA can further be processed into membrane. The resulting membranes were then characterized using SEM. In addition, the membranes were examined for filtering humic acid solution as surface water model. To improve the performance, CA membranes prepared from water hyacinth were modified by addition of chitosan (Chi) via blending in phase separation method. The resulting CA-Chi membranes were characterized using SEM and FTIR.

Keywords: polymeric membrane, local materials, tropical water hyacinth, chitosan, phase separation

1. Introduction

Membranes have increasingly been accepted as promising technology in a wide range of applications including high-quality water process production, removal or recovery of toxic or valuable components from various industrial effluents, dairy, biotechnological, pharmaceutical industries, food and beverage processing, and medical applications [1-2]. The emergence of membrane technology has made unit operations such as separation, and purification become industrially viable because of the high efficiency of separation, low energy of operation, simplicity of operation with modern compact modules [3]. As consequence of this increasing demand, efforts to use natural resources for membrane material are gaining more and more importance. Several previous membrane studies more focused on the process of membrane preparation, while the analysis of alternative materials that have economic value has been largely ignored even the presence of these materials are abundant in nature. In addition, environmental concerns such as pollution and decreases in natural resources, have led in recent years to an increased demand for renewable materials.

Cellulose, as natural renewable polymer, the main structural component of plant, is considered as an attractive raw material for the production of membrane, because of its availability in large quantities. Cellulose Acetate (CA), cellulose which has undergone acetylation process, is suitable as membrane material, since its advantages such as moderate flux, high salt rejection properties, cost effectiveness, relatively easy manufacture, renewable resource of raw material, and non-toxic [4] besides strongly hydrophilic and thus demonstrate lower fouling characteristic. CA membrane was the first high-performance asymmetric membrane [5]. It has been widely used for reverse osmosis (RO), microfiltration (MF) [6] and gas separation [7]. On the other hand, CA membranes yield a low flux and are susceptible to chemical and bacteriological agents in their first generation. In addition, the disadvantages of CA membrane are its stability over a narrow pH and their poor resistance to microbial attack [8] low oxidation, thermal and chemical resistances, [9, 10]. For this reason, the modification of CA membrane by blending CA with an appropriate polymer may be improves the performance of CA membrane.

The abundant aquatic weed species, Water hyacinth (*Eichhornia crassipes*) in tropical weather conditions such as Indonesia, is a major problem in open water bodies like power generation, irrigation and boating. It is considered as worst aquatic weed, an incredibly fast growing plant. Under the climatic conditions, it is reported a daily average water hyacinth biomass productivity of 0.26 ton of dry biomass per hectare [11]. Water hyacinth constitutes a potential biomass resource for cellulose isolation, while it is rich in fibre content and has no major differences in the percentage of cellulose content in the shoot and root [12]. Therefore, water hyacinth has great potential to be used as cellulose source, which then further be converted into cellulose acetate (CA) via acetylation process.

Chitosan as biopolymer from renewable resources -which its existence is also very plentiful in Indonesia- has been used extensively to form membranes [13]. Owing to its high biodegradability, biocompatibility, nontoxicity and antimicrobial properties, chitosan is widely used as antimicrobial agent either alone or blended with other natural polymers [14]. The antimicrobial properties of chitosan can cover CA membrane infirmity. Our previous research has succeeded to synthesize CA membranes prepared from water hyacinth [15]. The produced CA was in accordance with commercial CA.

This research was intends to investigate CA membrane performance and to study the effect of chitosan addition on the CA membrane. The use of CA and chitosan for membrane preparation are expected to be a solution for the problem of membrane application in Indonesia which is still limited by the high cost of imported membrane.

2. Materials and Methods

2.1. Materials

Water hyacinth stem were collected from Rawa Pening lake, Semarang, Indonesia. $NaClO_2$, NaOH, H_2SO_4, CH_3COOH, HCl, Toluene 99.9%, ethanol 99.8%, acetone 99.8 %, $(CH_3CO)_2O$ (acetic anhydride) 98,5 % and PEG (polyethylene glycol) were purchased from Merck, (Hohenbrunn, Germany). While cellulose acetate as a reference was used for membrane preparation, bought from Aldrich Chemistry, USA. Chitosan $(C_6H_{11}NO_4)n$ with deacetylation degree of 80.4% and a viscosity of 118.4 cp, produced by Biotech Surendo, Cirebon, Indonesia. Distilled water for all experiments produced from home-made pure water unit.

2.2. Methods

2.2.1. Cellulose Acetate Preparation Method. Cellulose isolation was performed by extraction followed by acetylation resulting CA. The method was adapted from previous studies [15-16].

2.2.2. CA and CA-Chi Membrane Preparations. Preparation of CA membrane was conducted by wet phase inversion. CA solutions with concentration of 13-15 % were prepared using acetone as solvent then stirred for 3 hours until all the cellulose acetate dissolved. Polyethylene glycol (5%) was added drop by drop. The homogenous polymer solution was left without stirring until no bubbles were observed. The polymer solution was cast using a steel casting knife on a glass substrate, then left in room temperature with time varies i.e. 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. The method used to prepare CA-Chi membranes was similar with CA membrane preparation.

3. Results and discussions

3.1 Investigation of separation performance of cellulose acetate membrane
The applicability of the obtained membrane in the separation of representative surface water (humic acid of 25 ppm) was evaluated.

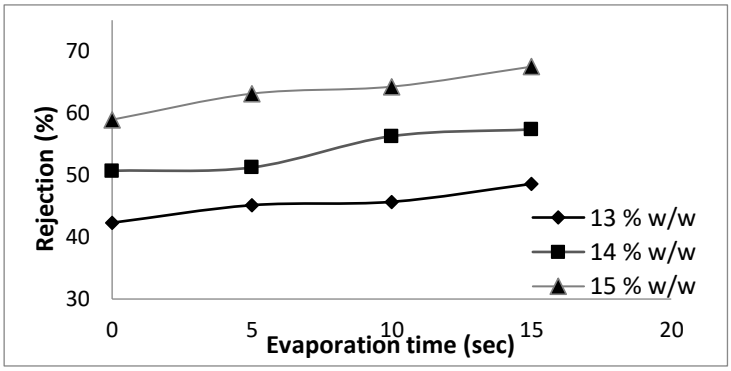

Figure 1. Effect of CA concentration and evaporation time on membrane separation efficiency.

The increase in concentration of cellulose acetate increase rejection. 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 [17]. In addition, the increase in CA 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 1 presents measurement data with the variation of evaporation time and CA concentration. On the other hand, rejection also increase along with the increasing evaporation time.

3.2 SEM imaging of CA membranes
Visualization of membrane surface by using SEM supports the preceding explanations that the increased evaporation time produced denser membrane. Fig 2 revealed that the membrane pore diameter has a size of 1-10 μm wherein the pore size is categorized as microfiltration membranes. With the same CA concentration (13% w/w) but with different time evaporation (0, 10 and 15 seconds), revealed that increasing time of evaporation reduced membrane pore diameter and quantity of membrane, so that the surface of membrane tends to denser.

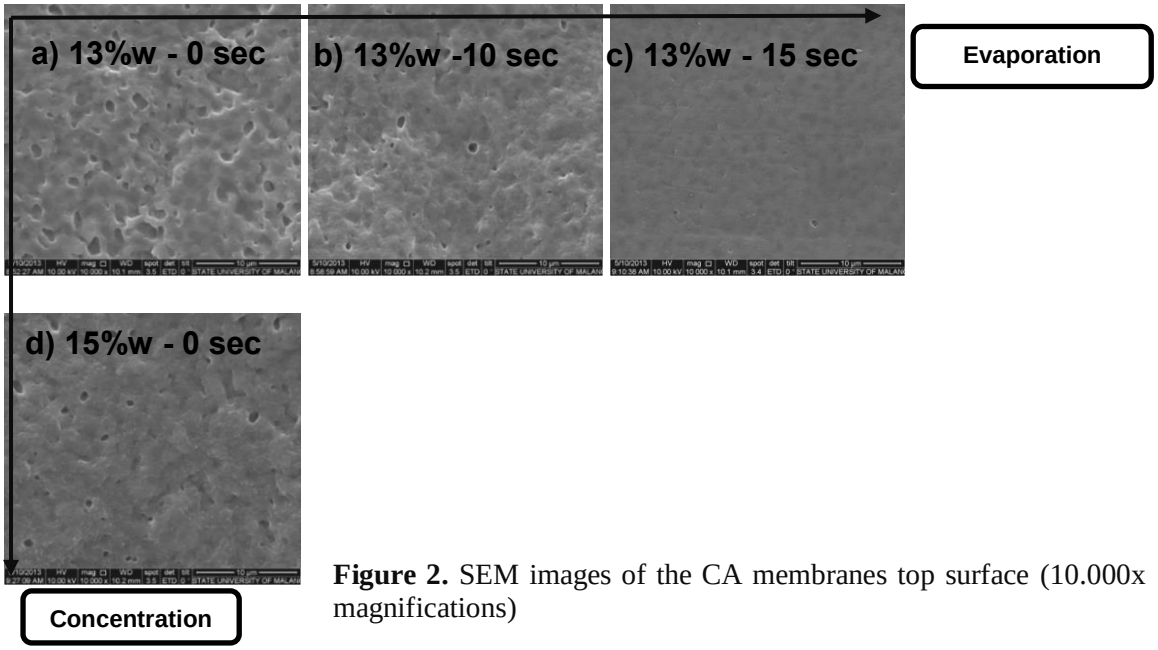

Figure 2. SEM images of the CA membranes top surface (10.000x magnifications)

Longer evaporation time causes an increase in the polymer concentration in the upper layer of the membrane and caused the membrane pores become smaller or narrower, due to interaction switchover solvent with the ambient air which is shorter compared to switchover solvent and non-solvent [18]. Likewise, comparison of membranes with different polymer concentrations, i.e. (concentration of 13% w and 15% w), it can be seen that the greater the concentration of the polymer, the number of membrane pore decreases and its diameter narrows. It proves that the more the polymer concentration causes increasing in rejection.

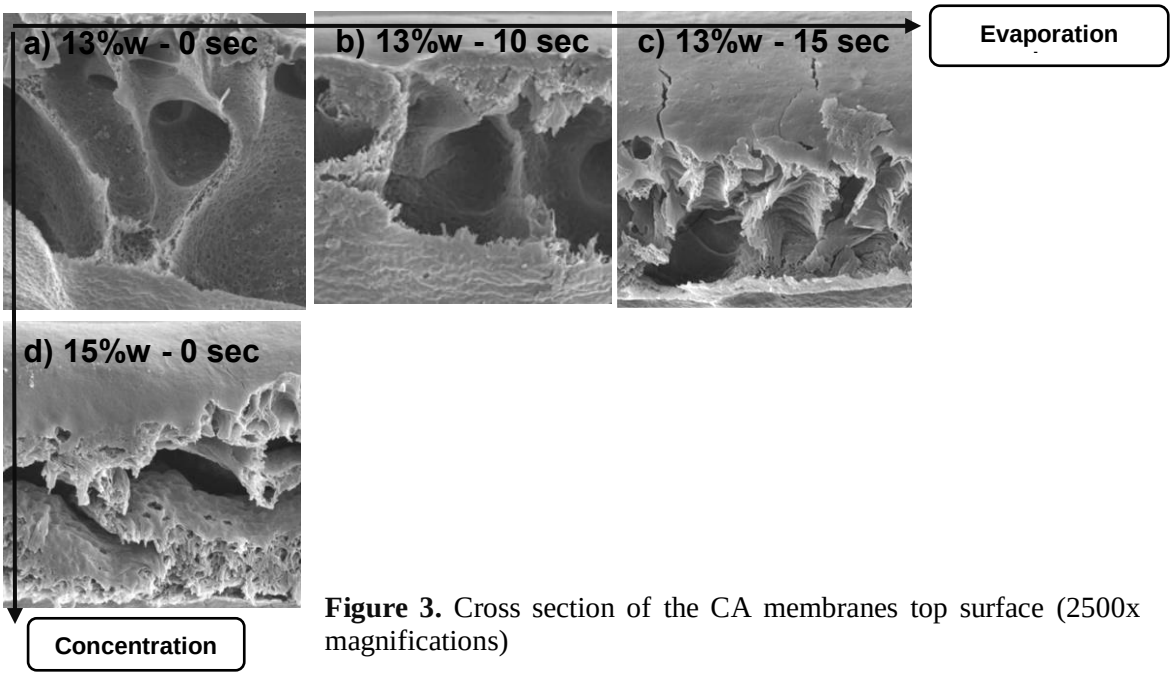

Figure 3. Cross section of the CA membranes top surface (2500x magnifications)

Figure 3 reinforces previous explanation that evaporation time affect the changes morphology of membrane structure. The larger the area of absorption (absorbance value) indicates that the polymer concentration in the membrane increases, resulting in more dense membrane. On the other hand, the

concentration of polymer also affects the morphology of the membrane structure. Higher polymer concentration resulted better morphology of membrane structure (catchment area of membrane with 15 % w polymer concentration greater than 13% w).

3.3. Cellulose acetate-chitosan (CA-Chi) membrane

CA-Chi membranes were prepared by polymer blending between cellulose acetate and chitosan. It is clearly observed from Figure 4 that pure water flux decreased with the addition of chitosan composition. The highest value, 68.79 L/m^2. hour was in flux membranes without chitosan (Chi 0%) was and lowest flux value was 5.70 L/m^2, produced by 1% Ca-Chi membrane. In other word, we can say that the addition of chitosan decreased water permeability of CA-Chi membranes. As the concentration of chitosan was increased, the water flux decreased. This phenomenon can be explained that addition of chitosan increases polymer concentration and solution viscosity.

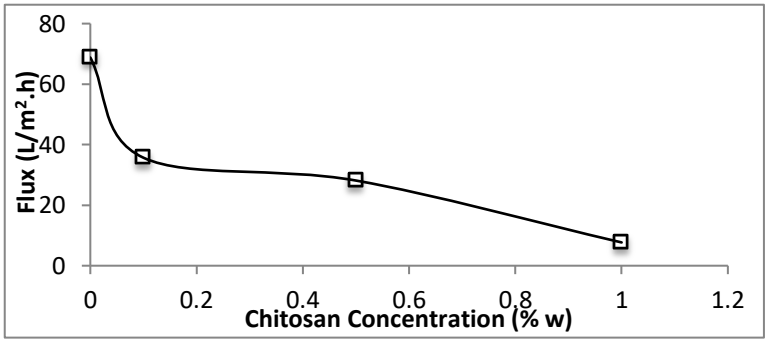

Figure 4. Water permeability of CA-Chi membranes as a function of chitosan concentration

The increase in polymer concentration increases polymer fraction in polymer solution, which will decrease the rate of liquid-liquid demixing resulting a membrane with lower porosity. The increase in solution viscosity causes reduction of mutual diffusivities between non-solvent and solvent in the system during solidification of the casting solution. Similar results have been reported in previous literatures [3, 19, 20]. In addition, the flux decline may occur due to the effect of chitosan addition in membrane preparation causing membrane properties being changed. Characteristic of cellulose acetate is more hydrophilic than chitosan, so this reason caused membrane flux reduction [21].

3.4. FTIR Analysis

Figure 5 shows infrared spectrophotometer images CA membrane without chitosan as control membrane and Ca-Chi membranes with various concentrations of chitosan. Interaction between cellulose acetate and chitosan in CA-Chi membranes can be seen from new or shifted peaks which are different from existing condition.

Special characteristics of cellulose acetate could be observed from the peaks at 1730 cm^{-1} representing the presence of carbonyl group (C=O), the highest peak at 1025 cm^{-1} representing C–O–C bond, and the peaks at 1360 and 1220 cm^{-1}, which indicate C–H bond from (CH_3). In addition, CA could also be observed by minor peaks at ~3500 and ~2840 cm^{-1} indicating O–H stretching and C–H bond stretching, respectively. This result agrees well with previous publications [21, 22, 23].

The addition of chitosan could clearly be observed by the peaks at ~1514 cm^{-1} (marked by black oval shaped). These peaks represent absorption band of amine bond (NH_2). The formed peaks in the range of 3687-3793 cm^{-1} indicate the presence of hydrogen bonds (OH) (also marked by black oval shaped). Moreover, slight movement of peak (from 1550 to 1514 cm^{-1}) is believed because both CA and chitosan present on the membrane surface. Similar results were reported by previous authors [24-27].

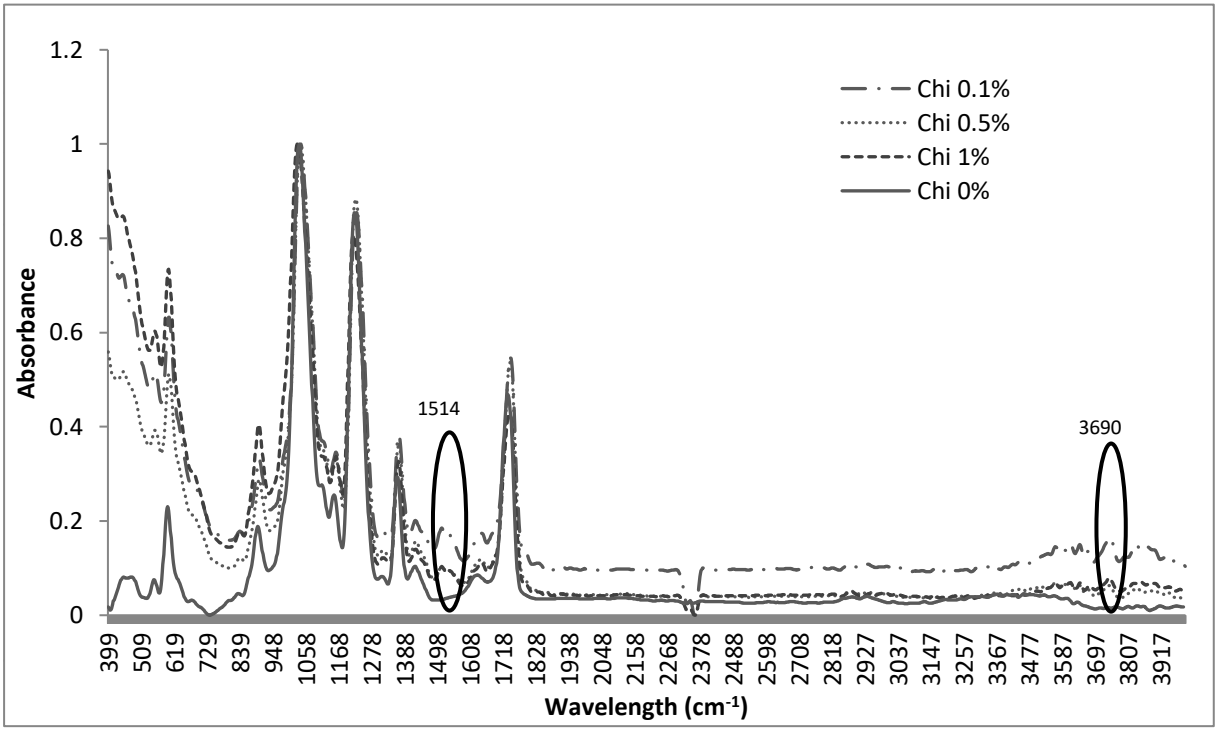

Figure 5. FTIR spectra of CA-Chi membranes.

3.5. SEM imaging of CA-Chi membranes

Visualization of membrane surface by using SEM (Figure 6) supports the preceding explanations (Section 3.4). It was observed qualitatively that addition of chitosan decreased membrane pore size as well as pore density. In addition, CA-Chitosan membrane (Fig 6.b.) revealed a rougher surface than CA membrane (without chitosan) (Fig 6.a.).

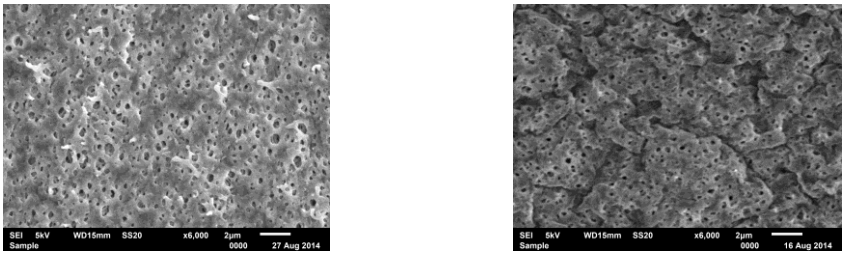

Figure 6. SEM images of membrane surface morphology (a) CA membrane, (b) CA-Chi membrane

4. Conclusion

This work provides a simple approach for obtaining modified nature polymer materials. Cellulose has been succesfully isolated from water hyacinth. The yield obtained can be processed into cellulose acetate (CA) which has similar chemical structure with commercial CA. Therefore, it possible to use it as material to prepare membranes. CA membrane with various concentration and time evaporation were also prepared and investigated. Addition of chitosan in the preparation of cellulose acetate membranes decreased membrane pore size as well as pore density.

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