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The Optimization of Sodium Carboxymethyl Cellulose (NA-CMC) Synthesized from Water Hyacinth (*Eichhornia crassipes* (Mart.) Solm) Cellulose

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ABSTRACT

One plant that has a high cellulose content that is equal to 64.51% is water hyacinth (*Eichhornia crassipes* (Mart.) Solm.). Water hyacinth has great potential to be used as a raw material for various products, such as sodium carboxymethyl cellulose (Na-CMC). Na-CMC is usually used in pharmaceutical industry as an excipient for pharmaceutical formulation. This study aims to isolate the alpha cellulose from water hyacinth and to optimize the synthesis of Na-CMC so that it can meet the standards of pharmaceutical excipients. The method of this research consists of the isolation of alpha cellulose with NaOH 25% and 12% NaOCl, the assay of cellulose, the synthesis of Na-CMC as pharmaceutical excipients using 40% NaOH, sodium monochloroacetate of 1:20:5 ratio, and the characterization. The results show the yield of 15.27% water hyacinth, and contain a high level of 61.176% alpha cellulose which is used for the synthesis of NaCMC with 95.33% yield. Characterization done by using Infrared Spectrophotometry, Scanning Electron Microscope (SEM) and Energy dispersive X-Ray Spectrometry (EDS) shows that the synthesized product gives the same spectrum as Na-CMC.

Keywords: *sodium carboxymethyl cellulose*, α-cellulose, water hyacinth

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INTRODUCTION

Data from International Pharmaceutical Manufacturer Group (IPMG) shows that pharmaceutical product market value in Indonesia in 2010 reached 2.5 billion US dollars [1]. One of the excipients that is usually used as a raw material for drugs and other pharmaceutical products is Sodium Cabrboxymethyl Cellulose (Na-CMC). Na-CMC is a cellulose derivative which is often used in pharmaceutical and food industry [2]. Na-CMC is a white or yellowish white colour powder, odorless, with hygroscopic characteristic. Na-CMC is easy to be dissolved in cold or hot water. Na-CMC is stable from pH 2 until pH10, and it is reacted with the salt form of metal ions to form undissolved film, transparence, and also reacted with organic compounds.

Na-CMC has already been used and has a lot of important effects in many fields especially in pharmaceutics, food, chemical, petroleum, and textile industries recently [3]. In pharmaceutics, the four important functional characteristics of Na-CMC were as a stabilizer, emulsifier, thickening and gelling agent [2]. Cellulose as raw material for Na-CMC is usually obtain from wood. Beside wood, Na-CMC also can be produced from other sources to minimize wood exploitation Alternative source which can be used to make Na-CMC is from water hyacinth. Water hyacinth has a big potential to be used as raw material for many products.. The cellulose content from water hyacinth bark was 64,51% before and 72,51% after grinding [4]. Based on the cellulose content of water hyacinth and the need to find an alternative source, this research need to be done. This research is conducted through several steps, which are material collection, optimization of cellulose isolation, water hyacinth cellulose characterization, synthesis of Na-CMC from cellulose of the water hyacinth, and Na-CMC synthesis characterization.

MATERIALS AND METHODS

INSTRUMENTATION

Analytical balance (Metller Toledo), grinding machine, magnetic stirer (Yellow MAG HS7), Oven (Heraus), pH meter (Mettler Toledo), waterbath (Mommert), Chromameter (Minolta, CR-300), Fourier Transform Infrared (FTIR) (Shimadzu, IR Prestige-21), Scanning Electron Microscope (SEM) (JEOL JSM-6510/LV).

MATERIALS

Water hyacinth, aquadestillata, sodium hydroxide (NaOH) (Bratachem), sodium hypochlorite (NaOCl) (Bratachem), potassium dichromate ($K_2Cr_2O_7$), concentrated sulfuric acid (H_2SO_4) (merck), Ferrro Ammonium Sulfate [$(NH_4)_2Fe(SO_4)_2.6H_2O$], isopropyl alcohol (Bratachem), Monochloroacetate ($NaCH_2COOCl$) (Merck), Methanol (Merck), Ethanol (Bratachem).

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METHODS

Collection of Water Hyacinth (*Eichhornia crassipes* (Mart.) Solm.)

The water hyacinth used in this research was obtained from Jatinangor District, Sumedang Regency, West Java, Indonesia.

Water Hyacinth Grain Preparation

Prior to the experiment, the water hyacinth was first taken into the determination process conducted in the Laboratory of Taxonomy, Department of Biology, Faculty of Mathematics and Natural Sciences at Padjadjaran University. The unnecessary hyacinth root part was then cleared from the stem, cleaned with water and dried. Next, the hyacinth was cut into smaller parts, and then subsequently dehydrated in the sunlight for 5-7 days and then in an oven at 95˚C for 12 hours. The grains were then filtered using mesh 50.

Determination of water content and ash content

The water hyacinth fine grain water-content examination was conducted in accordance with SNI (Indonesian National Standard) 08-7070-2005 code [5]. The water hyacinth ash-content examination was conducted by using thermographimetry method.

The Isolation Optimization of Water Hyacinth α-Cellulose

The isolation optimization was conducted by varying the NaOH concentration used in the process and its proportion. The NaOH concentration used in this research is 18% and 25%. The water hyacinth grain was first boiled with water, and filtered. The insoluble part was boiled again with natrium hydroxide for one hour, and then filtered. The residue from this process was then washed with aquadestillata until the pH level reaching 6-7. The cleaned residue was then put into a plastic container, and the natrium hypochlorite (NaOCL) bleaching solution was further added to the residue. Both the residue and the solution were stirred evenly for 4 hours in the closed container. The result was then filtered and again washed using aquadestillata until the chlorine scent was thoroughly undetectable. It was dehydrated in the oven at 50˚C. The final residue was what we called α-cellulose.

Alpha-Cellulose Content Analysis

The α-cellulose composition analysis was conducted by using titrimetry method in accordance with SNI 0444:2009 code [6] of conduct concerning alpha, beta and gamma cellulose in pulp examination method.

The Na-CMC Synthesis Optimization of Water Hyacinth Cellulose

The Na-CMC synthesis optimization was done by varying the amount of cellulose used in this research with the ratio as follows: isopropyl alcohol:NaOH:sodium monochloroacetate (1:1:0.25). Sodium carboxymethyl cellulose (Na-CMC) was synthesized from the water hyacinth cellulose in two-step reactions. In the first step, the cellulose was

put in the suspension process by stirring it with isopropyl alcohol using a mechanical stirrer at room temperature; NaOH 40% was also added in the stirring process. This mixture was stirred for 90 minutes, and the result was alkali cellulose. The stirring process was then continued by slowly adding natrium monochloroacetate ($ClCH_2COONa$) for 30 minutes, and after the addition the stirring process was continued for 3.5 hours at 55˚C. In the second step, 70% Methanol was added to the reactor and the mixture was neutralized with 90% acetic acid. Na-CMC was thus obtained by washing and filtering the residue 6 times using ethanol. The obtained Na-CMC through ethanol cleaning was then washed again with pure methanol and dehydrated in the oven at 60% [8].

The Na-CMC Characterization of Water Hyacinth Cellulose

The characterization of Na-CMC synthesized from water hyacinth cellulose was done by using *fourier transform infrared* (FTIR), *scanning electron microscope* (SEM), and *energy dispersive x-ray spectroscopy* (EDX)

RESULTS AND DISCUSSION

Collection of Water Hyacinth (*Eichhornia crassipes* (Mart.) Solm.) and Preparation

The Collection of water hyacinth was done by procuring the raw material from two regions in Jatinangor District in Sumedang Regency: Sayang and Jatiroke Region. Before the procuring process, the water hyacinth was first determined so that its taxonomical classification could be revealed. From the determination process, it was determined that the species of the water hyacinth is *Eichorma crassipes (Mart.) Solm.*

Determination of water content and ash content

The next step was determination of water content and ash content of Water Hyacinth. The result was showed in Table 1.

Table 1. Water Content Determination Result

Weight-Wet (kg)	Weight- Dry (kg)	Water content (%)
5,63	0,485	91,38

The ash-content level examination for the samples was performed by using the thermographimetry method. This ash making process was conducted in a furnace at 600˚C. This ash-content measurement was done to determine how big the mineral content in the sample was [9]. The result of the examination both samples from both regions can be seen in Table 2.

Table 2. Ash-Content Determination Results

Sample	Ash Content Percentage (%)
A	13, 58
B	11, 79

Note: A Sample = from Sayang region, Jatinangor
B Sample = from Jatiroke region, Jatinangor

From the Table 2 it can be seen that the ash-content level of the A sample possessed more ash than the B sample. This means that the mineral content in the former is greater than the latter. According to a research performed by Joedodibroto in 1983 [10], the ash content in water hyacinth reached 12%. The B sample in this paper, moreover, contained ash level 11.79%, which is smaller than the ash level in the experiment by Joedodibroto. Therefore, the water hyacinth fine grain sample used in this paper is the B sample.

The Isolation Optimization of Water Hyacinth α-Cellulose

The isolation optimizing process of water hyacinth α-cellulose was done by using alkali processing method, and the solution used is natrium hydroxide. Before the processing, the water hyacinth fine grain was first boiled in hot water as the early stage of hydrolysis (pre-hydrolysis) [11]. The next stage was the cellulose structure breaking process. This was done by boiling the insoluble part with natrium hydroxide (NaOH) 25% for one hour. This process would result in the formation of insoluble residue which was called α-cellulose. The usage of NaOH 25% was intended to eliminate or to dissolve other celluloses, for example β-cellulose, γ-cellulose, hemicellulose and holocellulose, without dissolving α-cellulose so that we can obtain α-cellulose [6]. The amount of lignin and carbohydrate still remain on the water hyacinth fibers can be eliminated by bleaching. From 50 grams water hyacinth fine grains used and boiled in 2000 ml NaOH 25% (1:40), it is obtained α-cellulose white grain with 15.278% rendement. On the other hand, the water hyacinth fine grain boiled in NaOH 18% resulted in 15.30% rendement. Even though the cellulose rendement boiled in NaOH 18% possessed higher rendement value, its color was yellowish white so that the cellulose used in the next process is the one isolated with NaOH 25%.

Alpha-Cellulose Content Analysis

The α-cellulose content analysis was conducted by using titrimetry method in accordance with SNI 0444:2009 pertaining cellulose alpha, beta and gamma content in pulp examination method. From the analysis, it was known that the content of α-cellulose contained in the water hyacinth used in this research was 66.873%. This value is higher than the value of water hyacinth α-cellulose found by Joedodibroto (1983), that is, 64.51%. The identification of the α-cellulose function cluster was performed by using infra-red spectrophotometer (FTIR), and the result can be seen in Figure 1. Essentially, from its structure, cellulose is a natural polymer which contains elements C, H and O as its building blocks [12].

The Na-CMC Synthesis Optimization of Water Hyacinth Cellulose

Sodium carboxymethyl cellulose (Na-CMC) was synthesized from water hyacinth cellulose in several stages including alkalization, carboxymethylation, heating, and neutralization consisting of washing and drying. Cellulose was suspended in isopropyl alcohol by using a mechanical stirrer at room temperature. The isopropyl alcohol acted as a media to make the alkalization and carboxymethylation reactions uniform, and also to increase the degree of substitution. Isopropyl alcohol can also be used to disperse cellulose, increase the kinetic speed of a reaction, and as a media for heat exchanges. The next stage was the alkalization process using NaOH 40%. This mixture was then stirred for 90 minutes

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and resulted in alkali cellulose. In the carboxymethylation process, the obtained alkali cellulose was reacted with sodium monochloroacetate ($ClCH_2COONa$). In this stage, apart from the formation of Na-CMC, several by-product compounds, such as sodium glycolate and sodium chloride, were also formed. The carboxymethylation process was done at 55˚C for 3.5 hours. The purpose of the heating process was to improve the result of the mixture reaction in order to facilitate the treatment for the following stages. After the heating process, 70% methanol was added into the reactor to wash and separate the formed Na-CMC from its by-products, natrium glycolate and natrium chloride. The crude of Na-CMC was neutralized by using 90% acetic acid. This step was intended to eliminate the glycolic acid content. The neutralized Na-CMC was then cleaned with 96% ethanol and absolute methanol in the cleaning stage to eliminate glycolic acid as a by-product of the reaction and other undesired contaminant. The Na-CMC yield by this process was 95,33%.

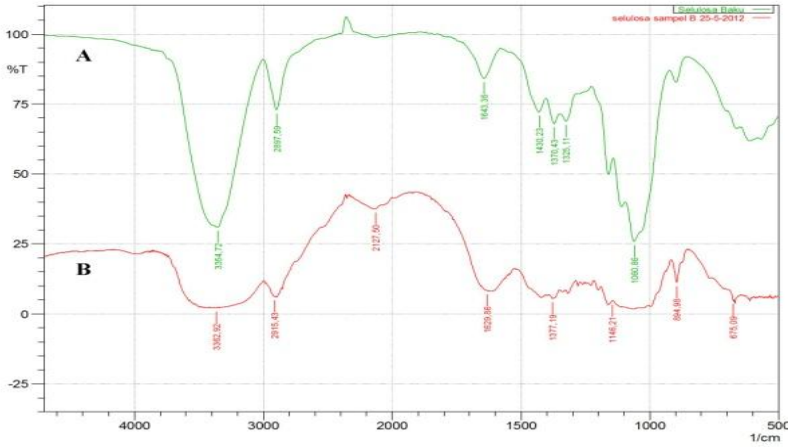

Figure 1. Infra Red spectrum of standard α-cellulose (A) and Isolated (B)

The Na-CMC Characterization of Water Hyacinth Cellulose

The determination of Na-CMC characteristics was conducted by using Fourier Transform Infrared (FTIR) and Scanning Electron Microscope (SEM). The analysis of the function clusters of Na-CMC grain obtained from water hyacinth cellulose synthesis and of standard Na-CMC was done by using Fourier Transform Infrared (FTIR).

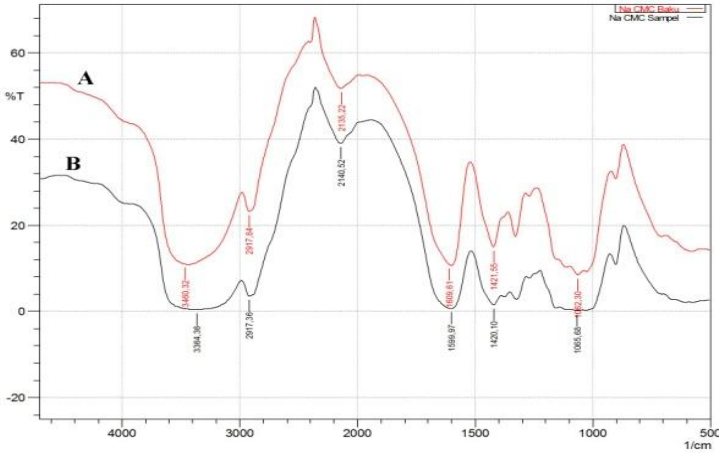

Figure 2. Infrared Spectrum of Standard Na-CMC (A) and Na-CMC Syntesized from Water Hyacinth Cellulose (B).

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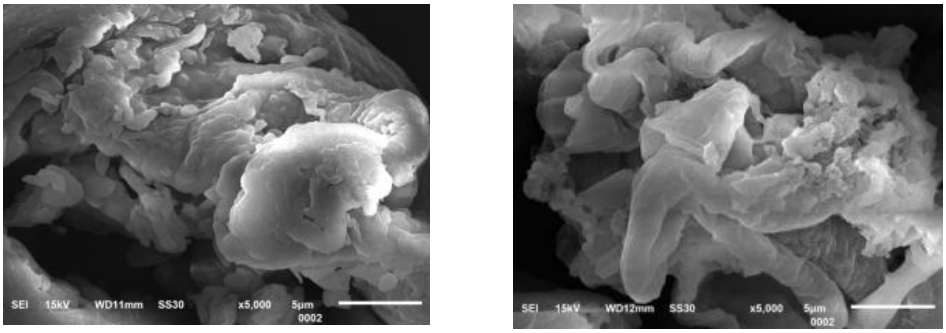
The infrared spectrum from the Na-CMC produced by the water hyacinth cellulose synthesis shows some absorption points at 1599.97 cm^{-1} and at 1420.10 cm^{-1} wave numbers. The peak of the spectrum at 1599.97 cm^{-1} wavelength shows the existence of carbonyl groups, and the peak at 1420.10 cm-1 shows the methyl. This indicates the presence of carboxymethyl in the Na-CMC sample structure. According to Peesok, Shields, Cairns and McWilliam (1976) in [8]), the carboxyl groups as the salt structure possess the wave number range from 1600-1640 cm^{-1} to 1400-1450 cm^{-1}.



(a) (b)

Figure 3. SEM Observation Results of (a) Standard Na-CMC and (b) Synthesized Na-CMC at 5000 times magnification

Based on the FTIR analysis, the unique absorption peaks of the samples, which are located at 3460.32 cm^{-1} and 3364.36 cm^{-1} wave numbers (OH groups) and located at 1062.30 cm^{-1} and 1065.68 cm^{-1} (C-O groups), show the existence of bonds in the structure of both samples [13] the infrared spectra of the Na-CMC obtained from the water hyacinth cellulose synthesis result and of the standard Na-CMC give similar spectrum results, and also show a similarity in the functional groups.

The microscopic testing to determine the morphology (the shape and size) and the topography (the texture of sample surface) of Na-CMC synthesized from water hyacinth cellulose, and comparing it with Na-CMC standard was done by using Scanning Electron Microscope (SEM).

From the observation using SEM, it can be seen in Figure 3 that both the particles of Na-CMC synthesized from water hyacinth cellulose and of standard Na-CMC are irregular in shapes, however, both show a degree of homogeneity on their morphology.

The curved plate shapes with big spaces and irregular or even rough particle surfaces caused Na-CMC to have a high degree of porosity and to be voluminous [13].The size of Na-CMC particles synthesized from water hyacinth cellulose ranges from 19 μm to 137 μm.

CONCLUSION

Based on the research, it can be concluded that water hyacinth cellulose can be synthesized to be sodium carboxymethyl cellulose (Na-CMC).

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