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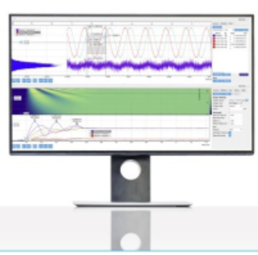

Utilization of *Imperata cylindrica* as an Alternative Low-Cost Cellulose Sources for Carboxymethyl Cellulose Production

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Abstract. Various non-wood plants were evaluated as alternative raw materials in cellulose production. Imperata cylindrica is a perennial grass which distributed mainly in South Kalimantan, Indonesia. This grass is a noxious weed both in crops and natural areas, causing severe economic and environmental damage. In this work, *Imperata cylindrica* was used as raw material to produce cellulose. Cellulose was extracted from *Imperata cylindrica* through the removal of lignin and hemicellulose. The purpose of this study was to synthesize carboxymethyl cellulose (CMC) obtained through alkalization using sodium hydroxide (NaOH) and carboxymethylation reaction using monochloroacetic acid (MCA). Na-CMC is cellulose-derived material which widely uses in many industrial application, such as pharmaceutical excipients, thickener, binder, and emulsifying agent. The carboxymethylation process of cellulose was confirmed by Fourier transform infrared spectroscopy (FTIR) and further characterized by X-ray diffraction (XRD), degree of substitution value, and levels of solubility. Based on the comparison of FTIR spectra, X-ray diffraction, solubility, and degree of substitution, the optimum condition for Na-CMC synthesis was found to be 15% NaOH and the ratio of MCA to cellulose 0.80. In conclusion of the characteristic study, *Imperata cylindrica* is an excellent potential alternative cellulose in the pharmaceutical industries.

INTRODUCTION

In the recent years, the transformation of cellulose into useful product has been increased consideration attention because of their low-cost, biorenewable character, abundant avaibility in various shape [1]. Cellulose can isolate from various sources, such as wood [2]-[3] and non-wood materials, such as cotton, straw and agriculture waste [4]-[6]. Presently, carboxymethyl cellulose (CMC) is the most broadly used cellulose derivative, with various valuable application in the pharmaceutical, food, cosmetics industries, and detergents [7]-[8]. CMC is produced from cellulose with monochloroacetic acid (MCA) in aqueous alkali conditions [9]-[10]. In this reaction, cellulose chain polymer has high activity and availability to chemicals, and the -OH group of cellulose are exchanged by $-CH_2-COOH$ group to produce carboxymethyl cellulose [11].

Imperata cylindrica is an abundant and low-value agriculture waste in the world. It is an aggressive, perennial invander and can grow rapidly in an infertile soil, which only minimal amount of nutrient and water. Currently, *Imperata cylindrica* cultivate through much of Kalimantan, Indonesia (more than 830.000 ha) and considered as ecological threat. According to the previous research [12], *I. cylindrica* consists of high content of cellulose (more than 40%), which can be extracted and used for numerous function. The aims of this research were to extracted cellulose from *I. cylindrica* for carboxymethyl cellulose production.

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In this research, the valorization of *I. cylindrica* to produce CMC, which have not been reported before, it could be an applicable use of agriculture waste to produce an economic and ecological advantages.

MATERIALS AND METHODS

I. cylindrica Preparation

I. cylindrica were collected from Landasan Ulin, Banjarbaru, South Kalimantan, Indonesia. The *I. cylindrica* stems were cleaned, washed, dried, and then stored in sealed plastic bags.

I. cylindrica Cellulose Isolation

The dried *I. cylindrica* stems were milled into powder and extracted with ethanol: toluene using a Soxhlet set extractor and then dried for 24 h. Cellulose extraction following the procedure used by Sunardi et al. [10].

Carboxymethyl Cellulose Synthesis

CMC was synthezed by alkalization and carboxymethylation process of cellulose. In the first step, 2 g of cellulose of *I. cylindrica* was added to 40 ml of isopropanol with constant mixing. NaOH solution (varying concentration 5-25%) was added and stirring was continued at room temperature for an hour. The second stage, the carboxymethylation process is carried out by adding MCA at 55 °C. The suspension is neutralized with acetic acid then filtered and dried at 60 °C.

Yield Measurement

CMC yield (%) was calculated using the Equation 1.

$$Yield = \frac{weight\ of\ dried\ CMC}{weight\ of\ dried\ cellulose} x\ 100\% \tag{1}$$

Substitution Degree Determination

The DS of the sample was determined by the standard methods according to Sunardi et al. [10].

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectra analysis of the cellulose and CMC samples using a Shimadzu FTIR-8201 PC spectrometer in the wavenumber range between 4000 and 400 cm^{-1}.

X-ray Diffraction Analysis

The X-ray diffraction (XRD) of the cellulose and CMC samples were analyzed using a X-ray diffractometer (Shimadzu XRD-6000) with a Cu Kα radiation (λ = 1.54 Å) at 30 mA and 40 kV.

RESULTS AND DISCUSSION

Effect of Concentration of NaOH on CMC

The effect of concentration of NaOH on the characteristics of CMC was confirmed in the range of alkali solution concentrations from 5, 10, 15, 20 and 25% (w/v). Fig. 1 shows that the yield of CMC synthesized using variation in

NaOH concentration relatively constant and ranged from 65.48-72.64%. The CMC yield is the amount of pure product after removal of dissolved materials during filtration process.

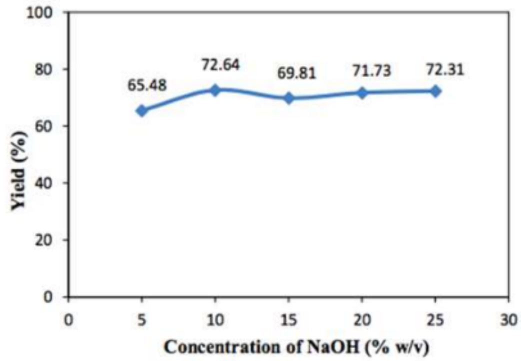

FIGURE 1. Yield (%) of CMC from *I. cylindrica* based on NaOH concentration

Fig. 2 shows the increasing of solubility of CMC at 5-15% (w/v) NaOH concentration. However, at the concentration 15-25% (w/v), CMC solubility tend to decreased. The increasing of solubility might be related with the number of Na^{+} ion that bind to the –OH group in cellulose to facilitate the carboxymethyl group substitution. According to Adinugraha et al. [13], the decrease in solubility at high concentration of NaOH was caused by more side product formed than main products.

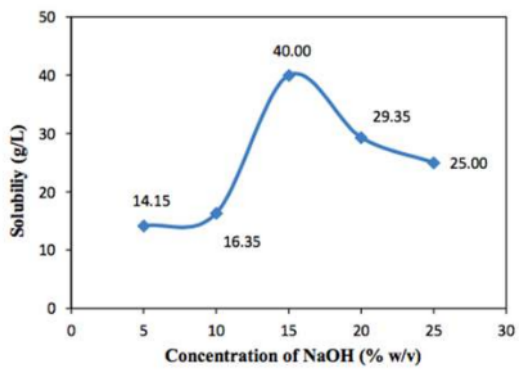

FIGURE 2. Solubility of CMC from *I. cylindrica* based on NaOH concentration

The CMC viscosity characteristic is an essential factor for the various purpose of this product. The value of CMC from *I. cylindrica* viscosity is not influenced by NaOH concentration up to 10% concentration. The viscosity of CMC is below than 50 Cps, is categorized as low viscosity. Nevertheless, the CMC viscosity of *I. cylindrica* significantly increased at 20% (w/v) NaOH concentration and than sharply decreased at higher NaOH concentration (Figure 3).

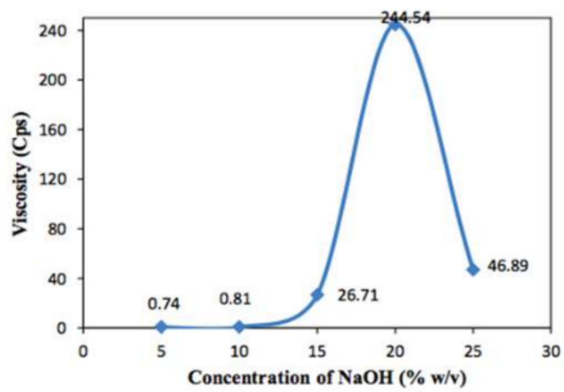

FIGURE 3. Viscosity of CMC from *I. cylindrica* based on NaOH concentration

Fig. 4 shows the degree of substitution of CMC from *I. cylindrica* based on NaOH concentration. Based on the Figure 4, the value of the degree of substitution of CMC decreased ith increasing the NaOH concentration. It was seen that the degree of substitution of CMC from *I. cylindrica* is very low at 25% NaOH concentration and it was spotted that the degree of substitution value sharply decreased with increasing the alkali concentration from 10 to 15% and then increased slightly from 15 to 20% (w/v) (Figure 4). This data can be described by considering of two competitive reactions in the process of carboxymethylation: cellulose activation with NaOH and cellulose reaction with MCA to produce CMC (reaction 2 and 3) [10].

$$R_{cell}OH + NaOH \rightarrow R_{cell}Ona + H_2O \quad (1)$$

$$R_{cell}ONa + ClCH_2COOH \rightarrow R_{cell}OCH_2COOH + NaCl + 2H_2O \quad (2)$$

$$2NaOH + ClCH_2COOH \rightarrow HOCH_2COONa + NaCl + H_2O \quad (3)$$

According to Pushpamalar*et* et al. [14], the extra of NaOH can produce glycolate as the side-product that can inactivation sodium monochloroacetate (reaction 3).

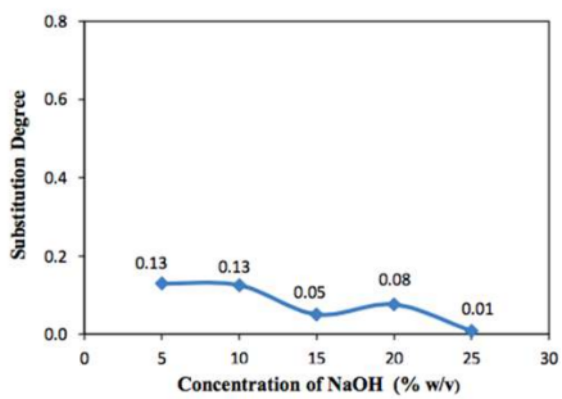

FIGURE 4. The degree of substitution of CMC from *I. cylindrica* based on NaOH concentration

The Effect of Ratio MCAto Cellulose

The effect of ratio MCA to cellulose on the characteristic of CMC produced by *I. cylindrica* was evaluated on 15% (w/v) alkali concentration as the optimum condition. The reactions were carried out by varying the ratio of MCA to cellulose at 0.6; 0.8; 1.0; 1.2 and 1.4. Fig. 5 showed that the yield (%) of CMC from *I. cylindrica* decreased with the inceasing of MCA to cellulose ratio. On the 0.6 to 0.8 ratio, the yield only slighty decreased but after that sharpy decreased.

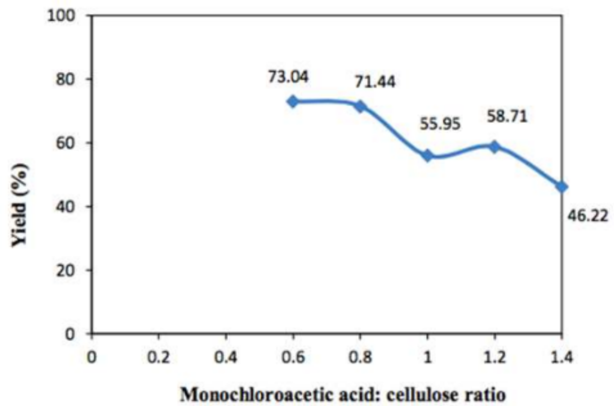

FIGURE 5. Yield (%) of CMC from *I. cylindrica* based on ratio of MCA to cellulose

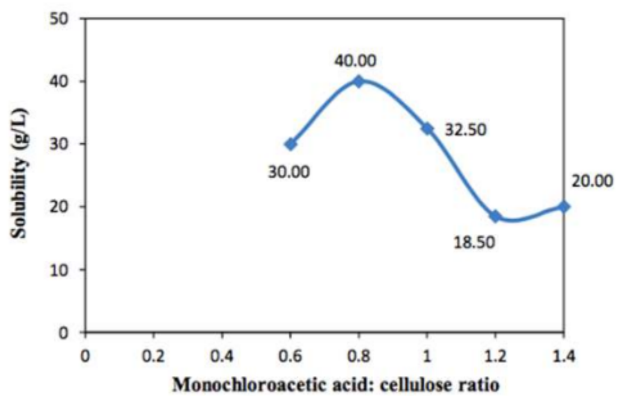

FIGURE 6. Solubility of CMC from *I. cylindrica* based on ratio of MCA to cellulose

Fig. 6 shows the increased solubility in addition to the MCA to cellulose ratio of 0.60 to 0.80 (w/w). This is possible at the time of the CMC synthesis process, the amount of carboxymethyl from MCA which substitutes alkali cellulose is more. The higher amount of cellulose-ONa that substituted by carboxymethyl, the polarity will increase and cause increasing the solubility of CMC in water. Whereas, with the addition of MCA (ratio 0.80 to 1.40), CMC solubility tends to decrease. This is presumably because more carboxymethyl from MCA reacts with NaOH to form side products so that the amount of carboxymethyl which can substitute alkali cellulose decreases. The results of CMC synthesis in this study obtained the optimum at ratio 0.80 of MCA to cellulose. Fig. 7 showed the effect of ratio of MCA to cellulose on the viscosity characteristic of CMC produced from *I. cylindrica*. The viscosity is a significant decrease with the increasing of MCA to cellulose ratio and then relatively constant.

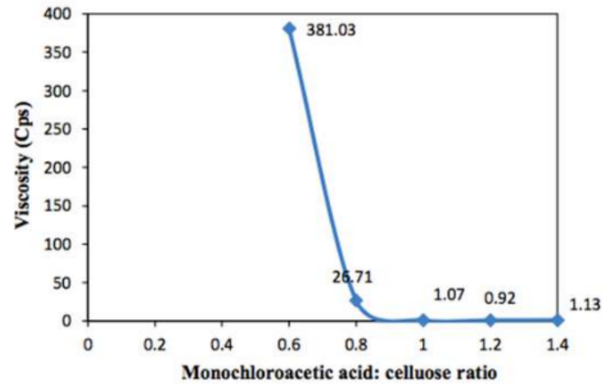

FIGURE 7. Viscosity of CMC from *I. cylindrica* based on ratio of MCA to cellulose

The effect of ratio of MCA to cellulose on the degree of substitution value was shown in Figure 8. It was observed that the degree of substitution is relatively low. The optimum condition of the degree of substitution value was obtained at 1.2 ratio of MCA to cellulose. The degree of substitution value significantly increased with increasing the ratio of MCA from 1 to 1.2 ratio and then decreased at 1.4 ratio.

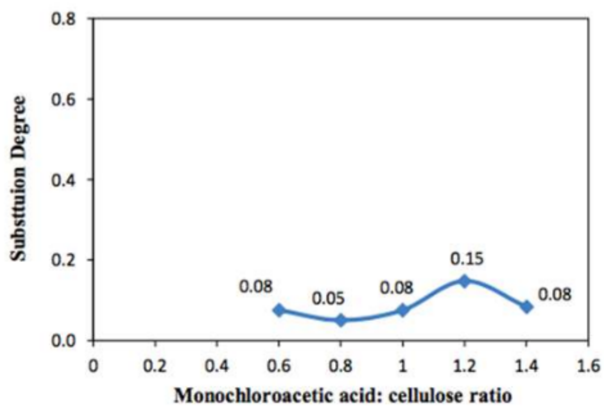

FIGURE 8. The degree of substitution of CMC from *I. cylindrica* based on ratio of MCA to cellulose

Evidence of Carboxymethylation Process

Fig. 9 shows the spectra of FTIR of cellulose and carboxymethyl cellulose from *I. cylidrica* and commercial carboxymethyl cellulose as a comparison. Absorption band around 3400 cm^{-1} (3402,43 cm^{-1} and 3402,43 cm^{-1} for cellulose and carboxymethyl cellulose, respectively) is because of stretching of the –OH group of the cellulose. The difference in the wave number in the -OH group occurs because of the difference in vibrational energy that causes a shift in the wave number. The FTIR spectra showed the characteristic band of cellulose backbone as well as the existence of the carboxymethyl ether group at 1604 cm^{-1}. The presence of a new peak at 1604 cm^{-1} approves the existence of COO^- group because of carboxymethylation reaction. Especially, two peaks around 1419 and 1327 cm^{-1} are assigned to $-CH_2$ scissoring and –OH bending vibrations, respectively [10],[15]. It is marked that the band at 3417 cm^{-1} is due to the stretching of –OH group and a band at 2924 suggests the C-H stretching vibration of CH_2 and CH_3. In addition, the peak at 1064 cm^{-1} is stretching of $>CH-O-CH_2$ [10],[14],[16].

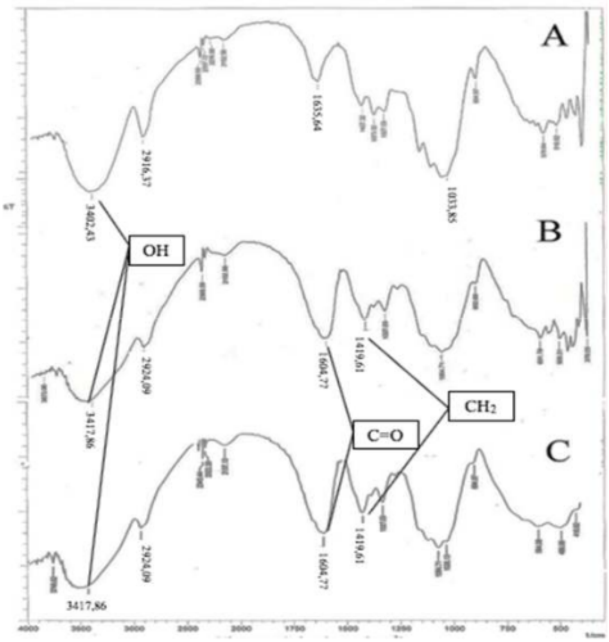

FIGURE 9. FTIR spectra of a) cellulose, b) CMC of *I. cylindrica,* c) commercial CMC

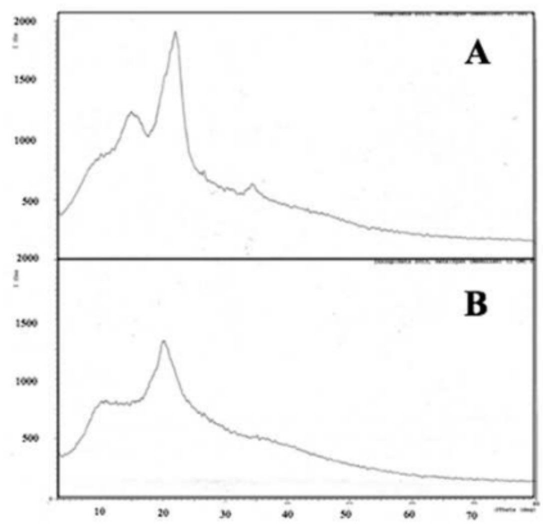

FIGURE 10. X-ray diffractograms of a) cellulose and b) carboxymethyl cellulose from *I. cylindrica*

Fig. 10 shows the cellulose and carboxymethyl cellulose from *I. cylindrica* X-ray diffractograms. The X-ray diffractograms showed that the crystallinity of cellulose was higher than CMC. Cellulose crystallinity is related with hydrogen bonding strength in the interaction of cellulose. It is also seen that the carboxymetylation process also changed the the degree of cellulose crystallinity of cellulose I (crystalline part) to cellulose II (amorphous part). This alteration was suggested with the peak shifting of 002 and 101 in 2θ degree X-ray diffractograms [10],[13].

CONCLUSIONS

CMC has been successfully synthesized from agriculture waste as cellulose source, alang-alang (*I. cylindrica*). *I. cylindrica* appears to be a prospective bioresources for fabricating cellulose derivative for a various utilisation. Based on the solubility data, the optimum conditions for CMC synthesized from *I. cylindrica* are using a 15% NaOH (w/v) concentration and MCAto cellulose ratio at 0.80 (w/w).

ACKNOWLEDGMENTS

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