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Preparation of Carboxymethyl Cellulose Produced from Purun Tikus (*Eleocharis dulcis*)

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Abstract. Sodium carboxymethyl cellulose (Na-CMC) is one of the important modified cellulose, a water-soluble cellulose, which is widely used in many application of food, pharmaceuticals, detergent, paper coating, dispersing agent, and others. The main raw material of modified cellulose is cellulose from wood and cotton. Recently, much attention has been attracted to the use of various agriculture product and by-product, grass, and residual biomass as cellulose and modified cellulose source for addressing an environmental and economic concern. *Eleocharis dulcis*, commonly known as purun tikus (in Indonesia), is a native aquatic plant of swamp area (wetland) in Kalimantan, which consists of 30-40% cellulose. It is significantly considered as one of the alternative resources for cellulose. The aims of present study were to isolate cellulose from *E. dulcis* and then to synthesise Na-CMC from isolated cellulose. Preparation of carboxymethyl cellulose from *E. dulcis* was carried out by an alkalization and etherification process of isolated cellulose, using various concentration of sodium hydroxide (NaOH) and monochloroacetic acid (MCA). The results indicated that the optimum reaction of alkalization was reached at 20% NaOH and etherification at the mass fraction ratio of MCA to cellulose 1.0. The optimum reaction has the highest solubility and degree of substitution. The carboxymethylation process of cellulose was confirmed by Fourier Transform Infrared spectroscopy (FTIR). In addition, changes in crystallinity of cellulose and Na-CMC were evaluated by X-ray diffraction (XRD).

INTRODUCTION

Cellulose is a linear, long-chain, water insoluble, and natural polymer and is the most abundant renewable material resources on earth. Cellulose is widely distributed in various plants, such as wood [1,2], cotton [3], straw [4], and grass [5]. Cellulose is commonly converted into useful chemical feedstock by etherification process. Sodium carboxymethyl cellulose (Na-CMC) is a useful water soluble derivative of cellulose with various valuable application in the detergents, paper, food, pharmaceutical, and cosmetics industries [6]. Sodium carboxymethyl cellulose is produced by aqueous alkali reaction with monochloroacetic acid in organic solvent [7]. Under alkaline conditions, cellulose structure shows the high accessibility and activity to chemicals and the hydroxyl group of cellulose are replaced by carboxymethyl group in the order of C2, C6, C3 [8].

Eleocharis dulcis (in Indonesia commonly known as purun tikus) is a native aquatic plants that can grow well in acidic water and swampy areas. Purun tikus consists of numerous upright tubular stems 90-150 cm tall and in advantageous conditions can grow rapidly, then secondary plants will begin to appear around the parent plant after 6 to 8 weeks [9]. Purun tikus is inexpensive and grow throughout much of South Kalimantan, Indonesia. Currently, the purun tikus are used as ruminant feed, and the fibers are used for traditional handicraft. According to Sunardi *et al*. [10], purun tikus consists of up to 40% cellulose, which can be extracted and used for various useful materials. The objectives of this study were to isolate cellulose from purun tikus and use for Na-CMC production. In an attempt to utilize this plant for useful chemical feedstock, this article seeks to determine the optimal condition for Na-CMC production from purun tikus. If purun tikus can transform to Na-CMC, it could be an effective use of natural resource, producing a significant economic benefit and ecological benefits in wetland agriculture.

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EXPERIMENTAL

Raw Materials

Plants of purun tikus were collected from Bati-Bati, Tanah Laut district, South Kalimantan, Indonesia. The plants were washed, cut manually into small pieces about 1-2 cm, and dried and used as raw material for the present research. Chemicals used in this research were monochloroacetic acid, acetic acid, isopropyl alcohol, ethanol, sodium hydroxide, sodium chlorite, etc. All the chemical were purchased from E. Merck, German, and used as they were.

Cellulose Isolation from Purun Tikus

The dried purun tikus plants were grounded into powder to pass through a 60 mesh sieves. Then the purun tikus powder was extracted with ethanol: toluene (by the volume ratio of 1 : 2) for 20 h using a Soxhlet extractor and dried for 24 h. After that, the ethanol-toluene extracts-free powder and $NaClO_2$ solutions (1.4%) were put in an Erlenmeyer flask and adjusted the pH 3-4 using CH_3COOH and heated in a water bath at 70 °C for 5 h. The mixture was then filtered and the residue was washed with distilled water until neutral and dried in the oven at 105 ± 3 °C. The samples from previous steps were dipped in an Erlenmeyer flask with KOH solution (5%) for 24 h at room temperature and then heated at 90 °C for 2 h. The suspension was cooling down and filtrated. The pure cellulose was washed with distilled water and dried in an oven at 105 ± 3 °C for 1 day.

Preparation of Sodium Carboxymethyl Cellulose

Synthesis of Na-CMC was carried out in two steps, alkalization and etherification of pure cellulose under heterogenous conditions. In alkalization step, 1 gram of cellulose powder of purun tikus was weighed and added to 20 ml of isopropanol with continuous stirring. Then, 4 mL of NaOH solution (5-25%; w/v) was added to the mixture while further stirring for an hour at room temperature. The carboxymethylation was started when monochloroacetic acid (0.6; 0.8; 1.0; 1.2; and 1.4 g) was added with continuous stirring for another at 55 °C for 3 hours. The slurry was neutralized with 90 % of acetic acid to pH 7 and then filtered, and washed with ethanol 70%, dried at 60 °C in the oven and kept in a dry place for further characterization.

Yield Measurement

Product yield (%) was measured based on the dry weight basis and calculated using the following equation:

$$\text{Yield (\%)} = \frac{\text{weight of dried Na–CMC}}{\text{weight of dried cellulose}} \times 100\% \tag{1}$$

Determination of the Degree of Substitution

The degree of substitution (DS) of carboxylic group in CMC is defined as the average number of the hydroxyl group in the cellulose structure which was substituted by carboxymethyl groups. The DS of the sample was determined by the standard methods [11] with slight modifications.

Determination of Viscosity

One gram of Na-CMC from purun tikus was weighed and dissolved in 50 mL of distilled water in a beaker. Then Ostwald viscometer was used to measure the viscosity of the dissolved Na-CMC.

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectra of cellulose and Na-CMC samples were collected using a Shimadzu FTIR-8201 PC spectrometer in the wavenumber range between 4000 and 400 cm^{-1}. Each sample was grounded and pelletized with KBr.

X-ray Diffraction Analysis

The X-ray diffraction (XRD) patterns for cellulose and Na-CMC samples were recorded with an X-ray diffractometer (Shimadzu XRD-6000) using a Cu Kα radiation (λ = 1,54 A˚) at 30 mA and 40 kV.

RESULTS AND DISCUSSION

In optimization process of carboxymethylation, each reaction parameter was varied one at a time. At first optimizing the NaOH concentration, reactions were carried out by varying NaOH concentration, while other parameters (i.e monochloroacetic acid and temperature) were kept to be the same conditions.

Effect of NaOH Concentration

The effect of NaOH concentration was tested in various concentrations of the NaOH solution. As shown in Figure 1, it was observed that the yield (%) of Na-CMC increased with NaOH concentration and attained a maximum yield of 79.59% at an alkali concentration of 25%. The yield is definitely a function of the amount of material lost during the filtration step [12]. At the concentration of 5-15% the yield of Na-CMC was sharply increasing, however, after 15% only slight increasing was observed.

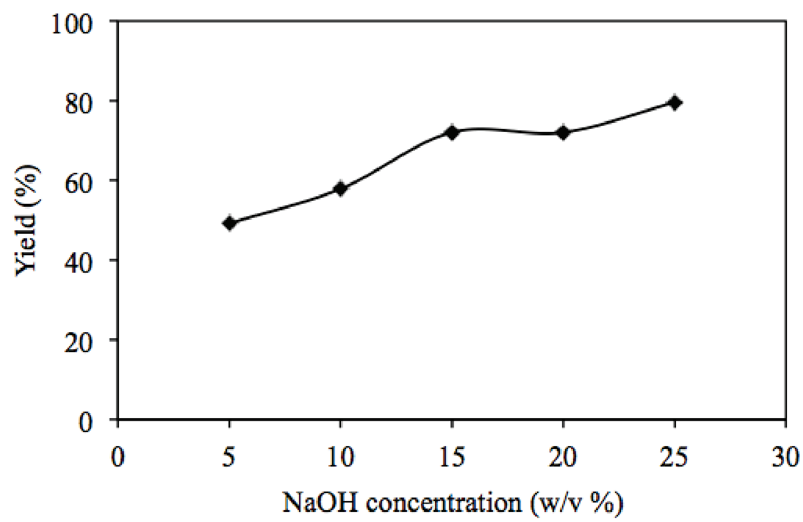

FIGURE 1. Yield (%) of sodium carboxymethyl cellulose synthesized with various alkali concentration

The viscosity of Na-CMC is an important parameter for the industrial application. It provided an information for flow characteristics of the Na-CMC solution flow involved in processing operation and products using certain concentrations of CMC. The viscosity of carboxymethyl from purun tikus is influenced by NaOH concentration, up to 20% concentration, the viscosity of Na-CMC is in a category of low viscosity (<50 Cps in 2% concentration of solution). However, the viscosity of Na-CMC from purun tikus sharply increased at 25% (w/v) NaOH concentration (Figure 2).

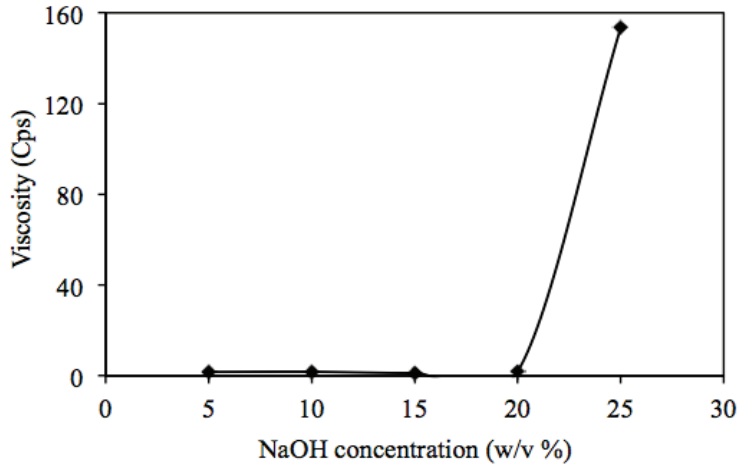

FIGURE 2. Viscosity of sodium carboxymethyl cellulose synthesized with various alkali concentration

It was observed that the DS value is very low at low concentration of 5% (w/v) NaOH solutions and it was observed that the DS value increased with increasing the alkali concentration from 5 to 10% (w/v) and then decreased slightly (Figure 3). At a specific alkali strength, the DS will be highest after which it will decline. This result can be explained by considering the carboxymethylation process, where two competitive reactions occur simultaneously. The first reaction is activation of cellulose with NaOH and reaction of cellulose with sodium monochloroacetate to form carboxymethyl cellulose as shown in reaction 2.

$$\text{Cell-OH} + \text{NaOH} \rightarrow \text{Cell-ONa} + H_2O$$
$$\text{Cell-ONa} + ClCH_2COONa \rightarrow \text{Cell-O-}CH_2COONa + NaCl \quad (2)$$

At higher concentrations of alkali, NaOH reacts with sodium monochloroacetate to form sodium glycolate as shown in reaction 3 [13] resulting in the inactivation of the monochloroacetate.

$$NaOH + Cl—CH_2COONa \rightarrow HO—CH_2COONa + NaCl \quad (3)$$

It appears that in the excess of NaOH, glycolate formation pre-dominates the product which means inactivation of sodium monochloroacetate.

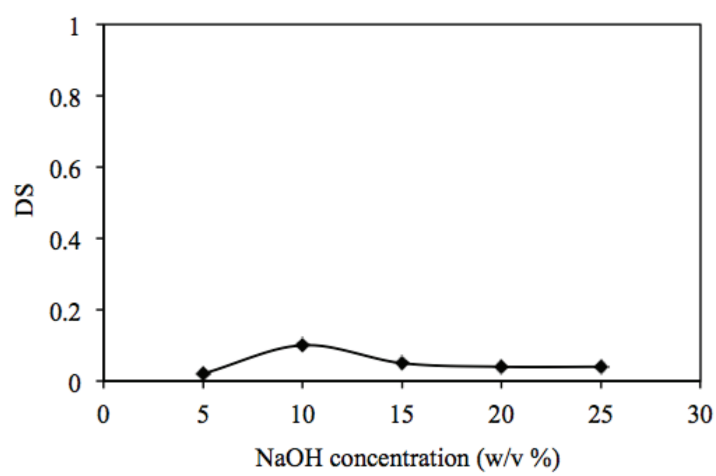

FIGURE 3. The degree of substitution of sodium carboxymethyl cellulose synthesized with various alkali concentration

The Ratio Effect of Monochloroacetic Acid to Cellulose

The ratio effect of monochloroacetic acid to cellulose produced by purun tikus on the characteristic of Na-CMC was examined on 20% (w/v) concentration of alkali. The reactions were carried out by varying amount of monochloroacetic acid (0.6; 0.8; 1.0; 1.2 and 1.4 g). As shown in Figure 4, the yield (%) of Na-CMC from purun tikus fluctuated and reached the maximum on the 1.2 g of monochloroacetic acid, being the ratio to cellulose by 1.2.

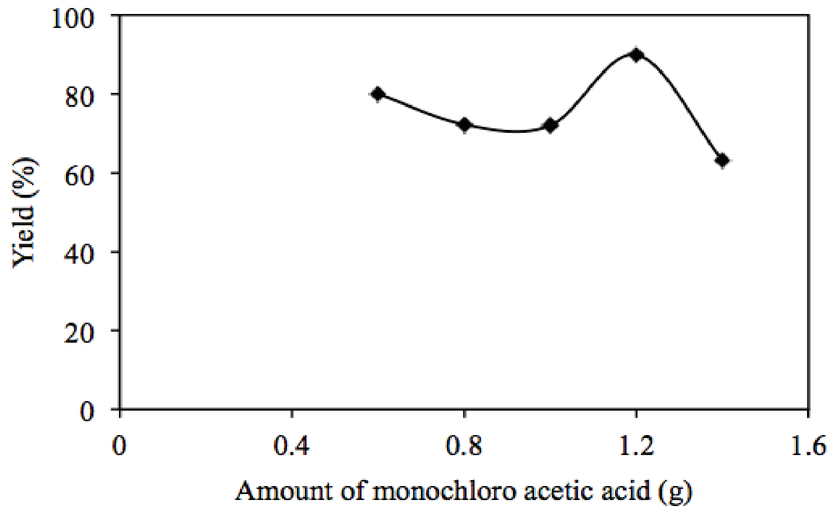

FIGURE 4. Yield (%) of sodium carboxymethyl cellulose synthesized with various amount of monochloroacetic acid

The ratio effect of monochloroacetic acid to cellulose produced by purun tikus on the characteristic of Na-CMC are shown in Figure 5. There is a significant increase in the viscosity up to 0.8 g of monochloroacetic acid but then significantly decreased thereafter.

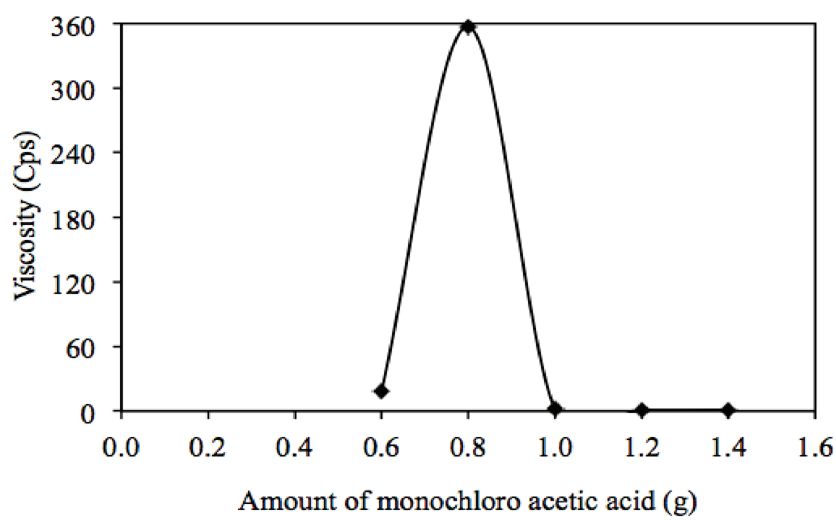

FIGURE 5. Viscosity of sodium carboxymethyl cellulose synthesized with various amount of monochloroacetic acid

Figure 6 shows the effect of the amount of monochloroacetic acid on DS value. It was observed that DS value is very low at the low amount of monochloroacetic acid. A maximum DS value was obtained with 1.4 g of monochloroacetic acid. There is an increase in the DS value with amount of monochloroacetic acid and it was observed that the DS value significantly increased with increasing the amount of monochloroacetic acid from 1 to 1.2 gram and thereafter slightly increased up to 1.4 g. The increase possibly is due to the greater availability of the acetate ions at a higher amount in the proximity of cellulose [8].

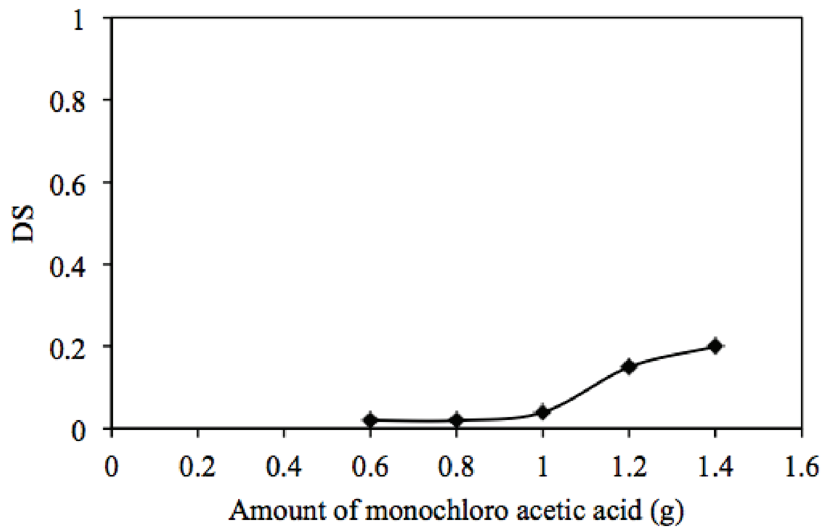

FIGURE 6. The degree of substitution of sodium carboxymethyl cellulose synthesized with various amount of monochloroacetic acid

The FTIR spectra of cellulose produced from purun tikus and the corresponding Na-CMC show the characteristic absorption of the cellulose backbone as well as the presence of the carboxymethyl ether group at 1627 cm^{-1}. Figure 7(a) shows the FTIR spectra of cellulose produced from purun tikus. Clearly, evidence is a broad absorption band at 3410 $cm^{-1,}$ which is due to the stretching frequency of the –OH group among intermolecular and intramolecular hydrogen bonds. The band at 2900 cm^{-1} is likely attributable to C-H stretching vibration. In particular, two bands around 1427 and 1319 cm^{-1} are assigned to $–CH_2$ scissoring and –OH bending vibrations respectively. In addition, the band at 1057 cm^{-1} is due to >CH-O-CH_2 [13].

Figure 7(b) shows a representative spectrum of the corresponding Na-CMC. It is evident that the peak at 3448 cm^{-1} is due to the stretching frequency of the –OH group and a peak at 2931 indicates the C-H stretching vibration of CH_2 and CH_3. The existence of a new band at 1627 cm^{-1} confirms the presence of COO^- group. The bands around 1427 and 1327 cm^{-1} correspond to $–CH_2$ scissoring and –OH bending vibrations, respectively. The band at 1072 cm^{-1} is due to >CH-O-CH2 stretching [13].

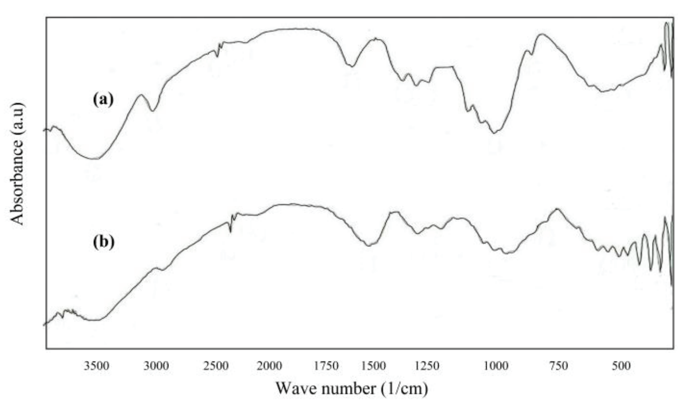

FIGURE 7. FTIR spectra of cellulose (a) and carboxymethyl cellulose from purun tikus (b)

X-ray diffractograms of cellulose produced from purun tikus and the corresponding carboxymethyl cellulose were recorded, and it was found that the crystallinity of Na-CMC decreased (Figure 8). The crystallinity of cellulose is associated with strong hydrogen bonding interaction of cellulose (intermolecular and intramolecular) and Van der Waals forced between adjacent molecules. The decrease of crystallinity on the alkalization and carboxymethylation process of cellulose were due to the cleavage of hydrogen bonds and this also results in the extending the distance between cellulose molecules. As shown in Figure 8, it is also observed that the degree of crystalinity of cellulose I (more crystalline) was changed to cellulose II (more amorf). This transformation was also indicated with the shifting of peaks of 002 and 101 in 2θ degree [14].

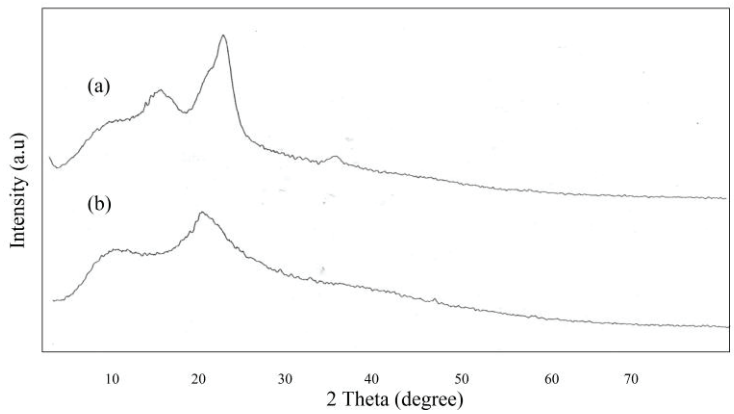

FIGURE 8. X-ray diffractograms of cellulose produced from purun tikus (a) and its carboxymethyl cellulose (b)

CONCLUSION

Sodium carboxymethyl cellulose could be synthesized from alkalization and carboxymethylation of purun tikus (*E.dulcis*) cellulose. Purun tikus seems to be a potential chemical feedstock for producing this cellulose derivative for a various industrial application. The characteristic of water-soluble cellulose derivative obtained by carboxymethylation reaction has the different yield, viscosity and degree of substitution depending on the reaction conditions. Optimization of other reaction condition for preparing carboxymethylation of purun tikus cellulose should be carried out to determine the optimum condition which will give the highest yield and DS value.

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