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Synthesis and characterization of carboxymethyl cellulose with high degree substitution from Vietnamese pineapple leaf waste

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Abstract:

In this work, cellulose was successfully extracted from pineapple leaf waste by 0.75 M NaOH at 90°C and 5 M HNO_3 at 70°C for 1.5 h and 5 h, respectively. The obtained cellulose fibres, with average diameters of 150-300 nm, were converted to carboxymethyl cellulose (CMC) by esterification. The pure cellulose was soaked in a solution mixture of isopropanol and NaOH for 2 h. It was then reacted with chloroacetic acid (MCA) at 60°C for 1.5 h. The optimum conditions for carboxymethylation were found to be 5 g cellulose, 1.5 g MCA, and 15 ml 16% w/v NaOH. The obtained CMC had a high degree of substitution (DS) of 2.3. The properties of CMC were determined.

Keywords: **carboxymethyl cellulose, cellulose degree of substitution, Vietnamese pineapple leaf waste.**

Classification number: **2.2**

Introduction

CMC is one of the most common derivatives obtained by the carboxymethylation of the hydroxyl groups of cellulose. CMC exhibits a great potential as thickening additives, film former, binder, suspending aid, and biodegradable materials [1-4]. In order to obtain CMC, first, cellulose was swollen in a NaOH solution, and then reacted with monochloroacetic acid in alcohol [5]. In this reaction, the sodium carboxymethyl groups substitutes the hydroxyl groups in C-2, C-3, and C-6 of the anhydro-glucose unit. It seems that substitution in the C2 position is slightly more dominant [6]. The solubility of CMC in water is a key parameter in their applications and a higher DS will normally improve the solubility of the CMC. Theoretically, the maximum DS is 3. CMC is soluble in water when DS is higher than 0.4. Most research [5-7] has achieved a DS ranging from 0.5 to 2.0. The DS of commercially available CMC is in the range of 0.4-1.4. Recently, many researchers are trying to find a way to achieve CMC with higher DS in order to improve commercial products. It has been shown that cellulose sources have a very important role since the crystalline content and the size of cellulose are the most crucial parameters for attaining CMC with a high DS [5]. Finding raw materials based on agricultural by-products to produce CMC has been obtaining more and more interest from researchers. For example, the use of cellulosic sources as an alternative to virgin softwood pulp to synthesize CMC has been reported [4-10]. N. Haleem, et al. (2014) [7] obtained cellulose fibre with sizes of 15-20 µm from cotton waste by acid hydrolysis with 10 M H_2SO_4 at 70-80°C for 1 h. Generally, cellulose extraction is a complicated process, and several steps have to be performed to gain a high degree of substitution. Thus, finding new, available, and cheap cellulose sources for CMC preparation is of great significance.

Pineapple is one of the most popular tropical fruits in Vietnam. During harvesting, pineapple leaves are discarded. Their release into the environment, in turn, leads to pollution of our living environmental system [11, 12]. However, pineapple leaves are an abundantly available and potential source of cellulose. These leaves contain about 65-70% dry weight of cellulose [11, 13]. The process of extracting cellulose from pineapple leaf is simple [14-18], and the extracted cellulose has relatively low crystal content as compared to that of cotton waste [7], paper sludge [8], rice straw [19, 20], and other sources [3, 4, 6, 19]. These two factors positively affect the possibility of synthesis of CMC with high DS.

The purpose of this work is to confirm the potential of Vietnamese pineapple leaf waste as a raw material for industrial production of CMC with high degree of substitution.

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Materials and methods

Materials

The pineapple leaves were collected from the pineapple Dong Giao farm, Tam Diep, Ninh Binh, Vietnam. The pineapple leaves were cut into 5 mm using a grinding machine, then dried in an oven at 60°C for 24 h. The samples were kept in zipper polyethylene bags.

For this study, the following acids, such as nitric acid 65%, monochloroacetic acid (MCA) (UK) 99.7%, acetic acid 99.9% and sodium hydroxide 99.9% (Merck), as well as methanol 99.8% and ethanol 99.9% from Xilong Chemical, isopropanol 99.7% (Merck), and acetone 99.8% (Merck) were used. They were of high purity.

Methods

Cellulose extraction: The extraction process of cellulose from pineapple leaf waste is illustrated in Fig. 1.

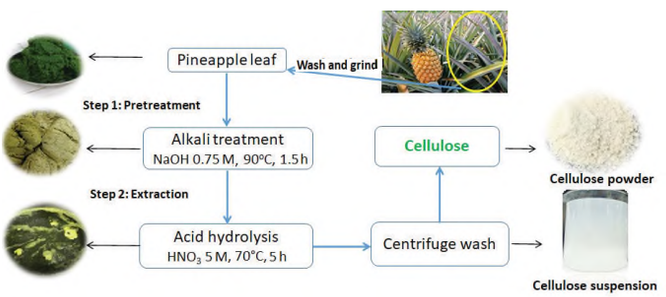

Fig. 1. Schematic illustration for the cellulose extraction process from pineapple leaf waste.

The dry pineapple leaf waste powder was treated with 0.75 M NaOH at 90°C and 5 M HNO_3 at 70°C for 1.5 and 5 h, respectively. This mixture was then centrifuged at 3000 rpm for 20 min to remove large particles and washed with warm distilled water until the indicator paper did not change colour. The residue was dried in an oven at 60°C overnight until the weight remained constant. Finally, the dried cellulose was ground and kept in a polyethylene bag for the next process modification.

The yield of the cellulose was gravimetrically determined and expressed as the weight of the extracted dried cellulose to 100 g of the dried pineapple leaf used for extraction. This was repeated 3 times for each extraction condition and the yield average and the standard deviation were calculated.

Equation (1) below was used for the determination of the yield of cellulose:

$$H(\%) = \frac{m}{m_0} \times 100 \quad (1)$$

where m_0 is the weight of initial dried pineapple leaf powder, m is the weight of obtained cellulose, and H is the yield of cellulose (named as HC).

Synthesis of CMC: Five grams of extracted cellulose from Vietnam's pineapple leaf powder was added to 150 ml of isopropanol under continuous stirring for 60 min. Then, 15 ml of 16% NaOH solution was dripped into the mixture and further stirred for 1 h at room temperature. The carboxymethylation was started when y grams of MCA (y=0.5, 1.0, 1.5, and 2.0 g) were added under continuous stirring for another 90 min at 60°C. The solid part was neutralized with acetic acid to pH=7.0 and washed two times by soaking in 20 ml of ethanol to remove undesirable by-products. The obtained CMC was filtered and dried at 60°C until it reached constant weight, and it was then kept in the polyethylene bag. Equation (1) above is also used to determine the yield of the CMC (HCMC) where m is the weight of the obtained CMC, and m_0 is the weight of the cellulose used for the CMC synthesis.

Infrared spectroscopy: FTIR analysis of the obtained cellulose and CMC were performed by a FT/IR-6300 spectrometer using KBr pellet methods. The spectral resolution was 4 cm^{-1} and the absorption region was 600-4000 cm^{-1}.

X-ray diffraction: The crystallinity index (CrI) of the obtained cellulose and CMC were analysed by Shimadzu XRD-6100 diffractometer. The diffraction angle ranged from 5 to 80° (0.05°/min). The measurement was carried out at 30 kV and 15 mA under Cu K_α radiation. The CrI of the samples was calculated by Eq. (2):

$$CrI\ (\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (2)$$

where I_{002}: (2θ=22.8°) and I_{am}: (2θ=18°) correspond to the crystalline and amorphous regions, respectively [21].

Particle size measurement: The particle size of the obtained cellulose was measured by a Shimadzu Sald-2001 Analyser. First, the cellulose suspension was diluted to 0.05-0.2 wt% concentration. Then, it was measured in a container.

Scanning electron microscopy (SEM): The surface of the separated cellulose is observed by the SEM images. The SEM images were done on a Hitachi S4800-NHE scanning electron microscope (Hitachi Co., Ltd., Japan).

Determination of Degree of Substitution (DS): Degree of Substitution of CMC is determined according to ASTM 1994 [22].

Sample preparation: 350 ml of ethanol was added to a 500 ml conical flask containing 5 g of CMC to the nearest 0.1 mg. The suspension in the flask was shaken for 30 min, then filtered through a porous funnel. The solvent was removed by heating at 100°C for 60 min. The sample was dried in an oven at 110°C until a constant weight was reached.

Procedure: 2 g of the dried obtained substance to the nearest 0.1 mg was put to a tared porcelain crucible. The crucible was carefully charred with a small flame, then with a large flame for 10 min. The cooled residue was moistened with 3-5 ml of concentrated sulfuric acid. Next, the crucible was cautiously heated until the fuming was finished. Then, the crucible was cooled to room temperature. About 1 g of ammonium carbonate was added. The powder was distributed over the content of the entire crucible. It was heated again with a small flame until the fuming stopped, and then was maintained at a dull red heat for 10 min. The treatment procedure was repeated with sulfuric acid and ammonium carbonate if the residual sodium sulphate still contained some carbon. The crucible was cooled in a desiccator and weighed. The sodium content, A, was calculated by Eq. (3):

$$A\ (\%) = \frac{a \times 32.28}{b} \quad (3)$$

where a is the weight of the sodium sulphate residue and b is the weight of the dry sample.

The degree of substitution was calculated by Eq. (4):

$$DS = \frac{162 \times A}{2300 - 80 \times A} \quad (4)$$

where 162 is the molecular weight of the glucose unit and 80 is the net increment in the anhydrous glucose unit for every substituted carboxymethyl group.

Results and discussion

Extraction of cellulose from Vietnam's pineapple leaf waste

The extracted cellulose yield was 55±1.75 wt.%. This yield value is much higher than that of cellulose extracted from other agricultural biomasses such as 37.67 wt.% from the Baobab fruit shell [19] and 32 wt.% from rice straw [20]. The high cellulose content would guarantee a lower price for cellulose derivatives.

The morphology of the obtained cellulose is shown in Fig. 2.

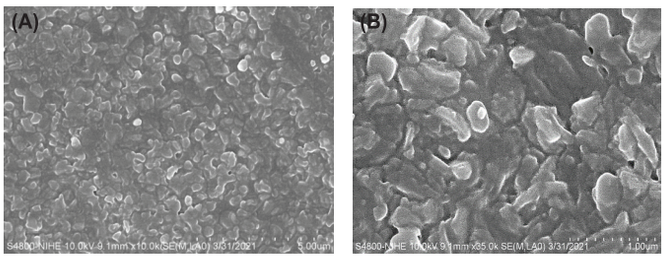

Fig. 2. SEM images of pineapple leaf cellulose at (A) 10,000 x magnification (5 µm size bar) and (B) 35,000 magnification (1 µm size bar).

As can be seen in from the SEM images, the obtained cellulose showed uniform size with average diameters of 150-300 nm, which was similar to that of another reported work [23]. It is worth mentioning that the separation of cellulose in this work is easier and the cellulose obtained had a significantly higher yield compared to that of previous reports [7, 14, 15, 16, 17]. Of course, this comparison is only relative because cellulose yield depends on the method and conditions of separation. The FTIR spectroscopy of obtained cellulose is displayed in Fig. 3.

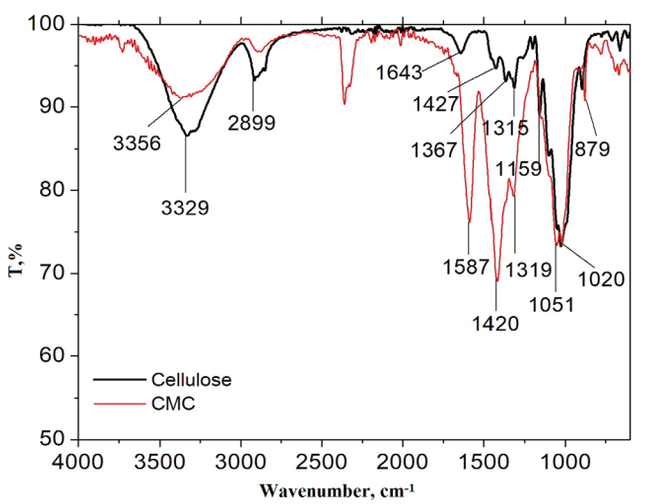

Fig. 3. FTIR spectroscopy of extracted cellulose and CMC from pineapple leaf waste.

As for cellulose, as shown in Fig. 3, there is a large band at 3329 cm^{-1} corresponding to the OH group. The peak at 2899 cm^{-1} represents the C-H stretching vibrations. The peak at 1159 cm^{-1} can be assigned to C-O-C stretching of the β(1,4)-glycosidic linkage. Besides, the peaks at 1367 and 1427 cm^{-1} are attributed to the -C-H and -C-O bending vibrations, respectively, in the polysaccharide rings. The vibration of the -C-O group of secondary alcohols in the cellulose chain backbone appears at 1105 cm^{-1}. The absorption band range of 879-1051 cm^{-1} is assigned to the

β-(4,1)-glycosidic linkages between the glucose units of cellulose [4-10]. In this study, the crystalline nature of the obtained cellulose was investigated by use of XRD [13, 14, 21]. The XRD diffractogram of pineapple leaf cellulose (PLC) is shown in Fig. 4.

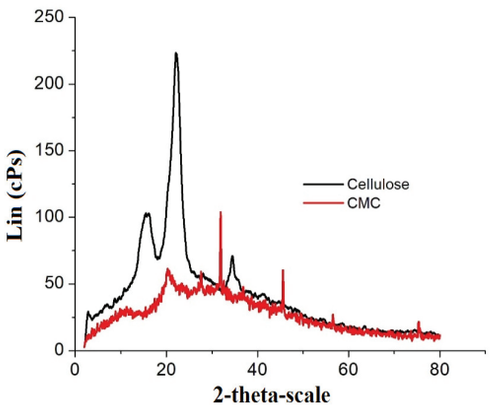

Fig. 4. XRD diffractogram of isolated cellulose and synthesized CMC from pineapple leaf waste.

As can be seen, the XRD diagrams of PLC showed peaks at 2θ=16.6°, 22.8°, and 35.4°, which are attributed to the characteristic peaks of cellulose. The crystallinity index (CrI) of PLC is 68.7 and this CrI value is significantly lower than 82.7, which was reported by M. Mahardika, et al. (2008) [24]. As we all know, the crystallinity of cellulose depends on the method of separation and treatment. Thus, the separation method used in this study gives cellulose with relatively low crystallinity.

Synthesis of CMC from Vietnam's pineapple leaf cellulose

Distribution size of cellulose in suspension: Cellulose size plays an important role in gaining higher yields and degrees of substitution of CMC. In the carboxymethylation process, cellulose is often dispersed in the suspension of the solvent. The solvent increases the accessibility of the etherizing reagent to the cellulose chains [4, 7, 8, 22]. To date, many researchers have focused on the effect of cellulose size on the DS of CMC in the solid state. However, to our knowledge, there is no publication reporting on this effect on the DS of CMC in suspension, as well as on the efficiency of the denaturation reaction. This study is dealing with the effect of solvent on the cellulose fibre size in suspension. The pineapple leaf cellulose, with an average size of 150-300 nm, was ultrasonicated and dispersed in water, ethanol, and isopropanol. Spectra of cellulose size distributions are shown in Fig. 5.

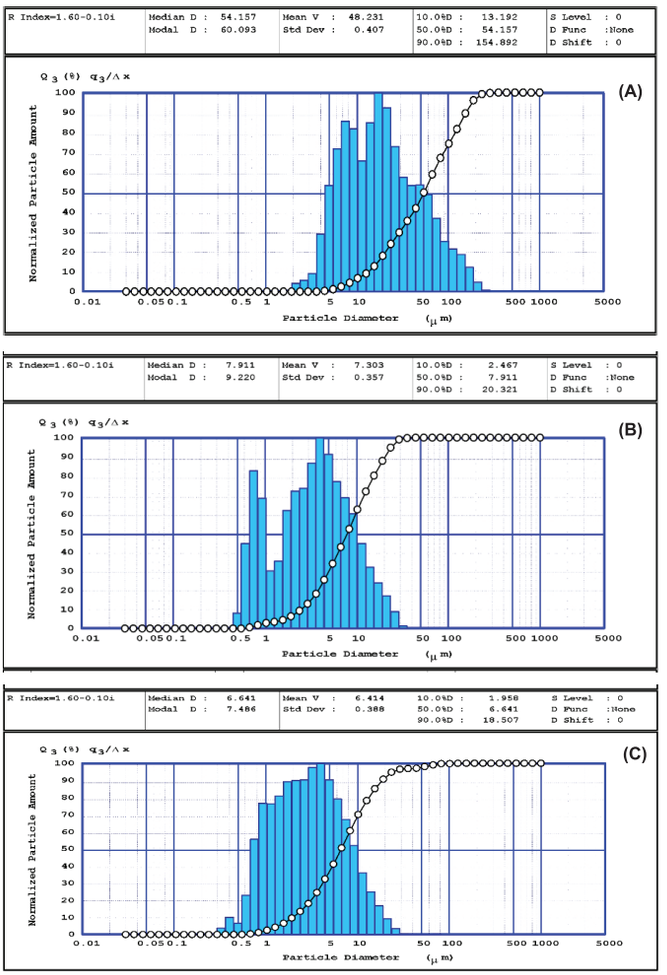

Fig. 5. Particle size distribution spectrum of cellulose in different solvents: (A) in water, (B) in ethanol, and (C) in isopropanol.

As can be seen, the average diameter of cellulose in water, ethanol, and isopropanol were 54.157, 7.911, and 6.641 *μm, respectively.* The cellulose size distribution is relatively narrow for isopropanol. Thus, isopropanol appears to be the best solvent to disperse cellulose. The differences in the particle sizes of cellulose can be due to the difference in the polarities and stereochemistry of the three solvents. The polarity index value of isopropanol, ethanol, and water are 5.0, 6.6, and 9.0, respectively. This implies that the lower the polarity of the solvent, the higher its dispersion for cellulose. These results are similar to those of other studies [4, 7, 8, 23] and serve as additional evidence of the successful synthesis of CMC in isopropanol [6, 25].

Effect of cellulose size on DS and yield of CMC: The reactant's accessibility and the presence of the activated hydroxyl groups are very important for the carboxymethylation reaction. As the particle size decreases, surface area and the free -OH groups for substitution increase, which leads to the reaction yield increasing.

Moreover, reduced cellulose particle size has larger specific surface areas meaning more cellulose accessibility for the reactants, and the reaction occurs at a faster rate [26-28]. In this work, the influence of the cellulose size in a suspension of isopropanol on the DS and yield of carboxymethylation reaction was studied. Cellulose was isolated from pineapple leaf waste at different concentration of HNO_3 (3, 4, 5 M) while other conditions were kept unchanged. The average sizes of the obtained cellulose in isopropanol were 42.421, 19.189, and 6.641 µm respectively. The DS and yield of CMC are shown in Table 1.

Table 1. The yield and DS of CMC synthesized with different sizes of cellulose in isopropanol.

Average diameter of cellulose, µm	6.641	19.189	42.421
H_{CMC}, %	136.6	121.2	115.1
DS	2.3	2.0	1.9

It is seen that the DS of CMC depends greatly on the size of cellulose in suspension. DS decreases with the increasing size of cellulose and reached 2.3 for cellulose with an average size of 6.641 µm, while cellulose with an average size of 42.421 µm produced a DS of only 1.9.

The yield of CMC greatly depends on the amount of monochloroacetic acid (MCA) used. The weight ratio of MCA to cellulose changed from 0.1 to 0.4. The yields of CMC and its dependence on MCA/cellulose ratios are shown in Table 2.

Table 2. The yield and DS of CMC synthesized with various amount of MCA.

Ratio of $m_{MCA}/m_{cellulose}$	0.1	0.2	0.3	0.4
H_{CMC},%	112.7	122.8	136.6	113.5

It can be seen from Table 2 that a maximum yield of 136.6% was obtained with an $m_{MCA}/m_{cellulose}$ ratio of 0.3. There was an increase in the yield of CMC with an increase of $m_{MCA}/m_{cellulose}$ ratio up to 0.3. The increase of CMC yield could be related to the greater availability of the acetate ions at higher concentrations. Nevertheless, as shown, further increase in $m_{MCA}/m_{cellulose}$ ratio leads to the CMC yield slightly decreasing. This could be due to the occurrence of undesired side reactions at high MCA amounts.

Structural characterization of CMC: The CMC structure was characterized by FTIR spectroscopy, and the spectrum (see in Fig. 3).

From the IR spectra of CMC, a broad absorption band at 3356 cm^{-1} was found, which indicated the presence of O-H groups. The band at 2898 cm^{-1} is attributed to the C-H stretching vibration. The spectra shows peaks at 1319 and 1159 cm^{-1}, which are assigned to the C-O-C stretch vibrations in the β (1,4)-glycosidic linkage. The absorption band at 1105 cm^{-1} is related to the C-O group of secondary alcohols and ethers in the cellulose molecules. The vibrations at 1051 and 1020 cm^{-1} are typical for the β-(1,4)-glycosidic linkages [8, 20, 29]. Besides, a new strong peak appears at 1587 cm^{-1}, corresponding to the COO- stretching vibrations, and also at 1420 cm^{-1} representing the salts of carboxyl groups. These two peaks are absent in the FTIR spectrum of cellulose (Fig. 3). A similar result was also shown by other researchers. For example, Ahmed [9] for Baobab fruit shell and S. Sophonputtanaphoca [20] for pineapple leaves.

Figure 4 presents the XRD diffractogram of CMC from pineapple leaf waste. It can be seen that the cellulose has greater crystallinity as compared to CMC. Besides, fewer peaks were found for CMC in comparison with cellulose. It is notable that the characteristic peaks at 2θ=16.6°, 22.8°, and 35.4° for CMC are broader and the intensity was significantly reduced. This means that this CMC represents a more amorphous structure than cellulose. Note that the typical peaks at 2θ=16.6° and 35.4° for cellulose are not present in the CMC curve. This shows that the formation of CMC - a product of carboxymethylation - has reduced the crystallinity of the reaction system. Indeed, the estimated crystallinity index was 68.7 for cellulose and 26.7 for CMC. The CMC being more amorphous than cellulose proves a more disordered molecular arrangement of CMC as compared to isolated holocellulose. This disordered molecular arrangement may be related to the cleavage of hydrogen bonds in cellulose by carboxymethyl substitution.

Conclusions

The cellulose extraction from Vietnamese pineapple leaf waste was successfully performed. The maximum extraction yield was 55±1.75 wt.% by using 0.75 M NaOH at 90°C for 1.5 h, and by 5 M HNO_3 at 70°C for 5 h. The average diameter of extracted cellulose was in the range of 150-300 nm. Pure cellulose was converted to CMC by esterification. The results showed that cellulose size and its distribution have a strong influence on the effectiveness of the carboxymethylation reaction. The DS and yield of CMC increases with decreasing the size of cellulose in suspension. The obtained CMC had a degree of substitution (DS) of 2.3 and a yield of 136.6%.

The study shows the successful separation of cellulose from Vietnamese pineapple leaf waste and the high-efficiency conversion of it into CMC, which both have great significance in utilizing pineapple leaf waste to create high-value products that contribute to environmental protection.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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