

Study on extracting hemicellulose, cellulose, and carboxymethyl cellulose from Vietnamese rice straw waste

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Abstract:

Cellulose and hemicellulose were successfully extracted from Vietnamese rice straw waste. The maximum hemicellulose yield of the process was 22.60% with 1.5 M NaOH at 90°C for 1.5 h. The pure cellulose obtained from the rice straw was prepared by refluxing the rice straw powder with a 1.0 M HNO₃ solution at 90°C for 1.5 h. The Vietnamese rice straw cellulose was converted to carboxymethyl cellulose (CMC) by etherification. The extracted cellulose was soaked in a mixed solution of isopropyl alcohol and NaOH solution for 1.5 h. After that, it was reacted with monochloroacetic acid at 70°C for 1.5 h. The optimum conditions for carboxymethylation were 5 g cellulose, 4.0 g monochloroacetic acid, and 15 ml 25% w/v NaOH and the obtained product had a degree of substitution (DS) of 0.70.

Keywords: carboxymethyl cellulose, cellulose, hemicellulose, Vietnamese rice straw waste.

Classification number: 2.2

Introduction

Vietnam is an agricultural country with a large amount of rice straw waste amounting to 55-60 million tons annually. Rice straw contains about 35-40% dry weight of cellulose and 25-30% hemicellulose and 10-15% lignin [1, 2]. Therefore, the potential of cellulose and hemicellulose recovery from this waste is quite feasible. Recovering cellulose from rice straw waste will upgrade the rice value chain by adding value to by-product of rice production. To date, many works have mentioned problems with cellulose, hemicellulose and lignin recovery from rice straw by-products [3, 4]. For example, Sun, et al. [3] reported that a two-stage treatment of rice straw with 0.25 M NaOH at 55°C for 2 h followed by 0.0-5.0% H₂O₂ at 45°C for 12 h at pH 11.5. From there, 49.3-74.3% of the residual hemicelluloses was released compared to 16.6-25.1 wt.% of the weight of the initial dried rice straw powder. Lignin was also extracted from Vietnamese rice straw using a combination of ultrasound irradiation for 30 min and 2 M NaOH at 90°C for 1.5 h, which yielded a lignin separation of 84.7% of the residual lignin [4]. Fan, et al. [5] extracted cellulose from rice straw and further converted it into microcrystalline cellulose (MCC) in the presence of a hydrochloric acid aqueous solution and the cellulose content reached up to 92.4% MCC. Although, many efforts have been made to identify a suitable solution for cellulose extraction, the determination of a procedure for separating the biomass constituents efficiently is still a major obstacle to its utilization. Therefore, studies on the simultaneous extraction of cellulose and hemicellulose from this waste is essential and important. The purpose of this work is to confirm the potential of using Vietnamese rice straw waste as a raw material for industrial hemicellulose extraction and CMC production.

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Experimental

Materials and rice straw source

The main chemicals used in this study include monochloroacetic (MCA) (UK) 99.7%, acetic acid 99.9%, nitric acid 65%, and sodium hydroxyl 99.9% (Merck). The solvents include methanol 99.8%, ethanol 99.9%, isopropanol 99.7%, and acetone 99.8% (Merck).

The rice straw waste was collected from Vietnam. Rice straw samples were dried in an oven at 60°C for 24 h before being ground into particles of 1 mm diameter by using a grinding machine.

Preparation methods

Hemicellulose extraction from Vietnamese rice straw waste:

Hemicellulose was recovered from Vietnamese rice straw by alkaline extraction. Ten grams of dried rice straw powder were mixed with 250 ml of diluted x M NaOH ($x=0.50$ M, 1.00 M, 1.50 M, 2.00 M, 2.50 M) at 90°C for different periods of time ($t=60, 90, 120$ min) under continuous stirring. The dark slurry obtained was filtered and washed with 250 ml of distilled water to the recover solid part. The residual solid part was put into a clean Erlenmeyer flask for separation of the cellulose. The filtrate was acidified to pH 6 with 25% acetic acid. The hemicellulose was precipitated by using cold ethanol 96% (volume portion of filtrate to ethanol was 1:2). The mixture was soaked overnight to allow the hemicellulose to precipitate (no stirring) and settle to the bottom. The precipitate layer was carefully removed by vacuum filtration. The precipitate was washed 3 times with 70% ethanol solution. The obtained hemicellulose was dried at 40°C for 24 h. The dried hemicellulose was ground into a fine powder. The yield of the hemicellulose was gravimetrically determined and expressed as a weight of the extracted dried hemicellulose to 100 g of the dried rice straw used for extraction. This process was repeated 3 times.

The yield of the hemicellulose was determined by using the below equation:

$$H_H(\%) = \frac{m_H}{m_0} \times 100$$

where H_H is the yield of hemicellulose, m_H is the weight of obtained hemicellulose, and m_0 is the weight of initial dried rice straw powder.

Cellulose recovery from Vietnam's rice straw waste:

Determination of optimum HNO_3 concentration: the solid residual part of the above process was treated with 150 ml of y M HNO_3 ($y=0.75$ M, 1.00 M, 1.25 M, 1.50 M) and cooked at 90°C for 90 min. This mixture was then filtered

and washed with cold distilled water until the indicator paper did not change colour. The residue was dried in an oven at 60°C overnight until the weight was constant. Finally, the dried cellulose was ground and kept in a polyethylene bag for cellulose modification in the next process.

The yield of the cellulose extraction was determined by using the below equation:

$$H_C(\%) = \frac{m_c}{m_0} \times 100$$

where H_C is the yield of the cellulose extraction, m_c is the weight of the obtained cellulose, and m_0 is the weight of the initial dried rice straw powder.

Synthesis of CMC:

Five grams of cellulose extraction obtained from Vietnamese rice straw powder was added to 50 ml of isopropanol under continuous stirring for 30 min. Then, 15 ml of (15%, 20%, 25%, 30% w/v) NaOH was added dropwise into the mixture and further stirred for 1 h at room temperature. The carboxymethylation began when y grams of MCA ($y=1.0$ g, 2.0 g, 3.0 g, 4.0 g and 5.0 g) was added under continuous stirring for another 90 min at 70°C. The solid part was neutralized with acetic acid to pH=7 and washed three times by soaking in 20 ml of ethanol for 10 min to remove undesirable by-products. The obtained CMC was filtered and dried at 60°C until the weight was constant and it was kept in a dry place.

The yield of the CMC was determined by using the below equation [6]:

$$H_{CMC}(\%) = \frac{m_{CMC} - m_c}{m_c} \times 100$$

where H_{CMC} is the yield of the CMC, m_{CMC} is the weight of the obtained CMC, and m_c is the weight of the cellulose used to synthesis CMC.

Research methods

Infrared spectroscopy (FTIR):

FTIR spectra were recorded on an FT/IR-6300 spectrometer, with 32 scans and a resolution of 4 cm^{-1} in the wavenumber range of 600-4000 cm^{-1} .

The degree of substitution, DS_{rel} of the carboxyl group in the CMC can be determined with FTIR spectra by means of taking the ratio of the absorption spectra as shown in the below equation [7]:

$$DS_{rel}(\%) = \frac{A_{1593}}{A_{2918}} - B$$

where is A_{1593} is the absorbance at 1593 cm^{-1} , which is assigned to the stretching vibration of the carboxyl group

(COO⁻), A_{2918} is the absorbance at 2918 cm⁻¹, which is assigned to the stretching vibration of methine (C-H), and B is a numerical constant corresponding to the A_{1593}/A_{2918} ratio of the cellulose, which was found to be zero. A linear relationship between the absolute and relative values of the degree of substitution was proved by Pushpamalar as shown in the below equation:

$$DS_{abs} = 0.4523DS_{rel}$$

Viscosity measurement method:

The average molecular weight (M) of the polymers was determined by viscometric measurements using an Ubbelohde Capillary Viscometer. This value was calculated according to the Mark and Houwink-Sakurada equation:

$$[\eta] = K.M^\alpha$$

where $[\eta]$ (dl.g⁻¹) is the intrinsic viscosity and K and α are the characteristic constants for the used polymer-solvent systems. For CMC at room temperature (25°C), the values of the constants K and α are 7.3×10^{-3} (ml/g) and 0.93, respectively, in 6% NaOH solution [1, 8].

Results and discussion

Hemicellulose extraction

Effect of NaOH concentration on the yield of hemicellulose extraction:

The results presented in Fig. 1A indicated that the concentration of NaOH solution had a significant impact on the hemicellulose yield from Vietnamese rice straw waste. The maximum yield of hemicellulose was obtained at 1.5 M NaOH. These results indicated that at a low NaOH

concentration (0.75 M), a very low yield of hemicellulose is obtained (about 7.8%). Increasing the concentration of NaOH to 1.0 M and 1.5 M increases the yield of extracted hemicellulose to about 18.3 and 22.4%, respectively. This increase can be attributed to the fact that at high concentrations of NaOH, the ester bond cleavage between ferulic acid and hemicellulose increases. However, with further increase of the NaOH concentration to 2 M and 2.5 M, the yield of hemicellulose reduced to 20.3% and 19.1%, respectively. The reduction in the retained hemicellulose at high alkaline concentration was due to the degradation of hemicellulose [9, 10].

Effect of treatment time on the yield of hemicellulose extraction:

The yield of hemicellulose extraction at different extraction times is shown in Fig. 1B. The extraction time was maintained at 60, 90, 120, and 150 min for each extraction. The other extraction conditions, such as the ratio of water to rice straw powder, extraction temperature, and NaOH concentration were maintained at 25:1, 90°C, and 1.5 M, respectively. These results show that the yield of hemicellulose increased with extraction time and reached its highest value of 22.4% at treatment time of 90 min. However, further increases in extraction time to 120 min and 150 min resulted in a slight reduction in hemicellulose yield. This could be due to the partial degradation of hemicellulose [10]. Thus, the optimum time of extraction for the maximum yield of hemicellulose was found to be 90 min.

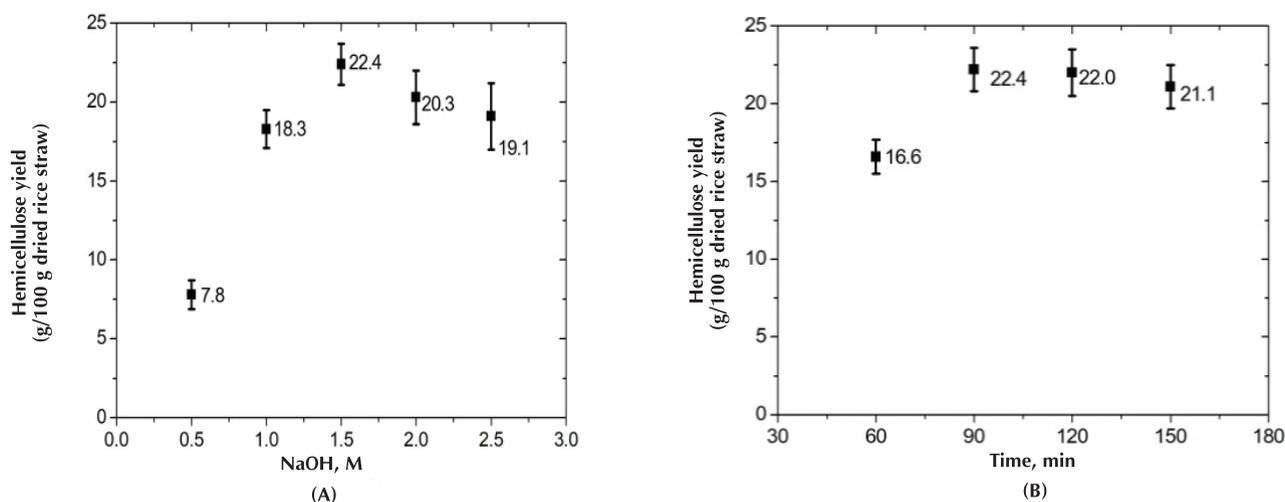


Fig. 1. Effect of (A) NaOH concentration during 90 min and (B) treatment time at 1.5 M NaOH on the yield of hemicellulose extraction.

Characterization of obtained hemicellulose:

The obtained hemicellulose was characterized by FTIR spectroscopy and the results are shown in Fig. 2.

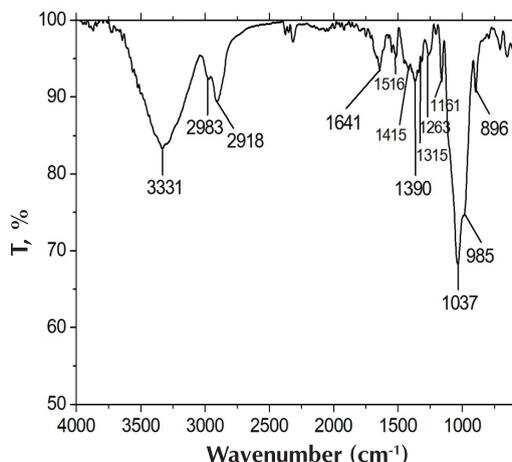


Fig. 2. FTIR spectroscopy of hemicellulose.

The peaks at 1415, 1390, 1315, 1263, 1161, 1037, 985, and 896 cm^{-1} are characteristic peaks of hemicellulose [11, 12]. A predominant absorption at 1037 cm^{-1} is due to the C-O-C stretching of glycosidic linkage of xylans [13]. A low intensity signal at 985 cm^{-1} also indicated the presence of arabinose units [14]. A peak at 896 cm^{-1} can be assigned to the β -(1,4)-glucosidic linkages between the sugar units in the hemicellulose polymers [15, 16]. The peak at 3331 cm^{-1} is represented by the OH stretching mode, while the peak at 2983 cm^{-1} is attributed to the stretching vibration of the CH_2 group. The peaks at 2918 cm^{-1} and 1315 cm^{-1} can be attributed to stretching and deformation vibrations of the C-H group in glucose unit. In the carbonyl stretching region, the peak at 1641 cm^{-1} is characteristic of absorbed water [16]. Furthermore, the peaks at 1390, 1263, and 1161 cm^{-1} represented C-H stretching and O-H or C-O bending vibrations. A very small peak at 1516 cm^{-1} is attributed to the aromatic skeletal vibration, implying the occurrence of a small amount of the lignin. The FTIR spectroscopy results are similar to other authors' results [4, 17].

Cellulose extraction

The process of cellulose recovery was conducted at various concentrations of HNO_3 solution to determine the optimum treatment conditions. The results are listed in Table 1.

Table 1. Cellulose yield with various HNO_3 concentrations.

Yield of cellulose	HNO_3, C_M			
	0.750	1.00	1.25	1.50
H_c (%)	28.50	32.50	30.13	26.20

In this experiment, HNO_3 was used to treat the solid residual part from the hemicellulose extraction process in the previous stage and the yield of cellulose reached the best result at HNO_3 1.00 M. It also can be seen in Table 1 that with the higher levels of HNO_3 concentration (1.25 M and 1.50 M), the cellulose yield decreases gradually. This might be due to the destruction of the cellulose structure at high concentrations of HNO_3 solution. In brief, the highest yield of the cellulose extraction is 32.50% at HNO_3 of 1.00 M.

Characterizations of cellulose by FTIR spectroscopy:

The FTIR spectroscopy of cellulose is displayed in Fig. 3. The band at 3313 cm^{-1} can be assigned to the OH stretching mode, while the signal observed at 2918 cm^{-1} and 1321 cm^{-1} is attributed to the stretching and deformation vibrations of the C-H groups in the glucose units. The band at 1159 cm^{-1} is assigned to -C-O-C stretch of the β (1,4)-glycosidic linkage is prominent for cellulose samples. The peak at 1105 cm^{-1} is assigned to -C-O group of secondary alcohols and ethers functions existing in the cellulose chain backbone. Lastly, the wavenumber range of about 895-1051 cm^{-1} is associated with the β -(4,1)-glycosidic linkages between the glucose units in cellulose [7]. FTIR spectroscopy of the cellulose extracted from Vietnamese rice straw waste is similar to the result of Vu, et al. [4]. In addition, the absence of peaks at 1600-1800 cm^{-1} , normally characterizing the C=O functional groups and the aromatic ring of hemicellulose and lignin molecules [18, 19], proved that hemicellulose and lignin were completely removed. This means that the recovered cellulose is of high purity. This pure cellulose was then used for CMC synthesis.

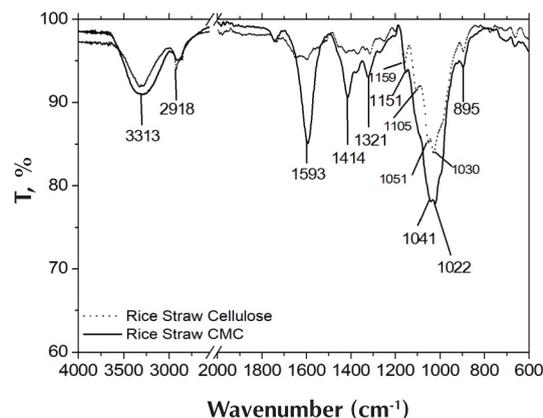


Fig. 3. FTIR spectroscopy of extracted cellulose and CMC.

CMC synthesis

Effect of NaOH concentration on DS and yield of CMC:

NaOH was used as an alkaline reagent to swell the cellulose chains, which provides the ability of substitution by sodium carboxymethyl groups in cellulose units. The DS of the CMC obtained with different concentrations of sodium hydroxide are shown in Table 2.

Table 2. The yield and DS of synthesized CMC with various NaOH concentrations.

	NaOH, %wt			
	15	20	25	30
H _{CMC} , %	32.1	52.3	63.8	56.6
DS	0.48	0.57	0.70	0.61

As shown in Table 2, the DS of the CMC increased with NaOH concentration and attained the highest DS of 0.70 at a NaOH concentration of 25% (w/v). However, upon further increase in the NaOH concentration, a reduction in DS value was observed. This can be explained by the degradation effect of high concentrations of the alkali reagent on CMC polymer chains. These results are similar to that of Xiao, et al. [17] and Sunardi, et al. [20].

Effect of MCA weight on DS and yield of CMC:

The effect of the MCA weight on the DS value was determined by changing the amount of MCA from 2.0 g to 5.0 g. The result is shown in Table 3, where the DS of the CMC increased with an increasing amount of MCA in a range of 2.0-4.0 g and then decreased slightly with further increase of the MCA amount. The highest DS value was observed at an MCA weight of 4.0 g. The reason behind this observation is that an undesired side reaction occurred that dominated CMC production with the greater availability of the MCA molecules. This range of DS value (from 0.48-0.70) is similar to another author's report [7] for bagasse waste. Table 3 also shows that the trend in the change of CMC yield is similar to that of the DS.

Table 3. The yield and DS of CMC synthesized with various amount of MCA.

	Amount of MCA, g			
	2.0	3.0	4.0	5.0
H _{CMC} , %	43.7	63.8	75.0	72.2
DS	0.50	0.61	0.70	0.67

The optimum condition for carboxymethylation was 5 g cellulose, 4.0 g chloroacetic acid, and 15 ml of 25% w/v NaOH solution. The obtained CMC had a DS of 0.70.

Characterizations of CMC:

The FTIR spectroscopy of the synthesized CMC is shown

in Fig. 3. The broad absorption peak at around 3313 cm⁻¹ in the spectra indicates the free OH stretching vibration as well as inter and intramolecular hydrogen bonds in the cellulose molecules. The band at 2918 cm⁻¹ is attributed to the stretching vibration of the C-H groups. The bands at 1041 cm⁻¹ and 1022 cm⁻¹ are relevant to the β-(1,4)-glycosidic linkages between the glucose units in cellulose [7, 18]. The presence of strong absorption bands at 1593 cm⁻¹ and 1414 cm⁻¹ are attributed to C=O stretching, which confirms the presence of the -COO and -COONa groups, indicating the successful etherification of cellulose. This peak does not exist in the FTIR spectroscopy of cellulose (Fig. 2). The above analysis results are similar to those of earlier publications of Xiao, et al. [17] for bagasse waste and Sunardi, et al. [20] for purun tikus.

The average molecular weight (M) is an important parameter of CMC. It affects swelling, the solubility of CMC in the water, its structure, and other properties. Fig. 4 displays the Mark and Houwink-Sakurada plots for synthesized CMC in 6% NaOH at 25°C.

Extrapolation of reduced viscosity [η_{red}] to zero concentration provides the intrinsic viscosity, [η], such that:

$$[\eta] = \lim_{C \rightarrow 0} \frac{\eta_{sp}}{C} = \lim_{C \rightarrow 0} \eta_{red}$$

where $\eta_r = t/t_0$, $\eta_{sp} = \eta_r - 1$, and t and t_0 are the flow time for the CMC solution and pure solvent, respectively.

The intrinsic viscosity as functions of average molecular weight are usually represented by the widely used Mark-Houwink-Sakurada empirical equation:

$$[\eta] = KM^\alpha$$

The Mark-Houwink constant, K , and α for CMC were 7.3×10^{-3} ml/g and 0.93, respectively [8].

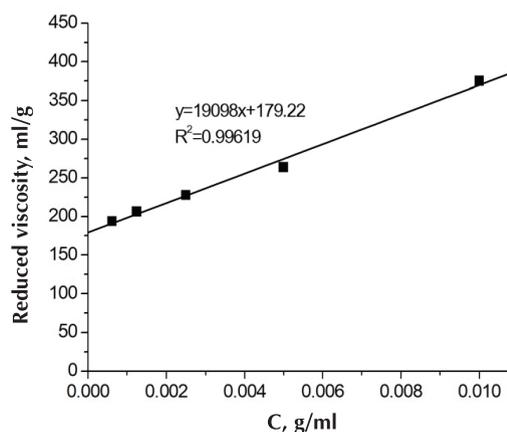


Fig. 4. Mark and Houwink-Sakurada plot for CMC in 0.1M NaOH at 25°C.

The $[\eta]$ values can be estimated from the intercept of the plot, where $[\eta]=179.22$ (ml/g). The average molecular weight of CMC is 52.535 ± 251 g/mol.

Conclusions

Hemicellulose was successfully extracted from Vietnamese rice straw waste with a maximum hemicellulose extraction yield of 22.4% with 1.5 M NaOH for 90 min at 90°C. The obtained hemicellulose was confirmed by FTIR spectra. Cellulose was successfully recovered from Vietnamese rice straw waste with yield of 32.5% at 1 M HNO₃ for 90 min at 90°C. CMC has been obtained by etherifying cellulose with monochloroacetic acid. The optimal condition for carboxymethylation was 5 g cellulose, 4.0 g chloroacetic acid, and 15 ml of 25% w/v NaOH solution. The optimised CMC products have a DS of 0.70. The chemical structure of the CMC was confirmed by FTIR spectra, which indicated the C=O group at 1593 cm⁻¹. These results show that the simultaneous separation of cellulose and hemicellulose from Vietnamese rice straw waste has great potential and feasibility from both economic and environmental viewpoints.

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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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