

Isolation and Characterization of Microcrystalline Cellulose (MCC) from Rice Husk (RH)

Zuliahani Ahmad^{1,a}, Nurul Nadhirah Rozaizan¹, Rozyanty Rahman², Ahmad Faiza Mohamad³ and Wan Izhan Nawawi Wan Ismail¹

¹Faculty of Applied Sciences, Universiti Teknologi Mara, 02600 Arau, Perlis, Malaysia

²School of Material Engineering, Universiti Malaysia Perlis, 02600 Arau, Perlis, Malaysia

³Faculty of Industrial Technology, Universiti Teknologi Mara, 40450 Shah Alam, Selangor, Malaysia

Abstract. Microcrystalline cellulose (MCC) was extracted from local agricultural residues, rice husk (RH). RH undergone alkaline, bleaching and acid hydrolysis treatments. Nitric acid was used in the hydrolysis process as a potential acid to replace strong acids such as hydrochloric and sulphuric acids. Hydrolysis of RH was carried out by using different molarity of nitric and hydrochloric acids (control). The properties of MCC obtained such as % yield, crystallinity index (CrI) and functional group present were studied. % yield shown a comparable result regardless of different acid used. Whilst Fourier transform infrared (FTIR) spectroscopy showed the progressive removal of non-cellulosic constituents. X-ray diffraction (XRD) analysis revealed that the crystallinity increased with successive treatments regardless different molarity and acids used. The results showed potential of nitric acid to be used in MCC isolation process.

1 Introduction

A lot of rice husk (RH) is generated during the milling process in rice milling industries. 78% of the paddy is received as bran, broken rice and rice. Other 22% of the paddy received as husk. Generally, RH made up of 33% cellulose, 26% hemicelluloses and 7% lignin [1]. Most of the RH widely used in building material, fertilizer, insulation material, oil spill absorbent, heat insulators as well as a fillers in composite preparation [2,3]. Nevertheless, large quantities of RH are usually burn in an open air, which creates environmental issues. Therefore, it is necessary to reduce environmental problem by fully utilize RH as cellulose derivatives source.

Cellulose is one of the biodegradable and renewable structural plant polymer which can be processed into whisker-like micro fibrils, microcrystalline cellulose (MCC), nanocrystalline cellulose (NCC) and many more [4,5]. It can be obtained from agricultural by-products such as cotton fiber, kenaf, hemp, corn stalk, bagasse and RH. MCC exhibits excellent properties in composite fabrication such as renewability, biodegradability, high surface area for bonding with resins [4-6].

The isolation technique is called hydrolysis method where the amorphous region of cellulosic material is disintegrated resulting with different degrees of crystallinity index. Many researchers reported on using strong minerals acids such as sulphuric acid (H₂SO₄) and hydrochloric acid (HCl) hydrolyzed the amorphous regions [6-7]. In this study, HNO₃ has been chosen as an alternative to the

^a Corresponding author : zuliahani@perlis.uitm.edu.my

strong acid because it is completely miscible with water, only small amounts needed to catalyze the hydrolysis reaction and less corrosive. The significance of this research is to encourage the utilization of MCC isolated from RH in composite preparation via acid hydrolysis using HNO₃ in comparison with HCl.

2 Materials

The rice husk was collected from BERNAS, a local rice mills in Simpang Empat, Perlis. NaOCl and NaOH were used as bleaching agents while HNO₃ and HCl were used for hydrolysis. All the chemicals was purchased from Fluka and was used without further purification.

2.1 Pre-treatment of RH

The alkaline treatment was performed to solubilise the hemicelluloses. 10 g of RH were refluxed with 120 mL of 1M NaOH at 80°C for 1h and 36 min. Following alkali treatment, the alkaline treated RH were refluxed with 140 mL of 5% sodium hypochlorite (NaOCl) at 80 °C for 18 min [8] in the bleaching process. The lignin become soluble in the alkaline medium and oxidized during bleaching.

2.2 Acid hydrolysis process

10 g of pre-treatment RH were treated with 61 mL of 1M and 2M HNO₃ at room temperature for 30 min under continuous stirring. It was washed repeatedly with distilled water until pH 7 is achieved. The resultant MCC were grounded into a fine powder by using rotary ball mill after the washing and drying process. The mass of dried RH were recorded and the same steps were used for 1M and 2M HCl.

2.3 Percentage yield

Percentage yield was calculated using the following equation:

$$\text{Percent yield (\%)} = \frac{\text{weight initial}}{\text{weight after hydrolysis}} \times 100\% \quad (1)$$

2.4 Fourier transform infrared (FTIR) spectroscopy

FTIR analysis was carried out using Perkin Elmer FTIR spectrometer 1650 with scanning ranges of 4000.0 cm⁻¹ to 400.0 cm⁻¹ at room temperature.

2.5 X-ray diffraction (XRD)

X-ray diffraction was performed to determine crystallinity index at different treatments. Diffraction patterns were obtained using a PANalytical X'PertPRO Multi-Purpose Diffractometer with Cu K α radiation. The crystallinity index (CrI) were calculated via Equation (2) [9]:

$$\text{CrI} = \left(\frac{I_{002} - I_{am}}{I_{002}} \right) \quad (2)$$

where I_{002} =intensity of the 002 peak (at about $2\theta=26$) I_{am} = intensity corresponds to the peak at about $2\theta = 8$.

3 Results and Discussion

3.1 Percentage yield

The yield of MCC sample was determined and the data was summarized in Table 1. Different molarity and acids were used to extract MCC from RH which were 1M HNO₃, 1M HCl, 2M HNO₃ and 2M HCl. 1M and 2M HCl gave 60.58% and 69.24% while 1M and 2M HNO₃ gave 80.64% and 83.26% of MCC yield respectively. Higher molarity of acids gave higher MCC yield. This is due to at higher acid concentration, more solubilised amorphous region of cellulose contribute to increase % of MCC yield. The percentage yield of MCC varied from sample to sample. Also, the difference was depending on the type of paddy, climatic, geographical conditions, sample preparation and method of analysis which could be the reason for this variation [7]. As a conclusion, 1M HNO₃ and 2M HNO₃ gave higher MCC yield as compared to HCl regardless of molarity.

Table 1. Yield of MCC sample at different molarity and acids used.

Samples	% Yield
1M HNO ₃	80.64
1M HCl	60.58
2M HNO ₃	83.26
2M HCl	69.24

3.2 FTIR

Figure 1 shows the FTIR spectra recorded for untreated RH and RH treated with different acids. All samples display two main absorbance regions at 2900-3500 cm⁻¹ and 450-1750 cm⁻¹ in line with Rosa et. al. [10] corresponding to OH bending, CH₂ groups, C-O-C stretching and C-H. The peak at 3350-3440 cm⁻¹, which was observed in all spectras, represents of the C-H and O-H groups. The absorption at region from 1637 until 1651 cm⁻¹ in all samples are corresponding to the absorption of water. According to Nurain Johar et. al. [7], this band is related to bending modes of water molecules due to a strong interaction between cellulose and water. This indicates that the cellulose components were present after the chemical treatment carried out on the rice husk fibres.

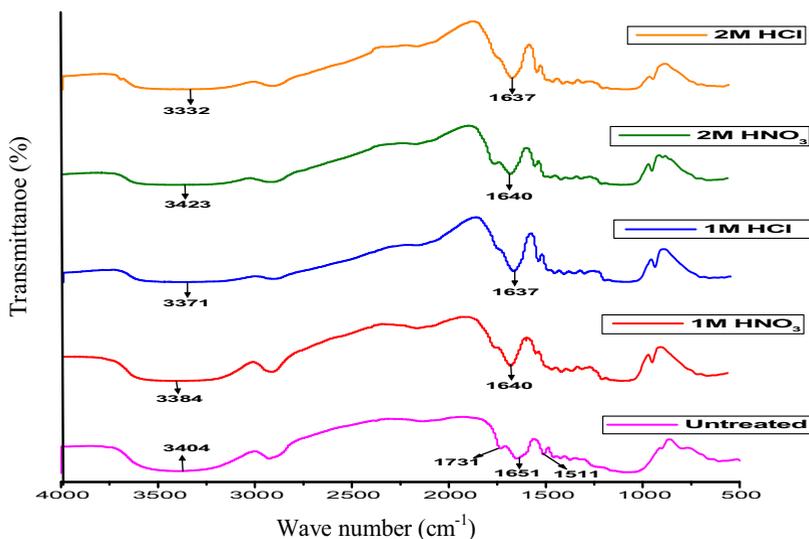


Figure 1. FTIR spectra of untreated rice husk and treated rice husk.

In addition, Rosa et. al. [10] found the absence of peaks located in the range of 1509-1609 cm^{-1} , which correspond to the C=C aromatic skeletal vibrations indicate the complete removal of lignin. The absorption band which corresponds to the acetyl or ester groups of hemicelluloses appears in the region 1700-1740 cm^{-1} as can be seen in untreated RH. Whilst the absence of this peak was found in treated RH indicates the removal of hemicelluloses was successfully done [10-11]. The peak located at 1049-1079 cm^{-1} was observed in five spectras referring to the C-H stretching vibration of C-O [12]. Based on FTIR spectras, lignin and hemicelluloses have been removed via bleaching treatment, alkali treatment and acid hydrolysis. In addition, no significance difference were observed in all samples at the cellulose region, which indicates the cellulose molecular structure remains unchanged from the treatment.

3.3 XRD

Figure 2 shows the diffraction patterns obtained for untreated and treated rice husk with different molarities and acid used. The peak at $2\theta = 16^\circ$, 22.5° and 36° is correspond to cellulose I region for all samples. This is supported by Rosa et al. [10] and Satyamurthy et al. [13] which there are typical of cellulose I with three well-defined crystalline peaks around $2\theta = 16^\circ$, 22.5° and 36° and indicated by the absence of the doublet located at 22.5° .

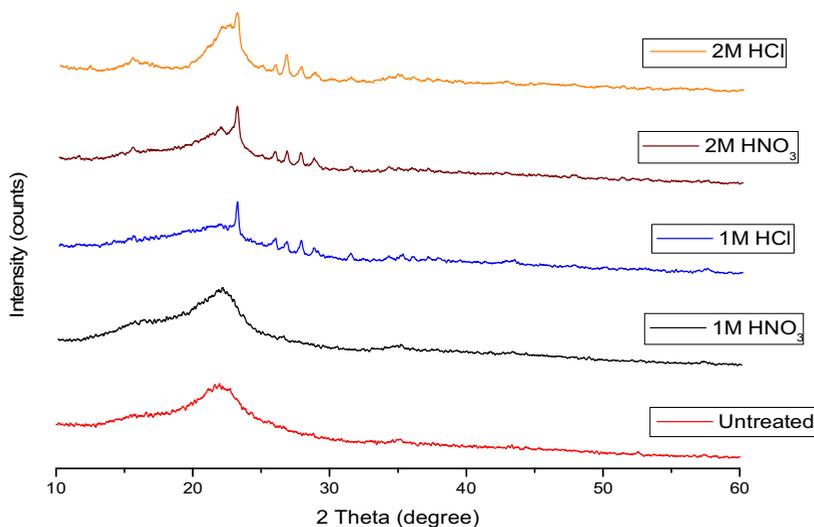


Figure 2. X-ray diffraction patterns of untreated and treated rice husk with different molarities.

The crystallinity index was determined for various samples and the results are summarized in Table 2. The crystallinity values of treated RH with 2M HNO₃ is 63.9% which is higher compared to others. It is due to the removal of amorphous regions of cellulose by acid hydrolysis, which prompts the hydrolytic cleavage of glycosidic bonds, finally releasing individual crystallites [6]. In comparison, 2M HNO₃ and 2M HCl shows comparable result and 1M HNO₃ gives higher percentage crystallinity compared to 1M HCl.

During the hydrolysis process, hydronium ions can penetrate the more accessible amorphous regions of cellulose and allow the hydrolytic cleavage of glycosidic bonds, which eventually releases individual crystallites [7]. In addition, during the preparation of cellulose the growth and realignment of monocrystals may occur in parallel and thus can improve the cellulose crystallinity [7]. An increase in crystallinity is related to increases in the rigidity of the cellulose structure, which can lead to higher tensile strength to fibers. This increase would be expected to enhance the mechanical properties of composites [10].

Table 2. Crystallinity index of treated and untreated RH.

Sample	Crystallinity (%)
Untreated RH	39.3
MCC-1M HNO ₃	42.0
MCC-1M HCl	37.0
MCC-2M HNO ₃	63.9
MCC-2M HCl	52.2

4 Conclusion

MCC has been successfully isolated from RH using chemical treatments involving alkali, bleaching and acid hydrolysis treatments. The results obtained from FTIR analysis confirmed that chemical structure of cellulosic fragments is not influenced by the acid hydrolysis. The crystallinity analysis shows that MCC give high crystallinity providing evidence that acid hydrolysis does not alter crystal structure from cellulose I of RH. The proposed HNO₃ gives comparable % yield and % crystallinity as compared to HCl making it a potential acid to be used in acid hydrolysis process.

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