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The Effect of Various Acids on Properties of Microcrystalline Cellulose (MCC) Extracted from Rice Husk (RH)

A S Nur Hanani[1], A Zuliahani[1], W I Nawawi[1], N Razif[1] and A R Rozyanty[2]

[1]Faculty of Applied Sciences, UniversitiTeknologi Mara (UiTM) Perlis, Malaysia
[2]School of Material Engineering, Universiti Malaysia Perlis, Malaysia

E-mail: nurhananiabuseman92@gmail.com,zuliahani@perlis.uitm.edu.my, wi_nawawi@perlis.uitm.edu.my, razifmn@perlis.uitm.edu.my, rozyanty@unimap.edu.my

Abstract. Microcrystalline cellulose (MCC) was successfully extracted from rice husk (RH) via acid hydrolysis process using nitric acid (HNO_3) in comparison with sulphuric acid (H_2SO_4) and hydrochloric acid (HCl). MCC-RH extracted using HNO_3 produced the highest percentage yield at 83.5% as compared to H_2SO_4 and HCl at 80.6% and 81.8% respectively. Analysis of Fourier Transform Infrared (FTIR) spectroscopy affirmed the successive elimination of non-cellulosic material from RH cellulose resulting highly purified MCC-RH. X-ray Diffraction (XRD) analysis showed MCC-RH treated with HCl gives the highest crystallinity index value of 54.2% while HNO_3 and H_2SO_4 produced comparable results of 52.4% and 49.7% respectively. The results indicate successive extraction of MCC-RH using HNO_3 that has great potential to replace strong acid such as H_2SO_4 and HCl in acid hydrolysis.

1. Introduction

MCC is a fine, white, odorless, crystalline powder and biodegradable material which composed of porous particles. It can be isolated from any material that contained high cellulose ranging from pure cellulose, commercial grade cellulose to lignocellulocis materials [1]. MCC is applied in pharmaceutical, cosmetics, food industries and acts as a water retainer, suspension stabilizer and reinforcement filler in composite preparation [2].

Generally, MCC is isolated from wood pulp and purified cotton linters via acid hydrolysis process [3]. Acid hydrolysis is commonly used to isolate MCC whereby the amorphous region of cellulose was disintegrated resulting a highly crystalline material with different degree of crystallinity such as MCC and nanocrytalline cellulose (NCC) [4]. Previous studies have been used strong acids such as H_2SO_4 and HCl to eliminate amorphous region during acid hydrolysis [1,2]. Lignin and hemicellulose were removed from RH undergone pre-treatments. Alkaline treatment was performed to solubilize hemicellulose while bleaching treatment was used to remove lignin [5].

Recent studies reported that MCC also can be obtained from the agricultural wastes such as coconut husk fibres, groundnut husk, rice straw and rice husk [6-9]. RH is an agricultural waste and a huge quantity of RH has been generated during the rice milling process. It was used as fertilizer, building material, heat insulator and produced RH ash for the production of silica [10]. However, only small amount of RH was recycled, whilst large quantities of RH are burn in open air which caused air pollution and resulted damage to the land.

RH is composed of 25-35% cellulose, 26-31% lignin and 18-21% hemicellulose [11]. In the rice husks cell wall, cellulose exists in a complex lignocellulosic matrix, surrounded by lignin and hemicellulose [12]. Since RH contains high composition of cellulose, it has great potential for producing MCC via acid hydrolysis process.

In this study, HNO_3 was used as an alternative to replace the usage of strong acids in the MCC isolation due to its miscibility in water and less corrosive characteristic. The significant of this study is to encourage the utilization of MCC isolated from RH via acid hydrolysis using HNO_3 in comparison with H_2SO_4 and HCl.

2. Materials

RH was collected from BERNAS, a local rice mill situated in Pendang, Kedah, Malaysia. Sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH) were used as bleaching agents while HNO_3, H_2SO_4 and HCl were used for acid hydrolysis process. All chemical were purchased from Fluka and were used without further purification.

3. Experimental Method

3.1. Alkaline and bleaching treatments of RH

The alkaline treatment was performed to solubilize hemicellulose. 10g of RH was reflux with 120 mL of 1M NaOH at 80 ℃ for 1 h and 30 min, and then washed with distilled water for removal of solubilized components until pH 7 was achieved. The alkaline treated RH then was undergone bleaching treatment and refluxed with 140 mL of 5% NaOCl at 80 ℃ for 18 min [13,14]. The cellulose obtained from the treated RH was filtered and rinsed several times using distilled water. It was dried in an oven at 70 ℃ until constant weight was achieved and the weight of the cellulose was recorded.

3.2. Acid hydrolysis

The obtained cellulose was hydrolyzed using 140 mL of 0.5M HNO_3 at a temperature of 80 ℃ for 30 min under continuous stirring. The MCC collected was filtered and rinsed with distilled water until pH 7 was achieved. It was then oven dried at 70 ℃ for 24 h. After constant weight was achieved, the weight of the MCC was recorded and it was grounded into fine powder using rotary ball mill. The same steps were repeated for 0.5M H_2SO_4 and 0.5M HCl [14].

3.3. Percentage yield

The percentage yield of MCC was calculated using the formula computed by recent studies [15].

$$\text{Percent yield of MCC (\%)} = \frac{A}{B}\ x\ 100\% \quad (1)$$

where,

A = weight of obtained MCC
B = weight of cellulose

3.4. Fourier Transform Insfrared (FTIR) spectroscopy

FTIR analysis of untreated RH and the obtained MCC was performed using Perkin Elmer FTIR spectrometer 1650 within the wavenumber range of 4000 cm^{-1} to 600 cm^{-1}. FTIR spectra of the samples were recorded using Nicolet's Avatar 360 at 32 scan with the spectra resolution of 4 cm^{-1}.

3.5. X-Ray Diffraction (XRD)

X-ray diffraction was performed to determine crystallinity index (CrI) of the obtained MCC using different acid used. Diffraction patterns were obtained using a PANalyticalX'PertPRO Multi-Purpose Diffractometer with Cu Kα radiation. CrI were calculated via:

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

where,

I_{002} = intensity of the 002 peak at about $2\theta = 22°$ and I_{am} is the intensity corresponds to the peak at about $2\theta = 18°$

4. Results and Discussions

4.1. Percentage yield of MCC

The percentage yield of MCC during acid hydrolysis process was determined and the data was summarized in Table 1. Different type of acid with same molarity was used in the isolation process of MCC from RH cellulose. The different acids used were HNO_3, H_2SO_4 and HCl with 0.5M concentration.

Table 1. Percentage Yield of MCC Isolated by Different Acids Used

MCC Samples	Percentage Yield [%]
0.5M HNO_3	83.5
0.5M H_2SO_4	80.6
0.5M HCl	81.8

Table 1 shows the highest percentage yield of MCC is obtained by 0.5M HNO_3 which produced 83.5% MCC. The MCC yield acquired from 0.5M H_2SO_4 and 0.5M HCl showed comparable result with 80.6% and 81.8% respectively. This is due to the ability HNO_3 to solubilize more amorphous region of cellulose that contribute to increase the percentage of MCC yield. Hydronium ions in mineral acids able to penetrate and remove the excessive amorphous regions of cellulose, resulting the increase in percentage yield of MCC [16]. In addition, the different in geographical conditions, climate, type of paddy used, sample preparation and method of analysis caused the variation of MCC yield [17].

4.2. Fourier Transform Infrared (FTIR) spectroscopy

Figure 1 shows the FTIR spectra of untreated RH, MCC-RH treated with 0.5M HNO_3, MCC-RH treated with 0.5M H_2SO_4 and MCC-RH treated with 0.5M HCl. For untreated RH, a broad absorption band appears at 3352 cm^{-1} is due to the stretching of –OH groups while the band at 2971 cm^{-1} corresponds to the C-H stretching vibrations. The band at 1636 cm^{-1} indicates the absorption of water and it is related to the bending modes of water molecules due to a strong interaction between cellulose and water [16,18]. All MCC-RH samples appeared at the same absorbance regions as untreated RH that represents –OH groups, C-H stretching and water absorption. Hence, it is affirmed that cellulose components are present in the MCC-RH samples and still remain even after being treated with several chemical treatments.

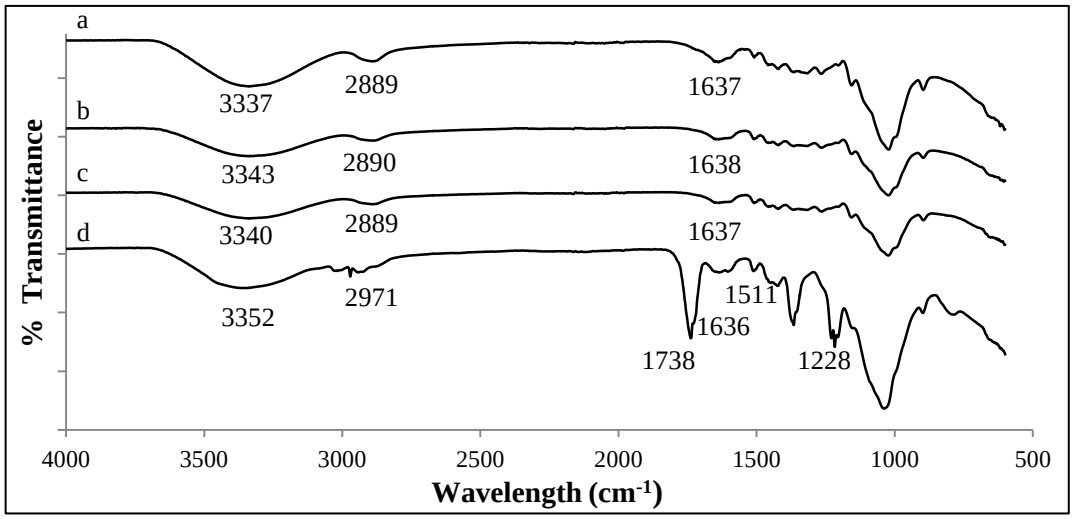

Figure 1. FTIR spectra of (a) MCC-RH treated with 0.5M HNO_3 (b) MCC-RH treated with 0.5M H_2SO_4 (c) MCC-RH treated with 0.5M HCl and (d) untreated RH

Besides, the absorption band located at 1738 cm^{-1} of untreated RH corresponds to the uronic ester and acetyl groups of hemicellulose. Based on previous study, this band normally appears at 1700 – 1740

cm^{-1} [19,20]. The absence of this band in all MCC-RH spectrums prove hemicellulose is successfully removed from RH cellulose during chemical treatments. A weak band at 1511 cm^{-1} and a strong band appeared at 1228 $cm^{-1}$for untreated RH spectrum are due to C=C aromatic skeletal vibration and C-O stretching of ester linkage of lignin. However, there is no absorption band is observed within the range of 1509 – 1609 cm^{-1} in all MCC-RH spectrum. According to previous work, absence of peaks located in range 1509 – 1609 cm^{-1} indicate complete removal of lignin [21]. Hence, lignin is successfully removed from RH cellulose during alkaline and bleaching treatments

4.3. X-Ray Diffraction (XRD)

The diffraction patterns of MCC-RH treated with 0.5M HCl, MCC-RH treated with 0.5M H_2SO_4, MCC-RH treated with 0.5M HNO_3 and untreated RH are presented in Figure 2. They are highly crystalline native cellulose I and no doublet presence at $2\theta = 22°$ [18]. The crystallinity index of the samples were calculated using Eq. 2. The highest crystallinity value is exhibits by 0.5M HCl at 54.2% as compared to HNO_3, H_2SO_4, and untreated RH at 52.4%, 49.7% and 44.1% respectively. The obtained result is in line with study carried out by Johar*et al* [16].

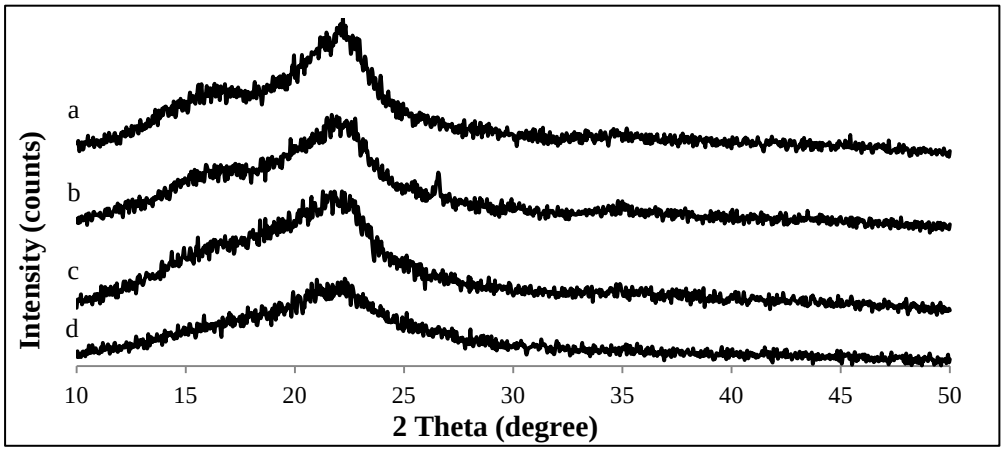

Figure 2. X-ray diffraction patterns of (a) MCC-RH treated with 0.5M HCl, (b) MCC-RH treated with 0.5M H_2SO_4, (c) MCC-RH treated with 0.5M HNO_3 and (d) untreated RH

The increase of crystallinity value is due the acid hydrolysis process that remove the amorphous regions of cellulose [14,18]. During this process, hydronium ions penetrate the accessible amorphous regions of cellulose and allow hydrolytic cleavage of glycosidic bonds which eventually releases individual crystallite [16]. Besides, the increase of cellulose crystallinity were expected to enhance rigidity, stiffness and strength. Thus, the increase of crystallinity value of the treated MCC-RH would be anticipated to provide good physical and mechanical properties of composites.

5. Conclusion

MCC-RH has been successfully extracted from RH using acid hydrolysis process via HNO_3, H_2SO_4 and HCl. The MCC-RH treated with 0.5M HNO_3 shows an optimum result in percentage yield of MCC and it is comparable H_2SO_4 and HCl. By reflecting FTIR results, chemical treatments that have been used in this study such as alkaline, bleaching and acid hydrolysis treatment were successfully removed hemicellulose, lignin and amorphous region from RH cellulose producing a highly crystalline MCC-RH. Whilst, crystallinity value of MCC-RH using HNO_3 is comparable with HCl and H_2SO_4. Thus, HNO_3 has great potential to replace H_2SO_4 and HCl during acid hydrolysis It is also affirmed that HNO_3 able to enhance the properties of MCC-RH in term of yield, purity and crystallinity.

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