EXTRACTION AND CHARACTERIZATION OF CELLULOSE AND MICROCRYSTALLINE CELLULOSE (MCC) FROM *Marantochloa cuspidata* LEAVES

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ABSTRACT

Microcrystalline cellulose (MCC) from *Marantochloa cuspidata* leaves were isolated and characterized. The physicochemical properties of the leaves were investigated. The functional groups analyses were carried out using Fourier Transform Infrared (FTIR) Spectroscopy and the crystalline structure were investigated using X-ray Diffraction (XRD). The morphology and thermal stabilities were investigated using Scanning Electron Microscope (SEM) and Thermo Gravimetric Analysis (TGA) respectively. The moisture content of the leaves was $7.16 \pm 0.12\%$. From FTIR, the spectra showed that the hemicelluloses and lignin were removed from the extracted cellulose. The peaks at 1733cm^{-1} and 1375cm^{-1} in the spectra of *M. cuspidata* leaves which were attributed to C = O stretching and C–O out-of plane stretching vibration of the hemicelluloses and lignin disappeared in the spectra of cellulose and MCC. XRD showed that the MCC produced is cellulose I polymorph. The SEM structures showed the microfibrils of the extracts to be crystallites. Cellulose and MCC were shown to have good thermal stability with a degradation temperature of 250°C and 260°C respectively.

Keywords: Microcrystalline cellulose, *Marantochloa cuspidata*, physicochemical properties FTIR, XRD, SEM, TGA.

INTRODUCTION

Cellulose is the most abundant polymer in nature, primarily composed of cell wall of plants, which gives support and rigidity to their structure. It is renewable and biodegradable. It exists in woods, cotton, hemp, husks, straws, sugarcane bagasse and many other plant based materials. Plant derived cellulose is usually found in a mixture with hemicellulose, lignin, pectin and other chemical substances while bacterial cellulose is quite pure, has a much higher water content and higher tensile strength due to higher chain lengths [1].

Native cellulose consists of amorphous and crystalline regions. The amorphous regions have lower density compared to the crystalline regions, so when cellulose fibres are subjected to harsh acid or alkali treatment, the amorphous regions breaks up, releasing the individual crystallites which may be microcrystalline cellulose or nano-crystalline cellulose depending on the condition of hydrolysis. These amorphous zones are regions in which the hydroxyl groups are more readily available for reaction than in the more highly ordered crystalline areas, which are less reactive [2]. Cellulose obtained from different origins and hydrolysis conditions differ in crystallinity, moisture content, surface area, porous structure, particle size and molecular weight [3] [4]. The ratio of amorphous cellulose to crystalline cellulose is called degree of crystallinity which depends upon the species and pre-treatment of the sample [5]. Crystalline cellulose is much stronger and stiffer, it is considered to be a

better reinforcing material than amorphous or the native cellulose itself [6].

Many researchers have extracted and studied the properties of crystallites such as microcrystalline cellulose (MCC) from various plant based materials. Thermally stable rice husk microcrystalline cellulose as adsorbent was studied [7]. Muli bamboo (*Melocanna baccifera*) as a new source of microcrystalline cellulose was investigated [8]. The cellulose and α -cellulose yields from original material were 62.5% and 54.8% respectively. The prepared MCC was characterized by FTIR, SEM, TGA and XRD. Results from these analyses indicate that the muli bamboo can be used as a green source of MCC. Physicochemical properties of microcrystalline cellulose from agricultural waste, orange mesocarp were investigated [9]. The results obtained showed that the yield of α -cellulose from the orange mesocarp was 62.5% and that of microcrystalline cellulose 25.3%. Microcrystalline cellulose from bagasse and rice straw using acid hydrolysis was investigated [10]. The different characteristics of prepared microcrystalline cellulose were determined and are found to be comparable with the characteristics of commercially available microcrystalline cellulose and the specifications given by Indian Standards. Cellulose and microcrystalline cellulose from rice straw and banana plant waste harvested in Egypt were investigated [11]. The results indicated higher α -cellulose content, 66.2%, in case of acid-alkaline treatment for rice straw compared to 64.7% in case of alkaline-acid treatment. MCC was prepared and characterized from tea waste by acid hydrolysis [12].

Microcrystalline cellulose (MCC) is a granular powder product with a size of about 10 μ m, obtained from the hydrolysis of the natural cellulose in an acidic medium, making the molecular weight reduced to a certain range. It is white, porous, tasteless, odourless, crystalline powder extracted from hydrolysis of native cellulose with diluted mineral acids or enzymolysis to produce alpha-cellulose, which is partially depolymerized and purified to obtain MCC. The MCC can be synthesized using mineral acids such as H₂SO₄, HCl and HBr as well as ionic liquids. The role of these reagents is to destroy the amorphous regions leaving the crystalline domain [13]. Mild acid gives microcrystalline cellulose (MCC) while strong acid treatment gives nanocrystalline cellulose. The results of FTIR, XRD and SEM analyses of microcrystalline cellulose (MCC) fibers from corncobs at various alkaline treatments were compared [14].

MCC is mainly used in the pharmaceutical industry as excipient, and in food industry as additives. The leaves of *Marantochloa cuspidata* are widely used in wrapping foods such as kola nut and moi-moi in African Communities.

MATERIALS AND METHODS

Raw Materials

The fresh leaves of *Marantochloa cuspidata* were harvested from a farmland in Nnong Eboh in Nsit Ibom L.G.A of Akwa Ibom State. It was washed, air-dried, ground and the ground sample was stored in an air-tight container prior its usage. The dried samples of the leaf are shown in Figure 1.

Figure 1: The dried leaves of *Marantochloa cuspidata*

Extraction of cellulose

Cellulose was prepared by the delignification process of sodium hypochlorite. 50g of the air-dried sample was measured and 1.2L of sodium hypochlorite was added. This was properly corked and left for 24hrs at room temperature, after which was filtered and

washed thoroughly with deionized water before 500mL of 18% NaOH and 500mL of 50w/w% hydrogen peroxide were added and left overnight. This was done to get rid of hemicelluloses and the residual lignin. Bleaching treatment further helps to remove most of the lignin.

Thereafter, the mixtures were filtered, washed with deionized water and was dried in an oven at a temperature of 80°C for an hour. The weight of the extracted cellulose and MCC were obtained, hence, the percentage yields calculated.

Extraction of microcrystalline cellulose from cellulose fibres

The cellulose obtained was acid hydrolyzed using 100mL of 25wt% H₂SO₄ at room temperature for 40 minutes.

FTIR Spectroscopy

This was carried out using FTIR spectroscopy (Perkin-Elmer, U.S.A). Infrared spectra of raw leaves, cellulose and microcrystalline cellulose from *Marantochloa cuspidata* between 4000cm⁻¹ to 600cm⁻¹ were recorded at a resolution of 4cm⁻¹.

X-ray Diffractometer

The X-ray diffraction patterns of raw leaves, cellulose and MCC were analyzed with a Siemens D 5000 Diffractometer, using CuK radiation ($\lambda=1.5418\text{\AA}$) at a 40KV and a current of 30mA, making measurements every 0.02° for 6s. The data was acquired in a 2 θ range from 2° to 60°.

The crystallinities of all samples were determined [15].

$$\text{Crystallinity} = \left[\frac{I_{\text{cry}} - I_{\text{am}}}{I_{\text{cry}}} \right] \times 100$$

where I_{am} represents the amorphous material.

Scanning Electron Microscope

The surface morphologies of the samples were determined using Scanning Electron Microscope (JOEL JSM 610 LA model) at magnification of 1000x /265. The differences in morphologies were obtained.

Determination of Thermal Property using TGA

A Mettler Toledo (model TGA/SDTA851e) thermogravimetric analyser was used to characterize the thermal stability of the samples. 2mg of each of them was placed in an aluminium pan and heated from 30 to 600°C at a heating rate of 10°C/min. All measurements were performed under a nitrogen atmosphere.

RESULTS AND DISCUSSION

The Percentage yields of extracted cellulose and MCC were 49% and 23% respectively. The results of

physicochemical analysis of *Marantochloa cuspidata* Leaves are shown in Table 1.

Table 1: Physicochemical Characteristics of *Marantochloa cuspidata* Leaves

Parameters	Results (%)
Moisture content	7.16 ±0.32
Cold water solubility	84.33 ±0.44
Hot water solubility	85.33 ±0.16
1% NaOH solubility	72.83 ±0.60
18% NaOH solubility	48.00 ±3.51
1:2 Ethanol : Benzene solubility	79.83 ±2.17

The molecular structures of the different samples were characterized by FTIR spectroscopy in the region of 4000 to 400 cm^{-1} (as shown in Figures 2a, b & c).

The prominent peak of 1733 cm^{-1} in the spectrum of raw *marantochloa cuspidata* leaves is attributed to the C=O stretching of acetyl group and uronic ester group of the hemicelluloses or the ester linkage of the carboxylic group of the ferulic and p-coumaric acids of lignin and/or hemicelluloses. However, this peak disappeared in the spectra of extracted cellulose and MCC and this is due to the removal of most of the hemicelluloses after alkali treatment.

FTIR analyses

Figure 2a: FTIR of raw sample from *Marantochloa cuspidata* leaf.

Figure 2b: FTIR of cellulose sample from *Marantochloa cuspidata* leaf.

Figure 2c: FTIR of MCC sample from *Marantochloa cuspidata* leaf.

X-ray Diffraction Analysis

The X-ray Diffraction results of raw leaves of *Marantochloa cuspidata*, cellulose and MCC are shown in Figures 3a, b & c.

Figure 3a: X-ray diffraction pattern of *Marantochloa cuspidata*.

Figure 3b: X-ray diffraction pattern of cellulose from *Marantochloa cuspidata*.

Figure 3c: X-ray diffraction pattern of microcrystalline cellulose.

The results of XRD of the leaves, cellulose and microcrystalline cellulose of *Marantochloa cuspidata* are shown in Figures 3a, b & c. These samples exhibited peaks around $2\theta=18^\circ$ and 24.5° while cellulose alone showed a peak around $2\theta = 35^\circ$, indicating a typical cellulose 1 structure. It can be seen that in all samples the peak around 24.5° was more prominent but more intense in MCC indicating higher crystallinity. The crystallinity of prepared raw leaves, cellulose and MCC were 25.15%, 28.63% and 35.2% respectively.

Morphological analysis

The electron micrographs of the leaves, cellulose and MCC from *Marantochloa cuspidata* are shown in Figures 4a, b & c at different magnifications.

Figure 4a: SEM Image of *Marantochloa cuspidata* leaves.

Figure 4b: SEM Image of cellulose from *Marantochloa cuspidata* leaves.

Figure 4c: SEM Image of Microcrystalline cellulose from *Marantochloa cuspidata* leaves.

Micrographs of the raw leaf samples (Figure 4a), shows the raw leaf with unexposed cellulose fibres at magnifications of 1000X while the micrographs

(Figure 4b), presents the treated samples with exposed microfibrils. The presence of the fibrils is an indication of the removal of the cementitious lignin material and the hemicellulose components of the native leaf sample. The fibrils are presented with a width to length ratio range between 80µm to 200µm (Figure 4c). The primary individual fibre presentation shows helicoidally structured strands which agrees with the natural ordered chains of cellulose. This structuring is as a result of the micro-ordered chains of pure native cellulose. This is investigative of the microcrystal nature of the extracted product. The microfibrils appear also as “spaghetti-like” clumps which is suggestive of their being crystallites.

Thermogravimetric analyses

The results of thermal analyses of raw leaves of *Marantochloa cuspidata*, cellulose and MCC are shown in Table 2, Figures 5a, b & c.

Table 2: Degradation temperature for *Marantochloa cuspidata* leaves, cellulose and MCC

Sample	1 st degradation temp./weight loss	2 nd degradation temp./weight loss
Raw leaves	275-430°C/65%	430-620°C/9%
Cellulose	250-340°C/80%	340-650°C/26%
MCC	260-390°C/92%	390-620°C/20%

An initial weight loss was observed from 50 to 100°C for all samples, caused by the gradual evaporation of residual moisture. The degradation behaviour of the MCC did not show significant difference from that of cellulose. Cellulose started to degrade at 250°C, while MCC started to degrade at 260°C and the raw leaves at 275°C.

Figure 5a: TGA/DTA curves of *Marantochloa cuspidata* Leaves.

Figure 5b: TGA/DTA curves of cellulose from *Marantochloa cuspidata* leaves.

Figure 5c: TGA/DTA curves of MCC from *Marantochloa cuspidata* leaves.

CONCLUSION

In this study, cellulose and microcrystalline cellulose were successfully extracted from *Marantochloa cuspidata* leaves. From XRD analysis, intense peak was observed for MCC, indicating a higher crystallinity while for TGA, the degradation temperatures for extracted cellulose and MCC were moderate, specifically below 400°C as required for suitability for biocomposite processing.

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