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Article *in* Der Pharma Chemica · November 2015

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Der Pharma Chemica, 2015, 7(11):1-7
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Extraction and characterization of microcrystalline cellulose from mango kernel: A waste management approach

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ABSTRACT

In this work, the compositional characteristics of mango kernel (MK) were established in terms of lignin, cellulose and hemicelluloses contents, to access its suitability for the extraction of microfibrils. Cellulose amounting to (25.2 %), hemicelluloses (34.06 %), lignin (15 %) were extracted. Microcrystalline cellulose (MCC) was extracted by hydrochloric acid hydrolysis of α-cellulose derived from the MK. The morphology of the MK-MCC was investigated using scanning electron microscope (SEM), and showed a compact structure and rough surface. X-ray diffraction (XRD) analysis showed that the MCC produced is of cellulose-1 polymorph, with 50.3% crystallinity. The physicochemical properties of the MCC suggests that the cellulose has good flow and compression properties, hence suitable for a range of applications such as green biodegradable nanocomposites reinforced with this form of cellulose and pharmaceutical tabletting.

Keywords: mango kernel; microcrystalline cellulose; morphology; physicochemical; crystallinity; pharmaceutical tabletting.

INTRODUCTION

Cellulose is the most abundant biopolymer on earth and the major component in the cell walls of wood and terrestrial plants. It is a linear homopolymer of glucose $(C_6H_6O_5)_n$ with repeating units consisting of D-glucose in a $^4C_1$ conformation, which is insoluble in water but degradable by microbial and fungal enzymes (Azubuike and Okhamafe, 2012; Li et al., 2012). Significant advances in cellulosic modifications (mechanically, chemically and even enzymatic) and the resultant production of derivatives with unique chemical, physical, physiological properties have dramatically increased interest in cellulose research over the past decade (Azubuike and Okhamafe 2012). This renewed focus on cellulose and its derivatives has resulted in the production of cellulose and its derivatives with varied physicochemical and functional properties (Azubuike et al., 2012).

Among other uses, cellulose is widely employed as a raw material to prepare a number of excipients (Azubuike and Okhamafe, 2012). Microcrystalline cellulose (MCC) is a fine white, odourless, crystalline powder, and a biodegradable material, which can be isolated from cellulose and used as a suspension stabilizer and a water retainer, in the cosmetics, food and pharmaceutical industries (Chuayjuljit et al., 2010; el-Sakhawy and Hassan, 2007). MCC produced from naturally occurring substance (cellulose) has proven to be stable, safe and

physiologically inert and has revolutionalized tabletting (Ejikeme, 2008). Microcrystalline cellulose can be made from any material that is high in cellulose ranging from pure cellulose, commercial grade cellulose and lignocellulosic materials (Ejikeme, 2008). Reports have shown that MCC can be produced from soybean, oath and rice hulls as well as sugar beet pulp, bagasse and corn cob, wheat, barley and oath straw, groundnut shell and rice husks, reed stalk, oil palm biomass, prickly pear fruit and cereal straw (Haafiz et al., 2013; Habibi et al., 2008; Hanna et al., 2000; Okhamafe et al, 1991; Okhamafe and Azubuike, 1994; Okhamafe et al., 1995; Proencal, 1999; Saleh and El-Ashmay, 1978;).

Mango kernel an agricultural waste abundantly found in Enugu metropolis, Enugu State, Nigeria. As a result of its abundance and easy accessibility, this material can be modified and applied as a cheap adsorbent for crude oil sorption in aqueous medium.

At the moment, to the best of our knowledge, there is no information on MCC derived from mango kernel. This study presents the preliminary information on the physicochemical, morphology and structural properties of MCC produced from mango kernel.

MATERIALS AND METHODS

2.1 Materials preparation

Mango kernels were collected from a mango plantation in Enugu State University of Science and Technology farms, Enugu, Enugu State, Nigeria. They were thoroughly washed with water to remove dust, fungus, foreign materials and water soluble components. The washed kernel were dried properly in sunlight for twelve hours (four hours for three days) and then left to dry at 65^{o}C in the oven. They were size reduced and sieved through No 30 British Standard Sieve (BSS Sieves). Reagents and chemicals used were from British Drug House (BDH) and include: Hydrochloric acid, sodium chlorite, potassium hydroxide, ethanol, chloroform, acetone and were used without further treatment.

2.2 Preparation of microcrystalline cellulose (MCC)

The extraction of α-cellulose was carried out with the methods of Sun et al., 2002. The dried and ground Mango Kernel (MK) was first extracted with chloroform-ethanol (2:1, v/v) in a Soxhlet extractor for 6 h so as to remove the extractable materials such as wax. The dewaxed Mango Kernel was delignified with two sequential processes as follows: the dewaxed sample (15 g) was soaked in distilled water (300 mL) and sodium chlorite (15 g, solid, 98%) was added into the suspension, the mixture was acidified to pH 4.0 with acetic acid and heated in water bath at 75 °C for 2 h, then sodium chlorite (7.5 g) was added again and the mixture was also acidified to pH 4.0 with acetic acid, heated in water bath at 75 °C for another 1 h. The residue was collected by filtration, subsequently washed with distilled water and 75% (v/v) ethanol, then oven dried at 55 °C for 16 h. The holocellulose obtained was soaked in distilled water with a solid-to-liquor ratio of 1:20 (g·mL-1), treated with KOH (1 mol) at 25 °C for 10 h. After filtration, the residue was washed with distilled water and 75% (v/v) ethanol and then oven dried at 55 °C for 16 h. After that, the dried filtration residue was subjected to further extraction with KOH (2 mol) at 25 °C for 10 h.
The α-cellulose powder obtained from mango kernel was hydrolysed at 105 ^{o}C with 2.5M hydrochloric acid under reflux for 15 min (Ejikeme, 2008) ; the solid-liquid ratio was 1:10. The hydrolysed cellulose was thoroughly washed with distilled water until neutral to litmus and then dried at 55^{o}C in an oven for 5 h.

2.3 X-ray diffraction (XRD)

The x-ray patterns were obtained using Phillips analytical diffractometer. The scanning region of the diffraction angle 2θ was from 5^{o} to 45^{o}. The crystallinity index (Ic) was calculated using Eq. (1).

$$\text{Crystallinity Index (Ic)} = \frac{I_{(002)} - I_{(am)} \times 100}{I_{(002)}} \quad (1)$$

Where I(002) is the maximum intensity of the diffraction from the 002 plane at 2θ = 21.5^{o}, I(am) is the intensity of the background scatter measured at 2θ = 18^{o}.

2.4 Scanning electron microscope
The morphology of the sample was examined using a Phenomprox electron microscope. Samples were prepared by attaching individual fibres with carbon tape and coated with gold to be conductive.

2.5 Physicochemical characterization
Bulk and tapped Density: A portion (20g) was accurately weighed and poured into a 100ml graduated cylinder. The cylinder was stoppered and the bulk volume V_o was recorded. For the tapped density, the cylinder was tapped on a hard surface to a constant volume (until no more settling of the material occured). The final constant volume (V_1) was noted to be the tapped volume.

The bulk and tapped densities D_{bulk} and D_{tap} were determined as follows;

$$D_{bulk} = W/V_o \quad (2)$$

$$D_{tap} = W/V_1 \quad (3)$$

True density: true density of the sample was determined by the liquid displacement method using xylene (a non-polar liquid) as the immersion fluid.

Carr's index and Hausner ratio: Carr's index and hausner ratio for cellulose were calculated from bulk and tapped densities using Eq. 4 and 5 (Ejikeme, 2008)

$$\text{Carr's Index} = \frac{D_{tap} - D_{bulk}}{D_{tap}} \quad (4)$$

$$\text{Hausner ratio} = \frac{D_{tap}}{D_{bulk}} \quad (5)$$

Moisture Content: A 2g each of the sorbents was measured into a wash glass. The samples will be placed in the oven for 24 hours at 105^{o}C. After 24 hours, the oven dried samples will be reweighed and the moisture content determined with the formula

$$Mc = [(W_o - W_1)/W_o] \times 100$$

where Mc is the moisture content; W_1 is the new weight after drying; W_o is the initial weight of the dry samples.
Porosity: the porosity of the materials was calculated using the formula for porosity.

$$\text{Porosity} = 1-(Dtap/Dtrue) \quad (6)$$

Determination of holocellulose content
Oven dried and extracted, EFB or Coir fibres were ground in a ball mill to pass a 100 micron mesh. Approximately 1 g of the powdered fibre was weighed out on a four figure balance and transferred to an Erlenmeyer flask to which was added 160 ml of deionised water, 0.5 ml glacial acetic acid and 10 ml of a 15% solution of sodium chlorite. A beaker was placed over the neck of the flask then flask and contents transferred to a water bath set at 75°C, and heated with occasional swirling for 1 h. Three further additions of 0.5 ml acetic acid and 10 ml sodium chlorite were made at hourly intervals. After heating for 4 h in total, the flask was transferred to an ice bath and the contents cooled to below 10°C. The delignified powder was filtered through a pre-weighed glass sinter crucible, washed with 200 ml of 95% ethanol, 200 ml ice cold deionised water and finally 200 ml acetone. The crucible and contents were oven dried overnight at 50°C, before weighing.

Determination of cellulose content
A sample (ca. 1 g) of dry delignified powder was weighed on a four figure balance, and transferred to a 250-ml Erlenmeyer flask, then 100 ml of a solution of 10% NaOH:15% $Na_2B_4O_7$ added. The flask was flushed with argon and the neck sealed with parafilm. The flask was maintained at a temperature of 20°C for 2 h, and contents agitated every 10 min during this period. The contents were then poured into a pre-weighed glass sinter crucible, washed

with 50 ml of the NaOH:$Na_2B_4O_7$ solution then several times with 100-ml portions of deionised water and finally 100 ml ethanol. The crucible and contents were oven dried overnight at 105°C, then weighed to give amount of cellulose. Weight of hemicellulose was calculated by subtracting weight of cellulose from weight of holocellulose.

Determination of lignin content

Approximately 1 g of powdered extracted fibre was weighed on a four figure balance, transferred to a 100-ml beaker, and 15 ml of a 6:1 v:v mixture of conc. sulphuric acid:phosphoric acid added. The mixture was stirred with a glass rod until gelatinised. The beakers were transferred to a water bath set at 35°C for 2 min, then added to 350 ml of deionised water in a 600-ml beaker. The contents of the beaker was then brought to the boil on a hotplate and left boiling for 20 min. The beaker was removed from the heat source and allowed to stand for 30 min, then the contents filtered through a pre-weighed oven dry glass filter pad, the lignin was washed with de-ionised water, oven dried at 105°C overnight and weighed.

RESULT AND DISCUSSION

Table 1: Chemical composition of mango kernel

Constituents	Dry weight %
Ash	3.88
Fat and wax	8.7
Lignin	15.0
Hemicelluloses	34.06
Cellulose	25.2

The constituents and chemical composition of mango kernel are presented in Table 1. Results from Table 1 showed that the main constituents of the kernel are hemicelluloses (34.06 %), cellulose (25.2 %), which are lower than hardwoods. An important amount of lignin (15.0 %) is similar to hardwoods. Fats (8.7%) was observed and the mineral constituents being the least (3.88%).

Table 2 physicochemical constituents of MK-MCC

Constituents	Dry weight
Moisture content (%)	5.2
Bulk density (g/cm3)	0.51
Tap density (g/cm3)	0.63
True density (g/cm3)	1.36
Porosity (%)	62.5
Carr's index	19.1
Hausner ratio	1.23

The physicochemical properties of the microcrystalline cellulose are reported in Table 2. The bulk density gives an estimate of the ability of the material to flow from a hopper into the die cavity of a rotary tablet compression machine, while tap density is a measure of how well a powder can be packed in a confined space on repeated tapping (Azubuike and Okhamafe, 2012). In general the higher the bulk and tapped densities, the better the potential for a material to flow and re-arrange under compression. This suggests that the microcrystalline cellulose sample may have good flow properties (Ejikeme, 2008). The density of the microcrystalline cellulose sample corresponds with those reported in previous studies (Azubuike and Okhamafe, 2012).

The Carr's compressibility and Hausner indices were estimated as the ratios of the difference between tapped and bulk density. The Carr's compressibility index gives an idea of how much a powder can be compressed, while Hausner index measures/estimates cohesion between particles; the value of both varies inversely with particle flow. For Carr's index, values in the ranges 5 to 10, 12 to 16, 18 to 21 and 23 to 28 indicate excellent, good, fair and poor flow properties of the material, respectively (Azubuike and Okhamafe, 2012). The index obtained in this study is in the range of 18 to 21, indicating fair flow property. On the other hand, for the Hausner ratio, a value less than 1.2 indicates good flowability whereas, a value of 1.5 and above suggests poor flow properties. In our study, the Hausner ratio, lie around the threshold of 1.20 (good flow property). Therefore, the value obtained for Hausner ratio, are consistent with that of Carr's index.

The moisture content of the cellulose in this work fall within the acceptable limits 5 and 7% (British Pharmacopoieia, 1993). The total porosity of a powder is made up of voids between the particles as well as pores within the particles. This as estimated for mango kernel MCC is high suggesting a poly-sized particles and easily compressible powder during tabletting. This also correlates the high tapped density obtained in this work.

3.1 X-ray diffraction

It is widely recognized that cellulose contains both crystalline and amorphous region (Klemm et al., 2005). The X-ray diffraction pattern of mango kernel MCC is presented in Fig 1. The crystallinity value recorded in this study is 50.3%. the diffractograms of the MCC exhibit diffraction pattern typical of cellulose I, with no cellulose II present, indicated by the absence of a doublet located at 22.6^o (Rosa et al., 2012; Satyamurthy et al., 2009). From Fig 1 it is clear that the diffraction peak located at 21.5^o is sharp, indicating a high crystallinity. An increase in crystallinity is related to increase in the rigidity of the cellulose structure, which can lead to a higher tensile strength of fibers. The crystallinity obtained in this study is moderate and high and is in agreement with results elsewhere (Haafiz et al., 2013).

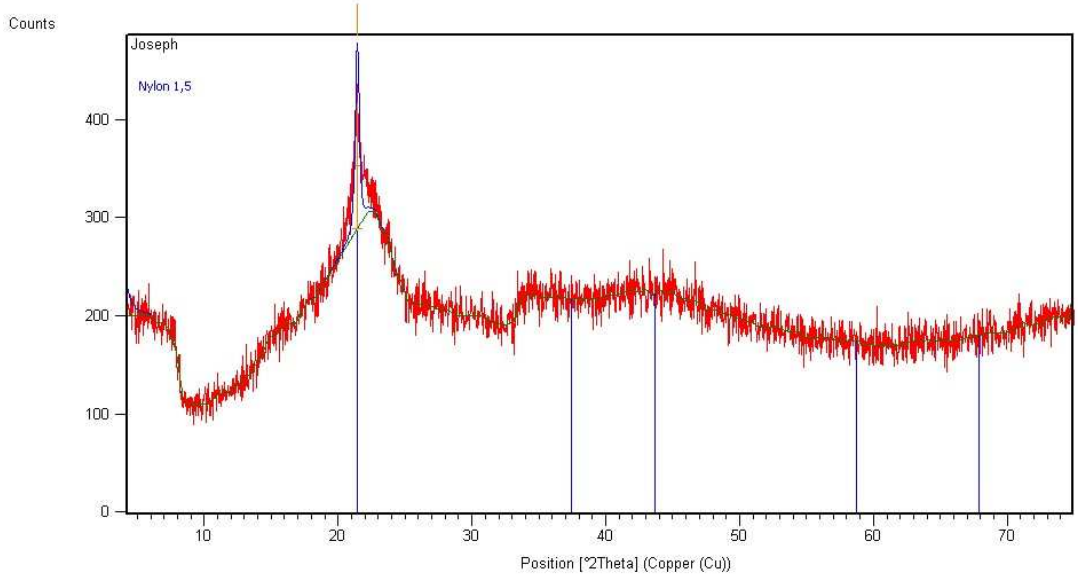

Figure 1: XRD pattern of MK-MCC

3.2 Morphological analysis

The morphology of MK-MCC was investigated using SEM and is presented in Fig. 2. The scanning electron micrograph shows that the morphology of the MK-MCC is rough with aggregates of irregular shaped fibrils. Cracks and damages were also observed at the surface and may be due to the removal of cementing materials (hemicelluloses and lignin) around the fibre bundles (Alemdar and Sain, 2008; Johar et al., 2012). The roughness of MCC favours the production of nanocrystals (Mathew et al., 2006). The morphology of MK-MCC are in agreement with findings elsewhere (Rosnah et al., 2009; Haafiz et al., 2013).

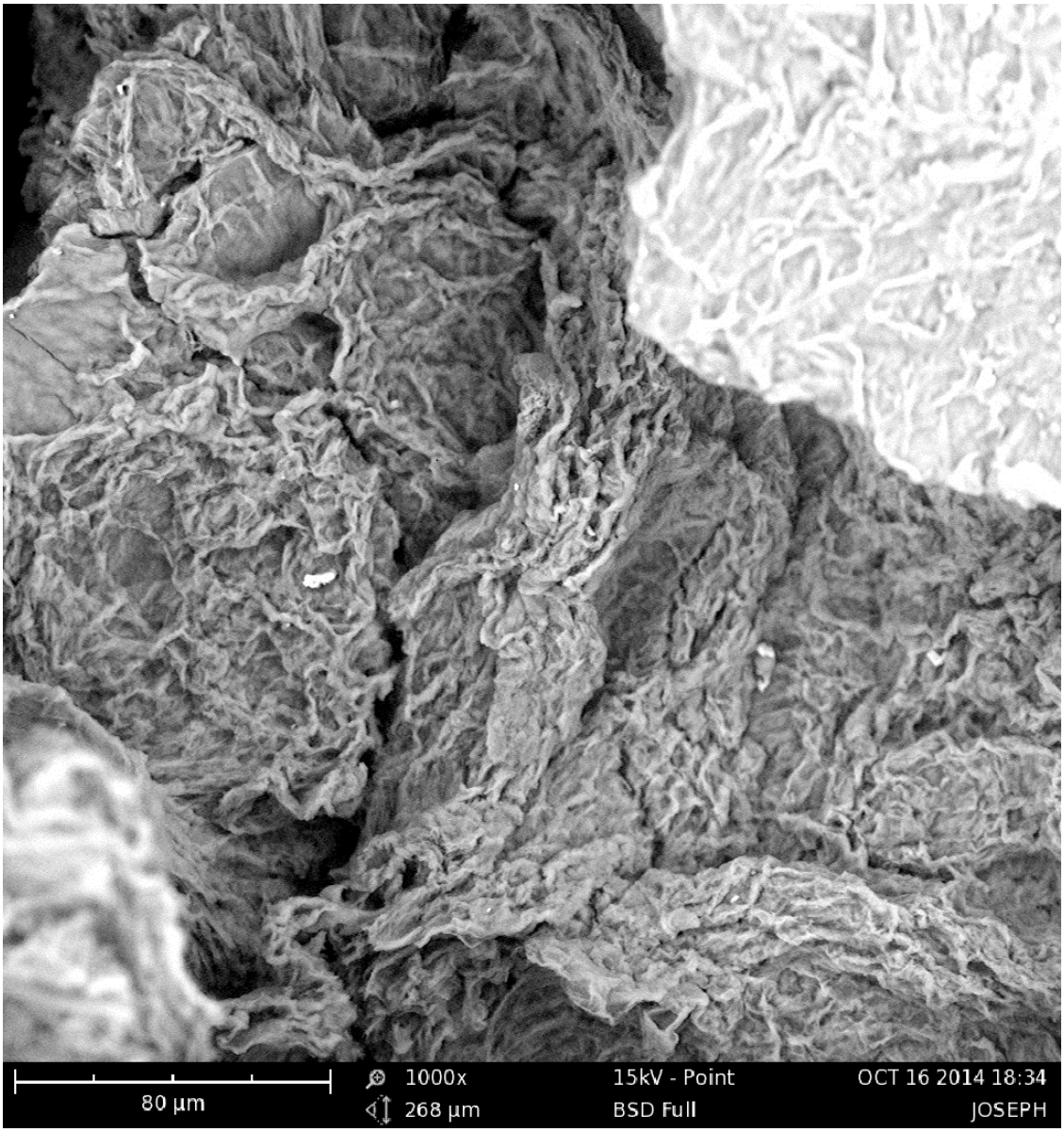

Fig. 2: SEM micrograph of MK-MCC

CONCLUSION

The microcrystalline cellulose has been successfully isolated from mango kernel an abundant biomass in Nigeria. The physicochemical analysis suggests that the cellulose has good flow and compression properties. SEM showed that the MK-MCC has a rough and compact structure. XRD analysis showed that MK-MCC consists of cellulose I polymorph with crystallinity index of 50.3. The high crystallinity suggests an enhanced mechanical property, thus its application in pharmaceutical tabletting, or as a reinforcing agent, considering that the material is cheap and available.

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