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Isolation and characterisation of cellulose nanocrystals obtained from sugarcane peel by SEM, XRD and CP/MAS ^{13}NMR

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Abstract

Sugarcane peels are agricultural waste materials discarded before taking the sugarcane juice. In the present study cellulose nanocrystal was isolated from sugarcane peel by sulphuric acid hydrolysis. Two pretreatments; alkaline treatment and bleaching with acidified sodium chlorite were applied. Sulphuric acid hydrolysis was performed at 45^0C for 45 mins using 64% concentration sulphuric acid. The resulting cellulose nanocrystal (CNC) of the sugarcane peel was characterised by studying the surface morphology using scanning electron microscope (SEM), SEM-EDX was used to identify the elemental composition of the sample. X-ray diffraction (XRD) was studied to identify the crystallinity nature of the CNC. CP/MAS ^{13}C solid- state NMR was used to evaluate the purity and molecular structure of the CNC. The SEM image of the nanocrystal showed that the fibre bundles were separated into individual CNC; with the size decreasing to a nanosize indicating an effective removal of the amorphous region. EDX showed the presence of 0.93 wt% of elemental sulphur impurity with the major components (carbon and oxygen). XRD diffraction pattern showed that the CNC retained the cellulose crystalline structure with crystallinity index of 99.22% and crystallite particle size dimension of 5.56 nm. The NMR spectra of the CNC revealed that all the signals were attributed to six carbon atoms of the glucose unit and the disappearance of several signals also indicated the disruption of the amorphous region. The results revealed effective synthesis of CNC from sugarcane peel, suggesting the leaching of the amorphous domain, apparent crystallinity and purity of the CNC. The cellulose nanocrystal obtained is considered to be a potential material for various industrial applications.

Keywords: sugarcane; cellulose nanocrystal; SEM; XRD; CP/MAS ^{13}C NMR

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1. Introduction

Over the past decades, there has been an increase in the development of nanotechnology from polymers. Cellulose, which is one of the most abundant polymers on the earth has attracted considerable attention in various applications in fields such as bio-composite, drug delivery, water treatment, food packaging, reinforcement, etc.(Sheltami *et al*., 2012; Julie *et al*., 2016). Cellulose is a semicrystalline long chain linear homopolymer, consisting of *D*-glucopyranose (glucose) molecules covalently linked through acetal functions formed by *β*-(1, 4)-glycosidic bonds (Flauzino, 2017). This natural polymer is the most obtainable on the earth and it is a vital physical constituent of the cell wall of several plants. Cellulose can be found in a wide range of living species, such as plant algae, fungi, bacteria, and tunicates. Naturally, cellulose is a tough, fibrous, and water-insoluble polymer and it plays an important role in sustaining the structure of plant cell walls. Moreover, it is a biodegradable, biocompatible, and renewable natural polymer, hence it is considered an alternative to non-degradable fossil fuel-based polymers (Johnsy and Sabapathi, 2015). Microfibrils are formed together from group of cellulose chains which are bundled together to form cellulose fibres. The long-chain cellulose polymers are bounded together by hydrogen and van der Waals bonds, which leads the cellulose to be packed into microfibrils.Natural fibres comprise majorly of cellulose, lignin, and hemicellulose and also include little amount of pectin, colourant and extracts. Enzymes biosynthesized cellulose chains are placed in a regular pattern and are totalled to form microfibrils. The microfibrils further totalled on the macroscale to produce fibres. The natural fibres behave as composite materials, accumulating in a primarily lignin matrix (Charreau *et al*., 2013).Nanomaterials from cellulose are known for their sustainability and are renewable. They have unique properties such as reduced toxicity, low density, low heat expansion, high aspect ratio, excellent mechanical properties, hydroxyl groups (-OH) on the surfaces that could be readily chemically functionalized (Anuj *et al*., 2014). Nanocrystalline cellulose (NCC) obtained from sulphuric acid hydrolysis of cellulose fibres, has been found as a new group of nanomaterials. Compared to cellulose fibres, nanocrystalline cellulose possesses many advantages, such as nanoscale dimension, high specific strength and modulus, high surface area, unique optical properties, etc.(Ng *et al*., 2015; Habibi *et al*.,2010). The synthesis of cellulose nanocrystals(CNCs) from cellulosic fibers often comprises of an acid-induced destructive method, including diffusion of acid molecules into cellulose fibres and cleavage of glycosidic bonds. The steps involved in acid hydrolysis are centrifugation, dialysis and ultrasonication. Several concentrated acids have been revealed to successfully degrade non-crystalline domains of cellulose fibres to release crystalline cellulosic nanoparticles, such as sulphuric acid, hydrochloric acid, phosphoric acid, hydrobromic acid and nitric acids, and a mixture composed of hydrochloric and organic acids (Habibi *et al*., 2010). Sulphuric acid (H_2SO_4) is the most common acid for nanocellulose preparation through chemical hydrolysis. There is one general method to produce CNC from sulfuric acid which is by using a 64 wt.% sulphuric acid solution at 45°C for 45–60 min with constant stirring, then stopping the suspension with 10-fold deionized water, the CNC suspension is concentrated through centrifugation and dialysis against deionized water until constant neutral pH is achieved, individualised crystals are achieved from repeated sonication (Dong *et al*., 1998). This study aims at isolating cellulose nanocrystals from a renewable, low cost, sustainable and underutilized raw material, sugarcane peel; no study has been reported on the isolation of cellulose nanocrystals from sugarcane peel. The resultant nanocrystals were characterised by SEM, XRD and NMR. The SEM instrument was used to determine the morphology of the sample. XRD was used to identify the crystallinity of the material while the nuclear magnetic resonance spectroscopy was used to evaluate the purity and molecular structure of the compounds. These techniques were used to investigate the potential use of cellulose nanocrystals isolated from sugarcane peel with a view to using them for various industrial applications.

2 Experimental

2.1. Materials and methods

Sugarcane peels (SP) used in this study were collected from different sugar cane farms at Papalanto and Sagamu areas in Ogun State, Nigeria. The sample was dried in sunlight for days, ground and sieved with a 30 mesh sieve. The agro-waste was preserved at 25^0C in a tight polyethylene bag. The chemicals used were: toluene, ethanol,

sodium hydroxide, sodium chlorite, acetic acid and sulphuric acid. All the reagents were purchased from Sigma Aldrich and Merck South Africa, they are all of analytical grade. All experiments and solutions were prepared ultra-pure water (Millipore Milli-Q UF Plus).

2.2. Isolation of chemically purified cellulose

Chemically purified cellulose (CPC) from sugarcane peel was isolated according to the previously reported methods with minor modifications (Lu and Hseih, 2012; Rahimi *et al*., 2016; Shaheen and Emam, 2018; Anuj *et al.,* 2014; Abe *et al*., 2007; Abe and Yano, 2009). The peel of sugarcane was prepared by washing with warm water, followed by sun drying. The clean dried sample was milled and allowed to pass through a 30 mesh screen. The sugarcane peel (30 g) was extracted with 2:1 v/v toluene and ethanol mixture for 6 h to remove wax, oil and pigments and then allowed to dry in an oven at 60°C for 16 h. The dewaxed fibre was successively treated with 300 mL water at 55°C, to remove water-soluble components with the residue being filtered and washed until neutral pH. The sample was then dried in an oven at 60°C for 16 h. The dewaxed sample was soaked in 50 g/L of 5% sodium hydroxide solution at 25°C for 24 h and heated at 90°C for 2 h to remove hemicellulose and silica. This was washed with copious amount of distilled water until the filtrate became neutral, followed by drying at 50°C for 16 h. The residual alkaline treated sample was then delignified using 2.5 % w/v of acidified sodium chlorite with pH adjusted to 4 with acetic acid using material to liquor ratio 1:20 for 4 h at pH 4.5 and 100°C. The delignified cellulose was, thereafter, washed with water to remove the excess/unreacted chemicals and dried in the oven at 50°C for 16 h. Finally, the product (chemically purified cellulose CPC) was stored in an air tight container.

2.3. Synthesis of cellulose nanocrystals

Chemically purified cellulose(α-cellulose) produced from peel of sugarcane was synthesised into cellulose nanocrystal (CNC) by acid-hydrolysis, according to the method adopted (Ilyas *et al*., 2018; Naduparambath *et al*., 2018; Rahimi *et al*., 2016; Anuj *et al*., 2014; Lu and Hseih, 2012) with little modifications. The cellulose isolated from sugarcane peel was separately hydrolysed with 64 wt.% sulphuric acid at a 10 mL/g acid-to-cellulose ratio at a temperature of 45°C for 45 minutes with vigorous mechanical stirring. Reaction of hydrolysis was stopped by diluting with 10-fold ice water. The resultant cellulose nanocrystal gel was centrifuged at 45000 rpm for 30 minutes to concentrate the cellulose nanocrystal and to remove excess aqueous acid, the filtrate was then decanted. The resultant precipitate was dialysed with cellulose dialysis membranes of 12–14 kDa molecular weight cut off (Sigma –Aldrich, South Africa) against ultra-pure water (Millipore Milli-Q UF Plus) until reaching neutral pH (pH 6-7). The suspension was sonicated at an amplitude of 40% in an ice bath to disrupt solid aggregates and avoid overheating. The resultant CNC suspension was freeze-dried (–47°C, 0.2 mbar). The dried sample was stored in an air tight container for characterisation.
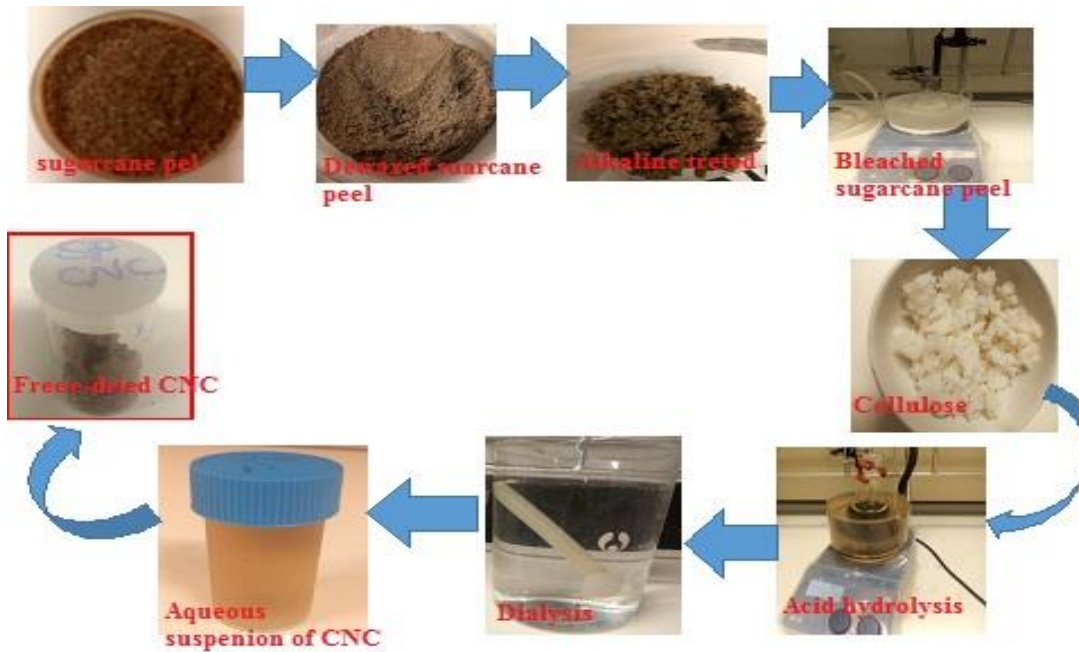
Fig. 1. Schematic representation of the preparation of cellulose nanocrystals from sugarcane peel

3. Characterisation

3.1 Analysis of chemical composition

The chemical composition of sugarcane peel was determined according to the method by Ayeni *et al.* (2015). The raw fibre, alkali-treated fibre and the bleached fibre were measured at different stages of treatment. The percentage extractives (wax), percentage hollocellulose, percentage lignin and percentage cellulose were determined.

3.2. High resolution scanning electron microscopy (HRSEM)

HRSEM is an instrument used for observing surface morphology of materials at a very small scale such as nanometer and micrometer. The samples were prepared by coating with carbon to make SEM work conductive; Emitech K950X Carbon evaporator was used for the coating process. HRSEM produces a beam of electrons that hits the specimen resulting in the emission of X-rays. The electron recorder takes up the rebounding electrons. The information from the electron recorder is translated onto a screen as three dimensional images. Metal samples can be studied directly while a non-conducting material must undergo a pre-preparation. Apart from images, HRSEM can also use energy dispersive X-ray spectroscopy (EDX) to determine the elemental composition and elemental mapping. In this study, AURIGA Field Emission High Resolution Scanning Electron Microscope was used to analyse the surface morphology of the untreated, treated and the nanocrystal. The sample images from HRSEM were taken at different magnification.

3.7. X-ray diffraction (XRD) spectroscopy

X-ray diffraction (XRD) is a technique used to identify the crystalline nature of a material, which could be mineral, organic or inorganic. In this study, the analysis was carried out to check the crystalline nature of the raw, CPC and CNC samples. Also, it is used to check the particle sizes of the untreated and treated samples. X-ray diffraction is based on the principle of bombarding material with accelerated electrons which invariably leads to the

dislodgement of inner shell electron of the material, hence generating X-rays in relation to the rotating angle of the sample and the detector. For this research, X-ray was carried out using Philips X-pert MPD X-ray diffractometer with Cu-K radiation operated at 40 kV and 40 Ma. The sample was scanned over a range of 5° to 70° 2θ with the count step size set at 0.5 seconds per step/0.05 step size. The crystallinity index (C_I) was calculated from the maximum intensity of the principle peak of 200 (I_{002}, 2θ= 22.9°) and the intensity of diffraction of 110 peaks (I_{am}, 2θ=16°) using the Segal method ((Azubuike et al., 2012; Seagal et al., 1959).

I_{002} represents both crystalline and amorphous material, whereas I_{am} represents the amorphous material.

$$C_I (\%) = \left(1 - \frac{I_{am} \times 100)}{I_{002}}\right.$$

3.4. Nuclear magnetic resonance (NMR) spectroscopy

The nuclear magnetic resonance spectroscopy is a technique used to evaluate the purity and molecular structure of compounds. The NMR technique reads into the magnetic properties of atomic nuclei. If an atom in a molecule is surrounded by an intra-molecular magnetic field, the resonance frequency of the atom changes, thus giving insight to the electronic structure of the molecule. Samples for NMR can be solid (solid NMR) or liquid (liquid NMR). In this study, solid NMR technique was used to study the carbon group. For solid NMR, 20 mg of nanocrystals was dissolved in 500 µL. The ^{13}C CPMAS spectra were recorded on an 11.4 Tesla Bruker Avance III HD NMR spectrometer, operating at frequencies of 500 MHz (1H) and 125 MHz (^{13}C). Magic angle spinning (MAS) frequency was 10 kHz for all experiments. The cellulose nanocrystals were packed into standard zirconia 4 mm rotors (Bruker). The standard CP sequence in the Bruker pulse programme library was used with 1H 90° pulse length 2.5 µs, contact time 1.5 ms, for 1500 to 3000 scans. During acquisition, SPINAL64 decoupling at field strength 100 kHz was applied on 1H. Chemical shifts were referenced to external adamantane, using the downfield signal at 38.48 ppm relative to TMS (^{13}C).

4. Results and discussion

4.1. Chemical composition

The chemical composition of the sugarcane peel is shown in Table 1. The result revealed that the sugarcane peel fibre consisted of 7.15±0.01% cellulose, 27.515±0.015% hemicellulose, 47.725±0.025% lignin and 17.585±0.055% wax. The percentage cellulose yield of the sugarcane peel was low as compared to the values reported in several studies on sugarcane bagasse namely 35.28±1.2%, 37%, 39%, 26-47%, 43% and 49% respectively (Ayeni *et al*., 2015; Bon, 2007; Aguilar *et al*.,1989; Paturau, 1989; Klinke, 2007 and Mesa *et al*., 2010).Moreso, this research has not been reported elsewhere. Hemicellulose was removed by alkaline treatment. The value obtained for lignin was expected since sugarcane peel has high stiffness. Lignin lend rigidity and do not rot, rather they display strength to natural fibres (Gilberto *et al*., 2010). The removal of lignin was carried out by bleaching treatment with acidified sodium chlorite. The removal of hemicellulose and lignin from sugarcane peel affected the cleavage of the ester-linked substance of hemicellulose, thereby increasing the surface area of the sugarcane fibre and making polysaccharides more susceptible to acid hydrolysis. The modifications of chemical composition of sugarcane peel fibre after all treatment gave rise to a better crystalline degree of cellulose, and thus improved the strength and thermal properties of the fibre (Ilyas *et al*., 2018; Alemdar and Sain, 2008).

Table 1. Chemical composition of raw, chemically purified cellulose and cellulose nanocrystal of sugarcane peel

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Wax (%)
Sugarcane peel	7.15±0.01	27.515±0.015	47.725±0.025	17.585±0.055

4.2. Scanning electron microscopy (SEM) analysis

The smooth surface of the untreated sample of the sugarcane peel is due to the presence of some non-fibrous components in the fibre surface such as lignin, hemicellulose, wax, pectin, oil etc., Fig. 2a and b show the SEM images of the raw sample and the cellulose. On subsequent treatment with alkaline and bleaching with acidified sodium chlorite, it was evident that hemicellulose and lignin were removed as revealed by Ilyas *et al*. (2018), Arup and Debabrata (2011). The amorphous region of the lignocellulose material was removed, the fibre bundles were separated into individual cellulose nanocrystals.

The alkaline treatment revealed that the hemicellulose was hydrolysed and became water soluble, the fibrils were defibrillated. After the chemical treatment of the raw fibre, a narrow fibril and reticular structure of the fibre which is the chemically purified cellulose was seen, indicating that the procedure of purifying and bleaching did not completely break the cellulose structure and remove impurities. The surface morphology of the raw samples was different from that of the CPC with a decrease in diameter which may have ensued from the removal of lignin, hemicellulose and other non-cellulosic constituents (Adewuyi and Vargas, 2016; Chen *et al*., 2011).

More so, the surface of CPC also presented a lump like structure, which may be due to the strong intra-molecular hydrogen bonds that occurred in the molecule; also the smooth surface of the nanocrystals revealed that the addition of sulphuric acid into cellulose units of the CPC may have narrowed the production of the intramolecular hydrogen bonds (Adewuyi and Vargas, 2016). The features of the cellulose nanocrystal in the sugarcane peel, showed that there was a reduction in the fibrillar structure size and intermittent breakdown in fibrillar structure into individualised fibrils. Fig. 2c and d represents the freeze dried cellulose nanocrystal, the structure of the cellulose was absolutely shattered and the size was considerably reduced to nanosize as pointed out by Hongija *et al*. (2013).
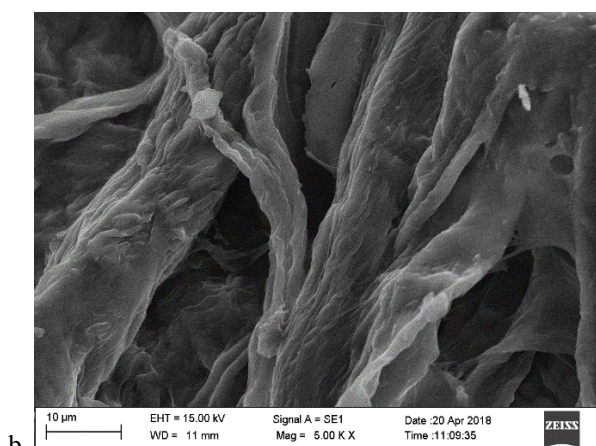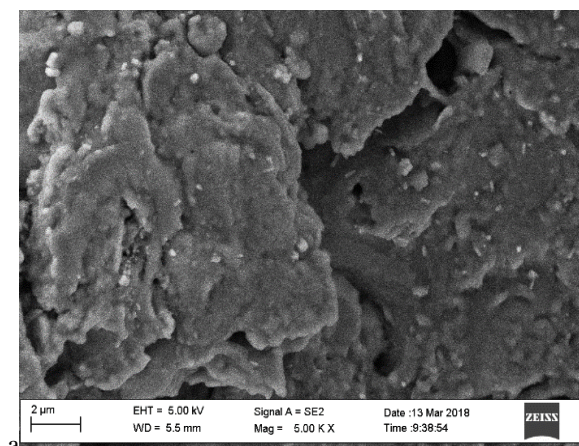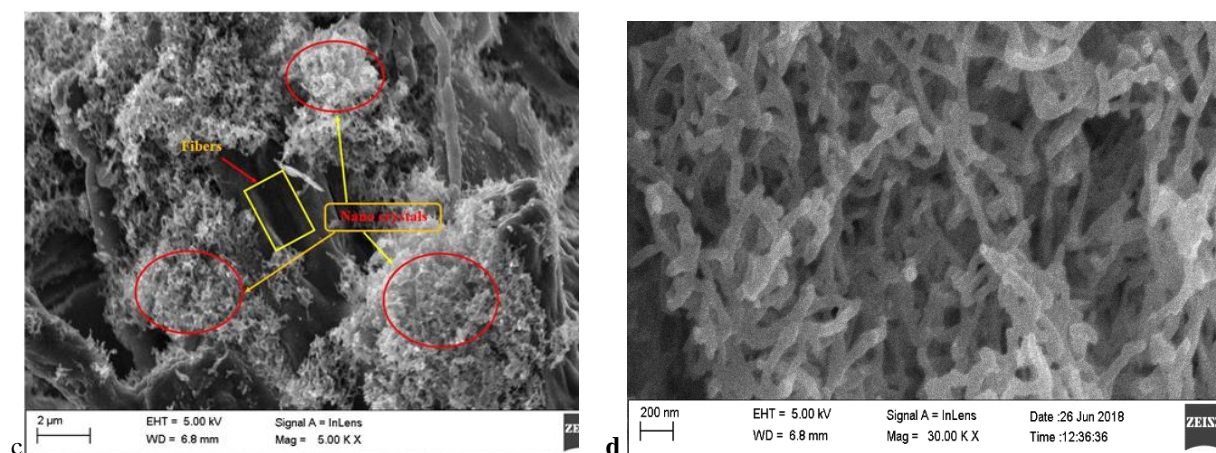
Fig. 2. SEM images of (a) raw sample(b) cellulose (c and d nanocrystal) of sugarcane peel

4.3. Elemental analysis of the cellulose nanocrystal

The elemental analysis of the sample was carried out using EDX coupled with HRSEM. The EDX spectra of the cellulose nanocrystal is shown in Fig.3. The results presented in Table 2 showed the presence of 0.93 wt.% elemental sulphur impurity with the major components having 68.25% carbon and 30.82% oxygen of sugarcane peel cellulose nanocrystal. The quantity of sulphur present might have emanated from the sulphate group during treatment with sulphuric acid hydrolysis.
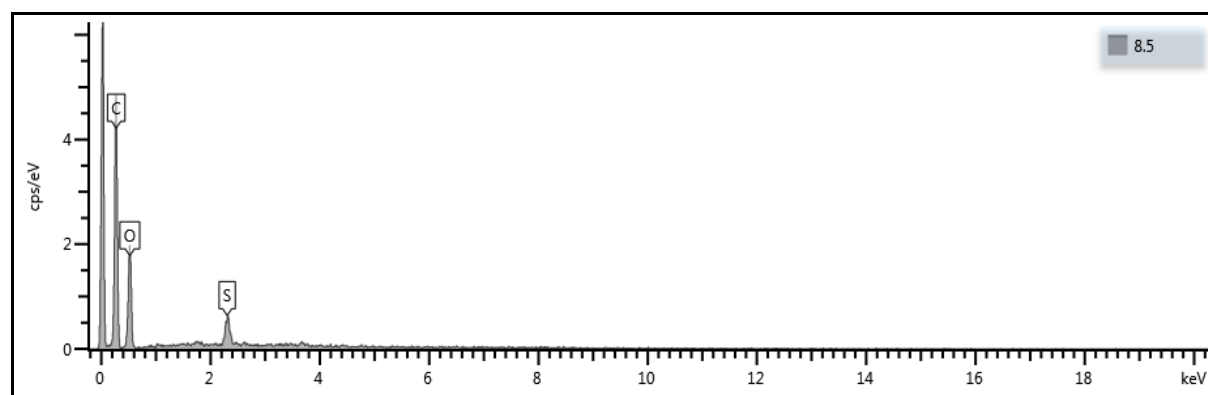

Fig. 3. Energy-dispersive spectroscopy spectrum of cellulose nanocrystal from sugarcane peel

Table 2. Chemical compositions obtained from EDX of cellulose nanocrystal from sugarcane peel

Element	Atomic%
C	68.25
O	30.82
S	0.93
Total:	100.0

4.4. X-ray diffraction analysis

Fig. 4 shows the XRD graph for the sugarcane peel (SP) (RSP, SPCPC and SPCNC). The characteristic peak of SP identified at $2\theta=16.89°$, and $34.70°$ of 110 and 004 lattice planes of cellulose I, indicates the presence of amorphous region, also the peak at $2\theta=16.71°$ of the SPCPC indicates the presence of amorphous region, and the disappearance of the peak at the lattice plane of 004 of the CPC indicates the partial removal of the amorphous region. The CNC showed a low peak height at $2\theta=16.71°$ indicating a complete removal of the amorphous region, leading to a broad surface and high tensile strength. After acid hydrolysis the same diffraction peak for sugarcane peel was recorded, but with lower intensity. This reflects that the crystal structure of the as-obtained CNC is cellulose I (Shaheen and Emam, 2018). It can be noted that the polymers show increasing coordination laterally to a particular axis as the non-cellulosic polysaccharides are removed and the amorphous regions disappears. The three diffractograms show two characteristic peaks around $2\theta = 16.71°$ (for 1 1 0 plane) and $2\theta = 22.47°$ (for 2 0 0 plane) (Arup and Debabrata, 2011). The peak at 2θ value of around $22.47°$ shows the crystallinity structure of cellulose I for all samples (Rahimi *et al*., 2016). The crystallinity index of SP, SPCPC and SPCNC was calculated to be 86.54%, 95.57%, and 99.22% and a particle size of 25.77 nm, 21.10 nm and 5.56 nm respectively. The benefits of having high crystallinity index (>70%) comprise the important increase of chemical and thermal stability and bacteria resistance (Mohammad *et al*., 2017). The crystallinity index increased progressively from the raw to the CNC which is similar to the result obtained by Nurian *et al*. (2012) and Rahimi *et al*. (2016). The increased crystallinity following the treated samples compared to the raw material was ascribed to the progressive removal of amorphous non-cellulosic materials (Nurian *et al*., 2012; Cherian *et al*., 2010b). The subsequent increase of the crystallinity index value upon acid hydrolysis is indicative of the removal of amorphous cellulosic regions. In the process of acid hydrolysis, hydronium ions penetrate the more available amorphous domains of cellulose and allow the hydrolytic cleavage of glycosidic bonds, which finally releases individual crystallites (Nurian *et al*., 2012, Lima and Borsali, 2004). Also, during the isolation of cellulose nanocrystals the progression and realignment of nanocrystals may occur in parallel and thus can improve the cellulose crystallinity (Li *et al*., 2009a,b; Nurian *et al*., 2012). The broad surface area of the nanocrystal is indicative of the ability of the sample to be a good adsorbent for the removal of metal ions from water.
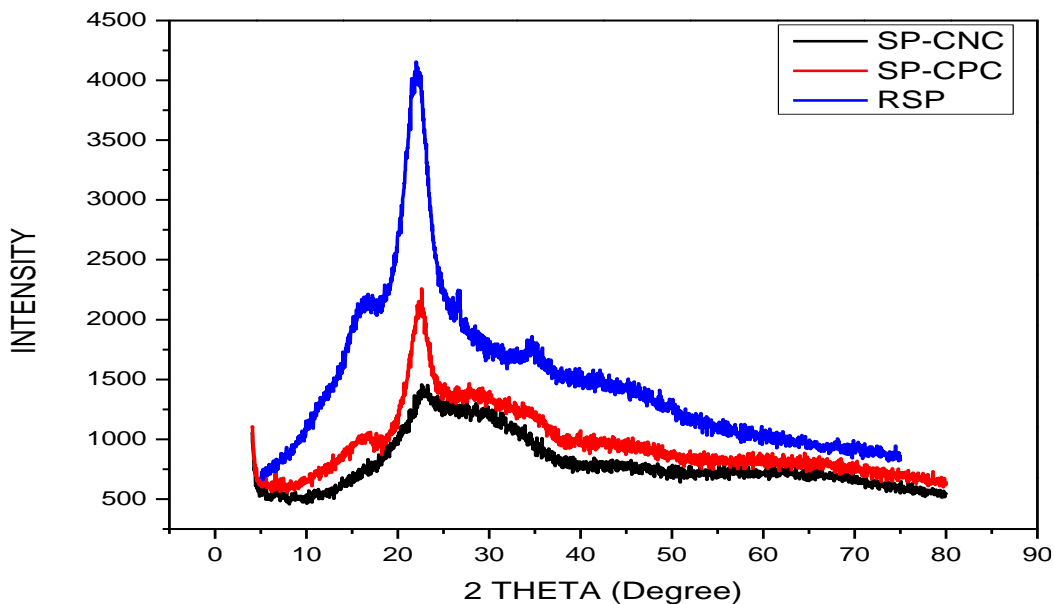

Fig. 4. X-ray diffraction patterns of raw sugarcane peel (RSP), cellulose (SPCPC) and nanocrystal (SPCNC)

4.5 CP/MAS 13C NMR spectra

Table 3 presents the signal assignments for the ^{13}C CPMAS NMR spectra of lignocellulosic material as reported by Wikberg and Maunu (2004).

Table 3. Signal assignments for 13C CPMAS spectra of lignocellulosic material

Chemical shift (ppm)	Assignment
173	COOH in acetyl groups
153	S 3/5e, G 4e
148	S 3/5f, G 3
146	G 4f
136	S 1/4e, G1e
133	S 1/4f, G1f
120	G 6
116	G 5
112	G 2
105	C-1 of cellulose
102	C-1 of hemicelluloses
89	C-4 of crystalline cellulose
84	C-4 of amorphous cellulose
72–75	C-2/C-3/C-5 of cellulose
65	C-6 of crystalline cellulose
62	C-6 of amorphous cellulose
56	methoxyl groups in lignin
21	CH3 in acetyl groups

S, syringyl; G, guaiacyl; e, etherified C-4; f, free phenolic C-4.

In summary, signals in the region between 60-110 ppm are from cellulose carbon. The signals from 60 to 70 ppm are ascribed to C-6, from 70 to 80 ppm to C-2, C-3, and C-5, from 80 to 90 ppm to C-4, and from 98 to 110 ppm to C-1 (Liu *et al*., 2006). Fig. 5 shows the spectrum of cellulose nanocrystal of sugarcane peel, the signal at 105.5 ppm corresponds to C-1 of cellulose, 89.3 ppm is attributed to C-4 of crystalline cellulose, 75.5 ppm corresponds to C-5 of cellulose and 73.4 and 72.6 ppm correspond to C-2/C-3 respectively which are also those of cellulose. The signal at 65.7 ppm corresponds to C-6 of highly ordered cellulose of the crystallite interiors (Wikberg and Maunu, 2004; Idstrom *et al*., 2016; Yu *et al*., 2013).

It is clear from the ^{13}C CPMAS NMR spectra of the CNC that most of the removal of carbohydrates occurred during acid hydrolysis treatment. The shoulder at 102 ppm assigned to hemicellulose disappeared during acid hydrolysis indicating the removal of hemicellulose (Wikberg and Maunu, 2004). The absence of signal at 84 ppm of C-4 of amorphous cellulose indicates the complete disruption of the cellulose amorphous structure during sulphuric acid hydrolysis of sugarcane peel (Yu *et al*., 2013). The disappearance of signals at 21 and 173 ppm assigned to the carbon of the methyl group and carbon of the carboxylic from acetyl groups indicates that treatment with sodium hydroxide considerably removed the side chain of 4-*O*-methyl-glucuronic acid from hemicellulose and xylans (Liu *et al*., 2006). In addition, the absence of the signal at 56 ppm assigned to methoxyl group in lignin, indicates the removal of lignin during bleaching with sodium chlorite. The disappearance of signals at region between 110 and 160 corresponding to aromatic group of lignin reveals the disruption of lignin associated group (Liu *et al*., 2006; Wikberg and Maunu, 2004).
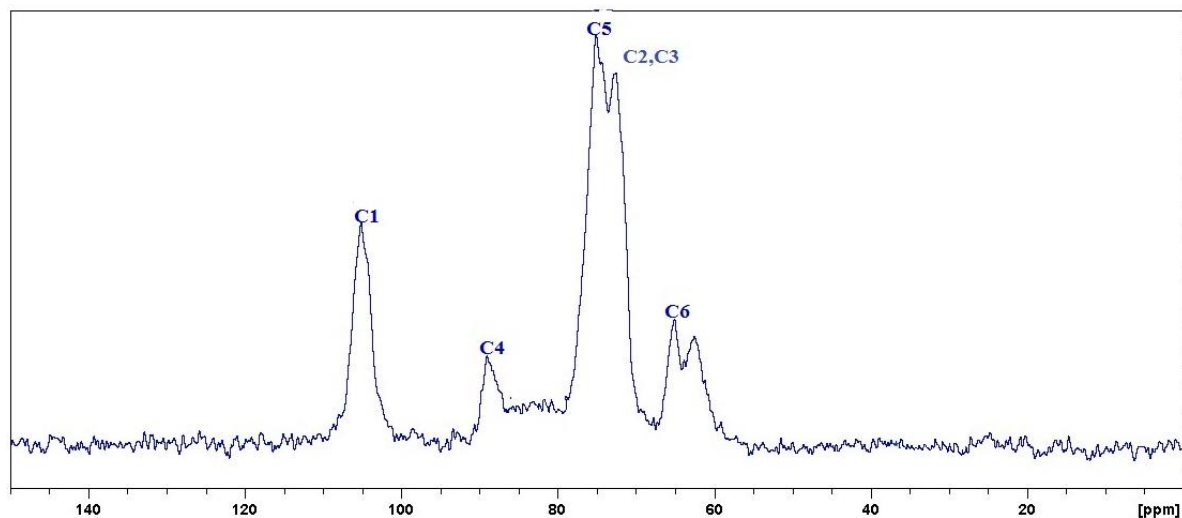
Fig. 5. CP/MAS ^{13}C NMR spectra of cellulose nanocrystal from sugarcane peel

5. Conclusion

The present study shows that cellulose nanocrystals were successfully prepared from sugarcane peel, proving the usage of sugarcane peel as novel material for the production of cellulose nanocrystals. The sulphuric acid hydrolysis conditions used, led to preparing a stable nanostructured crystals from sugarcane peel. The characterisation of cellulose nanocrystals which included morphological, crystal and molecular structure were investigated. The SEM image of the nanocrystal showed that the fibre bundles were separated into individual CNC; with the size decreasing from the untreated to the cellulose nanocrystals into a nanosize, indicating an effective removal of the amorphous region. EDX showed the presence of 0.93 wt.% of elemental sulphur impurity with the major components having 68.25% carbon and 30.82% oxygen of sugarcane peel cellulose nanocrystal. XRD diffraction pattern showed that the CNC retained the cellulose crystalline structure with crystallinity index from raw to CNC; 86.54, 95.57 and 99.22%, with crystallite particle size dimension of 25.77, 21.10 and 5.56 nm from raw to CNC respectively. The NMR spectra of the CNC revealed that all the signals were attributed to six carbon atoms of the glucose unit and the disappearance of several signals also indicated the disruption of the amorphous region. The results revealed effective synthesis of CNC from sugarcane peel (a waste material from agricultural process). Hence, suggesting the leaching of the amorphous domain, apparent crystallinity and purity of the CNC. The cellulose nanocrystal obtained is considered to be a potential material for various industrial applications.

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