



CELLULOSE NANOCRYSTALS PREPARED AND CHARACTERISED FROM UNDERUTILISED SUGARCANE PEEL

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Abstract

Peels of sugarcane are agrarian wastes, obtainable in a large quantity and are currently underutilised. This work was set out to discover the possible usage of sugarcane peel as a source of cellulose and nanocrystalline cellulose, hence, solving the problem of littering waste of sugarcane peels arbitrarily in the environment. Isolation of cellulose from sugarcane peel was prepared by using two pretreatments methods; alkaline and acidified sodium chlorite treatment. The extraction of cellulose nanocrystals (CNCs) was performed via acid hydrolysis at 45°C for 45 mins by 64% concentration sulphuric acid. The chemical composition of the sample was studied. The resulting CNCs of the sugarcane peel were characterised using; Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) spectroscopy and Transmission electron microscopy (TEM). The results indicated that the hemicellulose and lignin were removed comprehensively from the extracted cellulose. FT-IR and XRD revealed free noncellulosic contents and enhanced crystallinity for CNCs, respectively. The TEM revealed 20.6±9.47 nm as average particle size in width, a needle-like shape and a uniform nano dimension bundle of crystals. As a result, the CNCs from sugarcane peel residuals are of high-quality and auspicious resources for various industrial applications.

INTRODUCTION

Owing to the glitches involved in the recycling of polyethylene materials, there is a great importance in sustainable and ecofriendly materials. As an outcome in recent years, the advancement of biopolymers for applications in which synthetic polymers are conventionally used has been the purpose of thorough academic research (Wilson et al., 2013). Cellulose tends to be among the most significant available polymers, and it is known to be the most available renewable polymeric material on earth. Its yearly production is greater than 7.5×10¹⁰ tonnes (Brinchi, Cotana, Fortunati and Kenny, 2013). Cellulose has the formula [(C₆H₁₀O₅)_n, where n = repeating units]. It is a long chain linear homopolymer that is semicrystalline in nature, comprising of glucose molecules covalently joined via acetal functions made by β-(1,4)-glycosidic bonds. It contains several units of the monomer, glucose. D-glucose metabolises the body in order to survive but is not digested in the form of cellulose (Flauzino, 2017). A material particle or an object with at least a size less than 100 nanometers and is made up of atoms in the form of a single or poly-crystalline arrangement is referred to as a nanocrystal (Burt, 2005). Cellulose nanocrystals (CNCs) typically have a dimension of about 2–30 nm in width and may be numerous numbers of nanometers in length, this is made at the time of acid hydrolysis of cellulose materials in which there is a breakdown of the additional available, less-ordered parts (Mikaela and Gunnar, 2015). Acid hydrolysis eliminates the amorphous regions and only ordered-crystalline region will be left. During hydrolysis, firstly the acid disperses into the amorphous region of the cellulose material and hydrolyses the glycosidic bonds. After which simply available polymer fibres with glycosidic bonds are hydrolysed and then hydrolysis ensues at the reducing end group and at the superficial of the nanocrystals (Liu, Wang, Ma, Tian, Gu and Lin, 2014). Cellulose nanocrystals have been hydrolysed from several cellulose sources such as hardwood pulp, softwood pulp, sisal, cotton, rice straw, bacterial cellulose, algae, sugar beet and tunicate (Mikaela and Gunnar, 2015).



In this study, cellulose nanocrystals were extracted and characterised from sugarcane peel via acid hydrolysis to evaluate their suitability for various industrial applications. Diverse techniques were employed to characterise the cellulose and cellulose nanocrystals of sugarcane peel in order to examine their chemical composition, functional groups, crystallinity index, thermal transition, surface charge and shape and size.

2 METHODOLOGY

Materials and procedures

Locally obtainable lignocellulosic material such as sugarcane peel was collected from sugarcane farm at Agbara area of Ogun State, Nigeria. Peel was sorted, cleaned and air-dried for 10 days, milled and sieved with +30 mesh screens. Reagents used include; toluene, sodium hydroxide and sulphuric acid (Merck, South Africa). Ethanol and sodium chlorite were obtained from Sigma Aldrich, South Africa while acetic acid was obtained from Kimix, South Africa. All the chemicals were of analytical grade and were used as received.

Methods

Isolation of Chemically Purified Cellulose (CPC)

The ground sugarcane peel was isolated according to the previously reported methods by Rahimi, Brown, Tsuzuki and Rainey (2016); Shaheen and Emam (2018). The treated 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 oven-dried at 60°C for 16 h. The dewaxed fibre was successively heated with 300 mL water at 55°C for 1 h, to eliminate water-soluble constituents with the excess filtered and washed until neutral pH was attained. The sample was then oven-dried at 60°C for 16 h. The dewaxed sample was soaked separately in 50 g/L of 5% sodium hydroxide solution at 25°C for 24 h and at 90°C for 2 h for the removal of hemicellulose and silica. This was washed with distilled water until the filtrate became neutral 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 (acetic acid at pH 4.5) using fibre to acid concentration ratio of 1:20 for 4 h at 100°C. The delignified cellulose was subsequently washed with distilled water to eliminate the surplus chemicals and oven-dried at 50°C for 16 h. Lastly, the CPC was stored in an air tight ampule.

Synthesis of Cellulose Nanocrystals (CNC)

An aqueous solution of cellulose nanocrystal was prepared as follows; the isolated cellulose from sugarcane peel was synthesised to cellulose nanocrystal via sulphuric acid hydrolysis, according to the method by Ilyas, Sapuan and Ishak 2018; Naduparambath, Jinitha, Shaniba, Sreejith, Aparna and Purushothaman, 2018 with slight modifications. The cellulose isolated from sugarcane peel sample was hydrolysed with 64 wt% sulphuric acid at concentration-to-fibre ratio of 10 mL/g acid at a temperature of 45°C for 45 min with strong mechanical stirring. Tenfold ice water was used to quench the hydrolysis reaction. The resultant nanocrystal cellulose gel was centrifuged at 45000 rpm for 30 min to concentrate the cellulose nanocrystals and to remove surplus aqueous acid; the filtrate was then decanted. Dialysis membrane was used to separate the crystalloids from colloids in the subsequent solution with a 12–14 kDa molecular weight cut off (Sigma Aldrich, South Africa) against millipore water until neutral pH was attained (pH 6–7). The suspension was sonicated at 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 freeze-dried sample was kept in an air tight container for characterisation.

Analysis of Chemical Composition

The chemical compositions of sugarcane were determined according to the method by Ayeni, Adeeyo, Oresegun and Oladimeji (2015) with slight modifications. The raw samples, alkali-treated samples and the bleached samples were measured at diverse phases of treatment. The percentage extractives (wax), percentage hollocellulose, percentage lignin and percentage cellulose were determined.

Characterisation of Sugarcane Peel Fibres and Nanocrystals

Fourier Transform Infrared (FTIR) Spectroscopy

The Fourier Transform Infra-red Spectra were recorded using PerkinElmer Spectrum 400, FT-IR/FT-NIR Spectrometer. Untreated, bleached and acid-hydrolysed of the sugarcane peel fibre samples was fastened with the ATR holder onto the diamond crystal. Wavelength; 4000-650 cm^{-1} was programmed to scan 60 periods at a resolution of 2.0 cm^{-1} through the wavelength range of 4000 to 650 cm^{-1} .

X-ray Diffraction

X-ray diffraction was carried out using Philips Xpert Pro-MPD X-ray Diffractometer D8 Advanced Diffractometer Bruker, Germany with Cu-K radiation operated at 40 kV and 40 Ma. The sample was scanned over a range of 5° to 70° at 2 θ with the count step size set at 0.5 seconds per step/0.05 step size.

Transmission Electron Microscopy

Transmission electron micrograph was collected using HR-TEM (High Resolution Transmission Electron Microscope) FEI Tecnai G2 F20 X-Twin MAT, field emission gun (FEG), Germany, functioned in light-up field mode at a speed up voltage of 200 kV. This part should discuss methods used in carrying out the work.

3. RESULTS

Table 4.1 presents the chemical composition of lignocellulose of sugarcane peel with cellulose content of 7.15±0.01%. Fig 1 and 2 presents the FT-IR spectra and X-ray diffraction of the untreated and treated sugarcane peel. Plate 1 and Fig. 3 shows the TEM micrographs of the cellulose nanocrystal and cellulose of the sugarcane peel.

Table 4.1: Chemical Composition of Lignocellulose of Sugarcane Peel

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Wax (%)
Sugarcane Peel	7.15±0.01	27.522±0.015	47.733±0.02	17.592±0.055

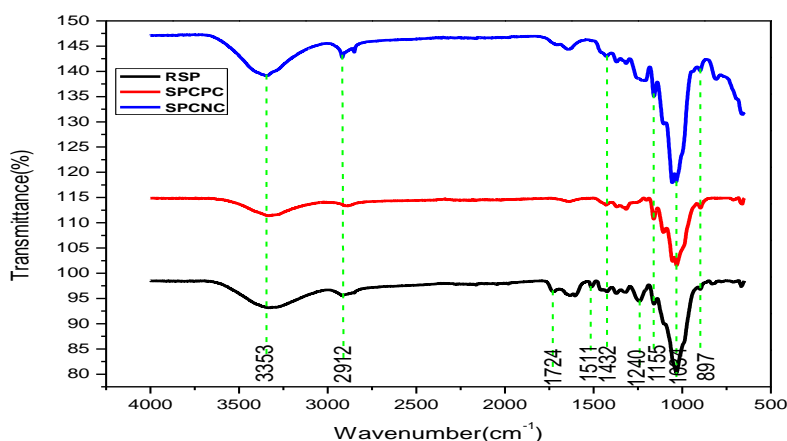


Fig. 1. FT-IR Spectra of Raw Sugarcane Peel, Cellulose Fibre and Cellulose Nanocrystal

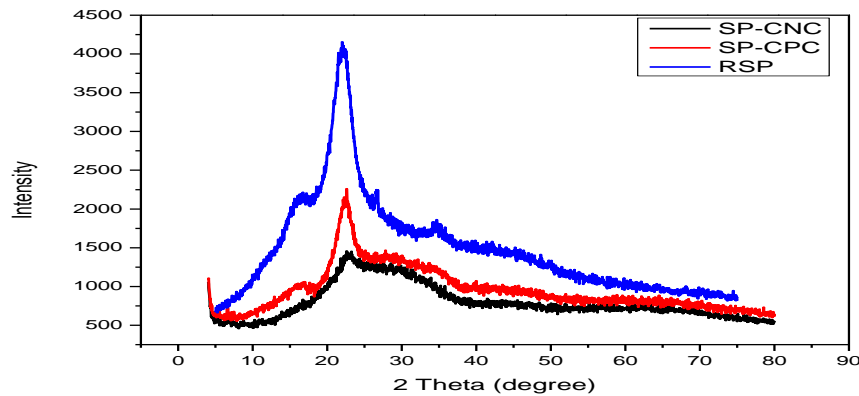


Fig. 2. X-Ray Diffraction of Raw Sugarcane Peel (RSP), Cellulose (SPCPC) and Nanocrystal (SPCNC)

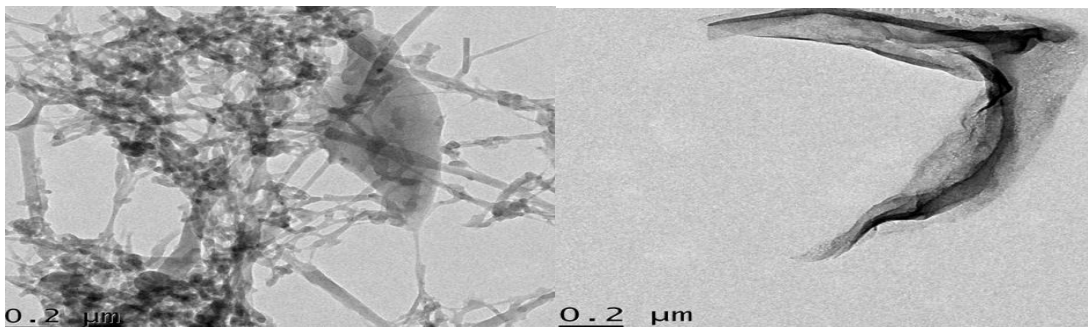


Plate 1. TEM Micrographs of (a) CNC of Sugarcane Peel (b) Cellulose of Sugarcane Peel

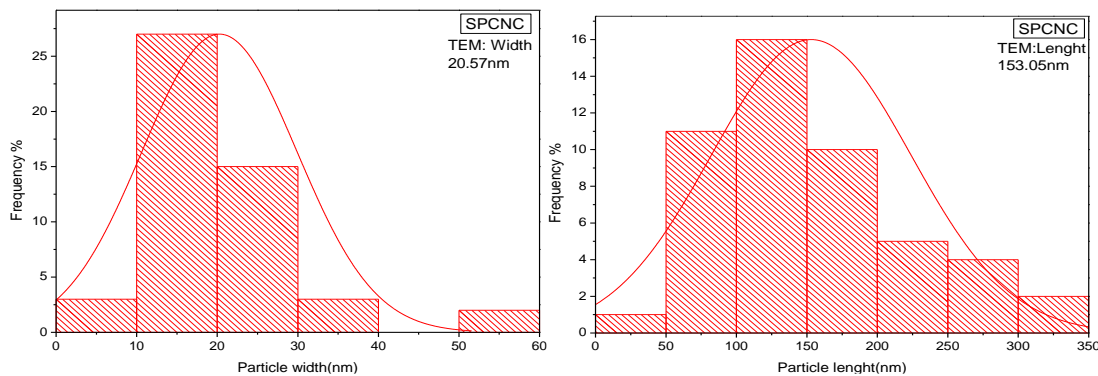


Fig. 3. TEM Histogram of SPCNC Width and Length

4. DISCUSSION

The results show that the sugarcane peel fibre consists of $7.15 \pm 0.01\%$ cellulose, $27.522 \pm 0.02\%$ hemicellulose, $47.733 \pm 0.03\%$ lignin and $17.592 \pm 0.06\%$ wax. The values obtained could not be compared with those from previous studies, as chemical composition of sugarcane peel has not been found elsewhere in the literature. The percentage cellulose yield for the sugarcane peel sample was low compared to the values of 39, 26-47 and 37%, reported in several studies on sugarcane bagasse (Aguilar, Ramirez, Garrote and Vazquez, 1989; Paturau, 1989; Bon, 2007).

FT-IR Technique

The FT-IR technique was used to conclude the available functional groups in sugarcane peel. Figure 4.1a represents the FT-IR spectra of the untreated and treated sugarcane peel. The number of peaks decreased and spectrum resolution increased in the nanocellulose FT-IR curve in comparison with the FT-IR spectrum of the raw sugarcane peel. The peaks around 1160 and 1450 cm^{-1} are indicative of sulphonates in nanocellulose (Morais et al., 2013). The absorption peak at 1511 cm^{-1} is linked with the aromatic C-C in plane symmetrical stretching vibration of aromatic ring available in lignin (Mandal and Chakrabarty, 2011) and in the spectra of SPCPC and SPCNC this peak disappeared which is indicative of the complete removal of lignin during delignification treatment. The peak between 3500 and 3200 cm^{-1} represents the characteristic OH stretching of the treated and untreated cellulose (Mandal and Chakrabarty, 2011). The strength of this band increased when modified with sodium hydroxide, attributing to the rise of hydroxyl concentration as the base decreased the hydrogen bonding in cellulosic OH groups (Buong et al., 2017), which attested to the removal of lignin portion and improved cellulose crystallinity. 2912 cm^{-1} of stretching frequency is attributed to the symmetric C-H vibration for all samples (Naduparambath et al., 2018). The characteristic peaks at 1034 and 1027 cm^{-1} confirms the presence of C-O-C pyranose ring in all the spectra.

X-ray diffraction (XRD)

Figure 4.10b shows the XRD graph for the sugarcane peel (RSP, SPCPC and SPCNC). The characteristic peak of RSP identified at $2\theta=16.89^\circ$ and 34.70° of 110 and 004 lattice planes of cellulose I, specifies the availability of amorphous region; the peak at $2\theta=16.71^\circ$ of the SPCPC also specifies the obtainability of amorphous region. The fading of the peak at the lattice plane of 004 for CPC designates the removal of the amorphous region. The CNC shows no peak height at 110 lattice planes of cellulose, indicating a complete removal of the amorphous region, leading to a broad surface and high tensile strength. 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 RSP, SPCPC and SPCNC was calculated to be 86.54, 95.57 and 99.22%, respectively. The crystallinity index increased progressively from the raw to the CNC and is similar to the result obtained from previous studies (Rahimi et al., 2016). The high crystallinity resulting from sugarcane peel treatments compared to the untreated fibre is attributed to the advanced removal of amorphous non-cellulosic fibre (Abiaziem et al., 2020).

High Resolution Transmission Electron Microscope (HR-TEM)

The width and length of the cellulose fiber was measured after sulphuric acid hydrolysis treatments using the TEM images by an image analyser, Image J. Over 70 measurements were used to obtain the width and the length of the image. The TEM images in Plate 4.2a revealed a needle-like shape, a uniform nano dimension bundle of crystals which resembled that reported by Rahimi et al. (2016). The particle size had an average value of 20.6 ± 9.47 nm in width and 153.1 ± 70.82 nm in length with a size range of 5.39-57.4 nm in width and 34.6-319.6 nm in length for sugarcane peel sample. The results were similar to those reported by other agro-waste sources such as sugarcane bagasse (35 nm) (Arup and Debabrata, 2011); rice straw (11.2 nm) (Lu and Hsieh, 2012); industrial waste cotton (10 nm) (Thambiraj and Shankara, 2017).

5. CONCLUSION

The present study shows that cellulose nanocrystal can be synthesized from sugarcane peels. Chemical treatment with alkali and sodium chlorite removed the non-cellulosic materials, hence its appropriateness for extracting CNC. The acid hydrolysis method used traversed to obtaining stable aqueous suspensions of CNCs which are negatively charged, owing to the presence of sulphate groups. The chemical composition of the sugarcane peel was determined and the cellulose content was found to be $7.15\pm 0.01\%$. Various characterization methods showed that the prepared sugarcane peel nanocrystals exhibited a high crystallinity index of 99.22%, a needle-like shape, uniform nano dimension bundle of crystals and an average value of 20.6 ± 9.47 nm in width. It can be concluded from these results that the cellulose nanocrystals obtained from sugarcane peels have great potentials to be used for diversified applications.



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