



Extraction and characterization of Nanocellulose obtained from sugarcane bagasse as agro-waste

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ABSTRACT

This study aimed to characterize nanocellulose extracted from sugarcane bagasse (SCB) by acid hydrolysis 60% (w/w) H₂SO₄ at 45 °C. The effect of hydrolysis time (20, 30 and 40 min) on the structure and properties of the nanofibers was investigated. Fourier transform infrared spectroscopy (FT-IR), and X-ray diffraction (XRD) results indicated that the hemicellulose and lignin were removed extensively in the cellulose whiskers. The morphology and dimensions of the fibers and acid-released cellulose nanowhisker (CNW) were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results showed that SCB could be used as source to obtain cellulose whiskers and they had needle-like structures. Longer hydrolysis time produced a lower yield of nanofibers; whereas the degree of crystallinity increased from 38.22% to 65.37% with increasing hydrolysis time due to removal of amorphous cellulose.

Keywords

Sugarcane bagasse- Cellulose whiskers- Acid hydrolysis- Nanocellulose

Council for Innovative Research

Peer Review Research Publishing System

Journal: Journal of Advances in Chemistry

Vol. 12, No. 3

editor@cirjac.com

www.cirjac.com



1. INTRODUCTION

In recent years, the quest for sustainable development has motivated efforts toward maximizing the efficiency of the use of raw materials and minimizing the creation of waste (1). In this context, the use of biomass residues as feedstock for the production of energy and materials has been the object of intensive academic and industrial research (2-5). The reuse of these residues allows a significant reduction both in the volume of waste accumulated in the environment and in the extraction of raw materials. Thus, an efficient reuse of these wastes is of great importance, not only for minimizing the environmental impact, but also for obtaining a higher profit. Sugarcane bagasse (SCB) is a residue from the refining process of sugarcane that contains about 40-50% of cellulose in its composition (6). This characteristic suggests the possibility of using the SCB as a source of cellulose fibers for the extraction of whiskers structures. It is known that the morphology and properties of the CNW depend mainly on the source of the original cellulose, of the extraction process and their parameters (7-8). Therefore, the isolation and further analysis of the characteristics of CNW from many kinds of cellulosic resources is necessary and relevant for the efficient comparison and exploitation of these resources (9-11). CNW have been isolated from different vegetable sources, such as cotton and wood pulp (7,12) and from animal sources such as tunicates (13). In addition, there are only a few papers which describe the isolation of whiskers from agricultural byproducts, such as soy hulls (10), corncob (11), rice husk (14) and sesame husk (15). Several processes (16-20) were used to extract cellulose nanowhiskers from biomass. They were generally based on successive cellulose fibers preparation and acid hydrolysis. Chemical treatments for cellulose fibers production at different routes were used to isolate nanowhiskers from mulberry (16), banana fibers (17), pea hull fibers (18), and sisal fibers (19-20).

The aim of this work was to isolate and characterize cellulose whiskers from bleached sugarcane bagasse treated with (17.5%) sodium hydroxide (NaOH) solution to extract cellulose followed by acid hydrolysis at a mild temperature (45°C), different time intervals (20, 30 and 40 min) and to investigate also the influence of extraction time on the morphology and crystallinity of the resulting whiskers.

2. EXPERIMENTAL

2.1. Materials

Bleached bagasse pulp was used for preparation of nanowhisker. It was kindly supplied by Qena Company for pulp and paper, Qena, Egypt. The pulp had the following composition: 26.8% hemicelluloses, 70.6% alpha cellulose, 0.82% ash content, 0.2% lignin. Sodium hydroxide (NaOH), acetic acid, sodium bicarbonate and sulfuric acid reagent grade chemicals were purchased from Sigma-Aldrich.

2.2. Isolation of Cellulose

For alkali pretreatment, bleached bagasse pulp was treated with 17.5% sodium hydroxide for 1 hr at room temperature to remove hemicellulose. At the end of extraction the insoluble residue (cellulose) was collected by filtration, washed thoroughly with water, dilute acetic acid (2% solution), with water again until neutral pH and finally air-dried.

2.3. Preparation of Cellulose Nanocrystals

The delignified and hemicellulose free cellulose was acid hydrolyzed at 45°C for 20 min, 30 min and 40 min with constant stirring. For each gram of cellulose 15 mL of 60% H₂SO₄ (w/w) was used. Immediately following the hydrolysis, the suspension was diluted 10-fold with distilled water to quench the hydrolysis reaction, and centrifuged twice for 10 min at 5000 rpm to remove the excess acid then washed with water, 5% sodium bicarbonate and finally with distilled water to pH about 6. Then, separating from the liquid phase at each washing by centrifugation. To obtain the dry nano-powder, the water dispersion of nanoparticles was sedimented, washed with acetone which can be separated from the solvent by centrifugation, and dried at 50 °C to constant weight. The cellulose nanocrystal samples were labeled SCBW20, SCBW30 and SCBW40 depending on the time of extraction. The mechanism of acid hydrolysis can be shown in figure (1)

3. Characterization And Measurements

Yield Analysis

The weight of the initial cellulose was designed as M₁, while the SCBW was dried at 50 °C up to constant weight M₂. The yield of SCBW is given as follows:

$$\text{Yield \%} = (M_2/M_1) \times 100\% \quad (1)$$

Fourier Transform Infrared Spectroscopy

FT-IR spectroscopy (6100, JASCO model, 50 scans, Japan) was used to examine the changes in the functional groups induced by the various treatments. The samples were ground and mixed with KBr at (1:100) by weight, respectively. The resultant powder was pressed into transparent pellets and analyzed in absorbance mode within the range of 4000-400 cm⁻¹.

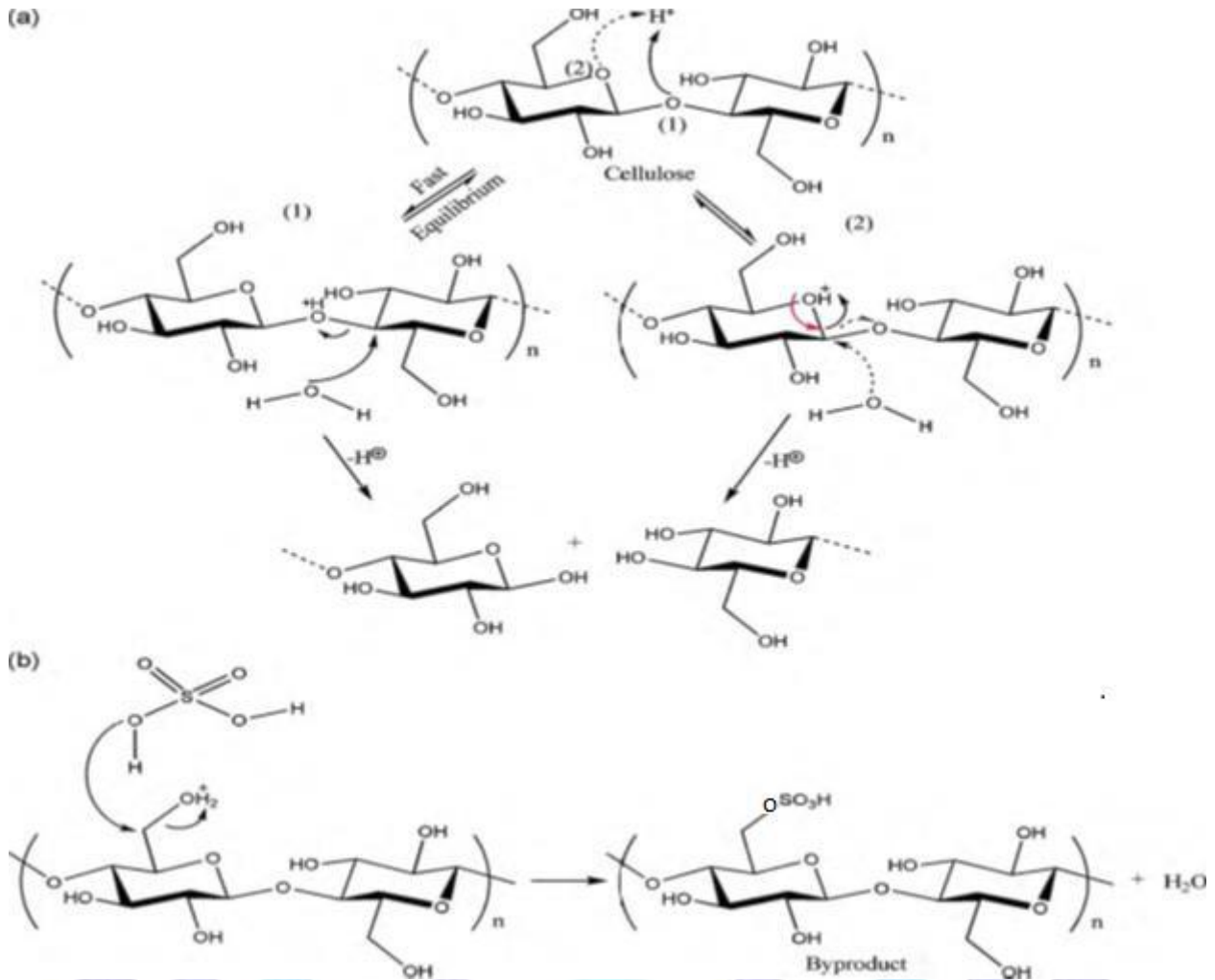


Fig (1): (a) Acid hydrolysis mechanism and (b) esterification of cellulose nanocrystals surfaces.

Microscopic Analysis

Morphological analysis of untreated, bleached and treated SCB was done by Scanning electron microscopy (SEM). SEM micrographs of fiber surface were taken using (JOEL JXA-840A electron probe microanalyzer with tungsten filament 30 Kv, Japan).

Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is the one of most important imaging tools of nanotechnology in which a thin specimen is imaged by an electron beam which is irradiated through the sample at uniform current density. The size and shape of cellulose nanocrystals were investigated by transmission electron microscopy (JEOL JEM-2100 Electron Microscope, Japan). After the suspension was mildly ultrasonicated in water bath for 20 min, A few drops of solution were dropped onto a TEM carbon coated grid and the residue was removed by a filter paper under the TEM grid.

X-ray Diffraction (XRD) Analysis

X-ray diffraction was used to determine the crystallinity of the SCB fibres after different treatments. Each sample in the form of milled powder was placed on the sample holder and levelled to obtain total and uniform X-ray exposure. The samples were analyzed using X-ray diffractometer at room temperature (RT) with a monochromatic Cu K α radiation source ($\lambda = 0.1539$ nm) in the step-scan mode with a 2θ angle ranging from 5° to 80° . To characterize the crystallinity of the different samples, the crystallinity index I_c , was determined based on the reflected intensity data following the equation of Segal et al. (21):

$$I_c = \left[\frac{I_{200} - I_{am}}{I_{200}} \right] \times 100 \quad (2)$$

Where I_{002} is the maximum intensity of the (002) lattice diffraction peak and I_{am} is the intensity scattered by the amorphous part of the sample. The diffraction peak for plane (002) is located at a diffraction angle around $2\theta = 22^\circ$ and the intensity scattered by the amorphous part is measured as the lowest intensity at a diffraction angle around $2\theta = 18^\circ$.

4. Results and discussion

4.1. Nanocellulose Yields

The yields of the SCBW, with respect to the initial amount of dried fibers, for SCBW20, SCBW30 and SCBW40 were 79.26, 74 and 65 wt% respectively; these values are consistent with the literature data (11, 12, 21). Among the several methods for preparing CNW, acid hydrolysis is the most well-known and widely used (22). This process breaks down the disordered and amorphous parts of the cellulose, releasing single and well-defined crystals. Thus, this process is based on the quicker hydrolysis kinetics presented by amorphous regions, as compared to crystalline ones (21-23). The decreasing yields with longer reaction time is expected as cellulose chains in the less ordered regions are hydrolyzed to separate the crystalline domains that reduce in sizes as the surface chains are further hydrolyzed, while cellulose fragments are broken into soluble oligo- and monosaccharides (24).

4.2. FT-IR Spectroscopy

Direct information about changes in chemical functionality can be obtained by FT-IR spectroscopy which has been extensively used for structural analysis of the material before and after chemical treatments. FT-IR spectra of SCB as raw material, chemically purified cellulose (CPC) and the SCBWs obtained by acid-hydrolysis are shown in Figure 2. The spectral bands at 3344-3490 and 2850-2970 cm^{-1} are characterized for the O-H stretching intramolecular hydrogen bonds (25) of hydroxyl groups and C-H stretching, respectively and the band at 1730 cm^{-1} represents the C-O stretching vibration for the acetyl and ester linkages in lignin, hemicellulose, pectin, etc. while the peaks at 1620-1649, 1512 and 1595 cm^{-1} are associated with the aromatic ring present in lignin and adsorbed water, respectively and the peak at 1250 cm^{-1} corresponds to C-O out of plane stretching due to the aryl group in lignin, which are associated with the SCB before the chemical treatments, are not observed for CPC. The effect of these chemical purification can be observed through main spectral bands specially the peak at 1735 cm^{-1} , which is assigned mainly to C=O stretching vibration of the carbonyl and acetyl groups in the xylan component of hemicellulose and also typical for structural features of lignin (26-27) disappeared after bleaching and alkaline treatments. Further absorption bands of lignin at approximately 1595 cm^{-1} (28) and, in particular, the band at 1512 cm^{-1} is absent (29-33). However, FT-IR spectra of SCBWs having sharp bands but similar to that observed in CPC. The spectral bands observed in the spectra of CPC and SCBWs in the region 1649-1634 cm^{-1} are assigned to the O-H bending due to the adsorbed water (31). The peaks at 1430-1420, 1382-1375 cm^{-1} and 893-902 cm^{-1} are allocated to the CH₂ scissoring motion in cellulose, C-H bending and C-O-C pyranose ring stretching vibration, respectively. While the two characteristics absorption bands at 893-902 cm^{-1} and 1155 cm^{-1} assigned to cellulosic β -glycosidic linkages and C-C ring stretching (33-34), respectively. The spectral bands observed at 1427 cm^{-1} and 897 cm^{-1} represent significant cellulose I content. Moreover, the bands at 1431, 1372, 1322, 1162, 1059 and 896 cm^{-1} are typical of pure cellulose (26-27)

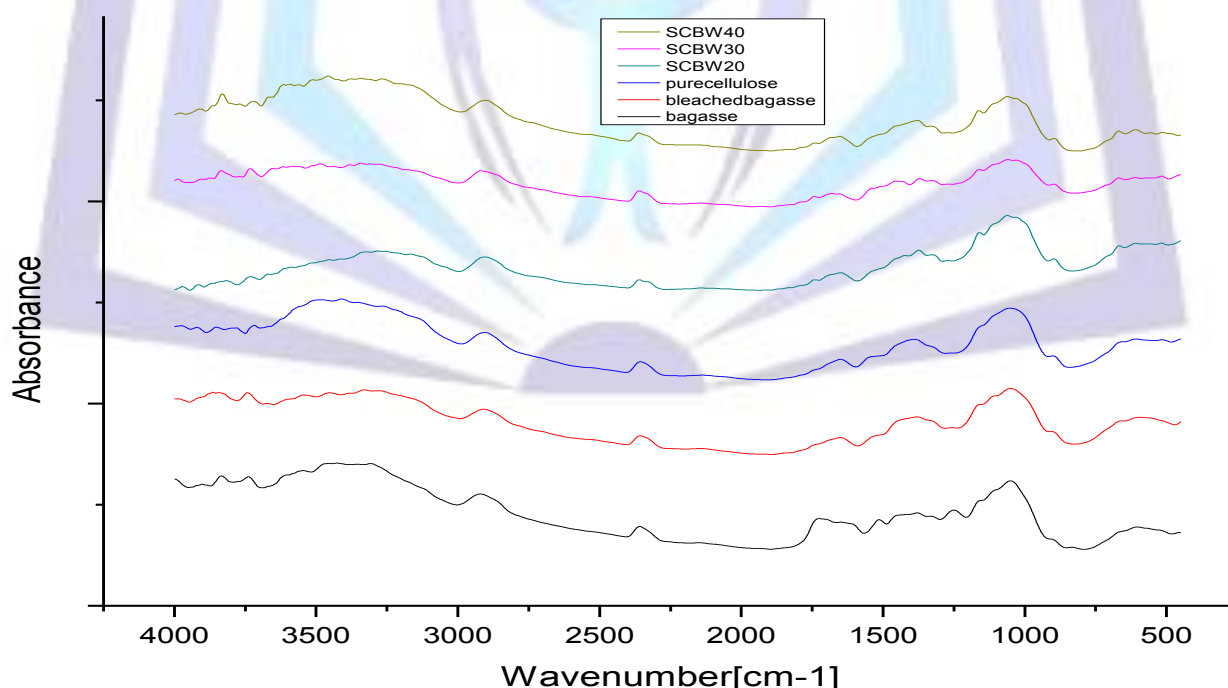


Fig (2): Infrared spectra of (a) bagasse (SCB) (b) bleached fibers (c) cellulose fib (d) SCBW20 (e) SCBW30 and (f) SCBW40.

4.3. Scanning Electron Microscopy (SEM) Analysis

The SEM micrographs of the original ground sugarcane bagasse (a), bleached bagasse pulp (b), pure cellulose after removal of lignin and hemicellulose (c) and nanocellulose produced by acid hydrolysis of the pure cellulose with 60% (w/w) H₂SO₄ at different time intervals (20,30 and 40 min.) while the temperature was kept constant at 45°C (d,e,f).

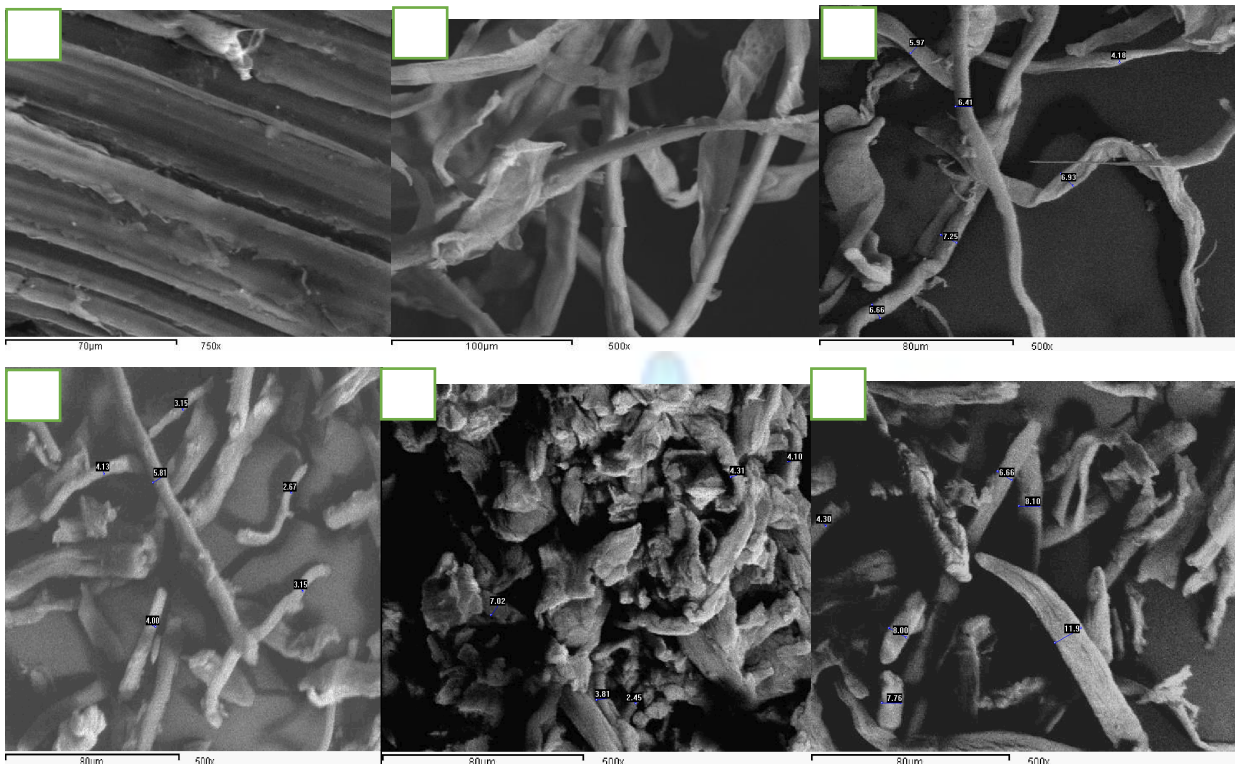


Fig 3. Scanning electron microscope of (a) bagasse (SCB) (b) bleached fibers (c) cellulose fibers (d) SCBW20 (e) SCBW30 and (f) SCBW40.

The diameter of the original sugarcane bagasse fiber was much bigger and each fiber appears to be composed of several microfibrils. Each elementary fiber possesses a compact structure; exhibiting an alignment in the fiber axis direction. In its natural state, and before chemical extraction, the overall surface of the fiber is found to be somewhat smooth due to the presence of waxes and oil (35-36) and other incrusting materials such as hemicellulose, lignin and pectin that form a thin layer to protect the cellulose inside. On treating with bleaching agent the lignin is removed through complex formation and depolymerization. On subsequent treatment with alkali the hemicellulose is hydrolyzed and becomes water soluble. These help in defibrillation of the fibrils and result in micrograph (b) and (c) whereby the diameter of the fibrils is reduced to a great extent, also possibly because of removal of non-cellulosic constituents. Untreated microcrystalline cellulose (MCC) displays irregular aggregated shape fibrils and a rough surface morphology with lower aspect ratio, these aggregates composed of strong hydrogen bonding between hundreds of individual cellulose whiskers (37-39). In the cellulose fiber, the sulfuric acid hydrolysis usually could cleavage the amorphous regions of microfibrils transversely, resulting in a diameter reduction of fibers from micron to nanometer (40) as shown in Table (1). Hydrolyzing of cellulose from tunicates and green algae produced whisker like particles with a length of micrometer, where higher plants cellulose from cotton and wood pulp gave shorter particles a few hundred of nanometers in length (8). The hydrolyzed fibers at different times have a rod-like shape. After acid hydrolysis of SCB at different time intervals, it's clear from typical SEM micrograph that the aggregation of MCC was broken down and the tendency of fiber separation can clearly be observed after these treatments gave rise to intermittent fibrillar structure and further reduction in intrafibrillar diameter especially after 30 minutes.

Table (1): Diameter (µm) determination by image j program from SEM micrograph.

Sample	Diameter (µm)
Bagasse	392.15
Bleached pulp	16.02
Pure cellulose	9.531
SCBW 20	4.748
SCBW 30	4.708
SCBW 40	5.28

4.4. Transmission Electron Microscopy (TEM)

In order to determine fiber length, and to indicate the aggregation state of the whiskers, highly diluted samples of the hydrolyzed suspension were analyzed by transmission electron microscopy. At least 10 measurements for each condition were used to determine average and standard deviation values.

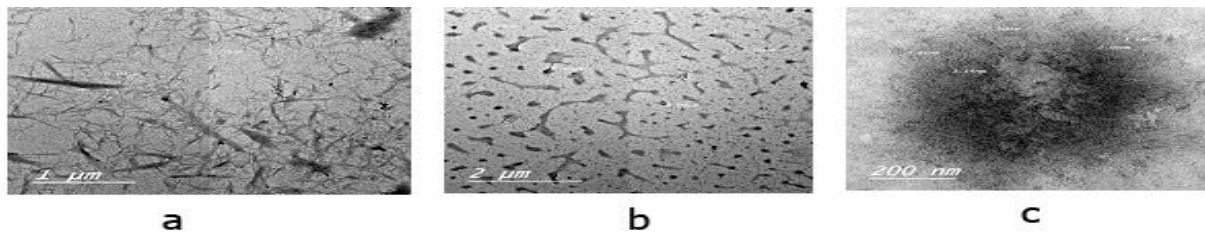


Fig 4. TEM image of cellulose nanowhiskers (a) SCBW20 (b) SCBW30 (c) SCBW40

These images evidenced the efficiency of the acid hydrolysis treatment, confirming that the bagasse cellulose nanowhiskers consisting mostly of individual fibrils and some aggregates. (40-41). The effect of preparation conditions on the dimensions of cellulose nanowhiskers were characterized by particle length (L), width (D) and aspect ratio (L/D). As pointed out by Dong et al. (42), the conditions of preparation govern somewhat the properties of the cellulose particles. It is expected that the prolonged acid attack can not only “dissolve” amorphous molecules but also partly destroy crystalline zones of the fibrils, ultimately resulting in a shortening of nanowhisker length. However, the results show that, for the tested conditions, the values are differences between the lengths of nanowhiskers obtained from the different conditions of preparation. Typically, bagasse nanowhiskers had lengths ranging from 7 to 80 nm and width from 1.7 to 40 nm.

4.5. X-ray Diffraction (XRD) Analysis

Cellulose has crystalline structure contrary to hemicellulose and lignin, which are amorphous in nature. According to Kumar et al. (29) pointed out that cellulose has a crystalline structure due to hydrogen bonding interactions and Van der Waals forces between adjacent molecules. X-ray diffraction (XRD) analysis was completed to evaluate the crystallinity of the SCB fibres after different chemical treatment stages. Chemical treatment performed on natural fibres can affect the crystallinity of cellulose. For example, dilute acid has no effect on the crystalline domains, but destroys the amorphous region of the fibre (43). On the other hand, the alkali treatment can be performed onto the plant fibres to increase the stiffness of fibre as the impurities present in the fibres can be removed during this treatment (44). Therefore, the crystallinity of chemically treated fibres can be determined and compared to untreated fibres to access the effectiveness of the chemical treatment. Fig. (5) Shows the diffraction patterns obtained for (a) untreated, (b) alkali treated, (c) bleached, and (d-f) acid hydrolysed SCB. The crystallinity index was determined for the various samples and the results are summarized in Table (2). A continuous increase of the CrI value was observed upon the successive chemical treatments. The highest value (65.37%) corresponds to cellulose nanocrystals, which also displayed the strongest and sharpest peak at $2\theta = 22^\circ$. The increased crystallinity following SCB treatments compared to the raw material was ascribed to the progressive removal of amorphous non-cellulosic materials. The subsequent increase of the CrI value upon acid hydrolysis of purified cellulose SCB fibres is indicative of the dissolution of amorphous cellulosic domains. During the hydrolysis process, hydronium ions can penetrate the more accessible amorphous regions of cellulose and allow the hydrolytic cleavage of glycosidic bonds, which eventually releases individual crystallites (45). In addition, during the preparation of cellulose nanocrystals the growth and realignment of monocrystals may occur in parallel and thus can improve the cellulose crystallinity (16). This phenomenon could explain the narrowing of the diffraction peaks. This increase in the cellulose fibres crystallinity was also expected to increase their stiffness and rigidity, and therefore strength. Thus, it was assumed that the potential mechanical properties and reinforcing capability of treated fibres increased (46-47).

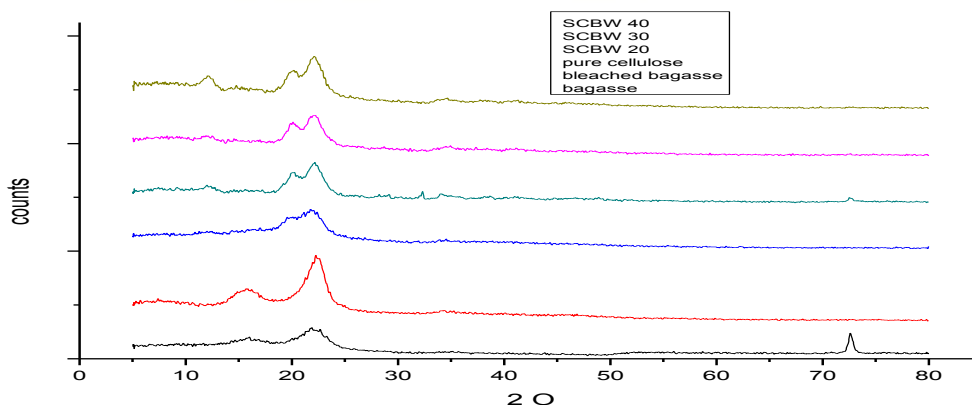


Fig 5. XRD of (a) bagasse (SCB) (b) bleached fibers (c) cellulose fib (d) SCBW20 (e) SCBW30 and (f) SCBW40.

**Table (2): Crystallinity index (I_c) of SCB fibres at different stages of treatment.**

Sample	I _c %
untreated SCB	38.22
Pure cellulose	48.41
Bleached SCB	53.44
SCBW20	54.03
SCBW30	57.99
SCBW40	65.37

CONCLUSION

Cellulose fibers were obtained from SCB fibers by alkali and bleaching treatment which are characterized by chemical analysis, FT-IR spectroscopy, and microscopic observations. Cellulose nanocrystals were successfully extracted from purified material using sulfuric acid while keeping the acid concentration and reaction temperature constant and varying the hydrolysis time. The chemical structure of the nanoparticles did not change during the acid hydrolysis process. Individually released cellulose nanocrystals showed an increased crystallinity when the reaction time was increased to 40 min. SCB whiskers were obtained at mild temperature (45°C) and shorter extraction times (20, 30 and 40 min). Their dimensions can be accurately measured by TEM and exhibited good crystallinity (65.37%) by XRD measurements.

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