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Isolation and Characterization of Cellulose Nano crystals from Baobab Pod Fibres using Acid Hydrolysis

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ABSTRACT

In this research, cellulose nanocrystals were isolated from locally grown baobab pod fibres. Fibres were treated chemically using NaOH and then hydrolysed using Nitric acid. The effect of NaOH treatment and acid hydrolysis on surface morphology, crystallinity, and thermal properties of fibres were investigated using Fourier Transform Infrared (FTIR), Scanning electron microscopy/Energy dispersive X-ray spectroscopy (SEM/EDS), X-ray Diffraction (XRD) and Thermogravimetric analysis (TGA/DTA). From the results evaluated, cellulose content of 17.9 % was recorded after NaOH treatment and 25.3 % was recorded after acid hydrolysis, the crystallite size was found to be 3.003 nm and thermal stability of the fibre was enhanced after chemical treatment and acid hydrolysis. Based on the results obtained, it shows that nanocellulose hydrolyzed from baobab pod fibres has excellent properties for use as polymer reinforcement and for other engineering applications.

Key words: Baobab pods, mercerization, acid hydrolysis, cellulose nanocrystals.

INTRODUCTION

Nanocellulose is a general term used for cellulose nanocrystals, cellulose nanofibers, and bacterial nanocellulose (Faridulhassan *et al.,* 2020). They have essentially different extraction procedures as well as different morphologies. Cellulose nanofibers can be isolated using mechanical processes such as high-pressure homogenization, grinding and refining (Wang *et al.,* 2007), whereas cellulose nanocrystals have been extensively isolated by using acid hydrolysis treatments (Habibi *et al*., 2009).

Cellulosenanocrystals production could be varied depending on the sources from which it is extracted, which provides researchers with a broad range of choices to study, such as types of cellulose sources, reaction parameters and processing methods (Razali et al., 2017). The size of cellulose nanocrystals depends on the source from which they are generated and can vary from 100 to 1,000 nm in length and 4 to 25 nm in diameter. Regarding the extraction of crystalline cellulosic regions, in the form of cellulose nanocrystals, a simple process mostly based on acid hydrolysis is generally utilized (Anteneh *et al*., 2021).

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Acid hydrolysis is therefore a well-known process to produce cellulose nanocrystals; it is believed that this method leads to isolation of celluloses with a high degree of crystallinity by removing the amorphous part of the raw material (Habibi *et al.,* 2010). Although acid hydrolysis is usually performed using HCl or H_2SO_4, microbial hydrolysis has also been utilized to produce nanocrystals (Satyamurthy *et al*., 2011). Cellulose nanocrystals derived from natural fibres found applications in food packaging, thin film composite and super adsorbent for water remediation (Septevani *et al.,* 2020). The improvement in binding efficiency shows the economic potential of cellulose nanocrystals in the pharmaceutical industry in the future (Low *et al*., 2019).

Previous studies have used other methods of isolation of nanocellulose from other natural fibers for biomedical applications from natural fibers like sisal, bamboo and jute using other procedures like chlorination, alkaline extraction and bleaching. This study aimed at using baobab pod natural fiber which is very rear to isolate cellulose nanocrystals that can be used for composite reinforcement in automobile industries and for other engineering applications.

MATERIALS AND METHODS

Materials Preparation

Baobab pods were sliced open mechanically using a knife. The fibres were screened out from the pods by hand, and then washed in a running tap water to remove the remaining pulp on the fibres. Finally, the fibres were allowed to dry for 24 h. The dried Baobab fibres were subjected to size reduction by grinding using local milling machine. The ground fibres were then sieved as shown in Figure 1 (b), in order to ensure equal distribution of the fibres.

Figure 1: The Images of (a) raw baobab pod fibres (b) ground baobab pod fibres

METHODOLOGY

The method adopted for the production of cellulose nanocrystals from baobab pod fibres involves three main stages as detailed in the flow chart shown in Figure 2.

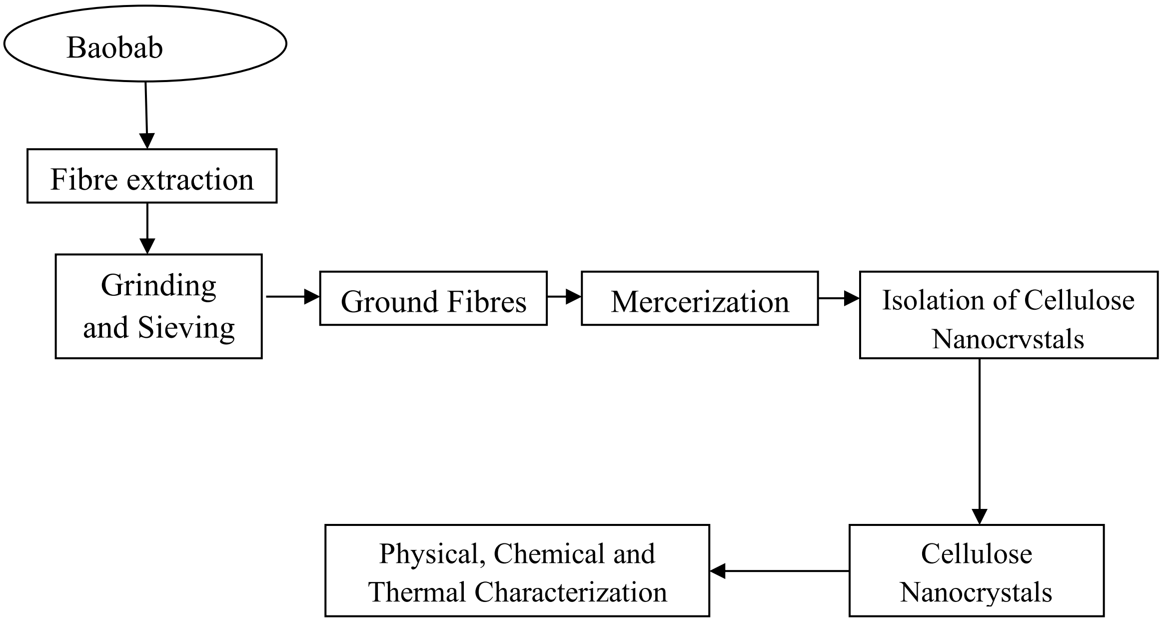

Figure 2: Block diagram for production cellulose nanofibers from Baobab pod fibre

The first stage involves pre-treatment of cellulose (baobab fibre extraction from pod, size reduction through grinding and sieving and mercerization), cellulose nanocrystals extraction after pre-treatment (acid hydrolysis) and characterization of cellulose nanocrystals using different techniques.

Chemical treatment (mercerization)

Mercerization method of fibre treatment was adopted for the purpose of this study; analytical grade NaOH was used. Different concentrations of aqueous NaOH were prepared (2 %, 6%, and 10 % by weight) by dissolving NaOH pellets in distilled water. Ground baobab pod fibres were then immersed into the solution and heated at 67.5 ˚C for 240 min with a solution to fibre ratio of 40 cm^3 to 1 g. After the immersion, the fibres were washed with distilled water to get a neutral pH. Subsequently, the fibres were dried at 60 *℃* for 24 h.

Isolation of cellulose nanocrystals from baobab pod fibres

Isolation of cellulose nanocrystals is the second stage in the production of cellulose nanocrystals from the fibre source. Isolation of cellulose nanocrystals usually involves acid hydrolysis at elevated temperatures, which is targeted to reduce polymerization by breaking down the accessible amorphous regions of the long glucose chains, liberating the crystalline materials from the fibre source (Qin *et al*., 2011).

Bleaching with sodium chlorite ($NaClO_2$)

Sodium chlorite was used for the bleaching of baobab pod fibre, it is an excellent bleaching agent which helps to remove lignin and produces holocellulose. 1.8 w/v% $NaClO_2$ was prepared in a 500 cm^3 beaker and baobab pod fibres were immersed into the solution and heated for 4 h at 70 ℃. The fibres were then washed with distilled water and dried in an oven for 2 h at 50 °C. The colour changes due to the removal of lignin and extractives as can be seen in the image represented in Figure 3

Figure 3: Image of bleached baobab pod fibres

Acid hydrolysis

A formulation of 60 % Nitric acid (HNO_3) and 40 % acetic acid mixture was used for the isolation of cellulose. 7 g of bleached baobab pod fibres were placed in a conical flask. 160 cm^3 of 40 % acetic acid and 240 cm^3, 60 % of nitric acid (w/w) were added and the flask was then closed using a cork. It was then placed on a heating mantel at a temperature of 83 °C (boiling point of Nitric acid) for 40 min. The flask was then removed from the heating mantel and cooled before 70 cm^3 distilled water was added. It was filtered and repeatedly washed with distilled water and ethanol to remove nitric acid. The residue was dried in an oven at 60 °C.

Centrifugation

A centrifuge was used to wash the hydrolysed cellulose five times; the centrifugation took place at 1000 rpm, 10 min and 10 ℃. the products were then neutralized to a pH of 7 using NaOH.

Characterization of cellulose nanocrystals using different techniques

FTIR Analysis

The surface chemistry of baobab pod fibres was investigated by using Fourier Transform Infrared (FTIR). It identifies the different functional groups present in the fibres. Shift in the spectre and the complete disappearance of some functional groups helps in detecting the changes that happens during chemical treatments.

SEM Analysis

Scanning electron microscopy (SEM) was carried out using a Phenom tm Prox scanning electron microscope. Samples were coated with a thin gold layer with a Quick Coater Metalizer Sanyu Electron SC-701. Scanning barrel was vacuumed to prevent interference of scanning picture due to the presence of air. Magnification, focus, contrast and brightness of the result were adjusted to produce the best micrographs at 50 and 200 µm.

X-ray Diffraction Analysis

The intensities were measured from 5° to 110° at 2θ with step size of 0.0167° and a scan speed of 0.015 deg/sec. The radiation used was full spectrum Co ($K\alpha_1$, $K\alpha_2$) with the K_β filtered out with a diffracted side Fe filter. The empirical Equation 1 was used to analyze the degree of crystallinity of baobab pod fibres cellulose nanocrystals.

$$I_{Cr} = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

Where

I_{002} is the maximum intensity of the 002 lattice reflection at $2\theta = 22.5°$

I_{am} is the intensity of diffraction of the amorphous material at $2\theta = 18.5°$.

The average crystallite particle size was determined from the XRD patterns of the cellulose nanocrystals using Scherer equation 2.

$$D = \frac{k\,\lambda}{\beta cos\theta} \quad (2)$$

Where

D = the particle size diameter

β = the full width at half maximum

λ = the wave length of X-ray

θ = the diffraction angle (peak position)

K = the Scherer constant = 0.94

TGA Analysis

Thermal analysis of the baobab pod fibres cellulose nanocrystals was carried out to further analyze the thermal properties. Thermogravimetric analysis was performed in an SDT Q600 instrument. For each measurement, approximately 5 mg of the baobab cellulose nanocrystals sample was used. Patterns were recorded under a nitrogen atmosphere at a flow rate of 100 mL / min by heating the material from room temperature to 500 °C at a heating rate of 20 °C/min.

RESULTS AND DISCUSSION

FTIR Analysis of Baobab Cellulose Nanocrystals

The FTIR spectrum of the baobab cellulose nanocrystals shown in Figure 4, displayed absorption patterns corresponding to the specific functional groups of cellulose, and was also in good agreement with the reported cellulose by Shehu *et al* (2017).

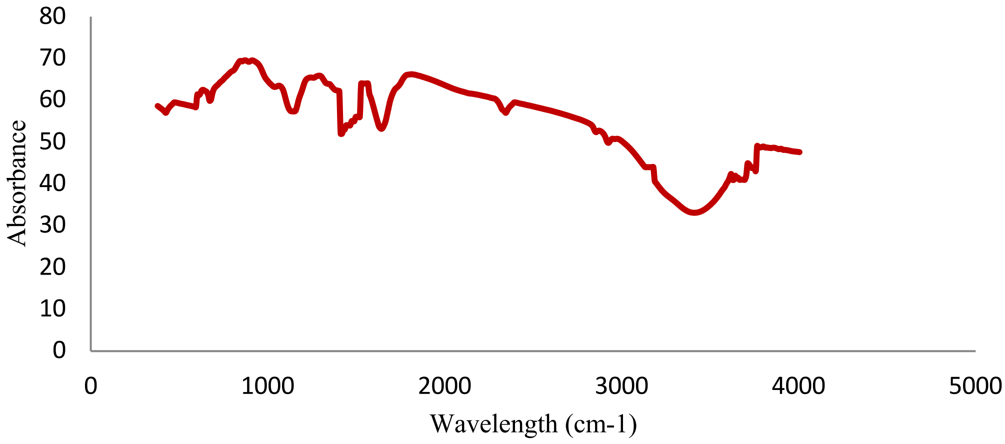

Figure 4: FTIR Spectrum for Baobab Cellulose Nanocrystals

The peak at 1635 cm^{-1} was formed due to the bending mode of adsorbed water. The peak at 1118 cm^{-1} may be due to CH_2 bending vibration. The sharp transmittance peak around 1384 cm^{-1} represents a bending of OH groups. The peak at 1174 and 1120 cm^{-1} corresponds to C-O asymmetric bridge stretching.

SEM of Baobab Cellulose Nanocrystals

Scanning electron microscopy (SEM) was employed to analyze the structure of nanocrystals of the cellulose formed. The SEM images in Figure 5 indicate changes in morphology of the baobab pod fibres.

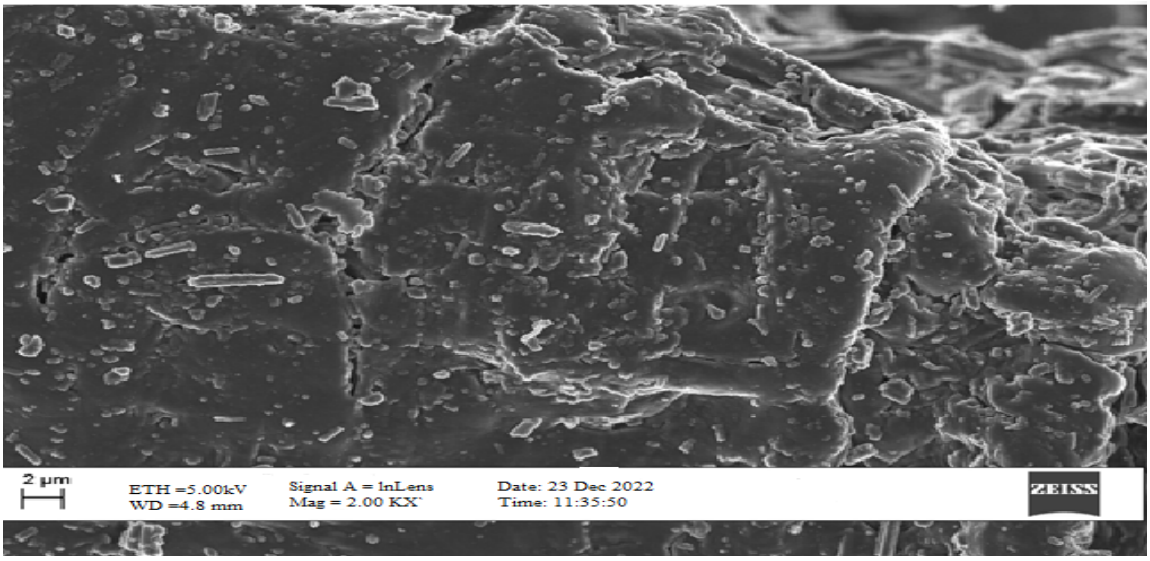

Figure 5: SEM images for baobab nanocellulose

X-ray Detraction Analysis of Baobab Cellulose Nanocrystals

The XRD of baobab pod fibres as shown in Figure 6, indicate peaks which are peculiar to natural fibres. The sharp and strong diffraction peaks in the XRD patterns of the cellulose

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nanocrystals confirm the high crystalline nature of the fibre. The spectrum also shows that the peak intensity increases as the samples are being modified.

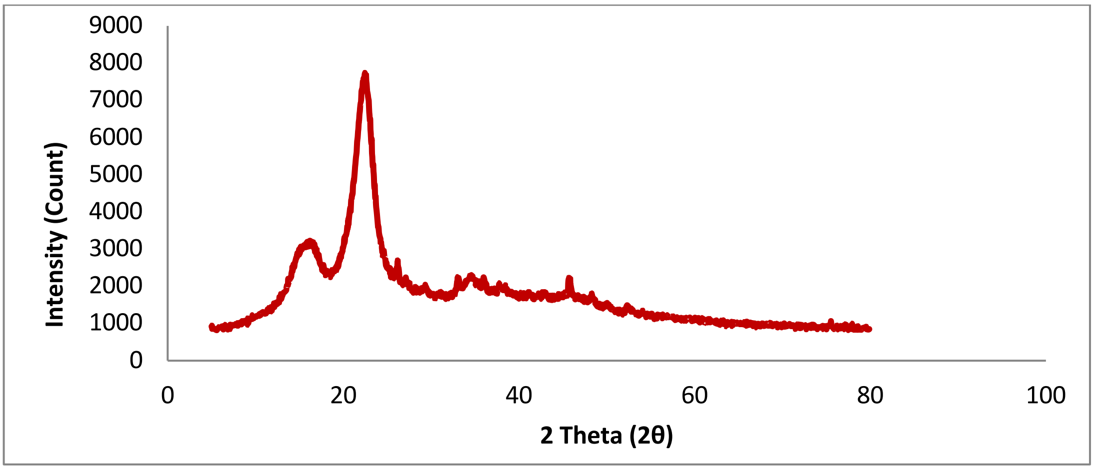

Figure 6: XRD pattern of baobab cellulose nanocrystals

The cellulose nanocrystals exhibited a typical cellulose I pattern at a sharp peak of 2θ =22°. The diffraction peak at 22° corresponds to the 002 crystallographic plane of the cellulose I lattice. The crystallinity index (CrI) was calculated according to the Segal empirical method. Table 1 shows the crystallinity index of the fibre cellulose nanocrystals.

Table 1: Crystallinity index of Baobab Cellulose Nanocrystals

Fibre	I (002)	I_{am}	CrI (%)
Baobab pod	5600	300	95

Source: This study

The Crystallinity index for the raw baobab pod fibres which is initially at 81% is higher than that reported by Elenga *et al*. (2009) of Wrighitia tinctoria seed fibres (49.2 %), ramie and (58 %). The percentage increased significantly after NaOH treatment and acid hydrolysis to about 95%. This increase shows the improvement in the cellulose structure of the fibre which in turn contributed to enhancing its mechanical properties. Crystallinity index of baobab pod fibre cellulose nanocrystals and crystallite size in comparison with other natural fibres is shown in Table 2.

Table 2: Comparison of crystallinity index and crystallite size with other nano crystals

Fibre	Crystallinity Index (%)	Crystallite Size (nm)	Reference
Baobab Pod	95	3.03	This study
Jack fruit peel	83.42	2.8	Trilokesh and Kiran, 2019
Brown Seaweed	78.7	2.8	He *et al*., 2018

TGA Analysis of Baobab Fibre Cellulose Nano crystals

The TGA spectrum is presented in Figure 7; it showed that the thermal behaviour exhibited by the cellulose nano crystals is in line with those that are used in the production of polymeric composites. The curve shows an endemic peak within the range of 110 ˚C to 140 ˚C, this can be attributed to evaporation of water. Exothermic peaks were observed at higher temperatures, which can be attributed to decomposition of hemicellulose and cellulose (Martins *et al.*, 2008).

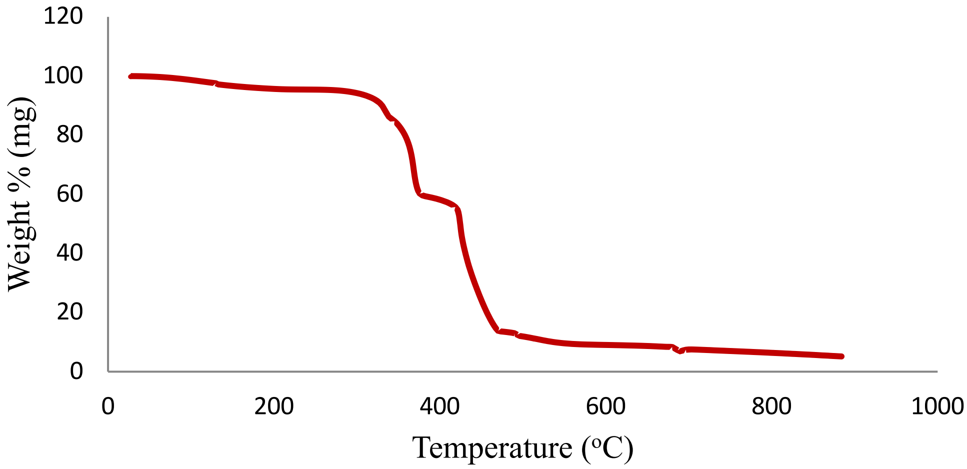

Figure 7: TGA of baobab Pod Fibre cellulose nanocrystals

The plot showed that there was an overall increase in the amount of heat generated, Tg value, degradation temperature of hemicellulose and cellulose. The TGA profile presents the same thermal behaviour in agreement with reported studies (Kargarzade *et al.,* 2012). The weight loss below 140–180 ˚C could be attributed to water evaporation; similarly, two degradation stages were evident around 230 and 350 ˚C.

CONCLUSION

Experimental results and analysis of the data shows that, NaOH treatment (Mercerization) of baobab pod fibres enhances the physical and mechanical properties of the fibres to a large extent. The optimal conditions were found when the fibres were soaked in 6.953 % NaOH concentration at 99.763 ˚C for 359.963 min in terms of tensile strength and Young modulus. The crystallinity index of the Baobab pod fibres increases significantly with NaOH treatment. Further increase of 95 % was recorded after the acid hydrolysis. Crystallite size which is also supportive of the description of crystallinity of the cellulose was found to be 3.003 nm

TGA results showed that chemical treatment and acid hydrolysis improved thermal stability of the Baobab pod fibres. The research serves as means of obtaining data on raw Baobab pod fibres which is very rear. It is suggested that further studies should be directed toward finding the capabilities of use of cellulose nanocrystals obtain from baobab pod fibres as reinforcing material for plastics and other matrix that can be used for various engineering applications.

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Conflict of Intrest:
The authors declare that they have no known conflict of intrest that hcould have appear to influence the work reported in this paper

Author contrıbutıon:
Author 1: Investigation, writting – original draft preparation, methodology, conceptualization and writting –review, editting. Author 2: Data curation, supervision, project administration, software, Author 3: Funding acquisition, writing – review editing.

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