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Potential of Anacardic Acid for Nanosized Cellulose Preparation Under Different Treatment Conditions

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Abstract

Herein, anacardic acid was applied for the preparation of nanosized cellulose using three different treatment conditions including ultrasonication, microwave irradiation, and reflux. Physico-chemical characterization was undertaken using FTIR, TEM, SEM, and XRD. FTIR, TEM, and SEM analyses confirm the preparation of nanosized cellulose with similar chemical but different physical properties as the cellulose starting material. In addition, calculated degrees of crystallinities from XRD data revealed crystallinities of 53.9, 54.4, and 54.7% for the nanosized cellulose prepared by ultrasonication (UNC), microwave irradiation (MNC), and reflux (RNC) respectively, which all are higher than the 53.3% of the precursor cellulose. Overall, the study shows that anacardic acid holds potential for the preparation of nanosized cellulose.

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1. Introduction

Nanosized cellulose, which is a material with at least one dimension < 100 nm, is traditionally prepared using mineral acids like sulfuric and hydrochloric acids [1-4]. However, the use of mineral acids comes with significant problems particularly operational hazards, generation of toxic wastes, and corrosion of reactors [5]. Consequently, growing attention is being paid to the development of environmentally friendly methods for preparing nanosized cellulose. Some of these methods are enzymatic and organic acid-based hydrolysis. Although enzymatic hydrolysis is environmentally friendly, significant mechanical energy is often required to break down the enzymatically hydrolyzed cellulose fibres into nanocrystals [6, 7]. In addition, dispersion and chemical modification of the product cellulose nanocrystal is challenging [5]. Consequently, significant consideration is being paid to organic acid-based hydrolysis [8, 9].

Attractive features of the organic acid-based method include ease of recovery, biodegradability, limited corrosivity, and convenient handling of the organic acid [10]. Fu and coinvestigators reported access to highly crystalline nanosized cellulose material in two steps using an ionic liquid and subsequently ox-

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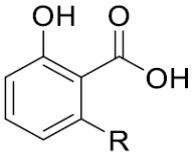

Figure 1. The general structure of anacardic acids (R = saturated or unsaturated alkyl chain)

alic acid under relatively mild conditions [2]. Robles's group described the ultrasonic-assisted hydrolysis of cellulose using citric, oxalic, and maleic acids. Though the yields of the prepared nanosized cellulose were poor to moderate (20 to 40%), the thermal stabilities were better than those obtained using sulfuric acid [11]. Holilah and coworkers observed that the yields, particles sizes, and crystallinities of the nanosized cellulose they prepared using organic acids (acetic, citric, and oxalic) were higher than that prepared using inorganic acids (hydrochloric, sulphuric, and phosphoric) [12].

Investigation into the discovery and development of bio-based alternatives to petroleum-derived heavy chemicals is becoming increasingly popular due to the need to achieve sustainable development. While many bio-based reagents can be employed to prepare nanosized cellulose, our attention was drawn to anacardic acid (Figure 1) because of the presence of the carboxylic acid group. In addition, the extraction of anacardic acid from the cashew fruit is well established [13-15] and applications of the acid [15-18] including those exploiting the carboxylic acid group [14] are growing.

As part of our work on the investigation of environmentally friendly methods for the preparation of bioderived materials, we wondered if anacardic acid could function as an effective hydrolyzing agent for the preparation of nanosized cellulose. Anacardic acid, a yellow liquid obtained from the nut of the cashew fruit, is composed of both saturated and unsaturated molecules. Herein, we report the preparation of nanosized cellulose by the hydrolysis of cellulose (derived from plantain inflorescence stalk) using anacardic acid under different conditions including ultrasonication, microwave irradiation, and reflux. Following this, the nanosized cellulose products were characterized using FTIR, TEM, SEM, and XRD. This study shows that anacardic acid is a potential candidate for the preparation of nanosized cellulose.

2. Materials and methods

2.1. Materials

The cashew (*Anacardium occidentale*) seeds were purchased from the local fruit market in Akure, Ondo State, Nigeria. Plantain (*Musa paradisiaca*) inflorescence stalk (PIS) was obtained from the Teaching/Demonstration Plantation of the Federal University of Technology Akure (FUTA). The materials were authenticated at the Department of Crop, Soil, and Pest Management, FUTA. All reagents were purchased from Sigma Aldrich and used as received.

2.2. Instrumentation

Fourier transform infrared (FTIR) spectra were recorded on Bruker© Alpha Platinum-Attenuated Total Reflectance IR spectrometer. X-ray diffraction (XRD) data were collected on a Panalytical Empyrean X-ray diffractometer employing a Co Kα radiation at 40 kV and 40 mA. Transmission electron micrographs (TEM) were captured using the JEOL 2100+ machine operating an acceleration voltage of 200 kV from samples prepared on a copper EM grid. Scanning Electron Microscopy (SEM) characterization was undertaken using LEO 1450 SEM, the samples were attached to a brass stub and coated with gold before analysis. Ultrasonication treatment was undertaken using a Bransonic ultrasonicator (Ranson 1210E- MT,USA) sonicator. Microwave irradiation was achieved using Russell Hobbs-ASDA (Leeds) microwave operating at a frequency of 2.45 GHz.

2.3. Preparation of plantain inflorescence stalk cellulose

Plantain inflorescence stalk (PIS) cellulose was prepared following the method reported by Oluwasina and coworkers [19]. Briefly, PIS powder and 5% NaOH (1:30 ratio by mass) were charged into a 15 L autoclave and heated at 140 ^{o}C under atmospheric pressure for 1 hour. The pulp obtained was washed with water until a neutral pH and finally dried. The dried PIS pulp (7.5 g), hot water (375 mL), $NaClO_2$ (4.45 g), and acetic acid (1.03 mL) in a 1 L beaker were heated at 80 ^{o}C for 1 hour. Next, $NaClO_2$ (8.9 g) and acetic acid (2.06 mL) were fed into the stirring mixture, and the whole suspension was heated for a further 2 hours. The bleached sample obtained was washed with water to a neutral pH and dried to give a white fibrous material labeled as plantain inflorescence stalk (PIS) cellulose.

2.4. Anacardic acid isolation

Anacardic acid was isolated from cashew nut powder following the combination of the methods reported by Shobha's [20] and Bezerra's [14] groups. Briefly, cashew seed nut powder (average particle size of 1 mm) was extracted with *n*-hexane for 12 hours to give a brown viscous liquid which was concentrated by distillation. A solution of the brown oil (70 g) in aqueous MeOH (300 mL, 5%) was warmed to 50 ^{o}C, after which $Ca(OH)_2$ was added in portions with continuous stirring for 3 hours. The crude product obtained was filtered and the resulting residue was washed successively with MeOH (150 mL), and water (200 mL) and stirred in concentrated HCl (400 mL, 11 M) for 1 hour. The organic component was extracted using petroleum ether (100 mL x 3), dried over anhydrous Na_2SO_4, and concentrated to furnish a dark brown liquid identified as crude anacardic acid.

2.5. Nanosized cellulose preparation

Nanosized cellulose was prepared by ultrasonication, microwave irradiation, and reflux. Typically, a suspension of PIS cellulose (5 g) and anacardic acid in acetone (50 mL, 80% v/v) was treated by ultrasonication, microwave irradiation, or reflux for 45 min. The resulting crude product was washed consecutively with acetone (100 mL), EtOH (100 mL), distilled water (100 mL), and oven dried at 60 ^{o}C for 8 hour to deliver a white

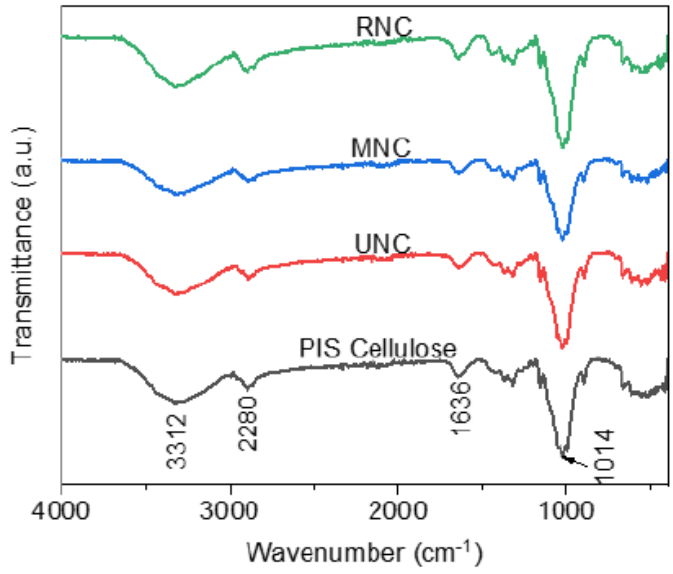

Figure 2. FTIR spectra show that plantain inflorescence stalk (PIS) cellulose and nanosized cellulose prepared by ultrasonication (UNC) microwave irradiation (MNC) and reflux (RNC) contain identical functional groups

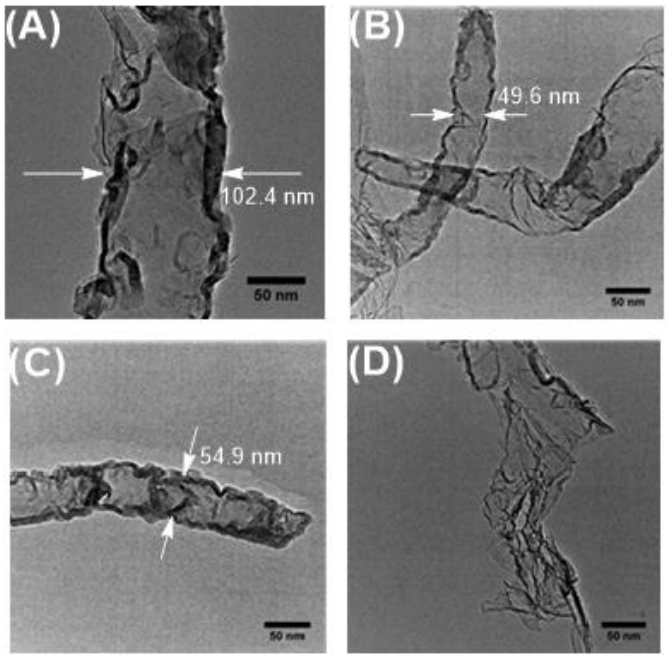

Figure 3. TEM micrographs of (a) plantain inflorescence stalk (PIS) cellulose and nanosized cellulose prepared by (b) ultrasonication (c) microwave irradiation and (d) reflux

powder labeled as ultrasonication-prepared nanosized cellulose (UNC), microwave irradiation-prepared nanocellulose (MNC) or reflux-prepared nanocellulose (RNC) to represent the preparation methods.

2.6. Determination of degree of crystallinity

The degree of crystallinity (DC) was determined using XRD data by the method described by Neto's group [21].

$$Degree\ of\ crystallinity(\%) = \frac{crystalline\ band\ areas}{(crystalline\ band\ areas + amorphous\ band\ area)} \times 100 \quad (1)$$

3. Results and Discussion

3.1. Chemical composition identification by FTIR

The chemical compositions of the PIS cellulose, RNC, UNC, and MNC prepared products were identified from their FTIR spectra (Figure 2). All the spectra show the presence of identical functional groups in all samples, an observation expected if the PIS cellulose is cellulosic and the RNC, UNC, and MNC are the nanosized products. Indeed, all spectra contain broad bands at 3312 cm^{-1}, weak/medium peaks at 2280 cm^{-1}, weak peaks at 1636 cm^{-1}, and sharp peaks at 1014 cm^{-1} representative of O-H stretching, C-H stretching, O-H bending, and C-O stretching vibrations respectively [22-25].

3.2. Morphology and fibre width determination by TEM and SEM

The fibre morphology and width were determined by TEM analysis (Figure 3). All fibres except for that prepared by reflux (RNC) appear as hollow tubes with thick edges. As expected, the PIS cellulose has the highest particle width of 102.4 nm. UNC and MNC have fibre widths of 49.6 and 54.9 nm respectively.The fibre width of RNC could not be determined as a sizeable micrograph was not obtained. The lower fibre width observed for UNC compared to MNC could be because ultrasonication involves the use of microbubbles of the anacardic acid solution which may be more efficient than the bulk solution involved with microwave heating for the splitting of PIS cellulose [26]. The observed nano sizes of the UNC and MNC fibers widths indicate that different materials have been successfully prepared from the PIS cellulose [27].

Further information on the morphology of the samples was obtained after SEM analysis. The PIS cellulose appears as fibre bundles cemented together to give a lightly rough surface (Figure 4). The nature of the PIS cellulose surface was attributed to the presence of lignin and hemicellulose. On the other hand, the RNC, UNC, and MNC samples appear as individual strands loosely bound into a bunch with deep longitudinal furrows and a higher degree of surface roughness than observed for the PIS cellulose. The loosely bound strands in the hydrolyzed cellulose samples can be attributed to the removal of the fibrous lignin and hemicellulose from the PIS cellulose by anacardic acid. Overall, the SEM micrographs support the TEM results showing that the cellulose derivative (RNC, UNC, and MNC) samples were prepared from the PIS cellulose using all methods employed.

3.3. Degree of crystallinity determination from XRD patterns

The X-ray diffractograms displayed in Figure 5 were collected to determine the degrees of crystallinity.The diffractogram for the PIS cellulose is similar (save the absence of a peak at 2Θ values below 20 ^{o}) to the diffractograms of cellulose sam-

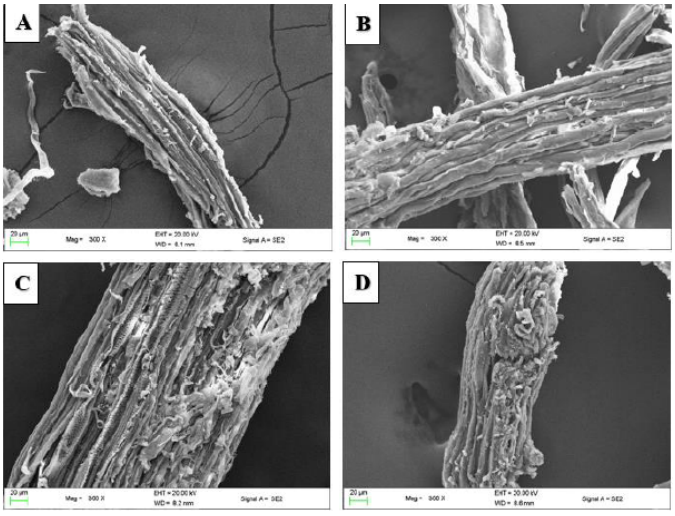

Figure 4. SEM micrographs of (a) plantain inflorescence stalk cellulose and nanosized cellulose prepared by (b) ultrasonication (c) microwave irradiation and (d) reflux

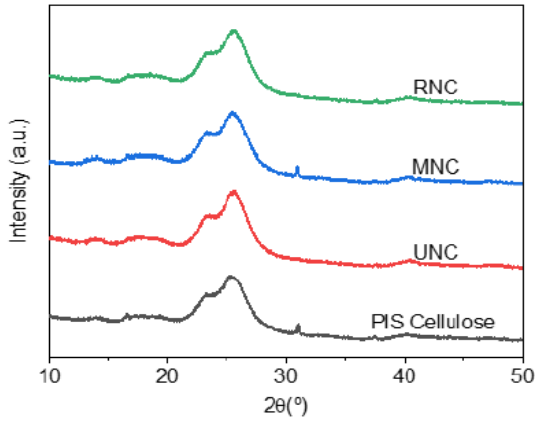

Figure 5. X-ray diffractograms of plantain inflorescence stalk (PIS) cellulose and nanosized cellulose prepared by ultrasonication (UNC), microwave irradiation (MNC), and reflux (RNC)

ples reported by Teixeira and coauthors [27] using sugarcane bagasseas a cellulose source. The PIS cellulose diffractogram looks identical to those of UNC, MNC, and RNC samples. The calculated DCs were as follows 53.3, 53.9, 54.4, and 54.7 % for the PIS cellulose, UNC, MNC, and RNC respectively. The DCs shows that the reflux method produced the most crystalline nanosized cellulose material. This could be because refluxing was most effective in the removal of non-cellulosic components from PIS cellulose.

4. Conclusion

The preparation of nanosized cellulose using anacardic acid under different treatment conditions including ultrasonication, microwave irradiation, and reflux was undertaken. Results from the physicochemical characterizations suggest that anacardic acid was most effective for the preparation of nanosized cellulose under reflux conditions. This study shows that a combination of anacardic acid as a hydrolysis agent and reflux provides access to nanosized cellulose with higher crystallinity compared to the precursor cellulose. Other conditions including pressure, reaction duration, and amounts of acid for the preparation of nanosized cellulose using anacardic acid could be investigated.

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