

***Euterpe oleracea* fruit processing residues as a source of nanocellulose**

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ABSTRACT

The species *Euterpe oleracea*, commonly known as açai, produces a fruit whose pulp is extracted and sold throughout Brazil. Its production generates a large volume of waste rich in chemical compounds that can be used as raw material in various industrial segments. In this sense, the extraction of plant nanocellulose has emerged as a suitable alternative to meet current environmental demands for sustainable development. Therefore, the objective of this study was to perform chemical characterization and obtain cellulose nanocrystals (CNC) from the waste generated in the açai production chain. For the production of nanocellulose, the waste was pretreated with NaClO₂ or H₂O₂, followed by hydrolysis with sulfuric acid (H₂SO₄). The quantities found for the chemical components in the waste were: 1.5% inorganic compounds, 11.11% total extractives, 25.58% Klason lignin, 62.01% holocellulose, 28.31% alpha-cellulose, and 33.40% hemicelluloses. The pretreatments delignified the material, and acid hydrolysis extracted CNC. The CNC yields from pretreatments with H₂O₂ and NaClO₂, followed by acid hydrolysis, were 58.76% and 0.5%, respectively. The crystallinity index reached 55.31% for the treatment with H₂O₂. Both pretreatments were effective in delignification and in obtaining nanocellulose, but the hydrolysis conditions in the treatment with NaClO₂ should be modified to increase the yield.

Keywords: Nanocellulose; Acid hydrolysis; Bioeconomy; Açai.

1. INTRODUCTION

A large portion of the natural resources extracted from nature is, in theory, partially utilized, and much of this amount is wasted during the processing stages, generating large volumes of waste that are discarded into the environment. Even though organic, these wastes cause environmental pollution. This process creates a double imbalance: on one side, the depletion of natural resources, and on the other, the increase in waste generated due to increased consumption [1].

Euterpe oleracea, popularly known as açai, produces a fruit from which the pulp is extracted through a battery system for national commercialization and export. Most of the açai pulp production is concentrated in the North of Brazil, accounting for approximately 92.1% of the national total. The state of Pará is the largest producer and exporter of the fruit in the world [2].

According to IBGE [3] approximately 220,000 tons of açai were produced in 2020 alone and, considering that 80% of the fruit consists of fibers and seeds, approximately 176,000 tons of waste were discarded. Most of this waste is not properly disposed of and is dumped into canals, rivers, or open-air landfills. It is necessary and essential to develop alternative approaches for the use of this material, since there is no adequate recycling process to handle the volume of waste generated daily.

Only a small amount of the waste generated in the açai processing chain is utilized in the form of agricultural substrates, raw materials for handicrafts, and as domestic fertilizer. This waste consists of seeds, tegument, and lignocellulosic fibers, which are rich in phytochemical compounds with antioxidant and antimicrobial properties [4].

Considering the search for sustainable and biodegradable materials as a solution to the problems caused by the use of petroleum-based materials, the lignocellulosic fibers present in the waste generated in the açai production chain can serve as a source of bioproducts, such as vegetal nanocellulose (NC). Cellulose is a widely recognized engineering material in the industry due to its abundance, biodegradability, and renewable nature, and it is currently employed in the form of NC as a platform for developing functional materials [5].

NC can be extracted in the form of cellulose nanocrystals (CNC) or cellulose nanofibrils (CNF), and its intrinsic characteristics can optimize chemical, physical, mechanical, optical, and thermal properties when applied in films, coatings, bioactive packaging, hydrogels, aerogels, wastewater treatment, automotive industry products, and other engineering applications [6–9].

Banana plant waste [10], sugarcane bagasse [11], rice husks [12], and nut shells [13], empty fruit bunches of palm oil [14], among other biomasses, have also been used as a source of lignocellulosic fibers for NC extraction. This approach adds value to the waste generated in their respective production chains and offers new alternatives to mitigate environmental liabilities.

CNCs are often extracted from lignocellulosic biomass using a two-step method: 1) purification of lignocellulosic biomass, which consists of removing non-cellulosic chemical constituents such as hemicelluloses, lignin, pectins, and low molecular weight substances to expose the cellulose fibers, and 2) acid hydrolysis using mineral acids such as H_2SO_4 [15], HCl [16], HBr [17], H_3PO_4 [18], and binary mixtures such as H_2SO_4/HNO_3 [19], $H_2SO_4/HCOOH$ [20] under controlled time and temperature conditions. CNCs hydrolyzed with H_2SO_4 showed high electrostatic stability, while those hydrolyzed with HCl , HBr , or H_3PO_4 showed higher thermal degradation temperatures [21].

CNCs have gained prominence as sustainable materials because they are obtained from renewable sources such as lignocellulosic biomass. In addition, this type of material has broad potential for use in the pulp and paper, food, pharmaceutical, cosmetic, biomedical, automotive, and other industries. This type of nanomaterial can improve the mechanical properties and oxygen and water vapor barrier properties of biodegradable films [22], substrates for the development of dressings, face masks, hydrogel manufacturing, scaffolds for tissue engineering and biosensors, drug delivery systems [23], can improve the flexural modulus and lead to lighter part designs for automotive applications, such as door panels, headliners, and underbody shields [24].

Several studies have proposed new methods for extracting CNC from lignocellulosic biomass, including extraction by strong acid hydrolysis with sulfuric and hydrochloric acids [16], hydrolysis with nitric acid [17], acid pretreatment followed by high-pressure homogenization [25], among other approaches. Although several residual biomasses have been studied as a source of cellulose for CN extraction, there are still few studies using *Euterpe oleracea* residue.

Thus, there are still gaps in knowledge that need to be filled in order to consolidate the potential of *Euterpe oleracea* waste as an alternative source for CNC extraction. In view of this, the present research aimed to perform the chemical characterization of the waste generated in the açai production chain and to obtain cellulose nanocrystals by the acid hydrolysis and ultrasonic processing method.

2. MATERIALS AND METHODS

Merchants from Castanhal, Pará, Brazil, kindly provided the (açai) *Euterpe oleracea*, (seeds and fibers). The açai residue was mainly composed of the mesocarp of the açai fruit. It was dried in an oven at 50 °C for 24 hours and ground in a Willey mill. The particle size classification was carried out using sieves attached to a magnetic shaker, employing a 40/60 mesh to determine the total extractives content [26], Klason lignin [27], hemicelluloses, calculated by the difference between holocellulose [28] and alpha-cellulose [29], and ash [30].

2.1. Sodium chlorite pretreatment

The sodium chlorite pretreatment was carried out as previously described [21], with some modifications. Thirty grams of açai residue, free of extractives, were added to an Erlenmeyer flask containing 10 g of sodium chlorite, 5 g of sodium acetate, 2.5 mL of glacial acetic acid, and 200 mL of distilled water. Subsequently, the mixture was subjected to a water bath reaction at 70 °C, with manual stirring every 10 minutes, for 2 hours. After the reaction time, the sample was washed with distilled water until the aqueous medium reached neutral pH. This procedure was repeated, totaling 4 hours of reaction. Due to the characteristics of the açai residue, an additional delignification step was required for the complete removal of lignin. This additional step consisted of applying a 2.5% sodium chlorite solution, with the pH adjusted to 4.5 by the addition of 55 drops of acetic acid, at 100 °C, for 1 hour. The resulting material, free of non-cellulosic chemical components, was then washed with distilled water and dried in an oven at 70 °C for 8 hours.

2.2. Hydrogen peroxide pretreatment

A mixture of 240 g of açaí residue and 2000 mL of distilled water was heated at 90 °C under magnetic stirring for 1 hour for the hydrogen peroxide pretreatment. Subsequently, the açaí residue was carefully washed with hot distilled water to remove impurities and then dried in an oven at 60 °C. The dried açaí residue was added to an Erlenmeyer flask containing a solution of 4% (w/v) sodium hydroxide and 27% (v/v) hydrogen peroxide, at a ratio of 1:40 (w/v), and subjected to a water bath reaction at 60 °C with mechanical stirring for 3 hours. The material was then washed with distilled water and dried in an oven at 60 °C for 24 hours. This procedure was repeated to achieve higher whiteness of the material.

2.3. Nanocellulose extraction from açaí elimination

The açaí residue fibers purified with sodium chlorite or hydrogen peroxide were subjected to the acid hydrolysis process to obtain nanocellulose. The previously treated açaí residue was subjected to acid hydrolysis by mixing it with a solution of sulfuric acid in a ratio of 1:10 (w/v), under mechanical agitation and heating in a water bath at 45 ° [31]. The reaction was then halted by adding cold distilled water, equivalent to five times the initial volume of the reaction. The diluted solution was centrifuged three times for 10 minutes at 10,000 rpm, replacing the supernatant with distilled water after each centrifugation cycle to remove excess unreacted sulfuric acid. Subsequently, the samples were dialyzed against distilled water until the medium was neutralized, as monitored with a pH meter. An additional dispersion step was conducted using an ultrasonic probe processor (SONICS Vibra Cell, model VCX 750), applying continuous sonication for 20 minutes at an amplitude of 30%, while keeping the sample in an ice bath during sonication. Table 1 presents the hydrolysis parameters used in each treatment, determined from experiments not included in this study.

The nanocellulose samples extracted from açaí residue treated with sodium chlorite were designated as ENaClO_2 , while the samples derived from residue treated with hydrogen peroxide were named EH_2O_2 (Figure 1).

2.4. Scanning electron microscopy (SEM) of the açaí residue

Samples of the açaí residue in natura were carefully fixed with carbon tape and covered with a thin layer of gold. Representative micrographs of the samples were taken using a Tescan scanning electron microscope (model VEGA3) with an acceleration voltage of 10 kV to study the morphology of the material.

2.5. Characterization of cellulose nanocrystals extracted from açaí residue

The yield of nanocellulose from the açaí residue after pre-treatment with NaClO_2 or hydrogen peroxide was determined by the ratio between the dry mass of the nanocellulose after lyophilization and the dry mass of the residue before sulfuric acid hydrolysis, as shown in Equation 1:

$$R\% = \frac{\text{PF}}{\text{PI}} \times 100 \quad (1)$$

Where:

R% = Nanocellulose yield

PF = Nanocellulose dry mass

PI = Dry mass of pre-treated açaí residue

Table 1: Hydrolysis parameters with sulfuric acid for extracting nanocellulose from *Euterpe oleracea* residue treated with sodium chlorite or hydrogen peroxide.

PRETREATMENT	PROPORTION (w/v)	TEMPERATURE (°C)	REACTION TIME (min)	CONCENTRATION H_2SO_4 (%)
NaClO_2	1:10	45	30	55
H_2O_2	1:10	45	60	45

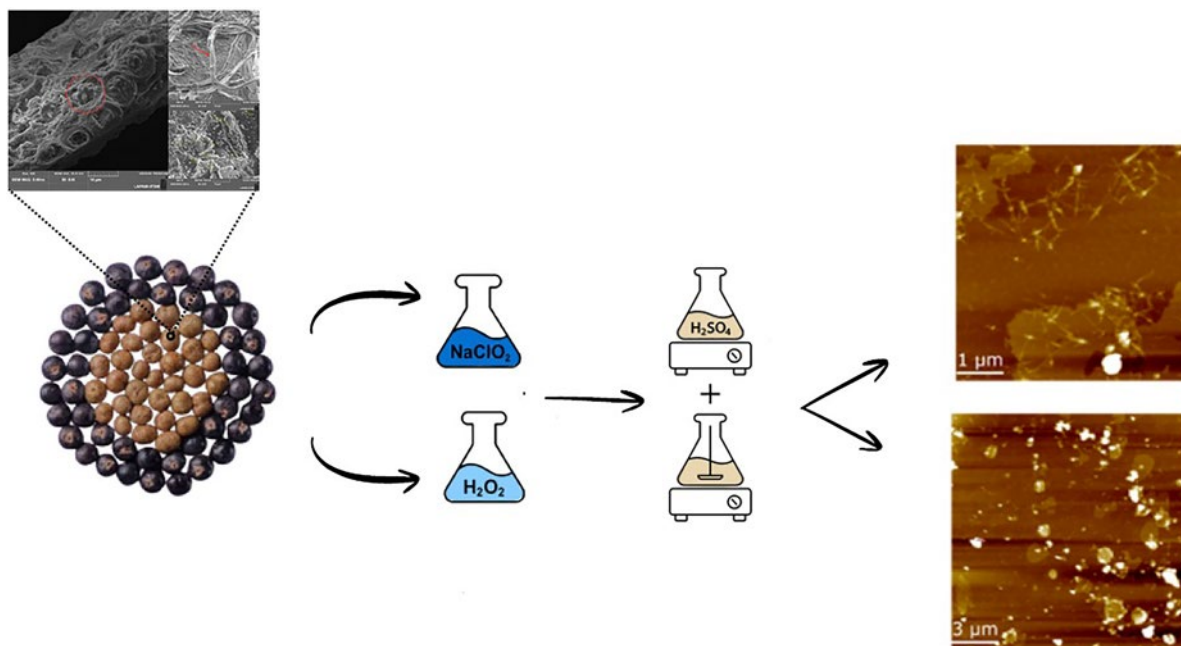


Figure 1: Schematic representation of the pre-treatment and extraction of nanocellulose from *Euterpe oleracea* residue by the acid hydrolysis method.

2.6. Fourier transform infrared spectroscopy (FT-IR)

Fourier Transform Infrared Spectroscopy (FT-IR) was performed using a Shimadzu Prestige IR device by the direct transmittance method, employing the KBr pellet technique. The spectra were recorded in the range of 4500 cm^{-1} to 500 cm^{-1} , with 45 scans and a resolution of 2.0 cm^{-1} .

2.7. X-ray diffraction (XRD)

The diffractograms were obtained by X-ray diffraction using a Rigaku Miniflex 300 device, with $K\alpha$ radiation ($\lambda = 1.54051\text{ \AA}$), a voltage of 30 kV, and a current of 10 mA. The analyses were conducted with a scanning speed of 0.5 s, a step of 0.03° , and an angular range of 5° to 100° .

The crystallinity indices (IC) were determined from the deconvolution of the peaks observed in the diffractograms. A Gaussian distribution function was used to represent the amorphous ($2\theta \sim 12^\circ\text{--}18^\circ$) and crystalline ($2\theta \sim 20^\circ\text{--}24^\circ$) peaks. Deconvolution was performed using Magic Plot (3.0.1) software, based on the peak positions [32]. The areas corresponding to the crystalline and amorphous peaks were estimated after baseline correction using OriginLab software. The IC was calculated according to Equation 2.

$$\text{IC\%} = \frac{A_c}{A_t} \times 100 \quad (2)$$

Where:

IC% = crystallinity index

A_c = sum of the areas under the crystalline curves

A_t = total area below the XRD standard

2.8. Atomic force microscopy (AFM)

The lyophilized nanocellulose was dispersed in 100 mL of distilled water using an ultrasonic probe processor (SONICS Vibra Cell, model VCX 750), applying continuous sonication for 10 minutes at 30% amplitude and keeping the sample in an ice bath during sonication. The solutions were then poured onto mica pieces and analyzed by atomic force microscopy using a Park NX10 microscope (Park Systems, Suwon – Korea) equipped with SmartScan software version 1.0. RTM13c2020-1, operating under environmental conditions of $21 \pm 5^\circ\text{C}$ and relative humidity of $55 \pm 10\%$. The images were processed offline using XEI software version 4.3.4 Build22.RTM1.

2.9. Thermogravimetric analysis (TGA)

TGA analysis of the raw açai residue and the nanocellulose produced from açai residue treated with NaClO_2 and H_2O_2 was performed using a TGA-100 instrument from Navas Instrument. A 50 mg sample of dried powder was subjected to heating from room temperature up to 1000 °C, at a heating rate of 10 °C/min and a nitrogen gas flow of 1 L/min, as previously reported [15].

3. RESULTS

The chemical characterization of the açai residue resulted in 1.5% ash, 11.11% total extractives, 25.58% lignin, 62.01% holocellulose (cellulose and hemicelluloses), and 28.61% alpha-cellulose.

The surface morphological structure of the raw açai residue was studied using scanning electron microscopy (SEM), and the micrographs are presented in Figure 2.

The NaClO_2 pretreatment resulted in low nanocellulose yield (0.5%) compared to the yield obtained with H_2O_2 pretreatment (58.76%). In relation to these results, it can be observed that the low yield of nanocellulose may be related to the second stage of treatment with NaClO_2 , which caused excessive degradation of the cellulose fibers.

Figure 3 shows the FTIR spectra of the natural açai residue and the nanocellulose extracted from the açai residue previously treated with hydrogen peroxide (EH_2O_2) or sodium chlorite (ENaClO_2). The characteristic peaks of hemicelluloses and lignin in the natural açai residue, EH_2O_2 , and ENaClO_2 indicate the partial removal of lignin and hemicelluloses after pretreatment.

In the treatment with NaClO_2 , it was not possible to calculate the crystallinity index, which shows that the material underwent degradation during hydrolysis, resulting in a predominantly amorphous structure. On the other hand, the treatment with H_2O_2 presented a crystallinity index of 55.31%, a value that indicates the presence of crystalline regions characteristic of cellulose nanocrystals (CNC). Figure 4 shows the XRD patterns of the amorphous material obtained with NaClO_2 and the CNC produced with H_2O_2 .

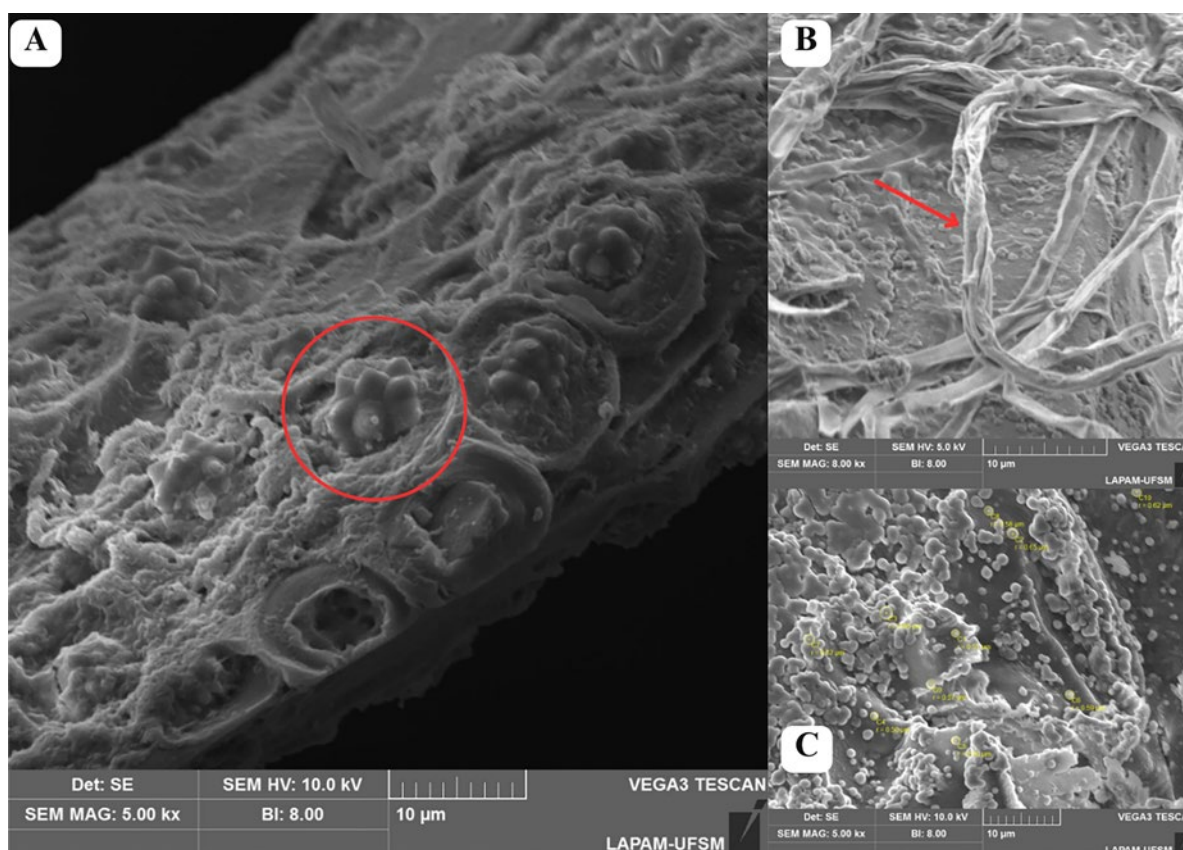


Figure 2: Scanning electron microscopy of (A) fibers from the in natura residue of *Euterpe oleracea*; (B) tegument and fibers; and (C) tegument coated with waxy substances.

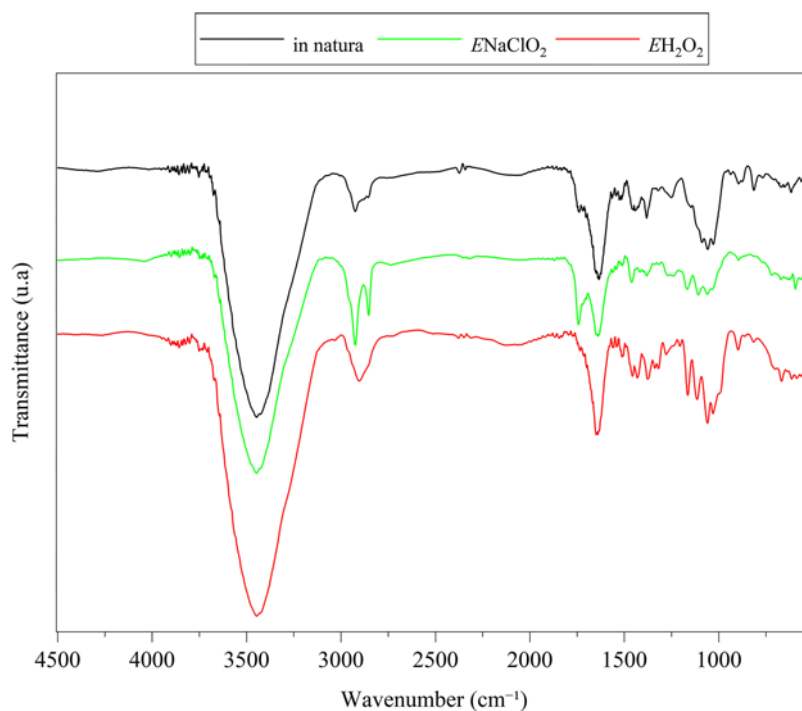


Figure 3: FTIR spectra of natural *Euterpe oleracea* residue and nanocellulose extracted from açai residue pre-treated with hydrogen peroxide (EH_2O_2) or sodium chlorite (ENaClO_2).

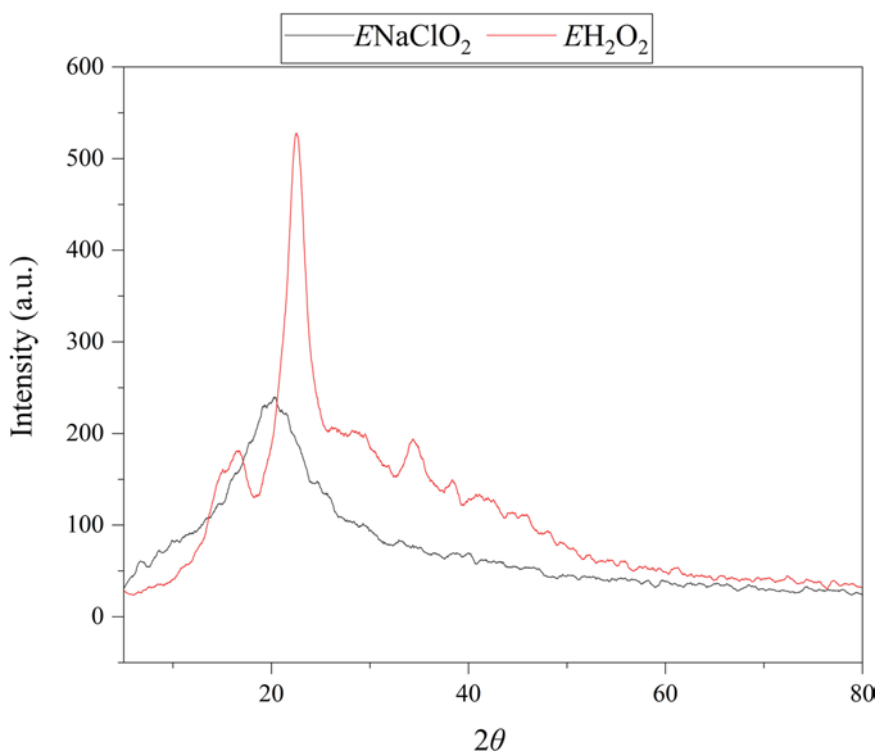


Figure 4: X-ray diffraction pattern of nanocellulose samples extracted from *Euterpe oleracea* residue pre-treated with hydrogen peroxide (EH_2O_2) or sodium chlorite (ENaClO_2).

Figure 5 shows representative AFM images of the EH_2O_2 and ENaClO_2 suspensions. The results indicated that acid hydrolysis successfully extracted nanocrystalline cellulose from the cellulose fibers of the açai residue, regardless of the delignification method applied to the residue. Figure 6 refers to the thermogravimetric curve of weight (%) (A) and differential thermogravimetric curves (DTG) (B) with sodium chlorite (NaClO_2) and hydrogen peroxide (H_2O_2).

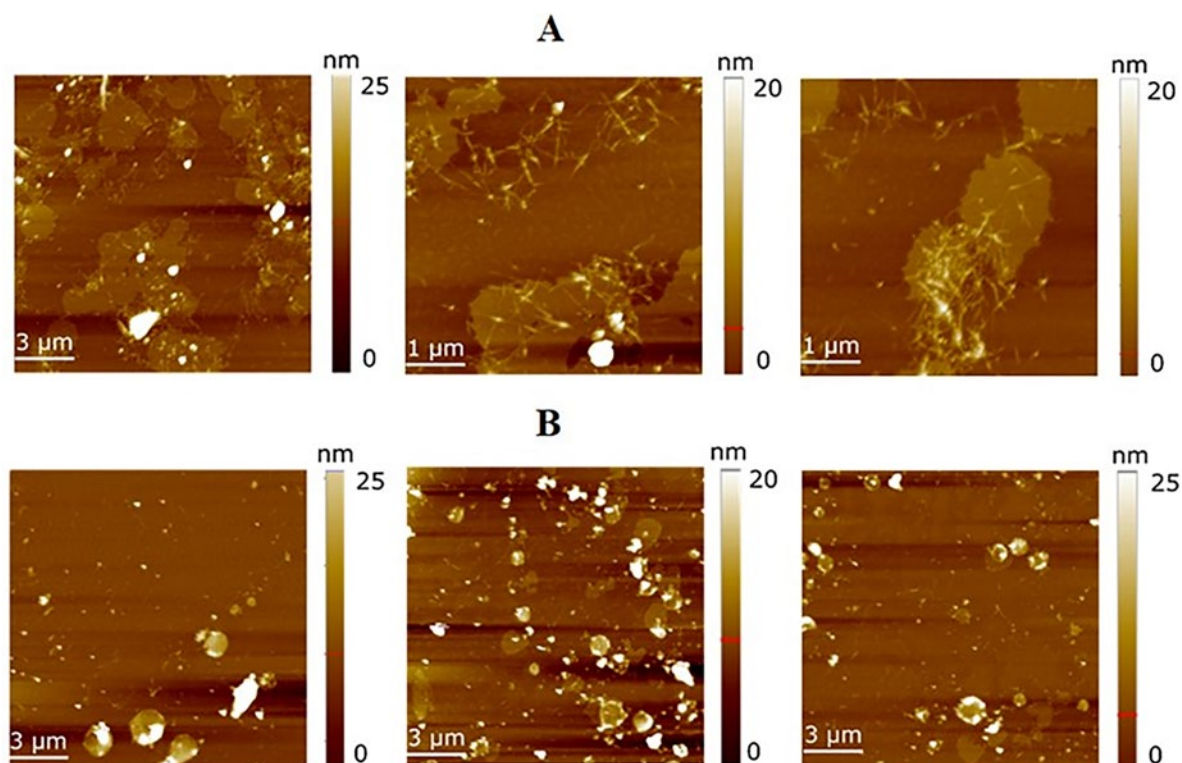


Figure 5: Atomic force microscopy images of cellulose nanofibril samples extracted from açai residue pre-treated with hydrogen peroxide (EH_2O_2) A or sodium chlorite (ENaClO_2) B.

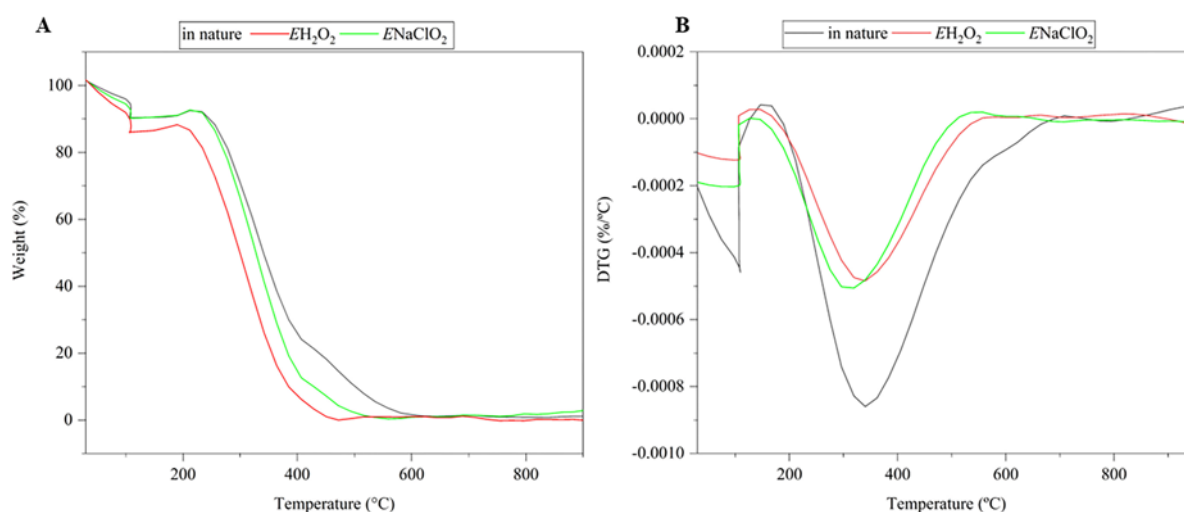


Figure 6: A) Thermogravimetric curve of weight (%) and B) differential thermogravimetric curves (DTG) of the residue of *Euterpe oleracea* in natura and nanocellulose extracted from the delignified residue with sodium chlorite (ENaClO_2) or hydrogen peroxide (EH_2O_2).

4. DISCUSSION

The proportions of the chemical components observed in the present research are generally typical of agro-industrial residues composed of fruit peels and seeds, with low mineral content, moderate extractive content, and high lignification [33]. Values ranging between 8.1–11.8, 29.7–44.1, 18.0–37.0, and 18.37–35.1 were found for extractives, cellulose, hemicelluloses, and lignin, respectively, for the same type of açai residue [34–39]. Açai showed low ash, extractive, and lignin content, and high alpha-cellulose content compared to other agro-industrial residues, indicating that they are a good material for nanocellulose production.

The pretreatment of lignocellulosic biomasses is the first step in the process of extracting plant nanocellulose and has been extensively studied for various types of biomass [38, 40] due to the importance of breaking lignocellulosic recalcitrance prior to acid hydrolysis.

In the representative micrograph of the raw residue in Figure 2, an individual fiber can be observed. The morphological surface of the fiber is rough and covered by a lipid layer, which is commonly found in this type of residue [4]. Throughout the fibrous structure, there are globular cells that are obstructed by a rosette-shaped structure (Figure 2A). These rosette structures have been previously described in the literature as silica rosettes, frequently found in fibers of açai residue [41].

In addition to the fibers, the micrograph also presents a representative view of the açai pericarp with a porous structure and irregular surface, which may be associated with the residue processing performed with a blade mill. This surface irregularity of the pericarp was also observed by other authors who studied the same type of açai residue and attributed this morphology to the mechanical processing in a blade mill and the friction of the solid particles of the açai residue during processing [42]. On the surface of the endocarp, rounded waxy punctuations can be observed, either individually or forming an aggregate of punctuations.

The yield of acid hydrolysis applied to the açai residue treated with sodium chlorite was 0.5% (ENaCl_2), while the material treated with hydrogen peroxide (EH_2O_2) resulted in 58.76%. This result demonstrates that the acid hydrolysis conditions applied to the material treated with sodium chlorite were too severe, leading to a low yield. On the other hand, the hydrolysis performed on the material treated with hydrogen peroxide had a high yield, indicating that the hydrolysis conditions were satisfactory for yield.

The yield may also have been affected by the acid's accessibility to the cellulose fibers. Pretreatment with sodium chlorite is often described as an efficient route for the delignification of both woody and non-woody lignocellulosic biomass, and for increasing the efficiency of nanocellulose extraction methods due to greater exposure of the cellulose fibers [43].

Therefore, lignin was excessively removed when the NaClO_2 pretreatment was applied to the açai residue. In contrast, the delignifying action of H_2O_2 pretreatment is milder; the chromophore groups of lignin are oxidized, resulting in only partial delignification of the lignocellulosic biomass [44].

The peaks observed from 3600 to 3000 cm^{-1} and at 2800 cm^{-1} correspond to the stretching vibrations of OH groups in cellulose and CH stretching vibrations, respectively, which are present in all analyzed spectra [45, 46]. The stretching of the carbonyl group ($\text{C}=\text{O}$) from hemicelluloses and the aldehyde group from lignin is indicated by the bands at 1745 cm^{-1} and 1637 cm^{-1} and is observed in all FTIR spectra [47]. Peaks at 1600 cm^{-1} , corresponding to aromatic skeletal vibration with $\text{C}=\text{O}$ stretching, and 1508 cm^{-1} , aromatic skeletal vibration, are characteristic of lignin and can also be observed [48, 49].

A peak is observed in all FTIR spectra at 1160 cm^{-1} , characteristic of the asymmetric COC stretches of cellulose [50]. The natural spectra and sharp peaks of EH_2O_2 appear at 1070 and 900 cm^{-1} , also corresponding to the amorphous structure of cellulose [45, 51, 52].

The reduction in the intensity of the bands 3600–3000 cm^{-1} in the bands corresponding to the material treated with NaClO_2 may be associated with the breaking of inter and intramolecular hydrogen bonds. This change corroborates the XRD results, in which low crystallinity index values are observed, possibly associated with changes in the supramolecular arrangement of cellulose. Furthermore, the bands at 1745 and 1637 cm^{-1} and 1600 and 1508 cm^{-1} that specify the $\text{C}=\text{O}$ of hemicelluloses and lignin and the aromatic skeleton of lignin, respectively, which were very accentuated in the curve corresponding to the *in natura* material, confirm the removal of hemicelluloses and lignin.

The XRD diffractograms showed significant differences between treatments. For the NaClO_2 treatment, it was not possible to calculate the crystallinity index, indicating that the material underwent severe degradation during hydrolysis, presenting an amorphous character. This behavior suggests that pretreatment with sodium chlorite did not preserve the crystalline structure of cellulose, compromising the formation of nanocrystals. The H_2O_2 treatment presented a crystallinity index of 55.31%, a value compatible with the presence of crystalline regions characteristic of cellulose nanocrystals. These results demonstrate that hydrogen peroxide was more efficient in removing lignin without causing significant degradation of the cellulose. Both pretreatments were effective in delignification and obtaining nanocellulose, but the hydrolysis conditions in the NaClO_2 treatment should be modified to increase the yield.

The morphology and dimensions of nanocellulose strongly depend on the type of technique, hydrolysis parameters, and the cellulose source. In general, stronger acidity, prolonged reaction time, and high temperatures reduce the width and length dimensions of nanocelluloses for acid hydrolysis techniques [53].

Figure 5A and B show thin fibrillar structures (diameter <100 nm) with several micrometers in length. These structures self-aggregate and form bundles of cellulose nanofibrils (CNC) through intra- and inter-molecular hydrogen bonds. Figure 5A shows CNC for EH_2O_2 suspensions. The CNC presented the longest lengths, with several hundred micrometers, and diameters ranging from 20 to 60 nm in these suspensions, produced by mild acid hydrolysis (45% H_2SO_4 , 45°C, and a reaction time of 60 minutes). The CNC was more dispersed and slightly entangled when the cellulose fibers from the açai residue delignified with sodium chlorite were hydrolyzed with concentrated sulfuric acid at 55%, 45°C, and a reaction time of 30 minutes. A slightly shorter length (<500 nm) and diameters between 6 and 20 nm were also observed. Similar results were observed when wood cellulose fibers were hydrolyzed with sulfuric acid at 50% at 45°C [54]. According to the same authors, the separated CNC had several micrometers in length, with diameters between 10 and 30 nm, and were highly entangled.

A weight reduction of less than 4% is observed in the temperature range between 30 and 106°C for all samples, which is related to the evaporation of water present in the samples. A further drop is observed in the TGA curves for the raw, EH_2O_2 , and ENaClO_2 samples at 146°C, extending to 275°C, which can be associated with the thermal degradation of hemicelluloses and the onset of cellulose dehydration and depolymerization. In the DTG curve of the raw sample, the peak associated with the thermal degradation of hemicelluloses is more pronounced compared to the DTG peaks of EH_2O_2 and ENaClO_2 in the temperature range between 146°C and 255°C due to the higher holocellulose content in the raw sample, as demonstrated in previous sections. The EH_2O_2 and ENaClO_2 nanocellulose samples exhibited DTG curves typical of thermal degradation of nanocellulose extracted using the acid hydrolysis method. In the DTG curves of EH_2O_2 and ENaClO_2 , a weight loss of over 70% can be observed by the broad and well-defined peak formation in the temperature range of 300°C to 427°C, followed by the formation of residue due to the preferential depolymerization of amorphous cellulose still present after acid hydrolysis. Additionally, the nanocellulose samples showed a rapid weight loss, which can be seen in the DTG curves of EH_2O_2 and ENaClO_2 at 319°C.

5. CONCLUSIONS

This study showed that it is possible to use the residue generated in the production chain of *Euterpe oleracea* as a source of cellulose fibers for the extraction of cellulose nanocrystals, due to its high alpha-cellulose content. Among the methods applied to perform the delignification of the residue, hydrogen peroxide pretreatment proved to be more efficient for cellulose fiber extraction, while the two-step sodium chlorite treatment was too aggressive, resulting in a low yield in the nanocrystal extraction process.

Thus, the research demonstrated that it is possible to extract cellulose nanocrystals from *Euterpe oleracea* residue by applying acid hydrolysis with sulfuric acid followed by ultrasonic processing as a way to add value to this lignocellulosic biomass source, which is still little explored. Future research should be conducted to optimize delignification conditions and to evaluate the effect of adding this nanocellulose to composites as a way to strengthen the potential of this raw material, contributing to the advancement of the circular bioeconomy.

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