

PREPARATION OF CELLULOSE NANOCRYSTALS
FROM DATE PALM TREE LEAFLETS (*PHOENIX DACTYLIFERA* L.)
VIA REPEATED CHEMICAL TREATMENTS

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Recently, there has been significant research interest in nanocellulose due to its unique properties and performance. Its special characteristics make it a desirable material for many advanced industrial applications. It is considered a precursor for many industrial products, such as textiles and leather, as well as for some smart applications, such as in the biomedical area, in photonics, and flexible optoelectronics. The preparation of the nanocellulose from bio-based degradable by-products is a great advantage from sustainability and environmental considerations. This work aimed to find the best utilization for locally available date palm tree by-products, in an attempt to turn them into a valuable material. We succeeded in preparing nanocellulose with considerable crystallinity from biomass by-products via chemical and physical processing. The properties of the obtained nanocellulose were investigated using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). It was found that the sonication process (20 kHz, 10 min, 100 °C) has a significant role to play in the nanocellulose formation. The nanocellulose was found to have a smaller diameter (20-508 nm) and smoother surface, compared to the untreated fibers, and reached the degradation temperature of 560 °C as a result of the removal of lignin and hemicelluloses. Therefore, cellulose nanocrystals (CNCs) were achieved from low-cost by-products and could be further applied as a biodegradable matrix material.

Keywords: nanocellulose, date palm tree leaflets, alkali treatment, cellulose extraction

INTRODUCTION

Dates harvested from date palm trees (*Phoenix dactylifera* L.) are one of the favorite foods in Saudi Arabia, therefore, date palms are widely cultivated in this region. According to the latest available statistics from the Ministry of Environment, Water, and Agriculture of Saudi Arabia, the number of palm trees exceeds 28 million on an area of 160 thousand hectares, which represents about 55% of the total domestic production of fruit produced by almost 120 thousand farms.¹

The local agriculture sector produces about 1.7 billion tons of date palm tree wastes and agricultural by-products every year.² Otherwise said, local farms generate huge amounts of palm by-products (leaflets, pods, stems, fruit bunch *etc.*, which are not valorized to bring benefits.

Because of global concerns regarding climate change and shortages of oil resources, the researchers' interest in developing eco-friendly materials has increased enormously within the last fifteen years and, in this context, date palm wastes can be also regarded as a valuable biomass resource.

Cellulose is considered as one of the bio-based solutions for sustainable resources. It is a major component of plant fibers, a natural hydrophilic polymer, which consists of linear chains of 1,4- β -D-anhydroglucose units.³ Within the last ten to fifteen years, researchers have directed their focus towards converting cellulose into value-added renewable materials.⁴⁻⁶ Also, researchers are interested in the preparation of cellulose nanofibers and nanocrystals due to their unique

properties and mechanical performance in advanced applications.⁷⁻¹¹ Biomedical devices, sensors, gas separation membranes, and food packaging are just a few of the possible applications.¹²⁻¹⁴ Cellulose nanofibers have been extracted from different biomasses. Rape and flax straws,¹⁵ rice husk,¹⁶ argan press cake waste,¹⁷ *Citrullus colocynthis* seeds,¹⁸ and oil palm tree parts¹⁹ have been the most commonly investigated raw materials in this context. The date palm is a cellulose-rich tree; the fiber can be obtained from four parts of the tree, namely, the mesh, spadix stems, midribs, and leaflets.

It has been reported that cellulose nanofibers (CNFs) obtained from different parts of the date palm tree have different characteristics in terms of structure, morphology, degree of polymerization, and surface properties.¹⁴ In this regard, date palm tree leaflets have been chosen (DPTL) in the present study. A variety of methods have been reported for extracting cellulose from agricultural biomass resources and turning it into nanocellulose. The most commonly used methods for nanocellulose production involve acidic hydrolysis using sulphuric and hydrochloric acids. The process is based on the hydrolysis of the amorphous (semicrystalline) or accessible cellulose.²⁰ Lani *et al.* obtained nanocellulose from empty fruit bunches under acidic conditions using 64% sulfuric acid and strong agitation at 45 °C, and then developed a blended nanomaterial with poly(vinyl alcohol)/starch.²¹ Hafemann *et al.* extracted cellulose nanocrystals (CNCs) from palm leaf sheaths, generated as a by-product after harvesting, through chlorine-free refining methods, followed by hydrolysis under strongly acidic conditions.²² Recently, researchers have developed a variety of methods for obtaining nanocellulose, such as oxidation,²³ esterification,²⁴ ionic liquids,²⁵ microwave-assisted, hydrothermal treatment, subcritical water,²⁶ and electron beam irradiation.²⁷ In general, the quest for alternative ways to reduce the efforts and costs of disposal of by-product wastes by turning these wastes into a valuable product is a noble goal. This goal can be achieved by encouraging the progress of studies on this issue.

This work is an attempt to add value to a cellulose-rich biomass by-product of *Phoenix dactylifera* L., namely, leaflets, by converting it into a nano-material. To achieve the objective, definite processes have been followed: extraction of the cellulose, purification, characterisation of

the isolated cellulose, preparation of nano-materials through hydrolysis with a strong acid, followed by sonication. The thermal and morphological properties and the crystallinity of the product have been investigated. Thus, this work aims to offer an input in the scientific and industrial areas from an eco-friendly perspective.

EXPERIMENTAL

Materials

The raw materials (leaflets) were collected from a local farm in Riyadh province, Saudi Arabia. Sodium hydroxide (NaOH), potassium hydroxide (KOH), sulphuric acid (H₂SO₄), acetic acid (CH₃COOH) and sodium chlorite (NaClO₂) were high grade laboratory chemicals, purchased from BDH Chemicals.

Extraction of cellulose

The collected raw materials were mechanically cut to small sizes (*ca.* 0.5-1 cm), washed with distilled water three times to remove dust and impurities, and then well dried in a sunny area for 12 hours. After complete drying, a stainless-steel grinder was used to mill the leaflets into fibers with an approximate size of less than five millimeters. An amount of 150 g of ground leaflets was placed into a round-bottom flask, one liter of distilled water was added and about 40 g of sulfuric acid was added gradually under heating for 2 hours at a fixed temperature (90 °C). This process was done to remove hemicelluloses.¹⁷ The residue was filtrated and washed with deionized water several times to a neutral pH.

Hydrolysis process using KOH

The hydrolysis process was carried out using 1000 g distilled water and 50 g of potassium hydroxide (KOH) at 90 °C for 2 hours to remove lignin and silica.¹⁷ Then, filtration and washing with deionized water were applied to ensure purification of the residue and obtaining a neutral pH.

Bleaching process

The bleaching process was carried out according to the method described by Battezzore *et al.*¹⁷ The process involves the treatment of cellulose with an aqueous solution of NaClO₂ (30 g/1000 g water) to remove lignin and amorphous cellulose. The pH was adjusted to 4.5 using acetic acid, and the solution was stirred for 4 hours at a fixed temperature (75 °C). The final product was filtered and neutralized through washing with deionized water several times. The residue was then dried in an oven at 80 °C until constant weight was reached.

Preparation of nanocellulose

Sulfuric acid 60 wt%, H₂SO₄, was used to prepare the nanocellulose at 45 °C for 45 min.²⁸ After the reaction, the sample was washed seven times with cold

deionized water to remove the residue of sulfuric acid. The washing was performed by centrifugation at 5,000 rpm for 20 min. The suspension was then transferred to dialysis tubes (6-8 kDa MWCO) against deionized water and equilibrated for 48 hours until a neutral pH value was reached (6.7-6.9). The sonication process (20 kHz, 10 min, at 10 °C) was carried out to scatter the nanocellulose. The ratio of the suspension to water was 20:1. The resulting nanocellulose was filtered by centrifugation at 10,000 rpm for 10 min. The precipitate, *i.e.* nanocellulose, was collected and dried in an oven at 60 °C for 2 hours, and then in the open air for one day to prepare it for characterization.

Characterization

Fourier transform infrared spectrometry (FTIR)

A Nicolet 6700 Fourier transform infrared spectrometer was used to record the FTIR spectra in the transmission mode, between 4500 and 400 cm^{-1} . The raw material, the extracted cellulose and the obtained nanocellulose were each scanned with a resolution of 4 cm^{-1} .

X-ray diffraction (XRD) analysis

The raw material, the cellulose and the nanocellulose were also observed by X-ray powder diffraction (XRD). Measurements were performed on a D8 Brucker diffractometer, with Cu-K radiation ($\lambda = 1.54178 \text{ \AA}$) in the range $2\theta = 10\text{-}70^\circ$ with 0.02° step size.

Scanning electron microscopy (SEM)

SEM images of the raw material, the extracted cellulose and the nanocellulose were recorded by a JSM-IT 500 HR (JEOL, Japan) at 10 kV accelerating voltage. The samples were placed on a metal holder

and coated with gold. The coating process lasted for 45 min to ensure good conductivity prior to analysis.

Thermogravimetric analysis (TGA)

The thermal stability of the raw material, the cellulose and the resulting nanocellulose was studied by a Perkin Elmer STA-6000 instrument. The TGA curves of the samples were recorded at a heating rate of 10 °C per min in the range from 30 °C to 1100 °C, under continuous nitrogen flow of 20.0 mL/min.

RESULTS AND DISCUSSION

The lignin content (%) of the raw material before and after the purification and bleaching processes is a significant parameter in the preparation of nanocellulose – lignin is insoluble in sulfuric acid and can obstruct the formation of the nanomaterial. Therefore, it is important to verify that the process used has been achieved satisfactorily. E. Hafemann *et al.*²⁴ reported that the fibers of royal palm date leaves had a lignin content of $10.4 \pm 0.9\%$. Thus, bleaching leads to a substantial decrease in the lignin content of the purified material. The nanocellulose obtained in this study remained suspended when mixed with water, without dissolving (Fig. 1). This behavior is due to the negative charge on the surface of the particles. When the solution was dried, very light and tiny crystals were obtained. In a 20:1 mixture ratio with water, the suspension became gel-like. If the water content is reduced, the suspended particles begin to get closer together and align spontaneously as an auto-assembly.

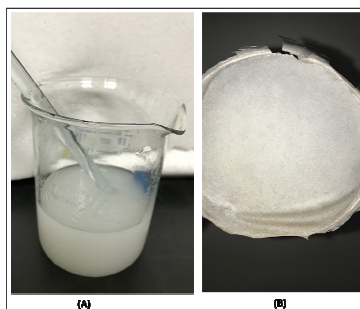


Figure 1: Nanocellulose (a) gel-like and (b) after drying

FT-IR analysis

Figure 2 shows the FTIR spectra of the raw material, the extracted cellulose and the nanocellulose. The spectra of all the samples show a similar trend of the absorption bands. In the region between 3630 and 3105 cm^{-1} , there is a broad band attributed to O-H stretching vibrations

(hydrogen bonding in the hydroxyl group).^{29,30} The band between 3300 and 3350 cm^{-1} corresponds to inter- and intra-chain hydrogen bonded 2OH, 3OH, 6OH groups.³¹ The peaks at the wavelength of 2840 and 2920 cm^{-1} are characteristic of $-\text{CH}$ and $-\text{CH}_2$ stretching vibrations in each sample. This indicates the

presence of the cellulose molecule.³² Due to their hydrophilic nature, the fibers show a peak at the wavelength of 1600-1650 cm^{-1} , which corresponds to the bending vibration of absorbed water.³³ The peaks at 1200, 1360 and 1630 cm^{-1} indicate the presence of lignin in the raw material, corresponding to the carbonyl group in aromatic skeletal vibration.³⁴ After alkali treatment and bleaching, the three peaks appear with low intensity. The small band at 900 cm^{-1} can be attributed to the glycoside bond (β -1 and β -4) in amorphous cellulose in the raw material. Strong peaks were observed around 1040 cm^{-1} , which became stronger after alkali hydrolysis (around 1039-1070 cm^{-1}).

XRD analysis

XRD data allow studying the sample crystallinity due to the diffraction peaks from cellulose crystals.³⁵ Figure 3 shows the XRD patterns corresponding to the raw material, the extracted cellulose, and the nanocellulose. There are two peaks at $2\theta = 22.3^\circ$ and 16.3° , indicating

the crystal structure of cellulose. The diffraction pattern of the raw material reveals the presence of a lot of amorphous regions, due to the presence of hemicelluloses and lignin in the untreated sample. The peak at $2\theta = 22.3^\circ$ is attributed to the cellulose, and the peak at 16.3° is due to the amorphous region corresponding to the crystallographic plane (101). This finding is similar to the results reported by Nazir *et al.*³⁶ and Mazlita *et al.*³⁷ To conclude, there is crystallographic interference in the XRD pattern of the raw material because it had been subjected to no pretreatment other than grinding.

The crystallinity index was estimated using the most commonly used method for cellulose – Segal’s method:³⁷

$$I_{cry} = \frac{I_{max} - I_{min}}{I_{max}} \times 100 \quad (1)$$

where I_{max} is the maximum intensity ($2\theta = 22.3^\circ$) of both crystalline and amorphous phase and I_{min} is the peak intensity ($2\theta = 16.3^\circ$) of the amorphous fraction.

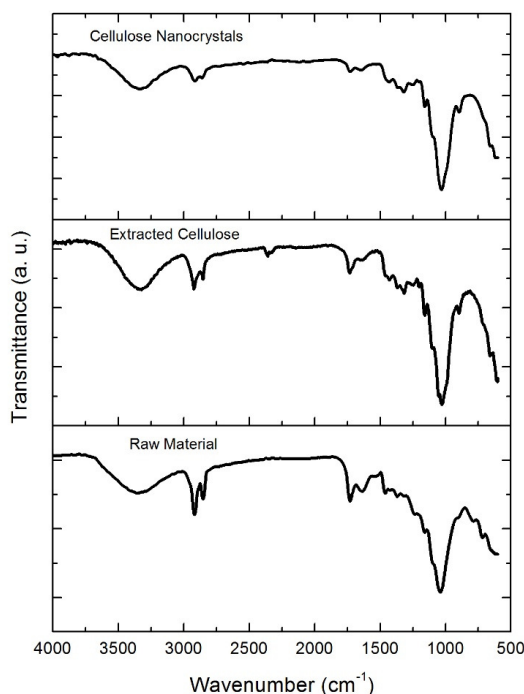


Figure 2: FTIR spectra for raw material, extracted cellulose and nanocellulose

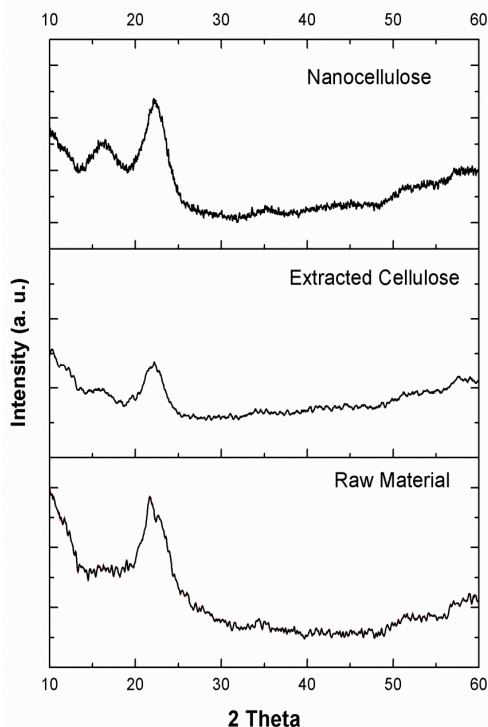


Figure 3: XRD pattern of raw material, extracted cellulose and nanocellulose

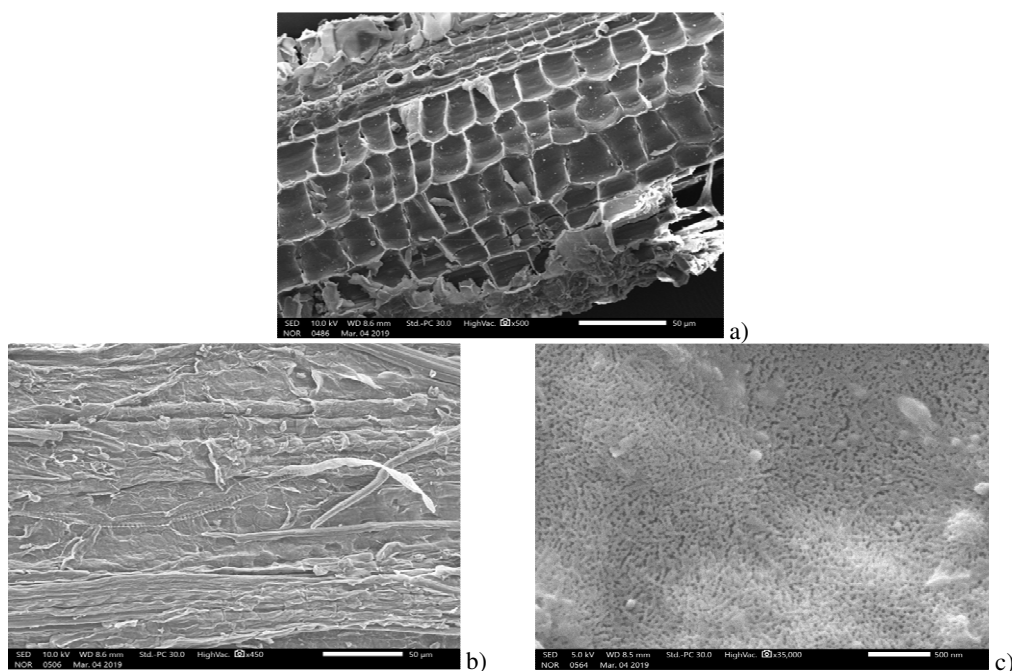


Figure 4: SEM images of (a) raw material, (b) bleached cellulose, (c) nanocellulose

Basically, the crystallinity index (I_{cry}) indicates the degree of crystallinity and it is used to compare the order of crystallinity for each of the materials under study. The crystallinity index of the samples was calculated, and it showed a remarkable increase as the raw material was subjected to the treatments. Therefore, the peak intensity increased in the following order: raw material < extracted cellulose < nanocellulose, indicating that nanocellulose exhibited the highest crystallinity. This finding is agreement with the results of SEM analysis (Fig. 4 (a-c)). Consequently, the removal of the non-cellulosic content was achieved, the amorphous region was degraded and a more ordered crystalline structure was obtained.³⁸

SEM characterization

The SEM images of the raw material, the extracted cellulose and the nanocellulose are shown in Figure 4. The images were taken at magnifications ranging from 500x to 10000x to determine the distribution of particle diameter. The image corresponding to the untreated raw material (Fig. 4 (a)) shows multi-cellular structures due to the presence of lignin and hemicelluloses. The SEM image of the extracted cellulose (Fig. 4 (b)) reveals that the white color surrounding the cellular structures decreased,

which is explained by the fact that the treatments removed a part of the hemicelluloses. Also, the surface of the leaflets becomes rough due to the removal of lignin, hemicelluloses, and other substances, such as waxes, fats, oils *etc.*

As shown in Figure 4 (a), the fiber length of the untreated sample is longer than 100 μm and approximately 20 μm wide. A significant change has been observed after bleaching and lignin removal (Fig. 4 (b)). Figure 4 (c) shows the presence of particles with significantly reduced sizes of ≤50 nm, as a result of acidic hydrolysis and sonication, therefore indicating successfully prepared cellulose nanocrystals (CNCs). The average diameter of the nanoparticles is lower than the average value for cellulose nanofibers and the XRD of the samples confirmed this result.

Thermogravimetric analysis

Figure 5 shows the TG curves for the three samples (the raw material, the extracted cellulose and the obtained nanocellulose). The mass reduction of all the samples starts at the expected temperature based on moisture release, as indicated by the cited data.³⁹ The figure indicates that the highest degree of degradation occurs in the temperature range from 300 to 400 °C, which is consistent with the fact that the material has been obtained from palm tree biomass (degree of

deterioration of cellulose and lignin-rich materials).⁴⁰ However, the chemical treatment removes the amorphous tissues, resulting in higher crystallinity and higher resistance to thermal degradation.³⁶ The TG curves also indicate that all the tested samples show slow deformation starting from a temperature close to

400 °C (around 380 °C), because α -cellulose has completely decomposed at a temperature lower than 380 °C. Overall, it may be concluded that the treatment performed increased the thermal stability of the material, which becomes more heat-resistant. This is in agreement with other previously reported results.^{41,42}

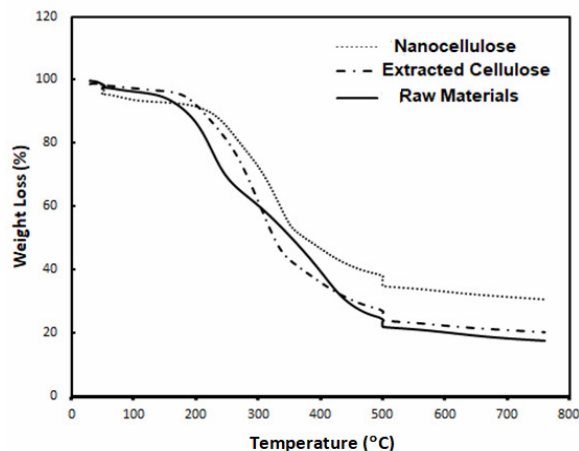


Figure 5: TG curves for raw material, extracted cellulose and nanocellulose

CONCLUSION

Agricultural residues, such as palm date leaves, are abundantly available in Saudi Arabia. It is important to take advantage of such a cellulose-rich resource. Cellulosic materials and CNCs have been obtained through repeated chemical treatments from date palm leaflets available as a by-product at local farms. The lignin and hemicelluloses were efficiently removed under alkaline conditions (KOH, 0.893 M). Acid hydrolysis with 60% (w/v) H₂SO₄, followed by a sonication process (20 kHz, 10 min, at 100 °C), was the procedure that led to nanocellulose formation. The results of the analyses revealed the formation of nanocellulose with uniform appearance and high degree of crystallinity. Therefore, a value-added product – nanocellulose – has been obtained from a low-cost agricultural residue.

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