

## EXTRACTION AND CHARACTERIZATION OF CELLULOSE FROM DATE PALM SEEDS (*Phoenix dactylifera* L.)

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Date palm seeds (DS) were subjected to mechanical grinding and then to sodium hydroxide delignification and sodium chlorite single step bleaching. The obtained holocellulose was treated with potassium hydroxide to extract cellulose. The structural features of the isolated cellulosic samples were examined by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The morphological characteristics of the cellulosic preparation were investigated with a fiber morphology analyser (MorFi). The degree of polymerization (DP) was determined by the standard test method for intrinsic viscosity. It was found that cellulose extracted from date seeds (CDS) contained fines (elements with the length under 100  $\mu\text{m}$  and width under 5  $\mu\text{m}$ ) with a degree of polymerization of 950. The extracted cellulose (CDS) was composed of 90% of amorphous phase and had a monoclinic crystal structure I $\beta$ . FTIR spectra showed that the extracted cellulose was free from lignin and hemicelluloses.

**Keywords:** date seeds, delignification, bleaching, cellulose I $\beta$ , characterization

### INTRODUCTION

Cellulose has a wide range of industrial applications in composites, textile, paper, food, additives and pharmaceutical industries.<sup>1</sup> It is the most promising plant components to substitute synthetic polymers due to its low cost, nontoxic, and biodegradable properties.<sup>2</sup> The repeating monomer of cellulose is composed of two D-glucopyranose units linked by  $\beta$ -1,4-glycosidic bonds. Each cellobiose contains six hydroxyl groups able to establish intra- and inter-chain hydrogen bonds, which result in various ordered crystalline arrangements, making cellulose a relatively stable polymer. Cellulose I or native cellulose has two polymorphs, a monoclinic structure I $\beta$  and a triclinic structure I $\alpha$ , which coexist in various proportions. In plant cell walls, cellulose is linked with hemicelluloses and lignin by covalent bonding, various intermolecular bridges, and van der Waals forces, forming the unique natural nanocomposite structure.<sup>3</sup> Depending on the species, the quantities of those three molecular components vary from 40-50%, 15-30% and 20-30%, respectively,<sup>4</sup> with the

exception of a few plants, such as cotton and hemp bast fiber, which are made up of  $\approx$ 80% cellulose, 20-40% hemicellulose, 20-30% lignin by weight.<sup>5</sup>

The major source of cellulose is wood. In 2011, 6.4  $10^8$  m<sup>3</sup> of wood were used to manufacture pulp and paper worldwide.<sup>6</sup> The society has become increasingly aware of the importance of environmental problems and demands an effort to be made by the cellulose industry to utilize non-wood sources and to implement new and less polluting processes for cooking raw materials and bleaching cellulose pulps. With a view to conserve the forest resource, investigations have been undertaken to extract cellulose fiber from diverse sources, including wheat straw and soy hulls,<sup>7</sup> sugar beet pulp,<sup>8</sup> bagasse,<sup>9</sup> banana rachis<sup>10</sup> and coconut palm leaf sheath.<sup>11</sup> Another interesting non-wood material is the date palm seed (*Phoenix dactylifera* L.), which constitutes approximately 10% of the fruit and has a small cylindrical embryo embedded in a sizable horny endosperm

of cellulose and hemicelluloses. In spite of its high fiber content, date seeds are still considered as a by-product and are usually thrown away after consuming the flesh of the dates or used as animal feed in certain countries. With a world date production estimated at 7.6 million tons in 2012, 755 thousand tons of date seeds are approximately produced and can be used as an alternative source of cellulose fibers.<sup>12</sup>

The aim of this study was to evaluate the suitability of date palm seeds as a source of cellulose and to predict the applicability domains of the isolated polymer. For this purpose, the extraction was conducted using an environment-friendly method and chemicals. The isolated cellulose was investigated with several analytical techniques to determine its morphology, crystallinity, degree of polymerization and thermal behavior.

## EXPERIMENTAL

### Seed material

Date palm fruits (*Phoenix dactylifera* L.) were obtained from the Regional Centre for Research in Oasis Agriculture (Degach, Tunisia). The seeds of the cultivar Deglet Nour were directly isolated from date fruit collected at the full ripeness stage. The obtained sample was washed with distilled water to get rid of any adhering date flesh, then air-dried and preserved at -20 °C until analyses.

### Methods

#### Preliminary study

A preliminary study was carried out on date seeds (DS) to evaluate the suitability of this raw material as cellulose source. For this purpose, transverse sections of DS were stained in Green Carmino of Mirande to distinguish lignified (green coloration) and cellulosic (red-pink coloration) structures, and then examined with optical microscopy. Carbohydrates were estimated by the Van Soest global method<sup>13</sup> using a Raw Fiber Extractor 6 Channel (VELP Scientifica, Italy). The Van Soest analysis is based on subsequent steps of chemical treatment. The residue was dried and used for the determination of neutral detergent fiber (NDF), acid detergent fiber (ADF) and acid digestible lignin (ADL). The NDF tests involve chemical extraction with a neutral detergent solution (sodium borate, sodium lauryl sulfate, disodium ethylenediaminetetraacetate, 2-ethoxyethanol, and disodium phosphate) under reflux. The unsolvable fraction contains cellulose, hemicellulose and lignin. The acid detergent solution (cetyltrimethylammonium bromide and sulfuric acid) digests the degradable hemicellulose and some proteins. The ADL method is based on solubilisation of the cellulose in 72% sulfuric

acid. Hemicellulose was calculated as NDF – ADF and cellulose as ADF – ADL.

### Chemical analysis

The moisture content was measured gravimetrically by drying 15 g of unground raw material overnight.<sup>14</sup> Total ash was determined according to the AOAC method<sup>15</sup> by calcinating the sample at 550 °C. The elemental analysis of mineral constituents (Ca, Cl, K, P and Mg) present in the date seeds was carried out by the Service central d'analyse, Institut des sciences analytiques ISA (Villeurbanne, France). Lipids were pulled out of the sample with petroleum ether using a Soxhlet apparatus,<sup>16</sup> then the solvent was removed with a rotary evaporator IKA RVO5 Basic (IKA Laboratory, Staufen, Germany). Total nitrogen was determined by the Kjeldahl method using Behr analysis equipment (Behr Labor Technik GmbH, Düsseldorf, Germany), followed by the protein calculation using the general factor of 6.25. The material was digested in H<sub>2</sub>SO<sub>4</sub> to convert the protein nitrogen to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at a boiling point elevated by the addition of K<sub>2</sub>SO<sub>4</sub> with a copper catalyst to enhance the reaction rate. Ammonia was liberated by alkaline steam distillation and quantified titrimetrically with standardized acid.<sup>17</sup> The cellulose content was evaluated by refluxing 1 g of date seed powder for one hour in 25 mL ethyl alcohol/nitric acid solution (4/1). After six cycles, the reaction mixture was filtered, washed with hot water, and dried at 103 °C until the crucible weight was constant.<sup>18</sup> Holocellulose was quantified with sodium chlorite treatment;<sup>19</sup> to 2.5 g ground date seeds, 150 ml of hot distilled water, 0.5 ml acetic acid, and 1 g of sodium chlorite were added. The mixture was heated in a water bath at 70 °C. After each succeeding hour, a fresh portion of 0.5 ml acetic acid, and 1 g of sodium chlorite were added under shaking. The delignification process took 6 hours of reaction. At the end, the holocellulose was filtered, washed and dried in an oven at 103 °C before weighing.<sup>20</sup> The lignin content was determined by the Klason method in accordance to the TAPPI norm:<sup>21</sup> to 1 g of the date seed powder, 14 ml of cold 72% sulfuric acid was added and stirred. The mixture was left to stand. After 2 hours, the mixture was washed in a conical flask and diluted to 3% sulfuric acid. Then, the mixture was boiled for 4 hours under reflux. The residue was washed and dried in an oven at 105 °C, then cooled and weighed as acid-insoluble lignin content.

### Cellulose isolation

Dried date seeds were ground into powder with a microphyte disintegrator FZ102 (Huanghua Faithful Instrument, Hebei, China) in order to pass a 495 µm sieve. The size of the samples must be small to make sure the reaction reagent and fibers are optimum during the extraction process. Powdered date seeds (20 g) were sequentially submitted to Soxhlet extraction with water and petroleum for 8 hours each<sup>22</sup> and then

subjected to alkaline extraction under the following conditions: consistency: 5%; NaOH: 2%; temperature: 70 °C and treatment time: 160 min. The bleaching step was performed with acidified sodium chlorite (1.7%). Cellulose was extracted from holocellulose with 10% KOH, containing 1% H<sub>3</sub>BO<sub>3</sub> for 10 hours at room temperature with a solid to liquor ratio of 1/25. Color measurement, on the external surface of DS and CDS, was performed using a Minolta CR-300 Chromameter (Konica Minolta Sensing, New Jersey, USA) calibrated against a standard white ceramic surface. The L\*C\*H\* color space was used to express the color of the dates.<sup>23</sup> It is a human based perception model in the form of a sphere. There are three axes: L\*, C\* and H\*. Coordinate L\* represents clarity (L\* = 0 black, L\* = 50 in the middle and L\* = 100 white). The C\* axis represents Chroma, this ranges from 0 at the center of the circle, which is completely unsaturated to 100 or more at the edge of the circle for very high color purity. This circular axis is known as H\* for Hue. The units are in the form of degrees, ranging from 0° (red) through 90° (yellow), 180° (green), 270° (blue) and back to 0°.

#### Measurement uncertainty

A-Type components of uncertainty were statistically quantified with the linearity of the measuring devices and repeatability of the measurements. B-Type evaluations are founded on *a priori* distributions quoted in manufacturer specifications and calibration certificate. The Expanded uncertainty (U) for each measurement was estimated using a coverage factor type (k=2) with 95% confidence.<sup>25</sup> Values of different parameters were expressed as the mean of at least three measurements ± expanded uncertainty. All used chemicals were of analytical grade.

#### Cellulose characterization

##### *Morphological properties of fibers (Morfi)*

The fiber and shive morphology analyzer MORFI LB-01 (Techpap, Toulouse, France) was used for the characterization of the extracted cellulose fibers. The equipment integrates a digital camera and a software package for image analysis, to automatically measure fibers in diluted suspension. Fiber analysis includes determining fiber length, width, curl, kink, coarseness, shives and fines. Fiber length and width were defined in the range of 200-10.000 and 5-75 µm, respectively. The fine was defined as the portion with the length shorter than 200 µm and the width less than 5 µm.

##### *Thermogravimetric analysis (TGA)*

The thermal stability of the initial material and the obtained cellulose was studied by a thermo-gravimetric analyzer STA 6000 (Perkin Elmer Instruments, Buckinghamshire, England), which measures the weight loss of the sample in relation to the temperature. A dynamic scan from 30 to 900 °C under

nitrogen atmosphere at a flow rate of 50 mL/min and a heating rate of 10 °C/min was performed.

##### *Degree of polymerization (DP)*

The value of DP of extracted cellulose was determined at 25 °C from the intrinsic viscosities [η] of cellulose solutions in cupri-ethylenediamine/water. A capillary-tube viscometer CT52 (Schott Instruments, Mainz, Germany) was used to determine the viscosities η and η<sub>0</sub> of the cellulose solution and of the solvent, respectively, at the same temperature. From the ratio of the viscosities η/η<sub>0</sub> and the mass concentration of the polymer, the limiting viscosity number [η] of testing sample was determined according to annex B of the recommended procedure.<sup>26</sup> The average degree of polymerization was calculated from [η] using the Staudinger–Mark–Houwink equation<sup>27</sup>  $DP^{0.85} = 1.1 \times [\eta]$ . The differences between DP calculated from duplicate runs were ≤ 2%.

##### *Fourier Transform Infrared Spectroscopy (FT-IR)*

Date seeds and cellulose samples were ground and mixed with KBr in an agate mortar (sample/KBr ratio of 1/100). The 13 mm KBr pellets were prepared under a pressure of 75 kN cm<sup>-2</sup> for 3 min. Spectra were obtained from 32 scans at a resolution of 4 cm<sup>-1</sup> and collected in the absorbance mode from 4000 to 400 cm<sup>-1</sup> using a Shimadzu FTIR-8200PC (Kyoto, Japan).

##### *X-ray diffraction (XRD)*

The X-ray diffraction analysis was performed on DS and CDS powder. Samples were placed in a 2.5 mm deep cell and the measurements were performed with a PANalytical, X'Pert PRO MPD diffractometer (PANalytical, Massachusetts, USA) equipped with an X'celerator detector. The operating conditions for the refractometer were: copper Kα radiation (1.5418 Å), 2θ (Bragg angle) between 5° and 60°, step size of 0.067° and counting time of 90 s.

## RESULTS AND DISCUSSION

### Preliminary study

The VanSoest proximate analysis allowed estimating 24.3%, 27.2% and 21.8% as cellulose, hemicellulose and lignin contents, respectively. Accordingly, it can be said that the carbohydrate content of the date seeds reveals that this material could be used as precursor for cellulose extraction. The microscopic study of the date palm seeds (Fig. 1) showed heterogeneous lignin and cellulose distribution. The endosperm was formed essentially of cellulosic structure, however the seed coat displayed a high lignin concentration. So, DS may be a good raw material for cellulose extraction by mechanical disintegration.

**Chemical composition**

The chemical composition of the date seeds was established according to standard methods and the results were summarized in Table 1. From this table, it may be concluded that the moisture content of the date seeds was of 10.4% and they contained 5.95% crude protein, 10.1% ether

extract, 1% ash, 23.9% cellulose, 26.8% hemicellulose and 21.6% lignin. In general, the amounts of protein, fat, ash and carbohydrates are within the range of values presented earlier in the literature.<sup>28-29</sup> However, other researchers<sup>30</sup> reported contents of 23% lignin, 20% cellulose and 55% hemicelluloses in date seeds.

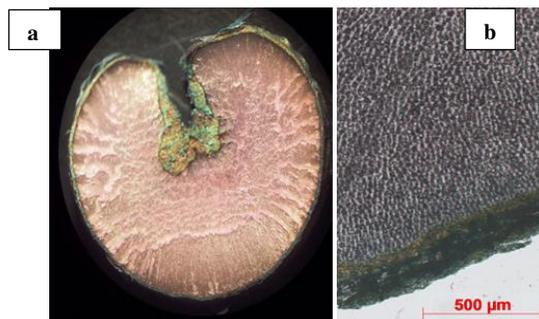


Figure 1: Light micrographs showing transverse sections of date seeds stained in Mirande reagent: a) Lignified (green) and cellulosic (red-pink) tissues identified at 4× magnification; b) Thick cellulosic cell walls surrounding lumina

Table 1  
Chemical composition of date seeds on dry matter basis (% db)

Component	Content (% db)	Method
Ash	1.0±0.1	(AOAC Method 942.05, 1995) <sup>15</sup>
Crude protein	5.95±0.01	(AOAC Method 2001.11, 2005) <sup>17</sup>
Hot water extract	10.5±0.1	(Tappi T264 om-88, 1988) <sup>22</sup>
Fat	10.3±0.01	(AOAC Method 920.39, 1997) <sup>16</sup>
Cellulose	23.9±0.1	(Pettersen, 1984) <sup>18</sup>
Hemicelluloses	26.8±0.1	(Wise <i>et al.</i> , 1946) <sup>19</sup>
Lignin	21.6±0.1	Klason and TAPPI (T22 om-88, 1998) <sup>21</sup>

Table 2  
Mineral contents of date seeds (%)

Constituent	Concentration (%)
Potassium (K)	26.68
Phosphorus (P)	11.96
Magnesium (Mg)	7.25
Calcium (Ca)	2.54
Chlorine (Cl)	1.86

Table 3  
Chromatic coordinates of date seeds (DS) and extracted cellulose (CDS)

Chromatic coordinates	L* (±0.1)	C* (±0.06)	H*(°) (±0.1)	ΔL* (±0.1)	ΔC* (±0.08)	ΔH*(°) (±0.03)
DS	64.2	21.89	67.2	31.6	-20.30	-143.40
CDS	95.8	1.59	-76.2			

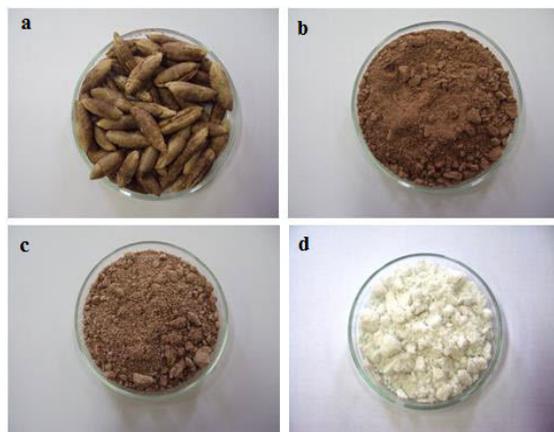


Figure 2: Photographs of a) untreated DS, b) ground DS, c) alkali treated DS, d) cellulose DS

Table 2 lists the content of minerals found in the date seeds. Potassium (K) was found in the highest amount, followed by phosphorus (P), magnesium (Mg), calcium (Ca) and chlorine (Cl). The low ash content determined (1%) could be appropriate to reach a suitable reaction rate in chemical processes.

#### Cellulose extraction and characterization

Figure 2 shows photographs of untreated (a), ground (b), alkali delignified (c) and bleached (c) DS. The yield of the bleaching step was estimated to be of 97.3%.

The chromatic coordinates of the date seeds (DS) and extracted cellulose (CDS) are presented in Table 3. The total color difference between DS and CDS was estimated using the overall color difference  $\Delta E_{94}$  (Eq. 1), as recommended by CIE for industrial use:

$$\Delta E_{94} = \sqrt{\left(\frac{\Delta L^*}{K_L S_L}\right)^2 + \left(\frac{\Delta C^*}{K_C S_C}\right)^2 + \left(\frac{\Delta a^*}{K_H S_H}\right)^2} \quad (1)$$

where  $K_L = K_C = K_H = 1$ ,  $S_L = 1$ ,  $S_C = 1 + 0.045C^*$ ,  $S_H = 1 + 0.015C^*$  and  $C^* = (C_{DS}^* C_{DS}^*)^{1/2}$ . The  $k$  coefficient accounts for the parametric effect, while  $S$  accounts for CIELAB lack of uniformity.<sup>31</sup> A color difference ( $\Delta E$ ) of 1 is said to be the smallest color difference that is visibly perceptible.<sup>32</sup> From Eq. 1,  $\Delta E$  was calculated to be 136. High values of brightness and total color difference between DS and CDS can be explained by the efficiency of the used process in cellulose extraction. The color change occurring during the treatment could be explained as originating in thermal and chemical oxidation.

Regarding the morphology, it may be noted that the cellulose extracted from the date seeds (CDS) contained fines (elements with the length under 100  $\mu\text{m}$  and width under 5  $\mu\text{m}$ ) in amounts, which are significantly lower than those of other fibers isolated from several annual plants. However, the DP of 950 is very close to that obtained for fibers extracted from annual plants.

#### FTIR spectroscopy

FTIR spectroscopy has been used as a simple technique for obtaining rapid information about the chemical structures. Peak wave numbers of the FTIR bands for DS and CDS, along with their assignments according to the literature, are presented in Table 4. The FTIR spectrum for DS (Fig. 3) shows a dominant peak at 3367  $\text{cm}^{-1}$  attributed to O–H stretching vibrations in hydroxyl groups. The band observed at 2924  $\text{cm}^{-1}$  is assigned to asymmetric C–H bands in methyl and methylene groups. Generally, these absorption bands show contributions from cellulose, hemicellulose and lignin. The peak at 2855  $\text{cm}^{-1}$  is assigned to symmetric C–H bands in methyl and methylene groups, attributed to cutin and waxes. The peak at 1744  $\text{cm}^{-1}$  is assigned to carbonyl C=O, due to either the acetyl, and uronic ester groups of hemicelluloses or the ester linkage of carboxylic groups of the ferulic and p-coumaric acids of lignin and/or hemicelluloses. The band at 1616  $\text{cm}^{-1}$  may represent C=C or C=N vibrations in the aromatic region. The peaks at 1522 and 1437  $\text{cm}^{-1}$  may be ascribed to C=C stretching of the aromatic skeletal mode. The peak at 1377  $\text{cm}^{-1}$  is due to the C–H stretching of cellulose.

The band at 1246 cm<sup>-1</sup> is attributed to C–O–H deformation and C–O stretching of phenolics. The band at 1061 cm<sup>-1</sup> describes the C–O stretching vibration of cellulose and hemicellulose. The absorption at 870 cm<sup>-1</sup> is related to the C–H

rocking vibrations of cellulose. In the CDS spectra, the peaks at 2855, 1744, 1616, 1520 and 1443 cm<sup>-1</sup> disappeared completely because of the removal of waxes, hemicelluloses, lignin and proteins.

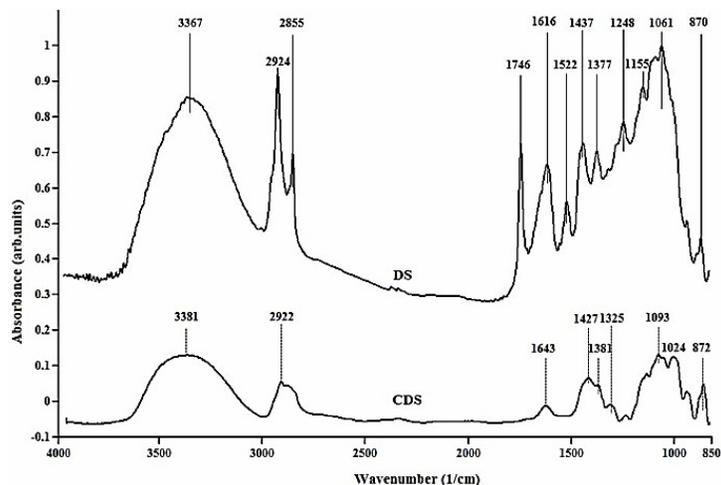


Figure 3: FTIR spectra of date palm seeds (DS) and extracted cellulose (CDS)

Table 4

Peak wavenumbers of FTIR bands for date seeds (DS) and cellulose extracted from date seeds (CDS), with their assignments according to the literature

Peak wavenumber (cm <sup>-1</sup> )		Band origin (assignment) with comments
DS	CDS	
3367	3381	O–H stretching vibrations in hydroxyl groups <sup>33</sup>
2924	2922	Asymmetric C–H stretch in methyl and methylene groups <sup>34-35</sup>
2855		Symmetric C–H stretch in methyl and methylene groups, cutin, waxes <sup>36</sup>
1746		C=O, due to either the acetyl, and uronic ester groups of hemicelluloses or the ester linkage of carboxylic groups of the ferulic and p-coumaric acids of lignin and/or hemicelluloses <sup>37-38</sup>
	1643	Adsorbed H <sub>2</sub> O
1616		C=C or C=N vibrations in aromatic region <sup>35-39</sup>
1522		C=C stretching of aromatic skeletal mode <sup>35-39</sup>
1443	1427	C=C stretching of aromatic skeletal mode <sup>35-39</sup>
1377	1381	C–H stretch of cellulose <sup>40</sup>
1248	1250	C–O–H deformation and C–O stretching of phenolics <sup>41-42</sup>
1151	1151	C–O–C vibration in cellulose and hemicellulose <sup>43</sup>
1061		C–O stretching vibration of cellulose and hemicellulose <sup>42,44,45</sup>
870	872	C–H rocking vibrations of cellulose <sup>46</sup>

**Thermogravimetric analysis (TGA)**

Cellulose, hemicellulose and lignin are the main organic polymers that decompose during thermal treatment. The three biomass polymers decompose independently without interfering with each other.<sup>47</sup> In the case of no interactions between the compounds, the decomposition behavior is a linear combination of the main

compounds and can be described by mass weighted average. The TG curve for DS shows three stages from 50 to 140 °C (8% weight loss), 140 to 480 °C (71% weight loss) and 480 to 900 °C (6% weight loss), respectively (Fig. 4a). The yield of the carbonized material represented 77% of the initial weight of the sample and the observed char was of 15%.

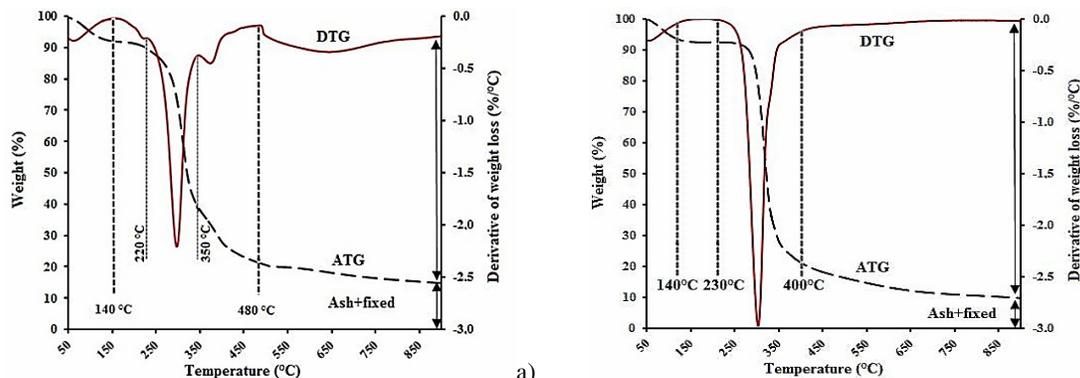


Figure 4: Thermogravimetric analysis (TGA) and differential thermogravimetry analysis (DTG) of date seeds (a) and of extracted cellulose (b)

In the first stage, the derivative weight (differential thermogravimetry analysis, DTG) had a separate peak of weight loss, which corresponds essentially to the loss of adsorbed and bound water. During the second stage, designated as fast thermal degradation, three zones can be distinguished. The first zone from 140 to 220 °C (3% weight loss) corresponds to the decomposition of pectin and probably to the beginning of the decomposition of cellulose and hemicelluloses. The second zone started around 220 °C and extended to 350 °C (48% weight loss), in this temperature range hemicellulose and cellulose decomposed. Hemicellulose degradation increases with residence time and temperature between 225 °C and 325 °C. Furthermore, the reported decomposition temperature range for xylan was between 200 °C and 350 °C.<sup>48</sup> Cellulose degradation occurs at higher temperatures, because of its crystalline structure; some publications have demonstrated that its decomposition occurs in the range of 315-400 °C, with maximum weight loss at 355 °C and the thermal decomposition of cellulose was complete under around 360 °C.<sup>49</sup> The third zone marked by a tiny degradation peak (from 350 to 480 °C) characterizes the degradation of lignin. However, some researchers reported that the degradation of lignin occurred in the temperature range of 100 °C to 700 °C with a tiny degradation peak at 340 °C. The thermal decomposition of lignin yields phenol via cleavage of ether and carbon-carbon linkages.<sup>50</sup> The overlapping observed in the DTG curves of hemicellulose, cellulose and lignin can be explained by the complexity of the polymeric material.

Figure 4b shows the TG-DTG curves of extracted cellulose. A small weight loss occurs between 50-140 °C, which is attributed to the

removal of absorbed water in cellulose. As depicted in the figure, the cellulose sample initiates a more pronounced degradation process at around 230 °C. The main decomposition step occurs in the range of 230 °C to 400 °C. In this stage, cellulose degrades producing anhydrocellulose and levoglucosan.<sup>50</sup>

#### X-ray diffraction (XRD)

The diffractogram of natural date stone (DS) does not exhibit a horizontal basic line. This shows that the major part of the matter is amorphous (Fig. 5). The XRD pattern of DS has been compared to those of native cellulose, xylene dehydrate given in the JCPDS crystallographic data base.<sup>51</sup> The peaks at (2θ) 16.1, 20.2, 39.2 may be attributed to native cellulose and hemicellulose dehydrate with different reticular distance (d), the peak at 33.3 corresponds to hemicellulose dehydrate and the peak at 25.4 describes the crystalline carbon.

The patterns of the isolated cellulose display one intense broad peak at ~22° (2θ). The peak broadening indicates poor crystallinity, as usually given in the literature.<sup>52</sup> Following deconvolution, the diffractogram shows the 14.7° 2θ reflection assigned to the (1̄10) crystallographic plane, the 16.00° 2θ reflection assigned to the (110) crystallographic plane, and the 21.8° 2θ reflection assigned to the (200) crystallographic plane.

The d-spacings were calculated using the Bragg equation (Eq. 2):

$$n\lambda = 2d\sin\theta \quad (2)$$

where n is the order of reflection, λ is the wavelength of the incident X-rays, d is the interplanar spacing of the crystal and θ is the angle of incidence.

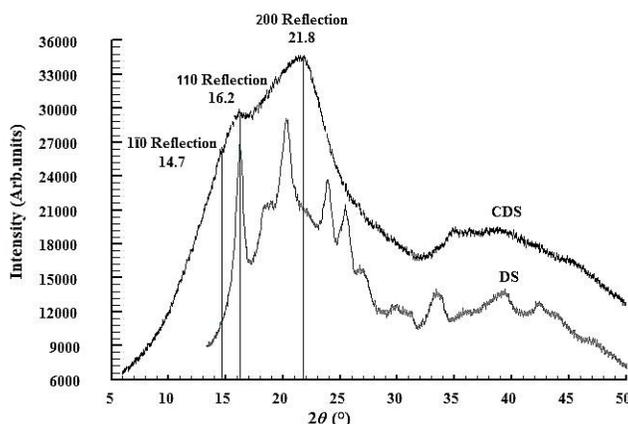


Figure 5: XRD diffractogram of date seeds (DS) and cellulose extracted from date seeds (CDS)

Table 5  
Parameters obtained from XRD analysis of date seed cellulose

Interplanar spacing d (nm)			Z value	Cr.I
L (1 $\bar{1}0$ )	L (110)	L (200)		
0.602	0.551	0.408	-25.91	10.3

To categorize cellulose as belonging to the I $\alpha$  or I $\beta$  predominant form, Z function (Eq. 3) was used:<sup>53</sup>

$$Z = 1693d_1 - 902d_2 - 549 \quad (3)$$

where  $d_1$  is the d-spacing of the (1 $\bar{1}0$ ) peak and  $d_2$  is the d-spacing of the (110) peak.

The approach used to determine the crystalline index (Eq. 4) was the empirical method proposed by Segal:<sup>53</sup>

$$Cr.I. = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \quad (4)$$

where  $I_{200}$  is the maximum intensity of the (200) lattice diffraction and  $I_{am}$  is the intensity diffraction at 18° 2 $\theta$  degrees.

Table 5 shows the parameters obtained from the XRD analysis of the date seed cellulose. For the extracted cellulose,  $d_1(1\bar{1}0)$ ,  $d_2(110)$  and Z-value were calculated to be 0.602 nm, 0.551 nm, and -25.91, respectively. The negative Z value indicates that the sample was rich in I $\beta$  polymorph.<sup>54</sup> The I $\beta$  is the dominant polymorph for higher plants, whereas the I $\alpha$  polymorph is a rare metastable form and can be converted into I $\beta$  by hydrothermal treatments in alkaline solution. The lower crystallinity index value (10.3) indicates that the structure of this cellulose is composed of a larger number of amorphous domains. Mechanical and chemical treatments affect the crystallinity of the cellulosic fibers.

## CONCLUSION

The aim of the above study was to characterize cellulose extracted from date palm seeds (*Phoenix dactylifera* L.). Carbohydrates are the main solids contained in the date seeds. The characterization done using Morfi, TGA, DP, FTIR, and XRD showed that the cellulose obtained was amorphous, microfibrillated, with a low degree of polymerization and good thermal stability. The cellulose obtained is not suitable for the papermaking process; nevertheless it may be a good precursor for cellulose derivatives or for the enzymatic process.

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