THE CELLULOSE FIBRE INDUSTRY: HARNESSING AGRICULTURAL WASTE FOR PRODUCTION

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Received October 2, 2024

This article investigates the potential of using agricultural residues from almond (*Prunus amygdalus* L.) and fig (*Ficus carica* L.) plants as sustainable sources for cellulose production. The study outlines the comprehensive pretreatment processes employed to extract cellulose fibres from these residues. Initially, delignification was carried out using a straightforward soda process, followed by sodium chlorite bleaching to enhance fibre purity. Subsequently, an alkali treatment was applied to remove hemicelluloses, ensuring the isolation of cellulose. The extracted cellulose was characterized through advanced techniques, such as X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), and thermogravimetric analysis (TGA). These methods confirmed the successful extraction and purity of the cellulose obtained from the agricultural waste materials. The results of the characterization processes revealed that the cellulose derived from almond and fig residues possesses suitable properties for various industrial applications. This includes the production of biomaterials, cellulose derivatives, and reinforced composite polymers. The findings underscore the potential of these agricultural residues as a valuable and renewable resource for cellulose production, contributing to the development of sustainable materials and promoting waste valorization in the agricultural sector.

Keywords: cellulose fibres, *Prunus amygdalus* L., *Ficus carica* L., characterization

INTRODUCTION

For years, biological waste and its recovery have become one of the most interesting new topics.[1] A compound is considered as a waste when it is disposed of without a plan to compensate for its intrinsic value. The growth of environmental pollutants is very high,[2] with irreparably damaging effects on it.[3] These natural residues can have harmful effects to the environment[4] as well as to living organisms[5] when improperly stored,[6] treated,[7] disposed,[8] managed[9] and transported.[10] Biological waste generally consists of significant amounts of chemical compounds[11] with the potential of being promising alternative raw materials as they are environmentally friendly,[12] biodegradable[13] and economically advantageous, and their use in different ways does not affect living organisms.[14] Biological waste can be removed in several ways, including microbial decomposition under aerobic or anaerobic conditions.[15] Bio-waste has garnered a great deal of attention from targeted academic and industry groups to identify approaches to transform low-value waste into new value-added compounds.[16,17]

Fig and almond are renewable and inexpensive annual resources for the production of natural fibres. These two natural biomasses could be the most important annual agricultural residues,

which are produced in many countries, such as the United States, Turkey, Syria, Spain, Italy and Tunisia.[18,19] The global almond harvest has experienced significant growth over the past five years, as indicated by data from FAOSTAT (2023). The almond cultivation area expanded from 1,822,021.0 ha in 2016 to 2,283,414.0 ha in 2021, representing a remarkable 25% increase. This expansion is primarily attributed to the establishment of new almond orchards in major producing nations, which predominantly consist of intensively irrigated plantations. Consequently, world almond production witnessed a substantial surge of 40%, rising from 2,860,346.2 tons in 2016 to 3,993,998.06 tons in 2021. Among Mediterranean countries, Spain, Morocco, and Tunisia stand out as the top almond producers, collectively accounting for a significant share of global production in 2021, as reported by FAOSTAT (2023). Spain takes the lead with an 83% share, followed by Morocco with 41% and Tunisia with 23%. These countries have significantly contributed to the overall growth and success of the global almond industry.

According to FAOSTAT (2023), the world's fig harvest has also steadily increased. A growth rate of up to 8% may be noted in the increase in fig cultivation from 278,207.0 ha in 2016 to 299,514.0 ha in 2021. A sharp 25% spike in global output has been attributed to this expansion of the cultivation area, as well as an increase in fig consumption globally. From 2016 to 2021, fig production escalated from 1,077,869.56 tons to 1,348,254.74 tons, according to FAOSTAT (2023). The Mediterranean area is where figs are most commonly found, and according to FAOSTAT (2023), Morocco, Spain and Tunisia will be the top producers of figs in 2021, as shown in Figure 1 (b).

In the present work, two different agricultural plants: almond and fig were pretreated within a pulping and bleaching process. Almond and fig wood were chosen considering their limited usage compared to bast fibres. In conclusion, the main objectives of this work are: (a) the extraction of cellulose, (b) the determination of the chemical compositions of the raw materials and (c) the characterization of cellulose. The resulting fibres have been characterized using X-ray diffraction (XRD), thermogravimetric analysis (TGA), and Fourier transform infrared (FTIR) analysis. The results obtained were discussed and compared with those available in the literature on wood, non-timber crops and annual crops.[20–23]

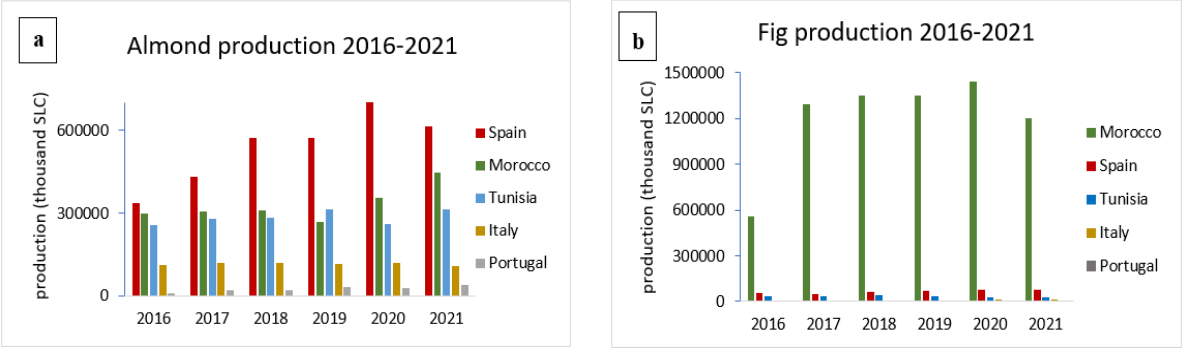

Figure 1: Almond and fig production in the Mediterranean region from 2016 to 2021; (a) Almond production; (b) fig production (FAOSTAT, 2023)

EXPERIMENTAL

Prunus amygdalus L. and *Ficus carica* L.

The raw materials, in this study, were obtained after the annual pruning of almond and fig tree plantations in the province of Mahdia, Ksour Essaf (Tunisia) in January 2022. Almond trimmings and shells, and fig trimmings were dried under natural conditions (average relative humidity = 65%, average temperature: around 25 °C). They were then washed in order to eliminate sand, dried again under the same conditions and stored until use. Before the raw materials were subjected to the pulping process, they were chipped in an automatic grinder to obtain chips of 1-2 cm length to facilitate the fractioning of the lignocellulosic components.

Preparation of cellulose fibres

The cellulose samples were obtained by a two-step methodology: (i) the delignification-bleaching, and (ii) the elimination of hemicelluloses from bleached fibres. In the present work, the delignification included the isolation and the extraction of cellulose pulp by following the chemical soda process. Usually, this process is recommended for annual plants.[24,25]

Starting with delignification, the biomass was subjected to a pulping process in a 15 L reactor, heated by an external heating jacket and rotated by means of a horizontal axis. The procedure described earlier[26] consisted in an alkaline pulping process using 10% NaOH (on dry matter) as a reactive agent, for 60 min at 170 °C and using a liquid/solid ratio of 8:1. Then, the ensuing pulp was extensively washed with water. After pulping, the treated chips were dispersed in a pulp disintegrator for 30 min at 1200 rpm. Once the chips were disintegrated, the pulp was filtrated by sieving through a netting of 50 µm mesh size. The cellulosic pulp was centrifuged to remove excess water and left humid in the fridge. Afterwards, the unbleached pulp was subjected to a bleaching process. For this purpose, 0.3 g of sodium chlorite per gram of pulp was added in a 0.3% pulp suspension in hot water of 80 °C for 3 h.[27] After cooling, the pulp was filtered and washed with distilled water in several cycles. This bleaching process allows the removal of practically all the lignin present in the fibre, while maintaining the entire carbohydrate composition. Each delignified pulp was carried out at least in duplicate to obtain a homogeneous bleaching.

The last step in the pulping process consisted of the elimination of hemicelluloses from the isolated fibres. This process was used to obtain high purity fibres from cellulose.[21,28] The bleached cellulose was mixed in 350 mL of a sodium hydroxide solution (4%). The reaction was performed with hot water of 80 °C, under mechanical stirring. After 2 h, the suspension was filtrated and washed with distilled water, until reaching a neutral pH or equal to that of distilled water. The treatment for the elimination of hemicelluloses was performed twice.[29] After delignification or bleaching steps, the pulping yield was calculated as the ratio of the weight of the o.d. material after washing to that of the o.d. initial raw material.

Figure 2: A schematic representation illustrating the various processes of the cellulosic fibres extraction

Characterization of cellulosic materials from almond and fig

Chemical composition

The raw materials and cellulosic pulp obtained from almond and fig were characterized in terms of the chemical composition: their content of cellulose (TAPPI T203 cm-99), holocellulose,[30] lignin (TAPPI T222 om-06), hot and cold water extractives (TAPPI T207 cm-08) and ashes (TAPPI T211 om-07). Since various standards can used to determine the chemical composition of the raw materials studied, we have chosen to briefly describe them below.

TAPPI T203 cm-99 is used to determine the alpha, beta, and gamma cellulose content in pulp. Alpha cellulose refers to the portion of the pulp that is resistant to 17.5% and 9.45% sodium hydroxide solutions under the specified test conditions. Beta cellulose is the fraction that dissolves, but then reprecipitates upon acidification. In this method, the pulp is sequentially extracted with 17.5% and 9.45% sodium hydroxide solutions at 25 °C. The soluble fraction, which includes both beta and gamma celluloses, is measured volumetrically through oxidation with potassium dichromate. The alpha cellulose, being the insoluble fraction, is determined by subtracting the soluble components.

TAPPI T222 om-06 is used to determine acid-insoluble lignin in wood and various grades of unbleached pulp. This standard applies only to raw materials and is not suitable for bleached cellulose. Acid-insoluble lignin is measured by subjecting the raw material to acid hydrolysis, followed by filtering off the insoluble lignin. The solid residue is then dried and weighed. Acid-soluble lignin can be quantified from the filtrate using a spectrophotometric method based on ultraviolet absorption, typically at a wavelength of 205 nm. Klason lignin is the sum of the acid-insoluble and acid-soluble lignins.

TAPPI T207 cm-08 is primarily used to measure the water solubility of pulp, wood, and annual plants that have not been extracted with organic solvents. If prior extraction with organic solvents is required, a solvent such as trichloroethane, which dissolves minimal water-soluble material, should be used. The raw material is extracted using a Soxhlet apparatus for 6 hours, and the amount of soluble products is determined gravimetrically.

TAPPI T212 cm-07 pertains to the solubility of pulp, wood, and annual plants in a 1% NaOH aqueous solution. This method involves boiling the raw materials in a 1% (w/w) NaOH aqueous solution for 6 hours. After filtering the solid phase, the amount of soluble products is determined gravimetrically. This TAPPI standard T211 om-07 is used for determining

the ash content, where the organic raw materials are combusted at a temperature of 525 °C.

Morphological analysis

Cellulosic fibres obtained from the two biomasses, almond and fig, were characterized from a morphological point of view using a MORFI (LB-01) analyzer, developed by Techpap (France). This analysis equipment employs an image analysis technique to determine the main morphological parameters (length, width, fines content) of fibres suspended in water. The measurement involves taking 1.2 g of dry pulp, diluted in 4 L of water. Then, one liter of the prepared suspension is taken and introduced into the device's tank, so that a quantity of 300 mg of dry fibres is analyzed. This procedure allows for working with highly diluted fibre suspensions. The test was done in triplicate.

X-ray diffraction (XRD) analysis

The X-ray diffraction (XRD) was performed to check the crystallinity of the extracted almond and fig fibres after various treatments. The samples were scanned with an X-ray diffractometer (D8-Advance Bruker AXS GmbH) at room temperature using a Cu Kα monochromatic light source (λ = 0.154 nm) in the step scan mode at an angle of 2θ from 10° to 50° with 0.04 pitch and 5.0 min scan time. The CrI crystalline index was determined using the methodology described previously.[31]

Fourier transform infrared (FTIR) spectroscopy

FT-IR analysis of extracted and treated cellulose was performed using a FTIR-ATR Perkin-Elmer Spectrum Two (Waltham, MA, USA), with a resolution of 4 cm^{-1} in the range of 500 to 4000 cm^{-1}. FTIR spectra were compared to evaluate the effects of raw materials and bleaching cellulose based on the intensity and shift of vibrational bands.

Thermogravimetric analysis (TGA)

The thermal stability of crude and bleached cellulose was assessed using a TA instrument Q-50 thermogravimetric analyzer (TA instruments, USA). Each sample was heated between 30 °C and 800 °C, at a heating rate of 10 °C/min under air atmosphere.

RESULTS AND DISCUSSION

Chemical composition of raw materials

The chemical composition of the various morphological parts of the biomass under study is presented in Table 1. The results reveal that the highest amount of cellulose (54.73%) was observed in fig trimmings and on the other hand, holocellulose was higher in almond shells (76.15%). In the case of lignin, the highest quantity was observed in almond stems (34.23%). α-Cellulose content of the raw material is the main selection factor for a pulping material. For the raw material examined, the α-cellulose content of the fig trimmings was considerably higher than those in the trimmings and shells of almonds.

Table 2 displays published data concerning various agricultural residues, including wood, non-wood materials, and both annual and perennial plants. Overall, cellulose remains the predominant component, accounting for varying weight percentages across agricultural residues and annual plants, ranging from approximately 35% to 70%. This data confirms the substantial cellulose content present in these sources. Additionally, the study revealed that both wood and non-wood materials exhibited higher lignin content compared to annual plants.

These data confirmed that the results obtained for almond trimmings and shells, and fig trimmings were similar to those for other agricultural residues.[18,21,42] The variations in the reported values for the studied raw materials can be attributed to the differences in the utilized processes, as well as the origin and variety of the raw material used.

Table 1
Chemical composition (wt%) of almond and fig materials

Component (%)	Tappi standard	Almond shells (AS)	Almond trimmings (AT)	Fig trimmings (FT)
Cold water extractives	T207 cm-08	8.92	17.12	10.08
Hot water extractives	T207 cm-08	14.59	18.34	14.16
1% NaOH extractives	T212 cm-07	23.48	30.08	23.36
Ash	T211 om-07	2.24	3.03	5.83
Klason lignin	T222 om-06	27.46	34.23	21.56
Holocellulose	[30]	76.15	67.14	74.7
α-Cellulose	T203 cm-99	48.54	44.71	54.73

Table 2
Chemical composition (wt%) of different raw materials

	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	References
Non-wood				
Phragmites	39.7	n.a.	23.6	[32]
Retama monosperma	42.7	n.a.	21.5	[32]
Posidonia oceanica	40	21.8	29.8	[33]
Date palm rachis	45	29.8	27.2	[33]
Banana pseudo-stems	40.2	n.a.	12.7	[34]
Wood				
Encalyptus globulus	52.7	n.a.	19.9	[32]
Hybrid poplar	41.7	20.2	29.3	[35]
Olive	41.0	n.a.	17.5	[36]
Pinus pinaster	55.9	n.a.	26.2	[32]
Annual and perennial plants				
Jute	71	14	13	[37]
Kenaf	36	21	18	[38]
Ramie	76	17	1	[39]
Sisal	73	14	11	[39]
Vine stems	35.0	30.4	28.1	[40]
Schinus mole	53.2	n.a.	21.4	[29]
Prunus amygdalus	40.7	n.a.	19.2	[41]

In conclusion, due to the acceptable amount of holocellulose, almond shells and trimmings, and fig trimmings may be considered as potential sources of cellulose for the cellulose derivatives production, cellulose pulp for paper, and natural fibres composite applications.

Pulping and bleaching

The cellulose samples from *Prunus amygdalus* L. and *Ficus carica* L. were prepared as described in the Experimental section. Several delignification and bleaching treatments were carried out, starting with an alkaline cooking process with 10% NaOH for 60 min at 170 °C. The resulting pulp from the starting material was then washed with water and disintegrated. The unbleached pulp was then bleached with sodium chlorite at 80 °C for 3 h to remove the lignin. Finally, the hemicelluloses were removed using a 4% NaOH solution at 80 °C. The obtained fibres were characterized and the results are reported in Table 3. From this table, it can be seen that almond shells present the highest delignification yield after cooking (65.66%), compared to the almond trimmings (44.20%) and fig trimmings (39.70%). These pulps were then treated with a bleaching step, leading to a final yield of over 33%, which is a typical value for chemical pulps from annual plants.[43]

The dimensions of the fibres extracted from almond shells, almond and fig trimmings are also given in Table 3, which summarizes the results obtained by Morfi Lab, in terms of arithmetic mean length, diameter and percentage of fine elements. The lengths of the isolated fibres are similar to those of other biomass sources, such as rice and wheat straw.[43] Almond and fig trimming fibres were longer than other annual plant fibres, such as those from Posidonia oceanica and/or Tamarisk sp.[40,41,43,44] The diameters of fibres extracted from almond and fig were smaller than the diameter of other fibres, such as those from date palm rachis (22.4 μm), grapevine stem (24.6 μm) etc. In all cases, the morphological characteristics of extracted bleached fibres, whatever the starting materials, are close to those of other fibres isolated from several annual plants,[43] while their average length (0.6 mm and 0.3 mm) is significantly lower. These properties impact the aspect ratio, whose value is around 20 to 23. In conclusion, despite the differences in chemical composition, these two residues can be considered as an interesting cellulosic source for the manufacture of durable materials or textile applications.

Fibre extraction and characterization

To confirm the chemical composition results, various analyses were conducted on the almond shells (AS), almond trimmings (AT) and fig trimmings (FT), as well as the extracted cellulose. Started with the XRD, the results showed four

diffraction peaks at 2θ = 15°, 22.6°, 30.2° and 35.4°, characteristic of cellulose crystal I. Removal of lignin and hemicelluloses from almond shells and trimmings and fig trimmings was indicated by the shoulder peak at 16.2° and a low peak at 34.2°. In addition, a new diffraction peak at about 2θ = 19.7°, which is generally attributed to the less ordered or amorphous region of the cellulosic chains, is shown in Figure 3.

Table 3
Yields and fibre dimensions for pulps from almond shells, almond and fig trimmings

Pulping results	Almond shells (AS)	Almond trimmings (AT)	Fig trimmings (FT)
Cooking yield (%)	65.66	44.20	39.69
Screening yield (%)	97.5	98.01	98.31
Bleaching yield (%)	33.34	25	33.34
Fibre length – arithmetic mean (mm)	0.411	0.574	0.545
Fibre width (µm)	26.5	19.3	22.7
Fine elements (% in length)	39	31.7	37.7

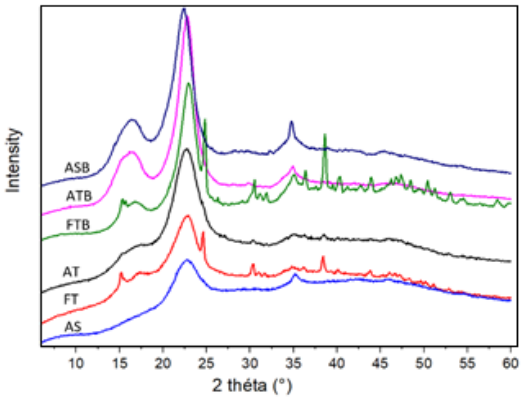

Figure 3: XRD patterns of raw materials and cellulose from *Prunus amygdalus* L. and *Ficus carica* L.

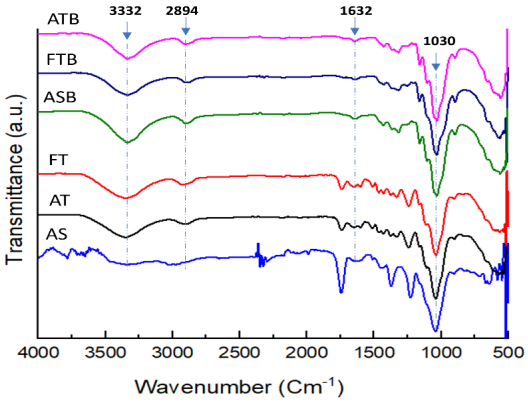

Figure 4: FT-IR of raw materials and cellulosic fibres from *Prunus amygdalus L* and *Ficus carica L.*

Fibres extracted from almond shells (ASB), almond trimmings (ATB) and fig trimmings (FTB) contain 54.99%, 70.21%, 70.17% crystalline cellulose, respectively. These values were comparable to the crystallinity levels observed in kenaf, cotton, and flax, which are 65%, 70% and 60% respectively.[42,45] However, other peaks have also been detected in the XRD curves. They correspond to the calcium and the magnesium elements. These impurities are the most common for lignocellulosic biomass, which can be easily removed after delignification and washing in several steps, as they are most likely related to carbonate anions. These results are consistent with those from TGA measurements.[19,21,39]

The FT-IR spectra are shown in Figure 4. The band at 1632 cm^{-1} was attributed to water in cellulose. The spectra provided an elastic band of CH_2 (2894 cm^{-1}) and an elastic band of O-H (3332, 3336 cm^{-1}) corresponding to the aliphatic fraction in polysaccharides. The band at 1632 cm^{-1} was assigned to the elongation vibration of the carbonyl group C=O located on non-conjugated structures and carboxylic acids.

The prominent band at 1030 cm^{-1} represented circular vibrations and C-OH bending. A small net absorption band at 900 cm^{-1} indicated β-glycosidic binding.[46] The increase in the intensity of these bands corresponded to the increase in the percentage of cellulosic components. Moreover, the FTIR curves of these biomasses (almond shells, almond trimmings and fig trimmings) confirmed that the three cellulosic materials appear to be comparable in chemical composition.

As for the thermal analysis of these agriculture residues, the results were illustrated in Figure 5, and clearly indicate that the three biomasses behaved in a similar manner. Thermal degradation curves can be divided into three zones: (i) up to 260 °C, (ii) between 280 °C and 380 °C and (iii) over 380 °C. The peak observed in the first region

was related to the moisture content found in the fibre, the increase in temperature resulted in an 8% weight loss for the three fibres examined. During the second degradation stage (200–280 °C), the decomposition of hemicelluloses and amorphous cellulose is observed. The decomposition of lignin also begins in the 280–380 °C range, with the formation of new structures that continue to decompose beyond 380 °C. The cellulosic samples behaved the same as ash-free pulps. Although the acid-free treatments used in this study only slightly reduced the ash content for each starting material, it remains high in both samples. We chose not to use acid treatments to preserve the structural integrity of the cellulose during extraction-bleaching treatments. However, for some applications, it may be necessary to decrease more or completely remove the ash content in order to avoid contaminating and affecting the purity of the final product. This will make the material more suitable for applications like producing cellulose derivatives.

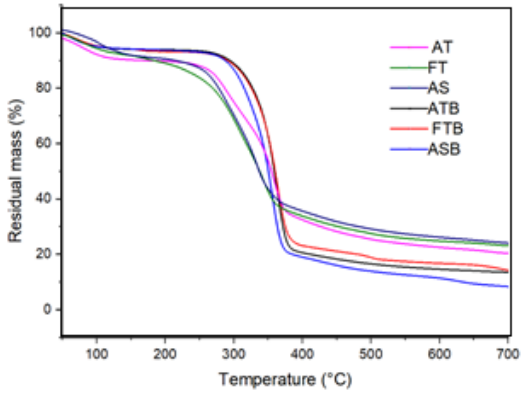

Figure 5: TGA curves of raw materials and cellulose from *Prunus amygdalus* L. and *Ficus carica* L.

CONCLUSION

This work leads to successful exploitation of agricultural waste widely available in Tunisia, specifically *Prunus amygdalus* L. and *Ficus carica* L. trimmings and shells. The use and recovery of these wastes can be a source for many economic activities associated with the generation of bio-products and bio-materials. The chemical composition results showed that these agricultural wastes are a promising source of cellulose (between 45 and 55% in weight), which encourages its use in various applications, such as composite or nanocomposite materials, paper making, nanocellulose, cellulose derivatives, *etc*. Several processes have been performed on the raw materials to obtain cellulosic fibres with high purity. The materials produced were characterized by a variety of techniques.

ACKNOWLEDGMENTS: The authors gratefully acknowledge the financial support provided by the University of Monastir, Tunisia, through a scholarship, and by the University of Cordoba for the financial support provided through the "Plan Propio de Investigación Enrique Aguilar Benítez de Lugo 2023, Submodalidad 2.4 UCOLIDERA" awarded to AgroCell project.

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