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Materials and Energy Valorization of Biomass and Waste: The Path for Sustainability and Circular Economy Promotion

Cellulose extraction by biomass valorization of prickly pear seed waste

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Abstract. The main objective of this work was the valorization of various biowastes to extract biocellulose for carbon fiber synthesis as a subsequent application. The effectiveness of cellulose extraction was investigated by two methods: maceration extraction and Soxhlet process. The extracted cellulose was characterized using a range of analytical techniques: thermogravimetric analysis/differential thermal analysis, scanning electron microscopy, Fourier transform infrared spectroscopy (FTIR), and energy-dispersive X-ray (EDX) analysis. The purity of extracted cellulose was successfully confirmed by FTIR and EDX results, which indicated the presence of major functional groups characteristic of cellulose structure. The cellulose extraction yield from prickly pear seeds was 39.3% by maceration and 23.18% using the Soxhlet extraction method.

Keywords. Biomass valorization, Cellulose, Extraction, Carbon fiber.

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1. Introduction

The valorization of agricultural wastes for producing lignocellulosic fillers (or fibers) is a promising strategy to develop green materials with appropriate performance and high sustainability from an economic and an ecological point of view. Biomass wastes were generally incinerated and discarded instead of being used productively, which intensifies environmental pollution. The growing environmental concerns and stringent regulations on waste dumping and emissions have stimulated researchers to valorize material from agriculture waste and obtain useful industrial substances. Through chemical and biochemical modification, the carbohydrate polymer from waste can be treated to obtain fine chemicals that would alleviate various socioeconomic problems [1]. Annually, 1.77–2.4 gigatons of waste from tubers, roots, cereals, and vegetables are produced [2]. They can be classified as lignocellulosic waste containing cellulose, hemicellulose, and lignin. Thus, in recent years, research has focused on the valorization of these natural and industrial wastes. Tunisia has a vast potential for biomass

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production from a variety of sources that can be used for the generation of bioenergy and other purposes. According to the International Renewable Energy Agency (2021) report, Tunisia produced approximately 6 million metric tons of biomass in 2019. This comprises 200,000 tons from wastewater treatment, 400,000 tons from poultry droppings, 2.2 million tons from agriculture and agroindustry, 1 million tons from olive oil production, and 2.2 million tons from household waste [3]. Numerous organic wastes are produced by Tunisia's agrifood industry, which presents opportunities for the production of useful materials, the mitigation of environmental issues, and the enhancement of resource circularity. Prickly pear seeds (PPS) from Tunisia's agrifood sector offer a promising opportunity among these wastes. An often overlooked byproduct of prickly pears arises from their ability to be turned into carbon fibers. This not only makes waste management more sustainable but also makes it possible to produce materials with high added value. Interesting characteristics like lightweight, mechanical strength, and electrical conductivity make carbon fibers made from leftover PPS valuable in a large range of industrial applications [4]. Cellulose extraction represents a significant opportunity for advancing sustainable and environmentally friendly solutions. Because of its special properties, including biodegradability, renewability, and exceptional mechanical strength, cellulose has attracted a great deal of interest in recent years. These properties make cellulose a desirable option for a variety of applications, including paper, textiles, bioplastics, scaffolding for biomedical procedures, and other advanced materials [5], The employment of cellulose for the production of carbon fibers is a promising area of research, offering many advantages in terms of durability and performance. Carbon fibers are highly sought-after materials in various fields of application (automotive, aeronautics, space, etc.) [6]. The advantages of cellulose include its reasonable budget, durability, and higher carbon content, making it a dominant precursor [7]. In this context, this study aims to extract cellulose from Tunisian lignocellulosic biomass including industrial biowaste and other waste sources for the potential application of carbon fiber synthesis. Two different extraction techniques were investigated: a conventional method using hot water maceration and a non-conventional method using the Soxhlet process. To assess the

effect of the extraction method on the quality of the extracted cellulose, the extract was finally characterized by various techniques: scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) analysis, Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA).

2. Materials and methods

2.1. *Materials*

For cellulose extraction, a variety of biomasses were used, such as olive stones, straws, palm petioles, sea balls (*Posidonia oceanica*), allied plants, and more specifically PPS, which were collected from an experimental plantation of the bioenergy industry in the Gabes region (Tunisia). The reagents utilized were sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2), which were acquired from the Laboratory of Promosciences, Tunisia.

2.2. *Methods*

In this study, two cellulose extraction methods, maceration and Soxhlet, were evaluated through continuous chemical treatment to eliminate lipids, hemicellulose, lignin, and other impurities. Both methods followed used the same steps shown in Figure 1. First, the pretreatment consisted of washing the biomass by distilled water for 24 h at ambient temperature, sun drying, grinding, and later storing in sealed plastic bags. Then, samples (25 g) were dewaxed using ethanol solution (95%) with a solid–liquid ratio of 1:10 (w/v) for 3 h at 75 °C to remove extractable sugars, fatty acids, tannins, and wax. The resultant extract was gathered, dried at 60 °C in an oven, and finally weighed. Subsequently, alkaline treatment was conducted to eliminate lipids, hemicellulose, lignin, and other impurities present in the raw fiber. The chemical treatment procedure was assessed three times: prior to treatment (% extractables), following alkaline treatment (% lignin), and following bleaching (% hemicellulose). The reaction occurred at a solid–liquid ratio of 1:10 (w/v), employing a 6% NaOH (w/w) solution at 95 °C for 2 h with continuous stirring. The obtained sample was washed repeatedly with distilled water until attaining neutral pH and then dried to a constant weight in an oven at 60 °C for 24 h. Finally, the extracted sample was bleached
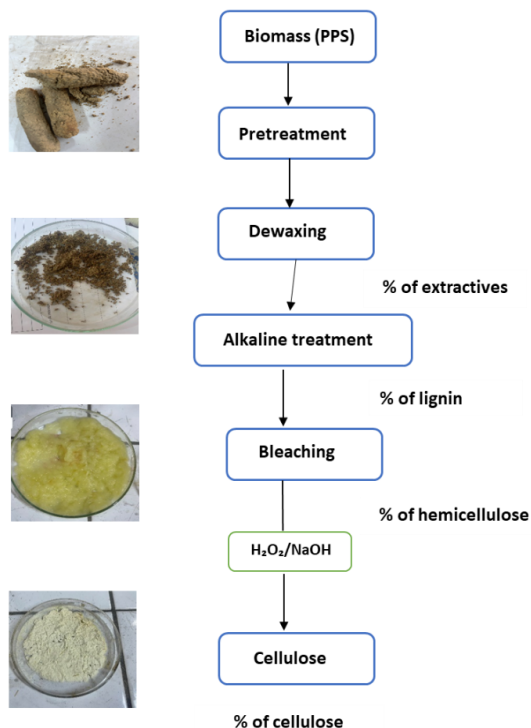
Figure 1. Extraction steps of cellulose.

using 1:40 solid–liquid ratio (w/v) of a mixture of 7.5% hydrogen peroxide (v/v) and 5% NaOH (w/w) for 2 h at 75 °C with stirring. The purified cellulose at pH 8.4 was rinsed with distilled water and dried at 60 °C in an oven for 24 h. The bleaching treatment was carried out five times under the same conditions and the samples weighed.

The cellulose content from the extraction methods was estimated by calculating the percentage of cellulose using Equation (1) [8]:

% Cellulose = 100
    − (% hemicellulose + % lignin + % extractive)   (1)

2.3. *Characterization*

The characterization of extracted cellulose was carried out by FTIR using a Spectrum two FTIR Spectrometer. The spectrum was recorded in transmittance mode over a range of 4000–400 cm^{-1}. Using a SETARAM thermal analysis system in a dinitrogen environment, the TGA/differential thermal analysis (TGA/DTA) method was performed throughout a temperature range of 30–1000 °C at a heating rate of

10 °C·min^{-1} and a flow rate of 20 ml/min. The weight loss and thermal properties of the samples were computed by the associated computer program. Model Tescan VEGA3 SBH (tungsten filament) equipped with a secondary electron detector and Bruker Flash 630M EDS was used to perform elemental analysis using EDX and SEM. Quantifying the cellulose's carbon, hydrogen, and nitrogen content and examining the biomass and cellulose morphology are the goals of these analyses. Ascertaining the ash content of cellulose is essential to evaluate its purity and appropriateness for different uses. The amount of ash measures the inorganic residue that remains after burning, which was mostly made up of minerals and other inflammable materials. The various percentages of extractives, hemicelluloses, lignin, and ash content were calculated using Formulas (2) and (3):

$$\% = \frac{m_i - m_f}{m_i} \times 100 \qquad (2)$$

$$\text{Ash content (\%)} = \frac{\text{Final mass of ash}}{\text{Initial mass of sample}} \times 100 \quad (3)$$

where m_i is the dried sample weight before extraction (g) and m_f is the dried sample weight after extraction (g).

3. Results and discussion

3.1. *Characterization of extracted cellulose*

3.1.1. *TGA–DTA analyses*

Thermograms of TGA/DTA, presented in Figure 2, provide a comparison of the thermal behavior between raw biomasses and extracted cellulose for different materials, including palm petiole, allied plant, olive stone, PPS, straw, and sea ball. The TGA curves show mass loss as a function of temperature while the DTG curves depict the rate of decomposition. For the raw materials, multiple phases of thermal degradation are observed: an initial phase around 100 °C, corresponding to moisture removal, followed by significant decomposition between 250 °C and 400 °C due to the breakdown of cellulose and hemicellulose, with further degradation beyond 400 °C related to lignin.

The DTA curve showed a slight exothermic reaction at the initial stage around 100 °C due to sample dehydration. Degradation of residual cellulose and hemicellulose was indicated by a strong exothermic reaction between about 270 °C and 375 °C.
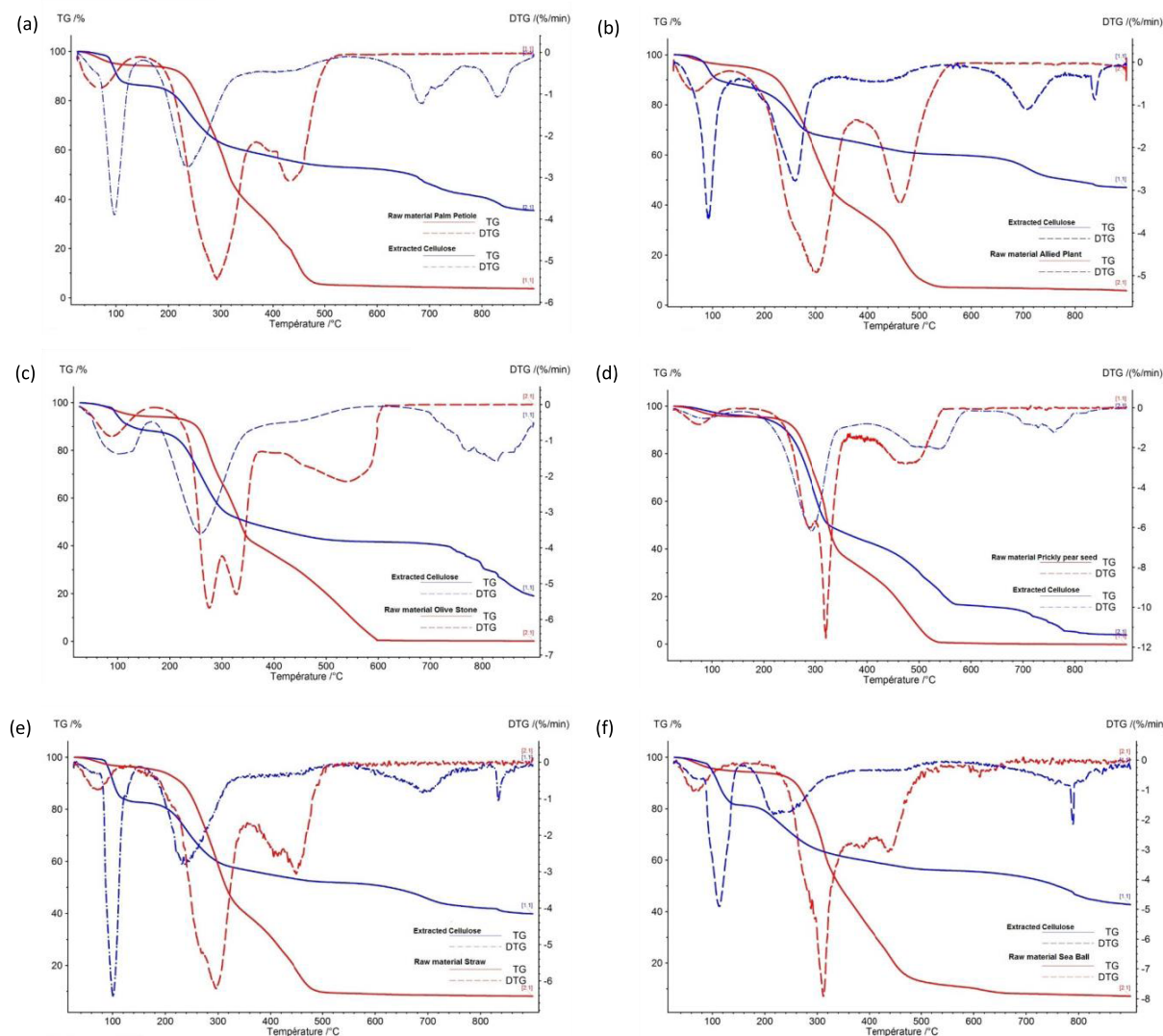
Figure 2. TGA/DTA curves of biomasses and their extracted cellulose: (a) palm petiole, (b) allied plant, (c) olive stone, (d) prickly pear, (e) straw, and (f) sea ball.

According to Safaei et al. [9], heat-induced modifications in cellulose structure mainly involved depolymerization (starting at 310 °C) as a result of chain breakage at the 1,4 glycosidic bonds, dehydration (starting at 280 °C), and glucose formation. According to the literature, the maximum decomposition of cellulose occurs at 338 °C [10], which was verified by the curves obtained. In fact, the DTG curves showed that a maximum rate of weight loss occurred between 228 °C and 400 °C. The third stage of degradation happened between 375 and 500 °C, which corresponds

to lignin, which was recognized for having higher thermal stability and resistance to degradation [11]. Thermal decomposition is normally deemed to be finished below 500 °C. In addition, the residue matter, without impurities at 1100 °C, of different biomasses were determined as follows: straw, 12.5%; petiole palm, 17.3%; PPS, 29%; allied plant, 11.6%; sea ball, 22.5%; olive stone, 22.3%. This observation indicated that PPS had significant cellulosic matter content, making it a good starting material for cellulose extraction. Consequently, this biomass was selected for

further investigation.

On the other hand, compared to the raw biomass curves, the thermal analysis (TGA/DTA) curves for the extracted cellulose exhibited significantly different degradation behavior. The first degradation process of the extracted cellulose was achieved in only two samples [12]. The first stage involved a minor mass loss around 100 °C, attributed to the evaporation of moisture. The second stage, in the temperature range of 300–400 °C, is related to the decomposition of cellulose, leading to the formation of hydrocellulose and levoglucosan [12].

This also confirmed the effective removal of other components such as hemicellulose and lignin from the raw biomasses indicating the purity of the extracted cellulose.

3.1.2. *Fourier transform infrared spectroscopy*

Figure 3(a) shows the FTIR spectra of the various raw material samples (untreated) and Figure 3(b) illustrates the spectra of prickly pear samples treated and bleached with H_2O_2/NaOH. All spectra (Figure 3a) show broadly similar peaks, indicating the existence of the same functional groups. There exist a broad peak around 3200–3600 cm^{-1}, indicating the presence of hydroxyl (OH) groups due to carbohydrates, organic acids, and water; peaks around 2800–3000 cm^{-1} corresponding to C–H bonds in hydrocarbons; a sharp peak around 1700 cm^{-1}, characteristic of carbonyl groups (C=O) in organic acids and esters; and peaks around 1000–1300 cm^{-1}, often associated with carbohydrates. More particularly for PPS, the two spectra in Figure 3(b) show broadly similar peaks, suggesting the presence of the same functional groups. This also proves that multi-step treatment does not alter the cellulose structure in PPS and that cellulose was successfully extracted after multistep treatment. The primary peaks indicating the presence of cellulose are located at 3440 cm^{-1} and 2950 cm^{-1}, and were attributed to the asymmetric stretching vibrations –OH and –CH, respectively, of the saturated aliphatic C–H group [13]. The value of the peak increases with deeper processing but often becomes sharper as it originates predominantly from the hydroxyl groups of cellulose, indicating an increase in the amount of cellulose and the content of –OH groups.

The peaks at 1658 cm^{-1} and 1232 cm^{-1} decrease as the extraction process advances, suggesting that

Table 1. Chemical composition and ash content of prickly pear seeds

Constituents	Percentage (%)
% Extractive	16
% Lignin	22.13
% Hemicellulose	22.57
% Cellulose	39.3
Ash	0.74

alkaline treatment and bleaching are the best means of removing hemicellulose and lignin [14].

The stretching vibration of the lignin carbonyl group and the ketone C=O group is represented by peaks at 1515 cm^{-1}. The intensity of this peak also decreased with time, suggesting that some of the lignin had been partially removed. As this is the spectral region of hemicellulose and lignin fingerprints, the absence of these peaks in the treated samples verified the total removal of hemicelluloses and lignin [15]. The O–H and C–O stretching vibrations of the polysaccharides present in cellulose were visible in the spectrum at 1024 cm^{-1} [16]. The C_1–O–C_4 bending vibration of the β-glycosidic bond in cellulose was represented by the peak at 865 cm^{-1} [17].

The presence of the cellulose group was strongly guaranteed by all these observed peaks [15].

3.1.3. *Chemical composition and ash content analysis*

The chemical composition and ash content of PPS during the extraction process were determined. Table 1 presents the significant alterations that were verified through yield computations for all extraction steps.

The chemical composition of PPS was investigated to assess its suitability to produce cellulose fibers for industrial use. To represent the inorganic impurity in the biomass that does not burn during the energy conversion process, an analysis of the ash content was done. In terms of reagent costs and the time needed to evaluate the purity and suitability of the materials, this approach has proved to be affordable. Determining the chemical composition of the samples is a critical step in understanding the organic components of the biomass. Additionally, analyzing the ash content provides insight into
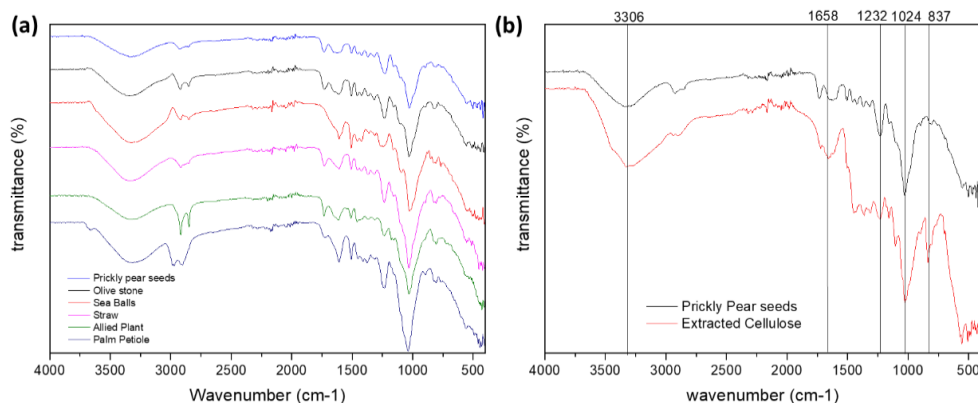
Figure 3. FTIR results of (a) raw material and (b) cellulose extracted from prickly pear seeds.

the amount of mineral matter present, resulting in a complete picture of the biomass composition.

3.1.4. *Morphological and elemental composition*

Scanning electron microscopy was used to study the morphology of PPS pericarp cells. The results revealed that the spindle-shaped sclerenchyma fibers were arranged in two different orientations. These tissues usually make up secondary walls. There are also a few single-helix spiral conducting vessels visible. As demonstrated in Figure 4, micrographs of cross-sections of Opuntia ficus-indica PPS reveal that the seed is composed of two distinct tissues: the pericarp (P) and the endosperm (E). The percentage of seeds in an entire Opuntia ficus-indica prickly fruit varies from 30% to 40% dry weight. This is a significant number of seeds, and about 90–95% of an entire seed is made up of pericarp [18]. Table 2 and Figure 5 present the elemental composition of the biomass, comparing the raw material (PPS) with the extracted sample. The results indicate significant variations in the content of carbon (C), oxygen (O), sodium (Na), and calcium (Ca), underscoring the impact of the extraction process on the chemical composition of the biomass.

The carbon content of the raw material decreases substantially from 49.97% to 7.65% post-extraction. This reflects a significant removal of organic matter, likely cellulose or lignin, which are major components of the biomass. This decrease suggests that the extraction process effectively removed a large proportion of unwanted organic compounds, thereby

Table 2. Cellulose and biomass elementary composition

Samples	C (%)	O (%)	Na (%)	Ca (%)
Raw material (PPS)	49.97	46.15	-	3.88
Extracted sample	7.65	28.64	14.38	-

enhancing the purity of the sample.

Additionally, the oxygen content also decreased, albeit less markedly, from 46.15% to 28.64%. Sodium, absent in the raw material, appears in the extracted sample at a notable concentration of 14.38%. This can be attributed to the use of sodium hydroxide (NaOH) during the alkaline treatment, which is employed to break down lignin or hemicellulose. Conversely, calcium, initially present at 3.88% in the raw material, was completely eliminated in the extracted sample. This suggests effective demineralization, with the removal of compounds such as calcium carbonate. The resultant fiber's EDX analysis reveals notable peaks for oxygen and carbon, pointing to the presence of a lignocellulosic biomass structure. It also shows that sodium is present in the cellulose that was extracted from PPS, most likely because of cations being drawn to negatively charged hydroxide ions during the bleaching process [19]. The presence of gold is explained by the metallic coating that was used to prepare the samples. Most of the contaminants were eliminated following the bleaching treatment, indicating that the dewaxing, alkalinization, and bleaching processes are success-
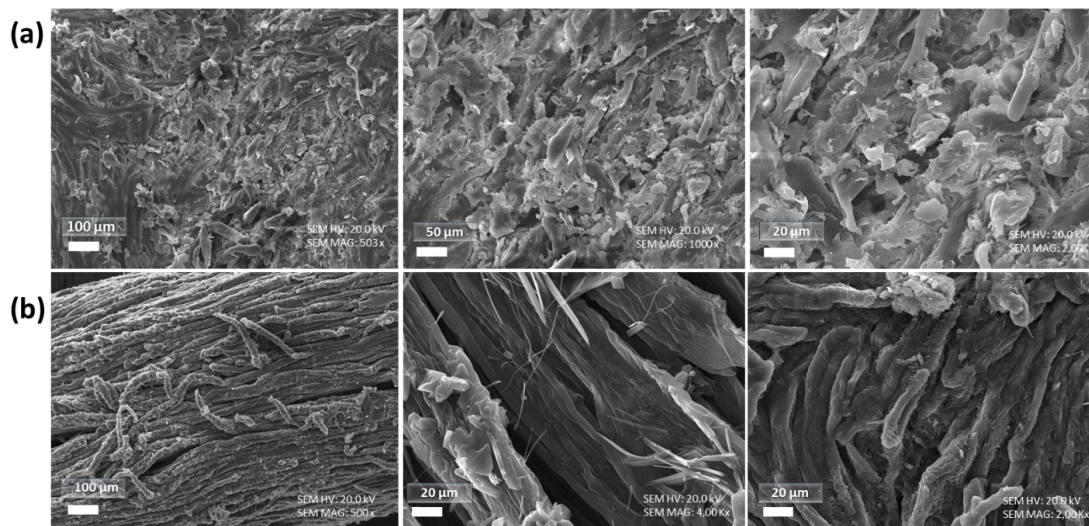
Figure 4. SEM of prickly pear seeds: (a) raw material and (b) treated samples.
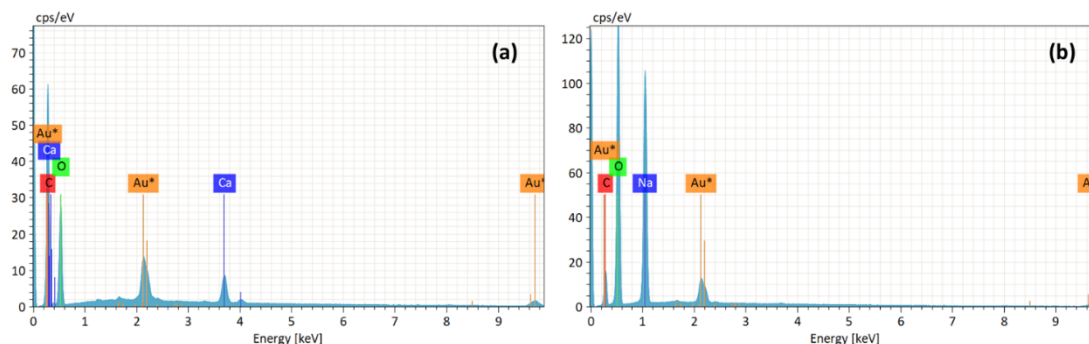

Figure 5. EDX spectra of (a) raw material of PPS and (b) cellulose extracted from PPS.

ful in yielding very pure cellulose with little to no residual contaminants. The outer layers of cellulose fibers, which contribute to the protection of cellulose, are composed of hemicellulose, lignin, pectin, and wax. As a result, untreated lignocellulose generally exhibits a dense structure. As shown in Figure 3(a), the waxy and lipidic substances present in PPS, even in the absence of chemical treatment, contribute to the smoothness and density of the fiber surface [15].

Figure 3(b) illustrates that after the dewaxing, alkalinization, and bleaching treatment with H_2O_2/ NaOH on prickly pear, some waxy and lipidic substances were removed. The dense and smooth structure of the cellulose surface was disrupted, resulting in an irregular surface. Hemicellulose, lignin, and pectin, which form the biomass coating, began to break down. After the alkaline treatment, part of the hemicellulose disappeared and the fiber surface became porous and rough. Strongly interwoven fiber bundles can be observed. The presence of lignin is indicated by the fiber bundles. There are van der Waals interactions, hydrogen bonds, and O–H covalent bonds between lignin and cellulose.

Alkaline hydrogen peroxide can act on lignin by penetrating lignocellulose, leading to the removal of hemicellulose, the formation of pores, and the complete breakdown of the biomass coating. The physical barrier of lignin was removed after the alkaline hydrogen peroxide bleaching treatment, resulting in a more uneven and rough fiber surface, a more visible pore structure, and a full exposure of the fiber's
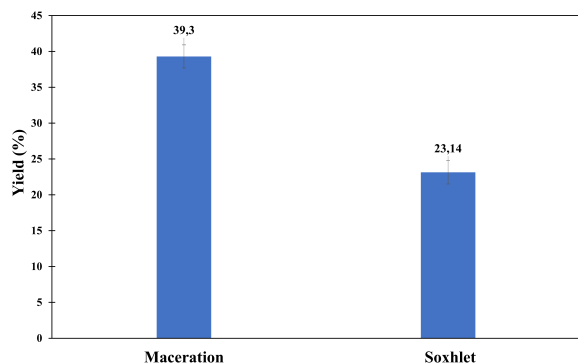
Figure 6. Yields of cellulose from prickly pear seeds after extraction with maceration and Soxhlet.

internal structure [17].

3.2. *Cellulose extraction using different methods*

The extraction of cellulose from PPS was evaluated using maceration and the Soxhlet method. The extraction yields are summarized in Figure 6. Both techniques provided significant extraction rates. The maceration technique presented a higher extraction yield equal to 39.3% compared to 23.14% obtained by the Soxhlet method. Maceration improves extraction kinetics because it occurs at a slightly higher temperature than Soxhlet extraction. Additionally, better external mass transfer between the solvent and the biomass might be the result of the direct contact between the two materials made possible by maceration [20].

The results of this study highlighted the importance of selecting the most appropriate technique for cellulose extraction as well as the potential for optimizing the extraction process to improve yields. Additionally, the findings underscored the significance of choosing the best method for maximizing cellulose extraction yields.

4. Conclusion

An environmentally friendly extraction technique was used in this study to extract cellulose from Tunisian industrial waste and other biological wastes such as PPS. Without the use of chlorine or hard acid, extraction was effectively completed through a co-operative chemical treatment of dewaxing (ethanol), alkalinization (NaOH), and bleaching (H_2O_2). Various characterization analyses were employed for the identification of extracted cellulose. The TGA analysis emphasized the stability of cellulose thermal properties and the composition of lignin and hemicellulose. The FTIR results verified the cellulose structure in relation to the removal of a significant amount of hemicellulose and lignin throughout the chemical treatments. The EDX analysis of crude cellulose and cellulose extracted from PPS proved the successful extraction of cellulose using $H_2O_2/NaOH$ with a yield of 39.3% by maceration and 23.14% by the Soxhlet method. The results of this study indicated that PPS represented a good source of high-quality cellulose and an effective means to produce large amounts of cellulose with superior thermal properties. Thus, the cellulose extracted from PPS exhibits a high potential for various sustainable applications. Because the extracted cellulose is exceptionally strong and light, it is a good choice for reinforcing composite materials used in aerospace, automotive, shipbuilding, and other industries requiring high-performance structural materials. These crystalline nanomaterials can be utilized to produce carbon fibers used as reinforcement and energy storage elements as in this work.

Declaration of interests

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