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Physicochemical Characterization of Cardoon "*Cynara cardunculus*" Wastes (Leaves and Stems): A Comparative Study

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Abstract: The disposal of vegetable wastes in nature is harmful for marine habitats and biota. These types of waste are frequently used as fuel, generating polluting products, with undesired side effects on the environment. Therefore, it is essential to find better alternatives for the capitalisation of these waste products. Their diversified chemical composition can become a potential resource of high added value raw materials. The knowledge of the physicochemical properties of these wastes is therefore essential. The present work aimed for characterising the physicochemical properties of a plant residue belonging to the Asteraceae Family, collected from a vegetable market in Fez city, Morocco. The vegetal tissues were analysed by Scanning Electron Microscopy coupled with EDX, X-ray Diffraction, Fourier Transform Infrared Spectroscopy, Inductively Coupled Plasma Atomic Emission Spectroscopy, and by Thermogravimetric/Differential thermal analyses. Other additional parameters were also measured, such as moisture, volatile matter, ash, and fixed carbon contents. Acidic and basic surface functions were evaluated by Boehm's method, and pH points at zero charge were equally calculated. The results revealed a strong congruence between the morphological and structural properties of this plant. These vegetal wastes comprise a homogeneous fibrous and porous aspect both in surface and in profile, with a crystalline structure characteristic of cellulose I. A mass loss of 86.49% for leaves and 87.91% for stems in the temperature range of 100 °C to 700 °C, and pH_{pzc} of 8.39 for leaves and 7.35 for stems were found. This study clarifies the similarities and differences between the chemical composition and morphological structure of these vegetal wastes, paving the way for future value-added applications in appropriate fields.

Keywords: waste; lignocellulose; capitalisation; characterization; environment

Citation: Hajji Nabih, M.; El Hajam, M.; Boulika, H.; Hassan, M.M.; Idrissi Kandri, N.; Hedfi, A.; Zerouale, A.; Boufahja, F. Physicochemical Characterization of Cardoon "*Cynara cardunculus*" Wastes (Leaves and Stems): A Comparative Study. *Sustainability* **2021**, *13*, 13905. https://doi.org/10.3390/su132413905

Academic Editor: Luis Jesús Belmonte-Ureña

Received: 25 November 2021
Accepted: 13 December 2021
Published: 16 December 2021

1. Introduction

Farms, cooperatives, the food industry, and markets generate large quantities of vegetal wastes, with undesired effects on human health and environment. These unwanted effects are mainly possible because of the poor management and illegal dumping of these organic wastes, mainly along coastlines [1].

In Morocco, this type of waste management still leaves much to be desired and is reflected on a daily manner in an insufficient collection rate, the presence of more than 300 unauthorized dumps, as well as by a poor coordination among the stakeholders involved in this sector [2]. The management of these wastes comprises a very stringent

issue, both nationally and internationally. This activity occurs as a result of an increasing volume of garbage being inadequately disposed, lack of financial and economic resources, failure of control systems, and a poor adequacy of treatment methods in field conditions [2].

The chemical composition of vegetal remains differs greatly among species, mainly as a result of climate. The chemical composition of vegetal residues influences the chemical capitalisation processes. For example, high ash content leads to negative effects on charcoal conversion processes, whereas high lignin concentrations in the lignocellulosic material affect the yield of cellulose extraction. The elemental characterization of these organic wastes is therefore necessary for an adequate choice of their proper capitalisation.

Cardoon is one of the most abundant plant species in Morocco, available throughout the year and comprises a basic food product for the local population. However, the consumable parts of the Cardoon comprise just one third of the plant, resulting in other two thirds that are wasted. The high abundance of this plant in most regions of the country, as well as its nutritional value make their wastes an important resource that needs to be better studied and economically exploited, given that the research on this topic is scant. The improper management of the organic remains of Cardoon led scientists towards finding adequate solutions for reducing their accumulation in the environment and for better capitalisation pathways, such as their use as adsorbents of organic dyes and heavy metals [3,4], feedstock for the sustainable production of levulinic acid and n-butyl levulinate [5], for energy production (e.g., solid biofuel, biodiesel, biomethane and ethanol), for cellulose, pulp and paper production, and for phytochemical and pharmacological purposes [6].

The first step in the current study was to characterize the physic-chemical properties of this plant, by measuring and describing its morphological, structural,3,3 and functional characteristics. An in depth knowledge of these properties can lead to a better exploitation of its wastes, through an adequate capitalization. The main characteristics of Cardoon wastes (i.e., leaves and stems) were measured by determining first their mineral compositions with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), followed by measuring the moisture (H%), the volatile matter (PF%), the ash (C%), and the fixed carbon (FC%) content, as well as their acid-base properties and pH point at zero charge (pH_{pzc}). The morphological and structural properties were also investigated by Scanning electron microscopy coupled with EDX (SEM/EDX), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA/DTA).

2. Materials and Methods

2.1. Materials

a. Cardoon wastes

Cardoon wastes were collected from a local vegetable market in Fez-city, Morocco, washed with water, dried at 50 °C in a Binder oven, then separated into leaves and stems. The dried material was homogenised with an automatic mill (IKA tube Mill control), and then sieved through a 1.25 mm mesh size sieve (Figure 1).

Figure 1. Cardoon waste states: (**A**) Fresh, (**B**) Dried, (**C**) Screened.

b. Chemicals

The different chemicals used in this study and their characteristics are listed in Table 1:

Table 1. Chemicals used in this study.

Chemicals	Purity (%)
Sodium Hydroxide (NaOH)	98
Nitric Acid (HNO_3)	67
Hydrochloric acid (HCl)	37
Sodium carbonate (Na_2CO_3)	99
Sodium hydrogen carbonate ($NaHCO_3$)	99
Sulfuric acid (H_2SO_4)	97 et 72
Sodium chloride (NaCl)	99
Hydrofluoric acid (HF)	94

2.2. Methods

2.2.1. Preliminary Analyses

a. Moisture and volatile matter contents

Moisture and volatile matter content were measured as follows: a mass m_0 of powdered sample was placed in a dry crucible and treated at 105 °C for 24 h. The moisture content (H%) was calculated using the Equation (1) [7]:

$$H\% = \frac{m_0 - m_1}{m_0} * 100 \quad (1)$$

where,

m_1 is the mass of the sample after drying at 105 °C.

The material was heated again to 1000 °C for 3 h in a muffle furnace. The volatile matter (PF%) content was calculated using the Equation (2) [8]:

$$PF\% = \frac{m_1 - m_2}{m_0} * 100 \quad (2)$$

where,

m_2: mass of the sample after treatment at 1000 °C.

b. Ash content

The ash content was measured as follows, a mass m_0 of each sample was calcinated in a furnace at 650 °C, the mass of the obtained residue m_1 representing the mineral content as ash. The ash content was calculated by Equation (3) [9]:

$$C\% = \frac{m_1}{m_0} * 100 \quad (3)$$

c. Fixed carbon

The fixed carbon (FC%) rate expresses the actual amount of pure carbon remaining after the complete decomposition of biomass. It was calculated using the Equation (4) [10]:

$$FC\% = 100 - (H\% + FP\% + C\%) \quad (4)$$

2.2.2. Determination of Surface Functions and pH at Point Zero Charge

a. Acid-base character: Boehm's method

- **Protocol for the determination of basic functions**

A mass of 400 mg of raw samples (leaves or stems) was dispersed in 50 mL in a HCl solution (0.02 M) under stirring for 48 h, the residue was filtered, and the filtrate recovered. The excess of HCl was dosed by a solution of NaOH (0.1 M), and the total amount of basic functions present in the sample is deduced by return dosage.

- **Protocol for the determination of the acid functions**

Quantities of 400 mg of leaves and stems were dispersed in a beaker containing 50 mL of a basic solution of $NaHCO_3$ (0.02 M) under stirring for 48 h; then, the mixture was filtered. The excess of $NaHCO_3$ was measured by a solution of HCl (0.02 M), the quantity of acid functions on the surface being deduced by return dosage. The same protocol is repeated for the same samples using basic solutions of Na_2CO_3 (0.02 M) and NaOH (0.02 M) separately [11].

b. Determination of pH point at zero charge (pH_{PZC})

A series of NaCl (0.01 M) solutions buffered at different pH_i values (2 to 12) were adjusted by the addition of NaOH (0.1 M) or HCl (0.1 M). A mass of 0.15 g was dispersed in 50 mL of buffered solutions under stirring and at room temperature, then the residue was filtered and the pH_f value of the filtrate measured. The pH_{pzc} was determined graphically by the intersection point of the $pH_f = f(pH_i)$ curve with the first bisector [12,13].

2.2.3. Physicochemical Characterization

The physicochemical characterization was done by scanning electron microscopy coupled to EDX (SEM/EDX), inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) (Regional University Centre of Interface of Fez).

a. Scanning electron microscopy coupled to EDX (SEM/EDX)

The morphology was performed using a scanning electron microscope (Jeol it500 HR), with acceleration range from 0.5 KV to 30 KV, a probe current ranges from 10 pA to 20 nA, equipped with a Schottky field emission gun camera. The coupling of the scanning electron microscope (SEM) with X-ray electron scattering (EDX), allows obtaining the qualitative elemental composition of the samples.

b. X-ray diffraction (XRD) analysis

X-ray diffraction analysis of dried samples was done with a Panalytical X'Pert Pro X-ray diffractometer equipped with a Cu-Kα (1.54 Å) monochromatic source (XPERT-PR) at a voltage of 40 kV and a filament current of 30 mA. The recording was performed from $2\theta = 10^\circ$ to $2\theta = 40^\circ$.

c. Fourier Transform Infrared Spectroscopy (FTIR)

The raw samples were analysed using a Bruker Vertex 70 FTIR spectrometer based on ATR mode. The recording of FTIR spectra is composed of 16 scans over a wavelength range from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1}.

d. Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

The samples, calcinated at 550 °C, were digested with a mixture of hydrochloric acid (37%) and nitric acid (67%) (V/2V) and then with hydrofluoric acid (94%), the volumes of these mixtures diluted with distilled water to 50 mL, ref. [14]. The elemental analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an Activa spectrometer from Horiba Jobin-Yvon, equipped with an Argon plasma.

e. Thermogravimetric analysis (TGA/DTA)

To study the thermal behaviour of the samples, we followed the mass losses recorded between 100 °C and 700 °C with a step of 10 °C, using a Nabertherm furnace. At the end of the analysis, curves illustrating the evolution of mass loss as a function of temperature were drawn.

3. Results and Discussion

3.1. Preliminary Analyses

The result of these analyses (Figure 2) showed that leaves were less hygroscopic compared to stems, with moisture contents (H%) of 9.63% and 11.32%, respectively. Volatile matter contents (PF%) were 80.69% for leaves and 77.76% for stems, implying that the samples comprised mostly organic matter. Regarding the ash contents (C%), they present 6.35% for leaves and 8.1% for stems. The values of fixed carbon (FC%) were 3.32% for leaves and 2.81% for stems. These results are consistent with those obtained by Panagiotis Grammelis et al. on Cardoon, who reported that the moisture was 8.2%, the volatile matter 70%, the ash contents 7.2% and the fixed carbon 14.6% [15]. However, Damartzis. Th. et al. found different results: 59.5% volatile matter for leaves and 77.7% for steams. The fixed carbon was 10.9% for leaves and 14.7% for steams and the ash contents were 29.6% for leaves and 7.6% for steams [16].

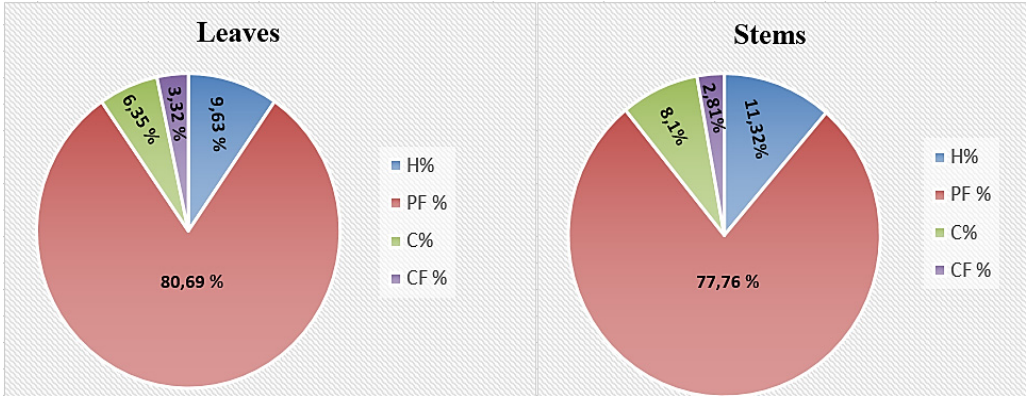

Figure 2. Piechart of preliminary analyses of leaves and stems.

3.2. Determination of Surface Functions and pH at Point Zero Charge

a. Acid-base character: Boehm's method

The results of the acidic and basic characters of the surfaces of the samples evaluated by the Boehm's method indicate that the basic functions are the majority at the surface of both leaves (1.25 mEq·g^{-1}) and stems (1.5 mEq·g^{-1}) (Table 2).

Table 2. Quantification of surface functions by Boehm's method.

Functions / Samples	Phenolic (mEq·g^{-1})	Carboxylic (mEq·g^{-1})	Lactonic (mEq·g^{-1})	Total Acidity (mEq·g^{-1})	Total Basicity (mEq·g^{-1})
Leaves	0.625	0.375	0.125	1.125	1.25
Stems	0.5	0.5	0.25	1.25	1.5

Table 3 presents the levels of carboxylic, lactonic, and phenolic compounds in Cardoon. The leaves contain 55.6% phenolic groups, 33.3% carboxylic groups and 11.1% lactonic groups, whereas the stems 40% phenolic groups, 40% carboxylic groups and 20% lactonic groups.

Table 3. Distribution of acidic oxygen groups on the surface.

Samples	Phenolic (%)	Carboxylic (%)	Lactonic (%)
Leaves	55.6	33.3	11.1
Stems	40	40	20

b. Determination of pH point at zero charge (pHPZC)

The results indicate that the leaves have a more marked basic character with a pH_{PZC} = 8.39 (Figure 3), whereas for the stems the pH_{PZC} value of 7.35 implies that the latter is rather neutral. These values are consistent with the quantification of surface functional groups via Boehm's method. These results are in agreement with those obtained by Ouldmoumna, A. et al., who indicated that the pH_{PZC} of Cardoon leaves is close to neutral [17].

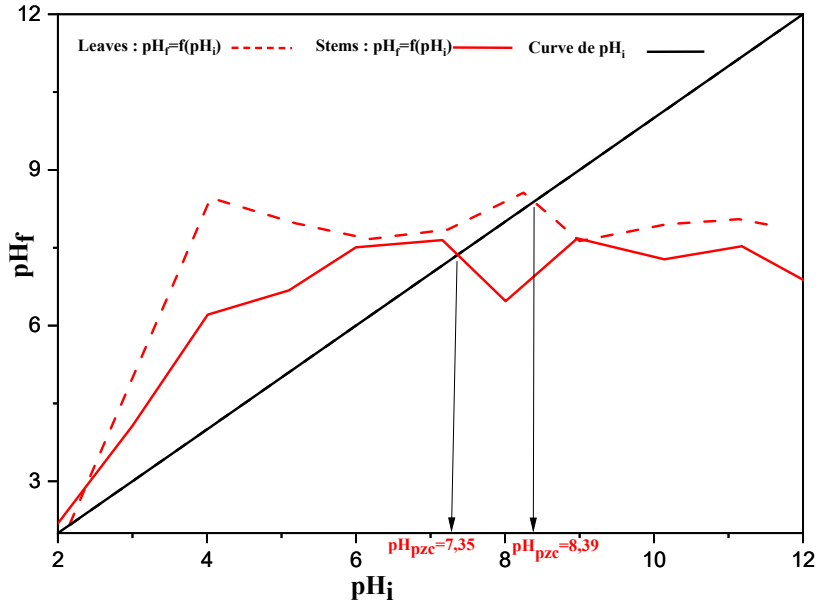

Figure 3. pH_{pzc} of Cardoon leaves and stems.

3.3. Physicochemical Characterizations

a. Scanning electron microscopy coupled to EDX (SEM/EDX)

SEM observations showed a heterogeneous fibrous structure of fresh leaf surfaces, with water pockets of 44.65 µm diameter (Figure 4A), which disappeared after drying them at 50 °C (Figure 4B). The observation of the stem in a cross section indicated the presence of long channels with diameters varying between 22.88 to 33.29 µm (Figure 5A). The longitudinal section of these channels showed a stratified fibrous structure, very homogeneous in thickness (Figure 5B,C). Similar observations were previously reported, the images show the presence of homogeneous parenchyma cells and fibro-vascular bundles in Cardoon leaves [6].

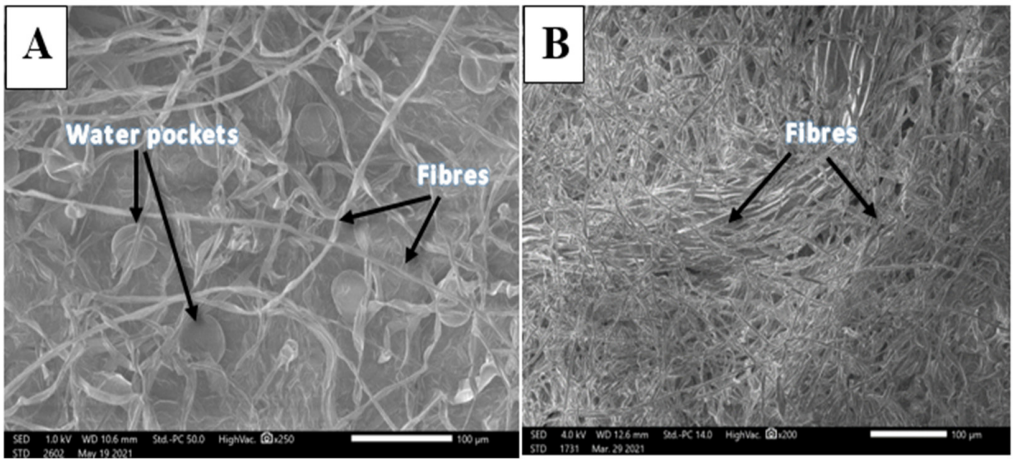

Figure 4. Morphology of leaf surfaces: (**A**) fresh leaf, (**B**) dried leaf.

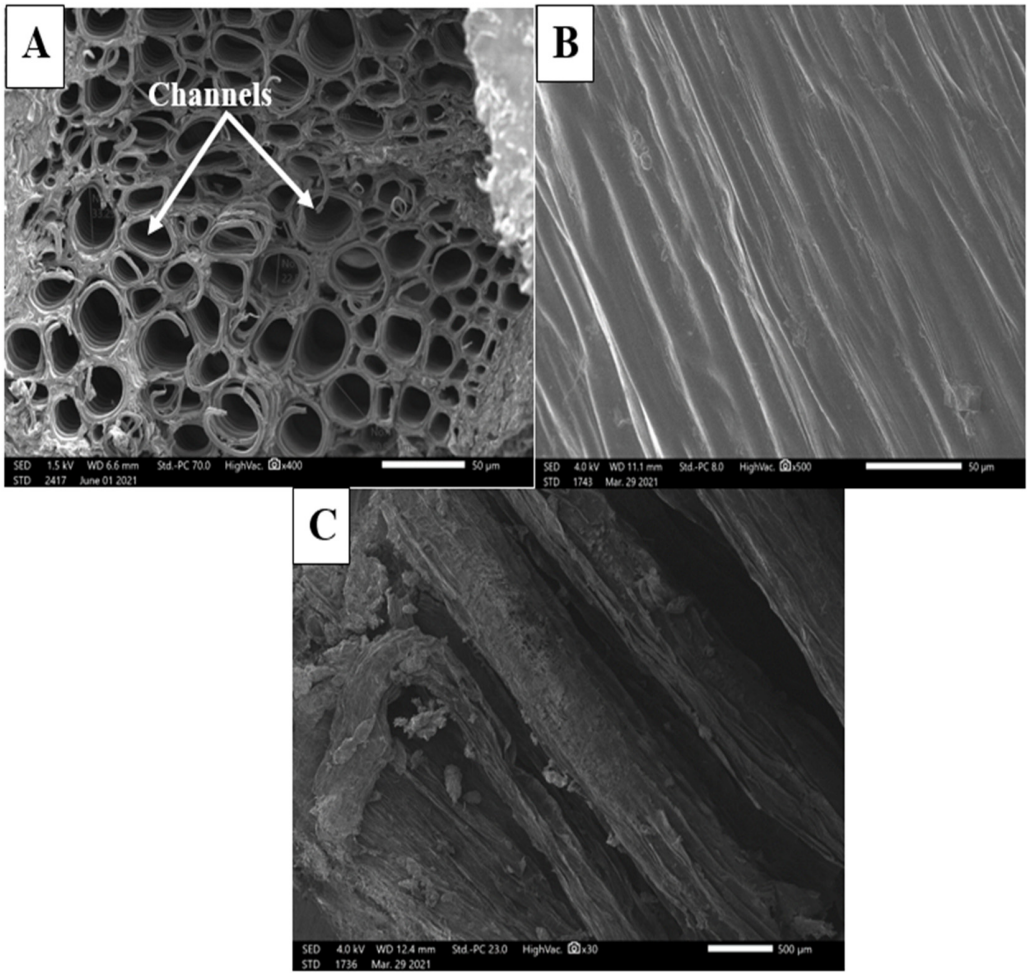

Figure 5. Morphology of the surfaces of the Cardoon stem. (**A**) Cross section, (**B**,**C**) longitudinal section.

The results of the qualitative analysis by surface electron scattering (EDX) (Table 4), revealed that the elements carbon and oxygen were dominant, which is consistent with the organic nature of these materials (i.e., carboxylic, lactonic, and phenolic compounds). The macro-elements (i.e., Magnesium, Potassium, Chlorine, Sodium, and Calcium) were present in relatively small quantities in both types of samples. Silica and Sulphur were not identified on the surface of stems. These results are similar to those obtained by previous studies, which showed that the average content of carbon was 41% and that of oxygen 49% [6–15].

b. *X-ray diffraction (XRD)*

The obtained diffractograms for both organs (leaves and stems) were similar (Figure 6). They showed three diffraction peaks of slightly different intensities, which are conventionally encountered in cellulosic compounds. The peaks positioned around $2\theta = 15.4^\circ$, $2\theta = 21.5^\circ$ and $2\theta = 32^\circ$, correspond respectively to the diffractions of the (101), (002), and (040) planes of crystalline cellulose I.

The crystallinity index (CI) was calculated according to the method of Segal, ref. [18] using Equation (5):

$$CI\% = 100 * \frac{I_{002} - I_{am}}{I_{002}} \quad (5)$$

where:

I_{002}: the maximum intensity of the diffraction peak of (200) plane
I_{am}: the intensity of the amorphous band at $2\theta = 18^\circ$.

Table 4. EDX microanalysis of elements in leaves and stems.

Elements	Leaves	Stems
	Mass Percentage %	Mass Percentage %
C	45.77	46.88
O	45.41	47.63
Na	0.73	1.27
Mg	0.11	0.28
Cl	1.63	1.39
K	2.63	1.72
Ca	2.91	0.82
Si	0.23	-
S	0.58	-

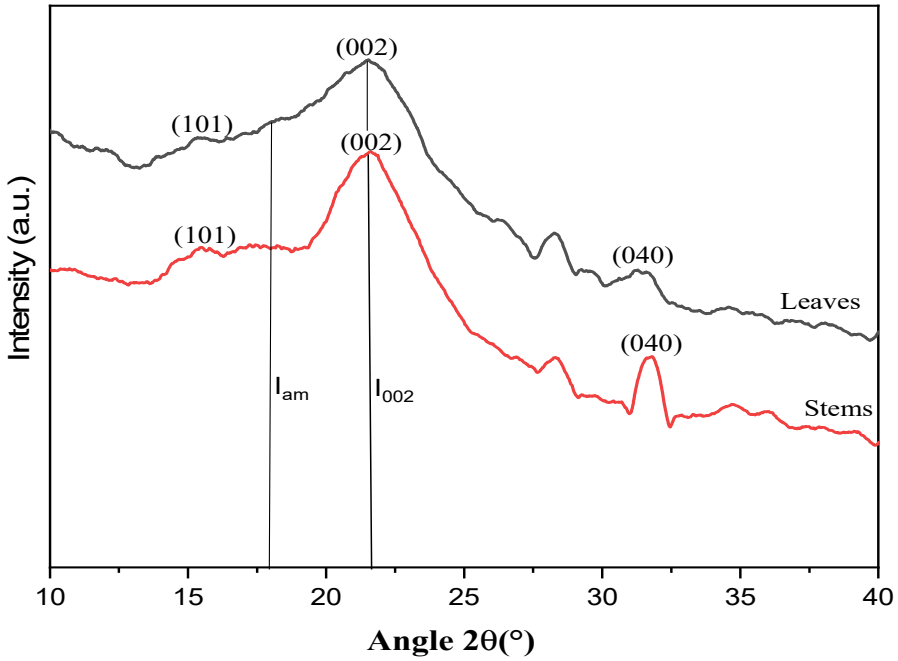

Figure 6. Diffractograms of leaves and stems of Cardoon.

The calculated crystallinity index is 10.24% for Leaves while it is about 13.22% for Stems (Table 5).

Table 5. Peak intensities and crystallinity indices of the samples.

Samples	I_{am}	I_{002}	CI (%)
Leaves	482	537	10.24
Stems	446	514	13.22

c. Fourier Transform Infrared Spectroscopy (FTIR)

The infrared absorption spectra had similar appearances, with practically the same absorption bands with only slight difference in intensity (Figure 7). In fact, a band was observed 3300 $cm^{-1,}$ attributed to the hydroxyl group -OH of cellulosic and hemicellulosic molecules (Table 6). The absorption bands at 2922 cm^{-1}, 2852 cm^{-1}, 1407 cm^{-1}, and 1367 cm^{-1} indicated the presence of C-H bond of cellulose, whereas another band around

1730 cm^{-1} was attributed to the carbonyl group C=O related to esters and/or carboxylic acids in hemicellulose and lignin. The band at 1600 cm^{-1} confirmed the cellulosic nature of samples.

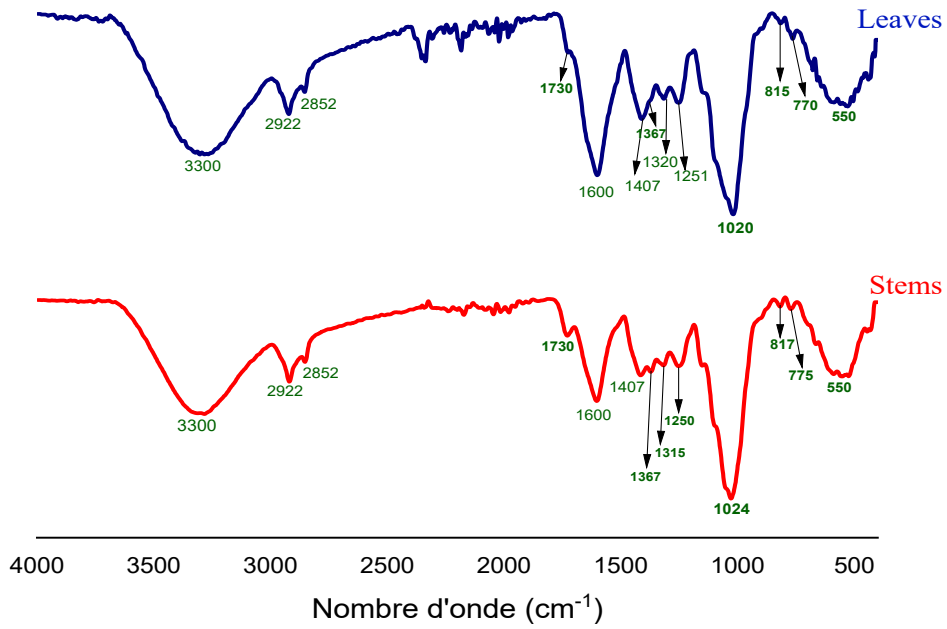

Figure 7. FTIR spectra of leaves and stems.

The absorption bands around 1250 and 1251 cm^{-1} were characteristic for the vibration of C-O bonds. Glycose ring stretching was recognized through the visible bands around 1020 and 1024 cm^{-1} and the low intensity bands at 815 and 817 cm^{-1} were attributed to the C-H vibrations of the glycosidic ring of β-glycosidic bonds [19]. The bands at 830 and 700 cm^{-1} were explained by the out-of-plane deformation mode of the C-H bond within the aromatic rings.

The same absorption bands were detected in the study of Ouldmoumna, A. et al. on Cardoon leaves [17].

Table 6. Absorption band assignments of infrared spectra of Cardoon leaves and stems.

Wavenumber (cm^{-1})		Assignment [19,20]
Leaves	Stems	
3300	3300	H-O (cellulose)
2922	2922	C-H (CH_2) (cellulose/hemicellulose)
2852	2852	C-H (cellulose)
1730	1730	C=O (carboxylic acid /ester) hemicellulose
1600	1600	O-H (cellulose)
1407	1407	C-H (cellulose)
1367	1367	C-H (cellulose)
1320	1315	O-H (cellulose)
1251	1250	C-O (the ester)
1020	1024	C-O (cellulose/hemicellulose)
815	817	C-H (glycosidic cycle)
770	775	C-H (aromatic ring)

d. Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

The results of the elemental analysis (Table 7) revealed that the leaves contained various elements, such as Sodium (Na), Calcium (Ca), Boron (B), Magnesium (Mg), Phosphorus (P), and Potassium (K), which dominated the vegetal mass with concentrations of 3.72 mg/g, 1.7 mg/g, 1.64 mg/g, 1.59 mg/g, 1.54 mg/g, and 1. 32 mg/g, respectively. The dominant elements in stems were Sodium (Na), Potassium (K), Calcium (Ca), Magnesium (Mg), Boron (B) and Phosphorus (P), with contents respectively of 2.7 mg/g, 2.03 mg/g, 1.07 mg/g, 0.91 mg/g, 0.64 mg/g, and 0.59 mg/g, along with other trace elements (i.e., Al, Fe, Sr, Zn, Mn, and Ti).

Table 7. Chemical composition of leaves and stems of Cardoon.

Elements (mg/g)	Na	Ca	B	Mg	P	K	Al	Fe	Sr	Zn	Mn	Ti
Leaves	3.72	1.7	1.64	1.59	1.54	1.32	0.27	0.1	0.07	0.03	0.02	0.01
Stems	2.7	1.07	0.64	0.91	0.59	2.03	0.25	0.02	0.02	0.01	0.008	0.01

These results agree with those found by surface electron scattering (EDX). The study of Angelova, V. et al. showed that the mineral composition of Cardoon also contained Calcium (1.6%), Magnesium (1%), Potassium (0.68%), and Nitrogen (0.13%) [21].

e. Thermogravimetric analysis (TGA/DTA)

The thermogram of leaves showed a mass loss of 86.49% in the temperature range 100–700 °C divided into three main steps (Figure 8):

- The first step: of 45.3% occurs around 230 °C and was attributed to the departure of volatile matter.
- The second step: of 9.06% at 280 °C, was due to the degradation of the hemicelluloses [22,23].
- The third step: of 30.41% at 350 °C, is usually attributed to the decomposition of cellulose and lignin [22,23].

For stems, the total mass loss was 87.91% within similar temperatures range. Equally, there were observed three stages, the first at 240 °C with a loss of 47.33%, the second at 280 °C with a mass loss of 16.43%, and the third at 410 °C with a mass loss of 23.83% (Figure 8).Damartzis et al. studied the thermal analysis (DTG curves) of stalks and leaves of Cardoon and noted that the pyrolysis occurred in the temperature range of 200 and 500 °C with two peaks, the former due the decomposition of hemicelluloses and the latter due to cellulose decomposition [16]. The study of Ouldmoumna, A. et al. confirmed our findings, by showing that the first stage of carbonization occurs in the temperature range of 200–500 °C (70% loss) and is due to the groups lignin, hemicellulose and cellulose [17].

The results showed that Cardoon stems and leaves consisted mainly in organic matter and had a basic character (pH_{pzc} = 8.39) for stems and neutral for leaves (pH_{pzc} = 7.35). The ash contents were 6.35% for leaves and 8.1% for stems. This type of vegetal waste contained 7% minerals, including Sodium (Na), Calcium (Ca), Boron (B), Magnesium (Mg), Phosphorus (P), and Potassium (K). The analysis by XRD and FTIR showed that Cardoon consists mainly of lignocellulosic compounds (i.e., cellulose, lignin, and hemicellulose), with an index of crystallinity for cellulose not exceeding 13%, indicating that this plant is rich in amorphous phase. The morphological analyses of Cardoon revealed a homogeneous fibrous and porous structure, both on the surface and in profile.

The results showed that Cardoon wastes have very interesting characteristics, making it a very valuable raw material in various economic domains with practical applications.

For example, the high content of ash indicates that Cardoon wastes could be used in the preparation of activated carbon. The findings of XRD and FTIR analyses encourage the extraction of cellulose, hemicellulose, and lignin from these wastes and their energetic capitalisation.

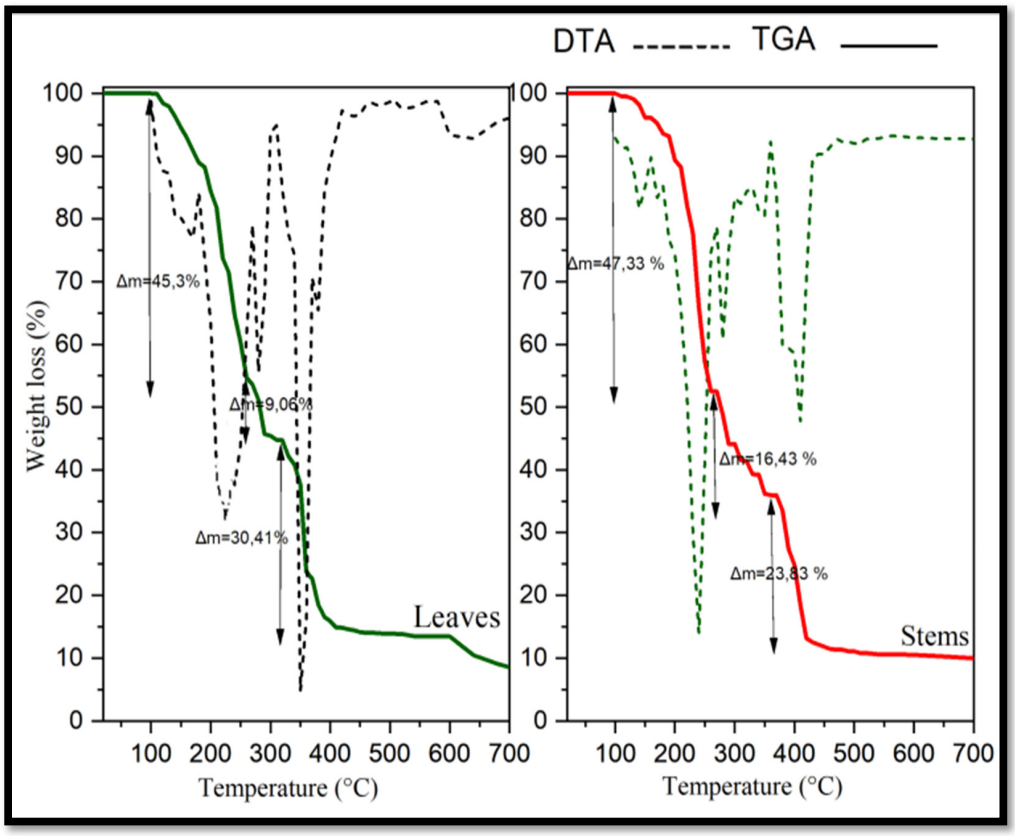

Figure 8. Thermograms (TGA /DTA) of leaves and stems of Cardoon.

4. Conclusions

In the current study the physicochemical, mineralogical, and thermal properties of leaves and stems of Cardoon wastes were determined. The leaves proved to have a heterogeneous fibrous structure, both in profile and surface, whereas the stems had a more porous surface and a channel profile. The pH points at zero charge indicated a basic character for leaves and neutral for stems, in agreement with the nature of the functional groups present on the surface, as was revealed by IR absorption spectroscopy. Preliminary analyses showed also that leaves had a slightly lower moisture and ash content compared to stems, but significant fixed carbon content. Nevertheless, the volatile matter contents in leaves and stems were nearly identical. These findings strongly support the great potential for an efficient capitalisation of these vegetal wastes in various economic sectors, such as wastewater treatment by adsorption, metal oxidation inhibition, and nanocomposites materials synthesis.

Author Contributions: M.H.N.: Formal analysis, Validation, Writing—original draft. M.E.H.: Data curation, Investigation, writing—review & editing. H.B.: Writing—review & editing. M.M.H.: Funding acquisition, Writing—review & editing. N.I.K.: Data curation, Investigation, writing—review & editing. A.H.: Funding acquisition, Investigation. A.Z.: Investigation, writing—review & editing. F.B.: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Supervision, Validation, Writing—review & editing. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to thank the Deanship of Scientific Research at Taif university for funding this work through Taif University Research Supporting Project number (TURSP-2020/119), Taif University, Taif, Saudi Arabia.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data are not be shared due to restrictions e.g., privacy and regulation.

Acknowledgments: The authors would like to thank the Deanship of Scientific Research at Taif university for funding this work through Taif University Research Supporting Project number (TURSP-2020/119), Taif University, Taif, Saudi Arabia.

Conflicts of Interest: The authors declare no conflict of interest.

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