

Waste Biomass Valorisation for the Development of Sustainable Cellulosic Aerogels and their Sound Absorption Properties

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Novel and more sustainable sound absorbing materials are produced through the valorization of waste biomass sources by following circular economy principles. Cellulosic nanocrystals (CNC) were extracted from *Posidonia oceanica* dead leaves, spent barely grains, and kale stems (KS) using a simplified purification protocol. These nanocrystals are used to prepare cellulosic aerogels, evaluating the effect of three parameters, namely, concentration (0.5–4%), CaCl_2 and poly(lactic acid) (PLA) incorporation (hybrid aerogels), on their sound absorption properties. Aerogels from 4% suspensions show the highest sound absorption, outperforming benchmark rockwool and polyester—two modern commonly-used sound absorbers. Moreover, PLA coating also improves the sound absorption performance of the most aerogels. CNC from KS aerogels are selected as the optimum at both high (500–6000 Hz) and low (100–1500 Hz) frequency ranges. Overall, these results represent a new proof-of-concept of waste biomass conversion to high-performance cellulosic aerogels that have excellent sound absorbing properties.

1. Introduction

Environmental noise pollution is an increasing threat to health and well-being (e.g., hearing loss, sleep disruption, or even cardiovascular diseases) in cities around the world. Unwanted noise is more present than ever before, and it will continue to increase in magnitude and severity because of population growth, urbanization, and the associated growth in the use of

increasingly powerful mobile sources of noise.^[1] As a result, a proper insulation becomes necessary to provide not only a good quality of life, but also optimum heat energy management, reducing the annual energy cost.^[2]

Importantly, approximately one third of the greenhouse emissions have been estimated to be produced by the building sector.^[3] Incentivized by this challenge, more sustainable materials have been studied as insulating alternatives over the past years to reduce emissions by providing more easily recyclable or even biodegradable solutions, such as cellulose fibers^[4] or foams derived from hardwood and softwood.^[5] Cellulosic aerogels^[6,7] have also recently gained attraction due to their outstanding thermal insulation properties thanks to their being light weight

and having high porosity (>95%). It should be highlighted that porous materials have also been shown to play a crucial role in absorbing broadband sound frequencies,^[8] which pinpoints the potential of aerogels as insulation materials. These cellulosic materials are usually derived from wood or other conventional crops, such as cotton, sisal or flax.^[4,5]

Waste biomass (i.e., agricultural or plant-based) is gaining attention over these conventional sources since waste materials

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Table 1. Composition of the different analyzed biomasses. Different letters at the same column denote significant differences between samples ($p \leq 0.05$).

	Lignin [%]	Holocellulose [%]	Ashes [%]	Proteins [%]	Lipids [%]
PO	18.1 (1.6) ^b	58.6 (0.8) ^a	13.2 (1.5) ^a	7.1 (0.8) ^{bc}	3.5 (1.2) ^c
BG	12.4 (0.7) ^c	58.4 (1.7) ^{ab}	4.5 (0.2) ^c	19.2 (0.1) ^a	10.0 (1.5) ^b
KS	24.5 (0.3) ^a	51.6 (2.0) ^b	4.9 (0.0) ^c	5.6 (0.1) ^c	22.3 (1.4) ^a
CG	13.1 (1.1) ^c	57.4 (0.8) ^{ab}	9.5 (0.0) ^b	9.2 (0.0) ^b	18.9 (3.6) ^a

do not compete with any other application while still maintaining a relatively high cellulose content, making them optimal for cellulosic nanocrystals (CNC) extraction by promoting circular economy principles.^[9,10] For example, some waste biomass like *Posidonia oceanica* dead leaves accumulate on sea shores, being detrimental for the quality of the beaches.^[11] On the other hand, agricultural biowaste, like kale stems (KS, *Brassica oleracea* or CG, from *Couve galega* sp.) are usually discarded when separated from the edible parts for food purposes, very similar to spent barley grains (BG, after beer production), being both derived to animal feeding purposes and compost. Interestingly, all these biomasses present a significant amount of cellulose, being $\approx 30\%$ for *P. oceanica*,^[12] $\approx 20\%$ for KS^[13] and $\approx 15\%$ for spent BG,^[14] while holocellulose contents are superior by 40% in all cases. Thus, in order to convert these waste biomasses into functional materials in a resource-wise manner, it would be worth applying an extraction protocol, where hemicelluloses are not specifically removed.^[15] This would increase the final yield as compared to conventional cellulose nanocrystal extraction processes and would thus also improve the cost-efficiency of the methodology. Additionally, the presence of hemicelluloses has been shown to improve some of the functional properties of cellulose-based aerogels.^[16]

Cellulose aerogels are known to present major drawbacks such as poor mechanical performance and low integrity when exposed to water or relatively high humidity conditions,^[17] thus precluding their application as building materials. To overcome this issue, a simple dipping method using poly(lactic) acid (PLA) has been recently proven to substantially improve both the mechanical (from 0.5 to 4.8 N mm⁻², up to tenfold improvement) and water resistance ($>100^\circ$ contact angle) properties of the inherently fragile and hydrophilic cellulosic aerogels,^[16] thus making them more suitable to mid or long-term building conditions. Other strategies, such as the addition of salts (like CaCl₂) have been seen to improve the performance of cellulosic aerogels by increasing the surface area while modifying the porosity,^[18–20] and might as well produce a positive response in the sound absorption capacity of the resulting aerogels.

Herein, we have extracted cellulose from several waste biomass sources including, kale stems (KS), barley grains (BG) and *Posidonia oceanica* (PO) by using a simplified purification protocol^[15] and the extracted cellulosic nanocrystals were used to develop cellulosic aerogels for acoustic applications. The sound absorption coefficients of the produced materials were measured and the influence of the biomass source, the solid concentrations and the addition of a coating (PLA) or cross-linkers (CaCl₂) on the acoustic behavior of the produced cellulose-based aerogels was studied. The results provide valuable insight for the optimization of bio-based sound absorbing materials by demonstrating, how completely biowaste-based material can exceed the performance of current market sound absorbers.

2. Results and Discussion

2.1. Characterization of the Different Biomass Sources

Initially, the composition of the different waste biomass sources was characterized, and results are shown in Table 1. It was observed that holocellulose was the predominant component (50–60%) in all the cases, confirming the suitability of these sources for obtaining CNCs. Notably, significant differences were observed for other components: PO was the richest in ashes, while BG showed the highest protein content. Both stems (KS and CG) showed the highest lipidic content, with minor differences between them. It should be noted that KS presented a significant amount of lignin (ca. 25%), which is expected to be removed with the purification protocol. Very similar compositions have already been reported for PO,^[21] BG^[14] in the literature. However, lower lignin and lipid contents ($\approx 12\%$) have been reported for KS.^[22] This discrepancy could be ascribed to a later stage of development and maturity of the lower parts of the stem.^[13,23] To the best of our knowledge the compositional characterization of CG has not been reported, but our compositional values seem to be consistent with the high similarity between KS and CG.

In addition, FT-IR and TGA analyses of all biomasses were carried out to confirm the compositional differences, and the results are shown in Figure 1. Briefly, similar spectra, typical for lignocellulosic biomass having holocellulose as the main component, were observed in FT-IR (Figure 1A). In particular, the broad band at 3500–3100 cm⁻¹, characteristic from O–H stretching,^[24] was clearly shown in all biomass sources, with a minor shift in PO spectrum as a result of the different equipment employed (see *Attenuated Total Reflectance (ATR) FT-IR Analysis*). In addition, several cellulose characteristic peaks were shown, such as those located at 1375, 1100 and 1030 cm⁻¹, corresponding to C–H bending, stretching and C–OH bending modes, respectively.^[25,26] It is also worth noting that the 1730 cm⁻¹ peak, which is typically ascribed to the presence of lignin,^[27,24] was more clearly visible as a broad shoulder in KS spectrum, which is reasonable given its higher amount of lignin, being partly or totally overlapped with the one corresponding to bound water located at ca. 1630 cm⁻¹.^[21] In addition, peaks at 1500 and 1600 cm⁻¹ typically corresponding to the presence of amides I and II were especially visible as an overlapped broad shoulder in the case of BG according to its higher protein content, as previously reported in the literature.^[28]

The thermal stability of the different biomasses was also evaluated, and results are shown in Figure 1B. Again, all sources showed derivative TG curves (DTG) curves characteristic of lignocellulosic biomass, with highest intensity of the degradation peak at $\approx 335^\circ\text{C}$, corresponding to the degradation

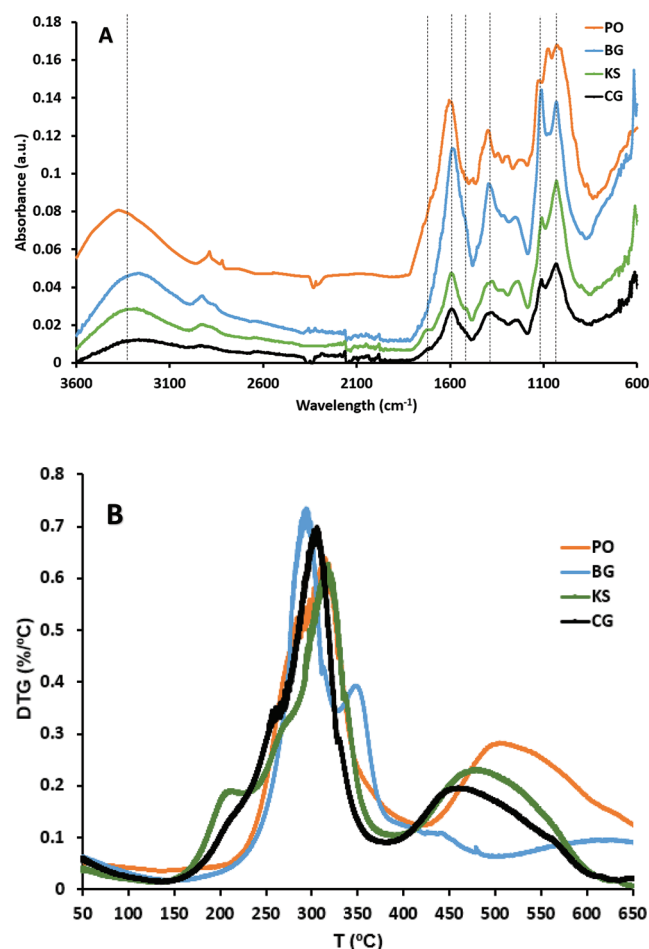


Figure 1. A) FT-IR spectra and B) DTG curves of the valorized biomasses.

of cellulose.^[21] On the other hand, broad shoulders located ≈ 200 – 250 °C have been related to the presence of hemicelluloses, while the presence of an additional degradation peak at ≈ 350 °C in the case of BG has been related to the presence of proteins,^[29] as it was previously characterized (Table 1). Peaks ≈ 200 °C present in the case of KS and CG in a lesser extent have been related to the degradation of water bound to pectin chains through hydrogen bonds.^[30] Finally, the broad degradation peak at 400 – 550 °C can be related to the presence of lignin, which presents high thermal stability due to the strong cross-linking between benzene-propane groups,^[21,31,32] and lipids,^[33] with minor differences between PO and both stems related to their variation on the lipid content (Table 1).

2.2. Characterization of Extracted Cellulosic Nanocrystals

After the initial characterization of the waste biomass, cellulosic nanocrystals (CNC) from selected biomasses (PO, BG, and KS) were purified. CG was discarded from this part of the study due to the high similarities with KS. Moreover, the other three biomasses were richest at one compound each (PO in ashes, BG in proteins, and KS in lipids), so they provide a great material platform to investigate the influence of the starting biomaterial

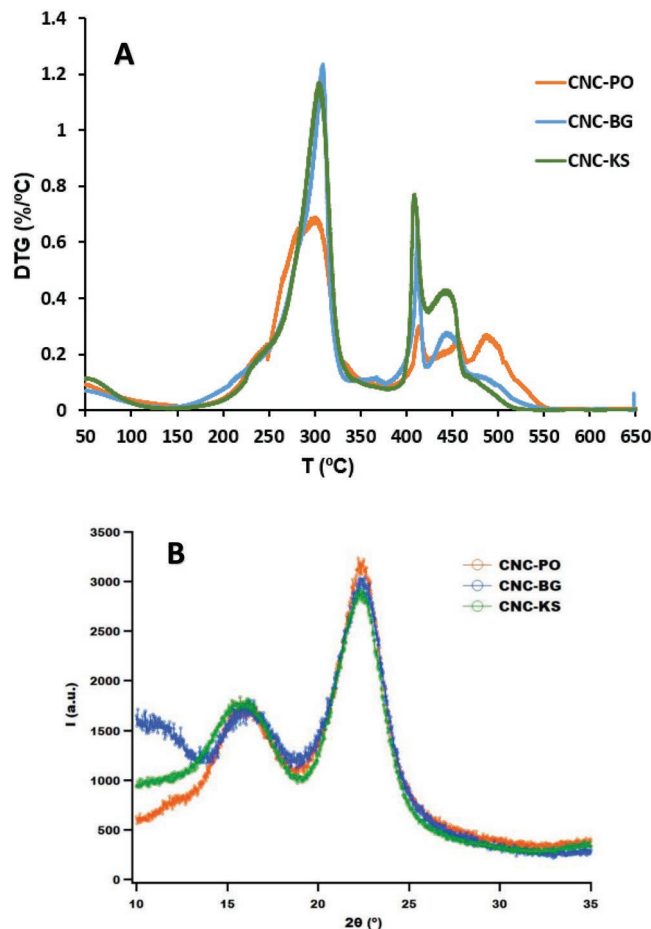


Figure 2. A) DTG curves and B) crystalline patterns of cellulosic nanocrystals obtained from the selected biomasses.

to the properties of the resulting CNCs and derived aerogels, as only lignin was specifically removed during the CNC extraction.

After applying the simplified extraction protocol, CNC were obtained with the following yields: $26 \pm 4\%$, $22 \pm 3\%$ and $36 \pm 3\%$ for CNC-PO, CNC-BG and CNC-KS, respectively. The higher yield in KS was attributed to its higher lipid content, since lipids are not expected to be removed with the simplified extraction protocol. In fact, the obtained nanocrystal suspension (CNC-KS) had a more viscous character, which might also be related to the higher presence of recalcitrant lipids (according to its higher content as shown in Table 1) and pectic polysaccharides that present a high water holding capacity.^[22] Similar yields ($\approx 27\%$) have been reported for CNC extracted from other lignocellulosic waste sources, such as vine shoots, using the same purification protocol applied in this work.^[27]

For a proper characterization of the extracted nanocrystals, their thermal stability was studied by means of TGA and the results are shown in Figure 2A. Again, the main peak at ≈ 310 °C, corresponding to the degradation of cellulose, was observed. This peak was less intense in the case of CNC-PO, suggesting a lower amount of cellulose in this case.^[21] A very similar broad shoulder between 200 – 250 °C was observed in all biomasses, corresponding to the degradation of hemicelluloses. A minor peak was still seen at ≈ 350 °C in the case of CNC-BG which

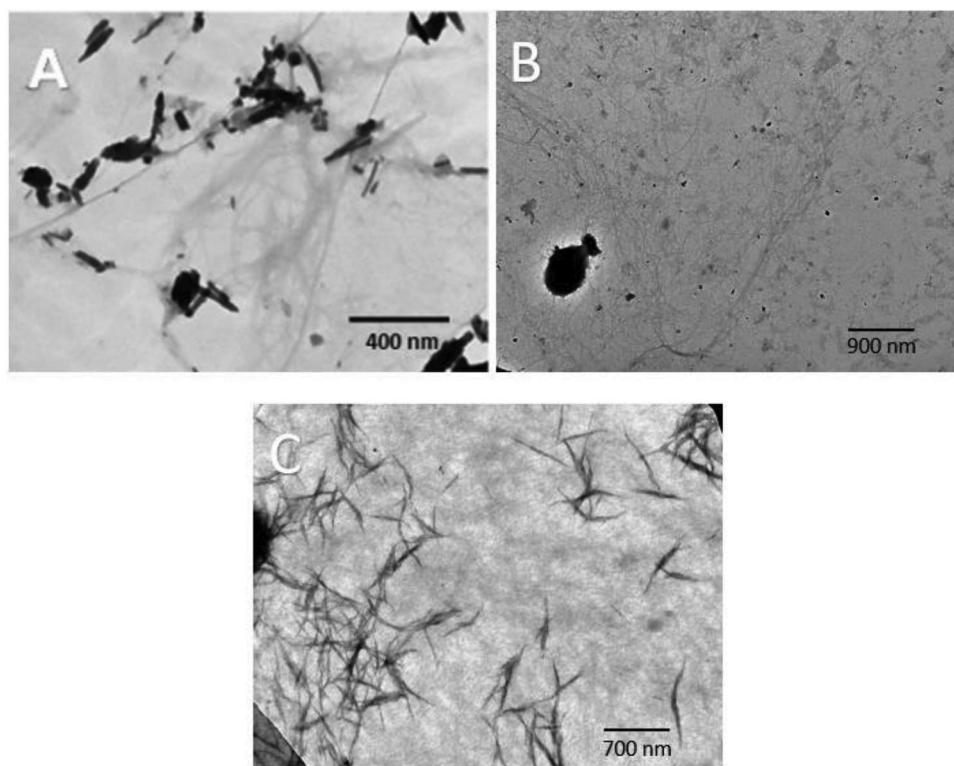


Figure 3. Representative TEM images of the obtained cellulosic nanocrystals: A) CNC-PO, B) CNC-BG, and C) CNC-KS.

can be related to the presence of some recalcitrant proteins.^[29] Finally, the region above 400 °C can be related to the degradation of lipids, like palmitic or linolenic acids (which are more abundant in KS),^[34,35] which were more abundant in KS and BG (Table 1). Degradation of lignin can also be ascribed at these temperatures but it was specifically removed during the purification process. On contrary, the sharp peak and broad shoulder at ≈ 400 and ≈ 450 °C, respectively, can be ascribed to the sodium azide addition, as they were shown in all three CNCs.^[36]

XRD patterns are shown in Figure 2B, and as expected, two differentiated peaks at 16° (which is actually composed of two overlapped peaks) and 22°, characteristic from the cellulose I_β crystalline allomorph, were clearly observed.^[37] In addition, crystallinity indexes were calculated, obtaining values of 54%, 49% and 59% for CNC-PO, CNC-BG and CNC-KS, respectively. The lower crystallinity of CNC-BG can be due to the potential effect of processing treatments applied to this biomass (see Section 2.1.) prior to the extraction of the nanocrystals on the cellulose structure. In comparison with other resources previously used to produce CNC using the same extraction protocol, such as vine shoots ($X_C \approx 85\%$), the crystallinity values here reported are significantly lower, evidencing the great relevance of the type of biomass source (woody versus herbaceous/grains) on the cellulose crystallinity.^[27,32]

The morphology of the extracted nanocrystals was studied by TEM and representative images are displayed in Figure 3. The different morphology of nanocellulose could be identified depending on the source. The average measured fibril dimensions of CNC-PO showed a length of 499 ± 96 nm and a width of 15 ± 5 nm,^[15] while bigger and more agglomerated

nanocrystals were observed in CNC-BG, with a length of 970 ± 185 nm and a width of 37 ± 7 nm. In both cases the structure of the nanocrystals corresponded to larger clusters typically reported after a simplified purification protocol where additional compounds have not been specifically removed.^[15,27] Interestingly, CNC-KS showed the most representative shapes of what is conventionally known as cellulose nanocrystals with a length of 669 ± 119 nm and a width of 28 ± 6 nm. These nanocrystals could also be seen to be more isolated, which is expected to affect positively the performance of the derived aerogels as a result of an enhanced dispersion and stronger interactions between them.

Finally, a complete characterization of the monosaccharide profile of the nanocrystals was carried out and the results are shown in Table 2. CNC-PO showed the lowest carbohydrate content, as already inferred from the TGA results (Figure 2A). This could be related to the significantly higher presence of ashes in PO biomass (Table 1), which were not completely eliminated by the simplified extraction method (Table 2), thus yielding nanocrystals with lower cellulosic and hemicellulosic contents but a significant amount of additional compounds such as ashes.^[38,39] On the other hand, as expected, CNC-BG showed major quantities of glucose and xylose, while other acid labile sugars like arabinose, typically present in the arabinoxylan structures even after the malting of the grains,^[40] were seen to be removed after the extraction of the nanocrystals. In this case, the presence of a significant quantity of recalcitrant proteins was still observed after CNC purification (Table 2). Lastly, CNC-KS showed remarkable differences, due to the contribution of primary cell wall polysaccharides, not present in the other biomass sources. This is reflected in the non-negligible

Table 2. Monosaccharide composition, ashes, and proteins absolute content (%) of the different cellulosic nanocrystals (CNC-PO, CNC-BG, and CNC-KS). Values in the same line followed by different letters are significantly different ($p \leq 0.05$).

[%]	CNC-PO	CNC-BG	CNC-KS
Galactose	tr*	tr*	1.8 (0.3) ^a
Glucose	40.5 (11.9) ^b	58.0 (3.0) ^{ab}	67.3 (4.9) ^a
Xylose	1.7 (0.4) ^b	11.2 (1.7) ^a	14.1 (1.5) ^a
Mannose	tr*	tr*	0.9 (0.4) ^a
Galacturonic acid	tr*	tr*	3.6 (1.7) ^a
Ashes	15.0 (0.1) ^a	6.2 (0.4) ^b	5.0 (0.5) ^b
Proteins	1.2 (0.2) ^b	4.8 (0.5) ^a	1.2 (0.2) ^b

*Fucose, Rhamnose, Arabinose, and glucuronic acid were not detected or only detected in trace amounts (tr) in all samples (<0.5%).

quantities of galacturonic acid and galactose, indicating some residual pectin was resistant to the relatively aggressive treatment. The xylose content could either arise from residual xyloglucan, very abundant at earlier maturity stages in the stem, or from glucuronoxylans to which the acid labile glucuronoxyl decorations were detached during the extraction process.^[22,23] In this case, the carbohydrate content was the highest of the three sources, which was expected to positively affect the final performance of the resulting aerogels.

2.3. Characterization of the Cellulosic Aerogels

Once the extracted nanocrystals were characterized, cellulosic aerogels were prepared by means of freeze-drying. Three different parameters were tested: cellulosic concentration (0.5–4% w/v), the addition of a salt (CaCl_2 , 10 mM–1 M in aqueous suspensions) and the addition of a hydrophobizing coating (by dipping the aerogels in 1–5% w/v PLA solutions). A complete characterization of the key parameters of these aerogels is summarized in Table 3. The measured densities yielded a wide range of values (18–287 mg cm^{-3}) mainly depending on the concentration and the addition of a reinforcing compound (CaCl_2 or PLA), increasing the bulk density in both cases. Similar values, such as 78 mg cm^{-3} , have been reported in the literature for cellulosic aerogels from other vegetal resources—cotton in this case,^[41] while aerogels from bacterial cellulose reinforced with PLA showed greater densities of 162 mg cm^{-3} .^[42] Densities of up to 230 mg cm^{-3} have been observed in PLA-coated cellulosic aerogels (2% w/v cellulose) from *P. oceanica* using the same methodology.^[16] The appearance of higher densities (up to 287 mg cm^{-3}) in this work for PLA-coated 0.5% w/v cellulosic aerogels (0.5% BG + 5% PLA or 0.5% PO + 5% PLA) was attributed to the shrinkage of the aerogels after the PLA dipping step. This shrinkage was avoided in the case of KS aerogels due to the presence of recalcitrant compounds such as lipids and pectic polysaccharides, which provided a higher integrity even at the lowest densities tested. Reference non-biobased materials, such as commercial rockwool and polyester, showed densities of 150 and 24 mg cm^{-3} respectively, the latter only being comparable to those from the cellulosic aerogels with the lowest solids concentration (0.5% w/v). On the contrary, commercial rockwool displayed higher density than all the studied cellulosic aerogels, being even higher than most of the PLA-coated aerogels.

Both CaCl_2 and PLA incorporation rates (%) were gravimetrically measured and results from this study are collected in Table 3. As expected, greater concentrations of salt (1 M) incorporated higher contents of salt (up to 330%), while lower concentrations (10 mM) had a minor effect ($\approx 20\%$). Similarly, PLA was incorporated to a greater extent when more concentrated solutions (5% w/v) and less dense starting materials (0.5% solids content) were used, related to their higher porosity.^[16] The higher shrinkage of 0.5% BG aerogels led to less porous structures, which was also reflected by lower incorporation rates of PLA.

Thermal stability of the aerogels was measured by means of TGA as it is a key factor for insulating materials and the main degradation peak (displayed by DTG) was also collected in Table 3. Interestingly, cellulose degradation peak was slightly displaced toward higher temperatures when the cellulosic concentration was increased (from 0.5% to 4%), suggesting stronger interactions between the $-\text{OH}$ groups of the more concentrated aerogels. In contrast, the addition of CaCl_2 had a detrimental effect on the thermal stability of the aerogels, showing most representative degradation peaks at $\approx 70^\circ\text{C}$ (in the case of 1 M) thus negatively affecting their performance. This observation was in accordance with the previously reported mass loss (in terms of moles of water) of CaCl_2 due to the presence of bounded water as a result of its hygroscopic behavior.^[45] This is expected to also have a detrimental effect on the sound absorption performance of the aerogels. Finally, PLA incorporation did not have a remarkable effect on the thermal stability of the aerogels due to their similar degradation peak (≈ 320 – 380°C),^[46] being more dependent on the biomass source. Reference materials, rockwool and polyester, have shown similar or lower thermal degradation rates at ≈ 250 ^[43] and 280 – 320°C ,^[44] respectively.

The specific surface areas of each aerogel derived from BET measurements are presented in Table 3. All the values were ranging between ≈ 0.5 and $\approx 9 \text{ m}^2 \text{ g}^{-1}$. It is known that the freeze-drying methodology yields aerogels with greater pore sizes with regards to other drying methodologies such as supercritical CO_2 (SC- CO_2), thus reducing their BET surface area (≈ 18 versus $\approx 100 \text{ m}^2 \text{ g}^{-1}$ with freeze-drying and SC- CO_2 drying, respectively).^[47] The lower values shown in this study can be related to the presence of hemicelluloses and other impurities such as ashes or proteins which might have provoked the formation of larger pores, thus reducing their BET surface area.

Table 3. Density, thermal resistance (first degradation peak), specific surface area, and thickness of the cellulosic aerogels. Commercial rockwool and polyester were also characterized as benchmark materials. Different letters in the same column and region are significantly different ($p \leq 0.05$).

	Density [mg cm ⁻³]	PLA/CaCl ₂ incorporation [%]	DTG [°C]	Surface area [m ² g ⁻¹]	Thickness [cm]
0.5% PO	18.5 (0.6) ^a	—	286	4.41	0.6 (0.1)
1% PO	25.9 (1.7) ^b	—	289	1.37	0.8 (0.0)
2% PO	36.9 (0.9) ^c	—	294	9.15	1.0 (0.0)
4% PO	53.5 (1.1) ^e	—	300	1.41	1.0 (0.0)
0.5% BG	30.5 (1.6) ^{bc}	—	340	3.54	0.4 (0.1)
1% BG	40.2 (2.2) ^{cd}	—	345	1.77	0.6 (0.1)
2% BG	42.3 (0.4) ^d	—	350	1.18	0.9 (0.0)
4% BG	69.5 (3.1) ^f	—	360	1.63	1.0 (0.0)
0.5% KS	20.5 (1.2) ^a	—	320	1.47	0.8 (0.1)
1% KS	28.8 (0.4) ^b	—	322	1.99	0.9 (0.1)
2% KS	39.5 (2.3) ^{cd}	—	322	0.91	1.0 (0.0)
4% KS	67.9 (1.8) ^f	—	323	1.57	1.1 (0.1)
2% PO + 10 mM	41.5 (0.9) ^a	16 (2) ^e	294	1.01	0.8 (0.0)
2% PO + 1 M	242.2 (5.9) ^e	330 (9) ^a	68	0.95	0.5 (0.1)
2% BG + 10 mM	74.5 (2.1) ^b	17 (0) ^e	329	2.88	0.6 (0.0)
2% BG + 1 M	191.1 (8.6) ^d	297 (8) ^b	73	1.48	0.9 (0.1)
2% KS + 10 mM	106.6 (8.2) ^c	26 (0) ^d	315	1.07	0.5 (0.1)
2% KS + 1 M	266.9 (6.0) ^f	235 (2) ^c	75	0.65	0.4 (0.2)
0.5% PO + 1% PLA	127.9 (4.2) ^c	45 (4) ^d	262	0.94	0.2 (0.1)
0.5% PO + 5% PLA	197.9 (6.9) ^e	227 (6) ^a	262	0.77	0.3 (0.1)
2% PO + 1% PLA	75.0 (4.8) ^a	29 (1) ^e	286	1.64	0.5 (0.2)
2% PO + 5% PLA	106.4 (4.5) ^b	153 (2) ^b	286	1.12	0.8 (0.1)
0.5% BG + 1% PLA	160.8 (8.2) ^d	21 (2) ^f	359	0.83	0.2 (0.1)
0.5% BG + 5% PLA	287.1 (6.0) ^f	141 (9) ^{bc}	350	0.46	0.2 (0.1)
2% BG + 1% PLA	60.8 (8.9) ^a	26 (1) ^e	362	1.03	0.8 (0.1)
2% BG + 5% PLA	103.4 (5.9) ^b	139 (5) ^c	350	0.69	1.0 (0.0)
0.5% KS + 1% PLA	110.9 (2.1) ^b	41 (1) ^d	300	0.46	0.4 (0.1)
0.5% KS + 5% PLA	136.2 (8.6) ^c	245 (8) ^a	300	6.14	0.6 (0.0)
2% KS + 1% PLA	68.8 (8.2) ^a	23 (2) ^{ef}	314	0.89	0.8 (0.0)
2% KS + 5% PLA	104.7 (6.0) ^b	139 (6) ^c	309	0.65	1.1 (0.1)
Rockwool	150	—	≈250 ^[43]	1.73	1.0 (0.0)
Polyester	24	—	280–320 ^[44]	0.81	1.0 (0.0)

However, it should be noted that these values were in range with those obtained from commercial insulating materials (≈ 0.8 – 1.7 m² g⁻¹).

Finally, the thicknesses of all tested aerogels were measured as thickness represents a key factor in determining the sound absorption properties of the materials and results are shown in Table 3. Briefly, all thicknesses were aimed to be standardized at ≈ 1 cm (like reference materials). However, some shrinkage took place unavoidably during freeze-drying and PLA coating of the less concentrated aerogels (mainly 0.5%) yielding aerogels with lower thickness and, as a result, higher densities (as previously commented on). Again, higher thicknesses at lower concentrations were indicative of more expanded and porous structures, which are expected to present higher sound absorption rates.^[8]

The morphologies of all aerogels (as well as reference materials) were characterized by means of SEM images and results are shown in Figure 4. Initially, the effect of the CNC concentration was investigated, and it was clearly seen that higher concentrations led to denser structures in all cases. In addition, greater and more abundant cellulosic and hemicellulosic fibers were differentiated in both BG and KS, while they were less present in PO (as expected by results previously shown in Table 2). It is worth highlighting that those aerogels produced from KS showed a more continuous layer on their surface which agreed with the higher viscous aspect as compared to the dispersions of nanocrystals extracted from other biomasses. This surface layer was more evident in 0.5% KS, 2% KS and 4% KS images and could be related to the higher presence of lipids (Table 1) and pectic polysaccharides such as galacturonic acid (Table 2).^[22]

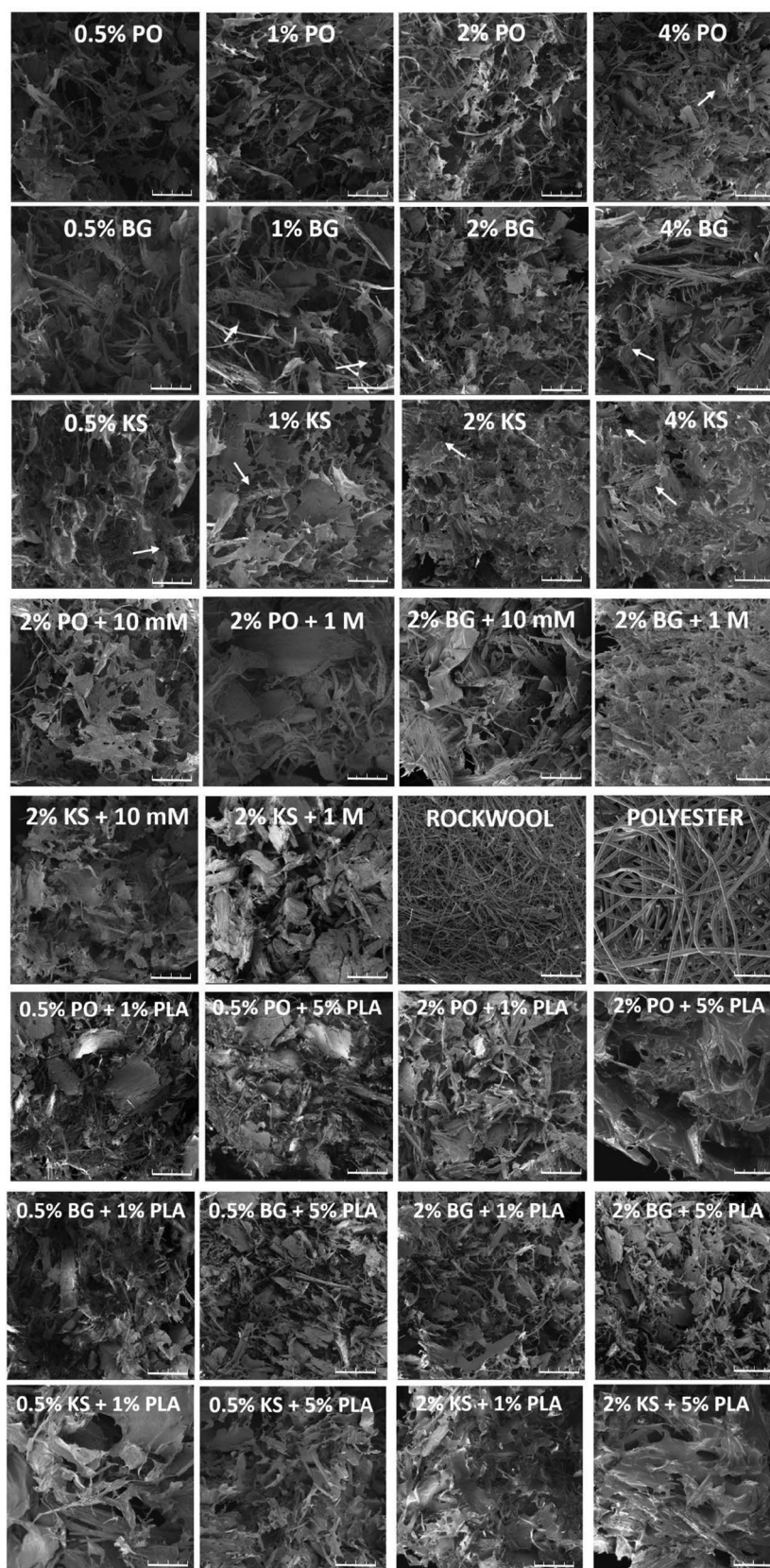


Figure 4. SEM images of all the produced aerogels and commercial rockwool and polyester. Scale bars correspond to 500 μm except for commercial materials (rockwool and polyester) which correspond to 200 μm . White arrows are pointing the (hemi)cellulosic fibers.

Again, these compositional differences were expected to significantly affect the sound absorption properties of the aerogels due to their clear differences in the microstructure.

The presence of salts (CaCl_2) at the highest concentration tested also significantly affected the microstructure of the aerogels due to an excess of salt with regards to the cellulosic weight ($\approx 3:1$ ratio, see Table 3). It could be seen that the addition of CaCl_2 1 M led to the formation of bigger clusters which were not apparently interconnected, especially in the case of KS. However, a continuous layer was formed in BG suggesting a better dispersion of CaCl_2 on these aerogels. On the contrary, the addition of 10 mM of the salt did not seem to have any observable effect on the morphology of the aerogels, and so, a significant effect on the sound absorption properties was not expected at this concentration.

Finally, PLA was incorporated into the cellulosic aerogels by means of a dipping procedure. Some remarkable differences between the coated aerogels could be noticed. BG aerogels showed minor differences regarding their porosity, while 2% PO + 5% PLA formed a continuous layer on its surface as a result of the PLA coating. In the case of KS, more continuous layers were clearly observed at all concentrations because of the inherent continuous phase previously described due to the presence of lipids and pectic monosaccharides, thus facilitating the incorporation of PLA more homogeneously. These coatings were also expected to significantly affect the sound absorption properties of the aerogels due to the strong interactions between cellulose and PLA, and were very similar to those previously reported from hybrid *P. oceanica* cellulosic aerogels using both 1% and 5% PLA solutions.^[16] The microstructure of both reference materials was also evaluated by SEM imaging showing in both cases long interspersed fibers (greater in the case of polyester, while those shown in rockwool were smaller and more compacted, thus yielding a much higher density as previously characterized in Table 3).

Finally, sound absorption capacity of all the tested aerogels was determined as a final proof of concept to validate our initial hypothesis on how differences in microstructure may affect their sound absorption properties. Initially, a frequency range of 500–6000 Hz was tested, and sound absorption coefficients are shown in Figure 4. Based on these data, a clear positive correlation between the initial CNC concentration and sound absorption coefficients emerged: The higher the aerogels' cellulosic concentration, the higher the absorption capacity was throughout the studied frequency range. This was evident in all biomasses, especially at 4% w/v. The best performance at lower concentrations (0.5–1%) was for CNC-KS aerogels. This can be related to their higher processability and resistance to shrinkage upon freeze-drying (higher thickness, as indicated in Table 3) with regards to their counterpart aerogels made from CNC-BG and CNC-PO. In this sense, the compositional differences (such as the presence of lipids and pectic polysaccharides) were shown to have a positive effect on the sound absorption capability of the aerogels as they led to the formation of more expanded aerogels with larger pore size distribution, as qualitatively observed from Figure 4.

It should be highlighted that all the 4% aerogels (with density values in a range of $50\text{--}70\text{ mg cm}^{-3}$) performed better than commercial rockwool (150 mg cm^{-3}), one of the reference materials tested. Exceeding the sound absorption properties of a

standard commercial material with a material of much lower density may prove to be impactful to all the industries in which the weight of the applied absorbers matters, such as vehicles and aerospace engineering. In addition, all the aerogels ($0.5\text{--}4\%$) performed better than polyester (24 mg cm^{-3}), thus showing cellulosic aerogels as a promising sound absorbing material due to them optimizing the interplay between sound absorption capacity while maintaining a low density.

Considering the studied additives, the addition of salts (CaCl_2) was seen to have a detrimental effect on the sound absorption capacity of the aerogels: minor decreases were observed in BG while worst performances were shown in PO and KS aerogels. In fact, 2% KS + 1 M samples could not be measured due to their low processability. On the contrary, PLA coating was demonstrated to have a positive effect on the sound absorption capacity of the materials (Figure 5). Both 0.5% and 2% aerogels were coated and significantly improved their performance when using a 5% PLA coating solution, like some 0.5% + 5% PLA aerogels which could even outperform raw 2% aerogels (in the case of PO and KS). It should be highlighted that 2% aerogels with the 5% PLA coating showed values similar or even higher than those previously reported from 4% raw aerogels without significantly increasing their density ($\approx 100\text{ mg cm}^{-3}$, still beneath the commercial rockwool), thus highlighting the potential of these mechanical and water-resistant materials to be used as sound absorbing materials in construction.

Regarding the literature, alternative materials such as natural coir fiber (153 mg cm^{-3}) with 30 mm thickness was measured showing similar results to those displayed in this work using 10 mm thickness,^[48] while 20 mm melamine foams reinforce with CNF showed the best performance near 4000 Hz but decreased at higher frequencies.^[49] In addition, composite cellulosic aerogels made from cotton fibers with aluminum hydroxide nanoparticles also showed remarkable sound absorption coefficients, with the highest capacity at 2500–3500 Hz for the raw cellulosic aerogels,^[6] confirming these materials as a promising although relatively unexplored source for more sustainable absorber alternatives.

Once we obtained the preliminary results in the high frequencies range, an additional test using the impedance tube with a larger diameter (100 mm) was carried out in order to determine the sound absorption coefficients at the low frequencies range (100–1600 Hz) to get a complete spectrum. For this study, CNC-KS was selected as the most optimal material due to its higher porosity and processability, slightly better performance at the high frequencies range (Figure 5) and highest extraction yield ($\approx 36\%$). As shown in Figure 6, thickness (progressively increased by the addition of 10 mm aerogels each, up to 40 mm) was shown to be a key factor, as expected, determining the sound absorption capacity of the aerogels. Figure 6 shows that 30 mm CNC-KS aerogel provided comparable sound absorption values to 40 mm commercial rockwool. When comparing the samples of equal thickness, CNC-KS clearly exceeded the performance of the commercial rockwool. Polyester was seen to present slightly better performance at lower frequencies (100–400 Hz) but showed again an overall poorer absorption capacity in comparison with rockwool or cellulosic aerogels. These results confirmed the potential of more sustainable and lighter materials ($\approx 40\text{ mg cm}^{-3}$) such as

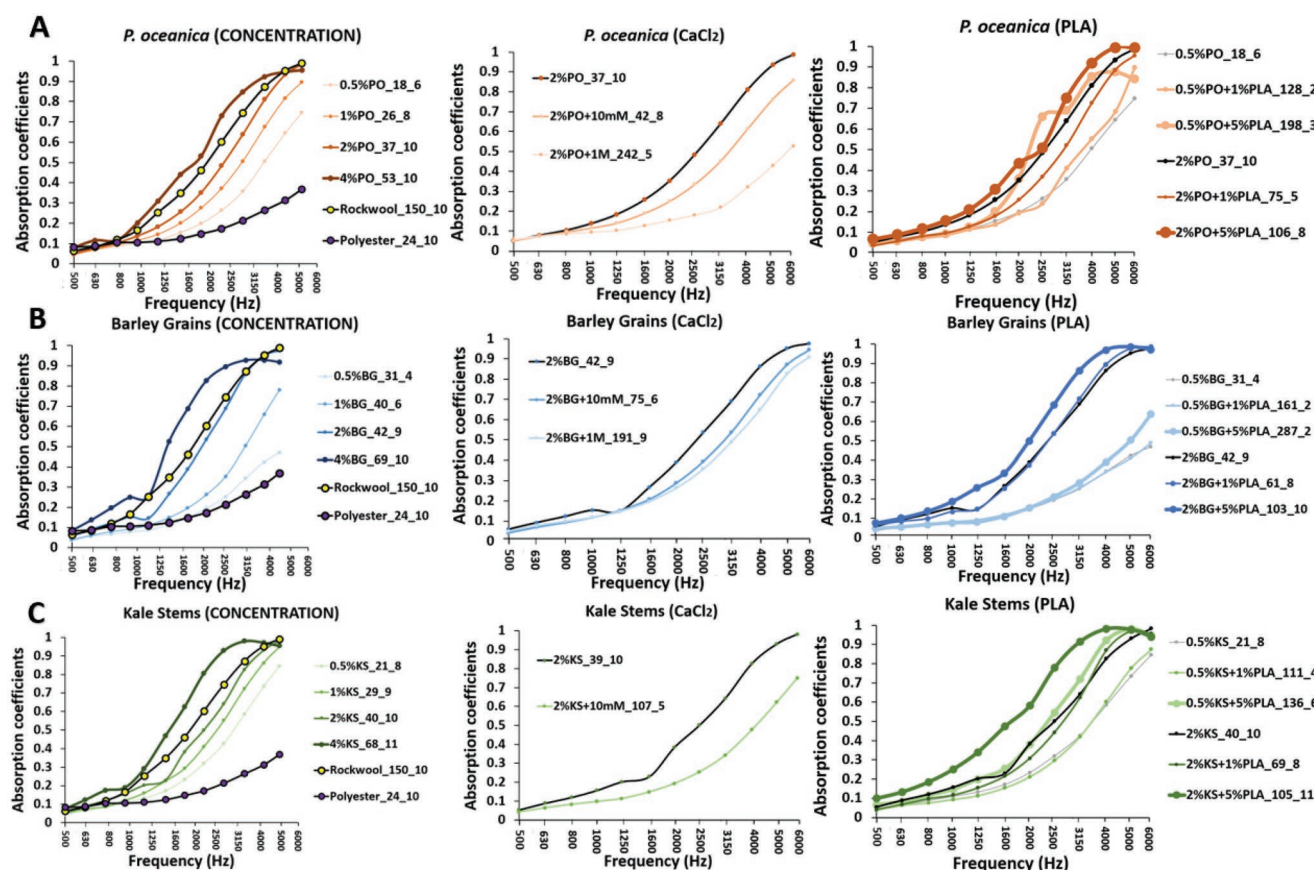


Figure 5. Sound absorption coefficients of A) PO, B) BG, and C) KS aerogels at different concentrations, CaCl_2 and PLA incorporation. Densities (mg cm^{-3}) and thicknesses (mm) were also added to the legends of each sample.

cellulosic aerogels (derived from waste biomass) as efficient alternatives to conventional and commercially available sound absorbing materials such as rockwool and polyester.

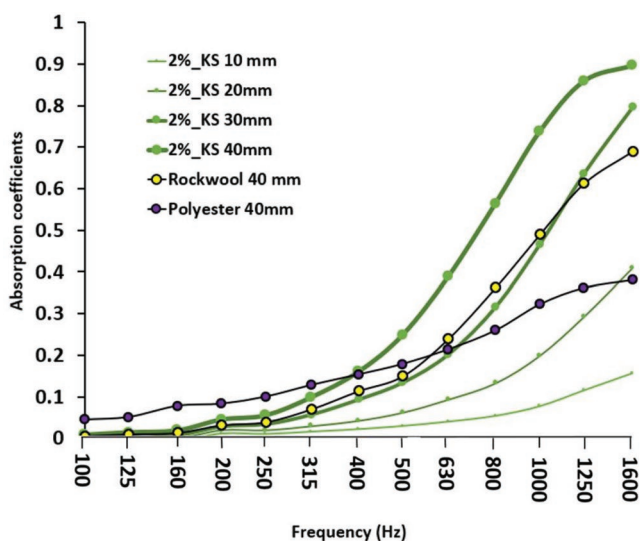


Figure 6. Sound absorption coefficients of selected aerogel (2% KS) with different thicknesses (10–40 mm) and reference materials (rockwool and polyester) at a low frequencies range (100–1500 Hz).

3. Conclusions

In this study, various waste biomass sources were valorized in order to produce more sustainable sound absorbing materials by following circular economy principles. *P. oceanica* (PO) dead leaves, spent barley grains (BG) and kale stems (KS) were characterized in terms of composition, FT-IR and TGA, with holocellulose remaining as the most abundant component in all of them, albeit having significant other differences. Subsequently, cellulosic nanocrystals (CNC-PO, CNC-BG, and CNC-KS) were extracted by using a simplified protocol and characterized. Both TGA and monosaccharide analyses showed lowest the cellulosic content in the case of CNC-PO, while CNC-KS showed a remarkable amount of galacturonic acid.

These nanocrystals were used to prepare cellulosic aerogels where three parameters were evaluated: solids concentration (0.5–4%), CaCl_2 incorporation, and PLA coating. All the aerogels were thermally stable (with degradation temperatures $>250^\circ\text{C}$) except those containing CaCl_2 (presumably due to their higher hygroscopic behavior), which was also detrimental for the sound absorption capacity of the aerogels. In essence, 4% aerogels showed the highest sound absorption results, outperforming commercial materials such as rockwool and polyester while maintaining similar or lower densities ($50\text{--}70\text{ mg cm}^{-3}$). PLA coating improved the sound absorption performance of most aerogels providing an efficient alternative while increasing

the mechanical processability and water-resistance of the raw cellulosic aerogels.

Out of the studied materials, CNC-KS aerogels were selected as the most optimal due to the positive effect that the recalcitrant lipids and pectic polysaccharides had in their structure (as confirmed by SEM images). These aerogels clearly absorbed more sound on wide frequency range (100–6000 Hz) than the commercial materials. Overall, these results show the potential of waste biomass to produce high-performance cellulosic aerogels by minimum processing that can be used as more sustainable sound absorbing materials with even better performance than those provided by commercially available reference materials.

4. Experimental Section

Materials: *Posidonia oceanica* (*P. oceanica*, labelled as PO) leaves were directly collected from the seashore in Denia, Alicante (Spain) in July 2019. The leaves were washed with water to remove salts and then milled, sieved (0.5 mm), and stored at ambient conditions (20 °C) until further use. Spent barley grains (BG) were previously mashed (≈70 °C, 1.5–3 h) and washed for wort's removal at Aalto University (Finland) while both Kale stems (KS) and Couve Galega stems (CG) were directly collected from a local orchard (Helsinki, Finland). These four biomasses were washed, milled, sieved (0.5 mm), and dried in the oven (105 °C) overnight to remove humidity prior to any further use. For comparison, commercial rockwool and polyester fibers (purchased from Rockfon and Ewona, respectively) were used as reference sound absorbing materials.

Compositional Analysis of the Different Biomasses: The Klason lignin content was determined according to the TAPPI T222 om-06 method. Briefly, 3 mL of 72% H₂SO₄ (v/v) were vigorously mixed with 300 mg of dry biomass in glass tubes. The tubes were then placed in a water bath at 30 °C for 1 h and vortexed every 10 min. After that, 84 mL of distilled water were added to each tube and mixed. The resulting material was autoclaved for 1 h at 121 °C and then cooled down with ice until reaching room temperature. The content of the tubes was subsequently filtered, and the solid material was dried in an oven at 105 °C overnight. The lignin content was calculated gravimetrically. The determinations were carried out in triplicate.

The holocellulose content was determined according to the ASTM D1104-56 method. Briefly, 1 g of dry biomass was added to 150 mL of distilled water, pre-heated at 70 °C. While stirring, 1 g of NaClO₂ and 0.2 mL of acetic acid were added every 1 h. This process was repeated three times, accounting for a total time of 4 h. The obtained material was then placed in an ice-bath to stop the reaction. After several washing cycles with distilled water (until obtaining a clear filtrate), the material was dried in an oven at 105 °C overnight. The holocellulose content was calculated gravimetrically. The determinations were carried out in triplicate.

The ash content was determined by dry biomass calcination, according to the standard TAPPI T211 om-07 method.^[50] Briefly, dry biomass samples were placed in a muffle at 525 °C for at least 4 h. The ash content was gravimetrically determined after combustion. The determinations were carried out in duplicate.

The lipid content was estimated by the Soxhlet extraction method. Approximately 9 g of dry biomass were placed in a Dumas filter and treated with 800 mL of a 2:1 toluene:ethanol mixture overnight. The lipid content was calculated gravimetrically after drying the extracted solid fraction. The determinations were carried out at least in triplicate.

Samples were analyzed for total nitrogen content using an Elemental Analyzer Rapid N Exceed (Paralab S.L., Spain). Approximately 100 mg of dry biomass were pressed into pellets and then analyzed using the Dumas method, which was based on the combustion of the sample and subsequent detection of the released N₂.^[51] The protein content was calculated from the nitrogen content multiplied by a factor of 6.25,

commonly used for lignocellulosic biomass.^[27] The determinations were carried out in triplicate.

Preparation of Cellulosic Nanocrystals: A simplified purification procedure previously reported for the extraction of cellulosic fractions from *P. oceanica* leaves was also applied to the spent barley grains and kale stems, generating cellulose-based nanocrystals containing hemicelluloses and lipidic compounds, as described in Ref. [15]. Briefly, all biomasses were subjected to a de-lignification step with NaClO₂, obtaining the cellulose-rich fraction, which was then subjected to a hydrolysis treatment with sulfuric acid (30% v/v) at 50 °C, under stirring conditions, for 1.5 h. The obtained nanocrystals were stored in the fridge as partially hydrated materials until further use. Some drops of sodium azide (1.7 M) were added to avoid the growth of microorganisms.

Preparation of Cellulosic Aerogels: Aerogels were produced by dispersing the required amount of or nanocellulosic materials in 15 mL of distilled water by ultra-turrax homogenization to obtain concentrations of 0.5 wt%, 1 wt%, 2 wt%, and 4 wt%. These suspensions were transferred to plastic falcon tubes (3 cm diameter), frozen at –80 °C for at least 4 h and then freeze-dried. The obtained nanocellulosic aerogels were labeled according to the concentration (0.5%, 1%, 2% or 4%) and type of nanocrystals used as starting material (PO, BG, or KS). For instance, 2%_KS is designated for aerogel prepared from KS with concentration of 2%.

Additionally, selected aerogels (0.5% and 2% w/v) were used to produce hybrid cellulosic-PLA aerogels using a patented technology.^[52] Briefly, PLA was dissolved in chloroform at two tested concentrations: 1% and 5% (w/v) by stirring at 50 °C for 30 min. The cellulosic aerogels were dipped in the PLA solution for 1 min and the samples were then dried at room temperature in a fume hood until the chloroform was completely evaporated (at least 24 h). The obtained aerogels were stored in equilibrated relative humidity cabinets at 0% RH and 25 °C for at least three days prior to their characterization. The amount of PLA adsorbed by the aerogels was calculated as follows:

$$\% \text{PLA} = \frac{W_f - W_0}{W_f} \times 100 \quad (1)$$

where W_0 refers to the (nano)cellulosic aerogel initial weight and W_f corresponds to the final sample weight (aerogel + PLA).

Similarly, selected concentrations (2% w/v) were used to produce hybrid cellulosic-CaCl₂ aerogels. Briefly, CaCl₂ was dissolved in water and slowly added to water dispersions of the cellulosic nanocrystals prior to freeze-drying. Two concentrations were tested in order to observe clear differences (10 mM and 1 M). The amount of CaCl₂ incorporated was also calculated according to Equation (1). At least two samples were prepared for each cellulosic aerogel type.

Carbohydrate Composition of the Extracted Cellulosic Nanocrystals: The carbohydrate content and sugar composition of the cellulosic nanocrystals was determined after sulfuric hydrolysis, as previously described.^[53] The monosaccharides were analyzed using high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) with a ICS-3000 (Dionex) equipped with a CarboPac PA 1 column (4 × 250 mm, Dionex). Control samples of known concentrations of mixtures of glucose, fructose, galactose, arabinose, xylose, mannose, galacturonic acid, and glucuronic acid were used for calibration. All experiments were carried out in triplicate and the reported values are simple averages of the repetitions.

Attenuated Total Reflectance (ATR) FT-IR Analysis: Different biomasses (BG, KS and CG) were analyzed by FT-IR in attenuated total reflectance (ATR) mode using a Jasco FT/IR 4100 (Japan) equipment. *Posidonia oceanica* (PO) was analyzed in ATR mode using a Thermo Nicolet Nexus (GMI, USA) equipment. Before the measurements, the samples were dried in an oven at 60 °C for at least 24 h. The spectra were taken at 4 cm^{–1} resolution in a wavelength range between 400–4000 cm^{–1} and averaging a minimum of 32 scans.

XRD Diffraction: XRD measurements of nanocrystals were carried out on a D5005 Bruker diffractometer. The instrument was equipped with

a Cu tube and a secondary monochromator. The configuration of the equipment was θ -2 θ , and the samples were examined over the angular range of 3–60° with a step size of 0.02° and a count time of 200 s per step. Peak fitting was carried out using the Igor software package (Wavemetrics, Lake Oswego, Oregon) as described in a previous work.^[54] The crystallinity index was determined by the method reported by Wang et al.^[55]

$$X_c(\%) = \frac{\sum A_{\text{Crystall}}}{A_{\text{Total}}} \times 100 \quad (2)$$

where A_{Total} is the sum of the areas under all the diffraction peaks and $\sum A_{\text{Crystall}}$ is the sum of the areas corresponding to the three crystalline peaks from cellulose I.

Thermogravimetric Analyses (TGA): Thermogravimetric curves (TG) were recorded with a Setaram Setsys 16/18 (SETARAM Instrumentation, France). Prior to measurements, the samples were oven-dried at 60 °C for at least 24 h. The samples (ca. 10 mg of the raw biomasses, corresponding nanocrystals and aerogels) were heated from 30 to 1000 °C with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. DTG express the weight loss rate as a function of temperature.

Transmission Electron Microscopy (TEM): One drop (8 µL) of 0.003% aqueous suspensions of the obtained cellulosic nanocrystals was allowed to dry on a carbon coated grid (200 mesh). The nanocrystals were stained with uranyl acetate. TEM was performed using a JEOL 1010 (JEOL, Massachusetts, USA) at an accelerating voltage of 80 kV. Morphology of the observed nanocrystals was characterized using ImageJ-win64 software by means of at least 5 different images.

Scanning Electron Microscopy (SEM): SEM was conducted on a Tescan Mira3 instrument at an accelerating voltage of 3 kV and a working distance of 18–20 mm. Small samples (≈5 mm² area) of the aerogels were cut to observe their surface. The samples were then coated with a 5 nm layer of gold-palladium under vacuum before their morphology was examined.

Density of Aerogels: Aerogel densities were determined from the weight and volume of each individual aerogel. The weight was determined by an analytical balance (Precisa Gravimetrics AG SERIES320XB, Dietikon, Switzerland) and the dimensions were measured by simple averages of the values determined by a digital caliper at three different positions.

Brunauer–Emmett–Teller (BET) Analysis: The surface area and pore size of the commercialized and synthesized samples were determined from the nitrogen adsorption–desorption isotherms, which were measured at 77.35 K using BELsorp-mini II instrument (BEL, Japan). Prior to the measurements, ≈40 mg of each sample was placed in the sample cell and left in a degas system (BELPrep VAC II, Microtrac BEL) at 90 °C for 12 h under nitrogen flow.

Measurements of Sound Absorption Coefficients: The normal incidence sound absorption coefficients of the samples were determined using the impedance tube transfer-function method defined in the standard.^[56] The impedance tube used was a Brüel & Kjaer type 4206. All the samples were measured in the small impedance tube (diameter of 29 mm) providing results in the frequency range of 500–6000 Hz, while selected aerogels were also measured in a larger impedance tube (diameter of 100 mm) providing results in the frequency range of 100–1600 Hz. The excitation signal used in the measurements was a logarithmic sweep covering the frequency range 20–20 000 Hz. Impulse responses were computed as explained in Ref. [57]. The excitation signal was amplified using a power amplifier of the type Yamaha MX70. Two 1/4"-pressure microphones of the type Brüel & Kjaer 2670 were used to measure pressures at each microphone location. The measured signals were amplified using a pre-amplifier of the type Brüel & Kjaer Nexus. The audio interface used was the UltraLite-mk3 Hybrid. All the signal processing was performed in Matlab.

Statistical Analysis: Analysis of variance (ANOVA) followed by a Tukey-b test were used when comparing more than two data sets, after confirming the homogeneity of variances by the Levene test using IBM SPSS Statistics software v.26. All data have been represented as the average ± standard deviation. Significant differences ($p \leq 0.05$)

are denoted by showing the data provided in tables and figures with different letters.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aerogels, biomass valorisation, cellulosic nanocrystals, poly(lactic acid), sound absorption

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- [1] H. J. Jariwala, H. S. Syed, M. J. Pandya, Y. M. Gajera, *Indoor Built Environ.* **2017**, 1.
- [2] M. S. Al-Homoud, *Build. Environ.* **2005**, 40, 353.
- [3] S. Solomon, *Intergov. Panel Clim. Change (IPCC), Clim. Change* **2007**, 996.
- [4] D. J. Oldham, C. A. Egan, R. D. Cookson, *Appl. Acoust.* **2011**, 72, 350.
- [5] J. Cucharero, S. Ceccherini, T. Maloney, T. Lokki, T. Hänninen, *Cellulose* **2021**, 28, 4267.
- [6] C. He, J. Huang, S. Li, K. Meng, L. Zhang, Z. Chen, Y. Lai, *ACS Sustainable Chem. Eng.* **2018**, 6, 927.
- [7] T. Budtova, *Cellulose* **2019**, 26, 81.
- [8] I. L. Vêr, L. L. Beranek, *Noise and Vibration Control Engineering: Principles and Applications*, John Wiley & Sons, New York **2005**.
- [9] J. Sherwood, *Bioresour. Technol.* **2020**, 300, 122755.
- [10] J. Gröndahl, K. Karisalmi, J. Vapaavuori, *Soft Matter* **2021**, 17, 9842.
- [11] G. Balata, A. Tola, *J. Cleaner Prod.* **2018**, 172, 4085.
- [12] F. Bettaieb, R. Khiari, A. Dufresne, M. F. Mhenni, J. L. Putaux, S. Boufi, *Ind. Crops Prod.* **2015**, 72, 97.
- [13] S. Majumdar, S. Seth, D. K. Bhattacharyya, J. Bhowal, *Waste and Biomass Valorization* **2021**, 12, 3849.
- [14] G. Z. Dehnavi, J. L. Lauceric, D. Rodriguez, M. Beaton, M. J. Taherzadeh, C. Martin, *Cellul. Chem. Technol.* **2011**, 45, 339.
- [15] I. Benito-González, A. López-Rubio, R. Gavara, M. Martínez-Sanz, *Cellulose* **2019**, 26, 8007.

- [16] I. Benito-González, A. López-Rubio, L. G. Gómez-Mascaraque, M. Martínez-Sanz, *Chem. Eng. J.* **2020**, 390, 124607.
- [17] Y. Li, Y. Liu, Y. Liu, W. Lai, F. Huang, A. Ou, R. Qin, X. Liu, Xu Wang, *ACS Sustainable Chem. Eng.* **2018**, 6, 11979.
- [18] R. Nisticò, G. Magnacca, M. Antonietti, N. Fechner, *Adv. Porous Mater.* **2014**, 2, 37.
- [19] X. Wang, Y. Zhang, H. Jiang, Y. Song, Z. Zhou, H. Zhao, *Mater. Res. Express* **2017**, 4, 065006.
- [20] Y. Al Haj, S. Mousavihashemi, D. Robertson, M. Borghei, T. Paakkonen, O. J. Rojas, E. Kontturi, T. Kallio, J. Vapaavuori, *Chem. Eng. J.* **2022**, 435, 135058.
- [21] I. Benito-González, A. López-Rubio, M. Martínez-Sanz, *Int. J. Biol. Macromol.* **2018**, 118, 542.
- [22] A. Fernenia, K. W. Waldron, J. A. Robertson, R. R. Selvendran, *Carbohydr. Polym.* **1999**, 39, 101.
- [23] A. Fernenia, J. A. Robertson, K. W. Waldron, R. R. Selvendran, *J. Sci. Food Agric.* **1998**, 77, 511.
- [24] X. F. Sun, F. Xu, R. C. Sun, P. Fowler, M. S. Baird, *Carbohydr. Res.* **2005**, 340, 97.
- [25] N. Abidi, L. Cabrales, C. H. Haigler, *Carbohydr. Polym.* **2014**, 100, 9.
- [26] R. Khiari, Z. Marrakchi, M. N. Belgacem, E. Mauret, F. Mhenni, *Compos. Sci. Technol.* **2011**, 71, 1867.
- [27] I. Benito-González, C. M. Jaén-Cano, A. López-Rubio, A. Martínez-Abad, M. Martínez-Sanz, *Int. J. Biol. Macromol.* **2020**, 165, 1540.
- [28] H. Gholizadeh, A. A. Naserian, M. Yari, A. Jonker, P. Yu, *Anim. Feed Sci. Technol.* **2021**, 275, 114855.
- [29] M. Jackowski, L. Niedzwiecki, M. Lech, M. Wnukowski, A. Arora, M. Tkaczuk-Serafin, M. Baranowski, K. Krochmalny, V. K. Veetil, P. Seruga, A. Trusek, H. Pawlak-Kruczek, *Energies* **2020**, 13, 2058.
- [30] A. Nesic, J. Ruzic, M. Gordic, S. Ostojic, D. Micic, A. Onjia, *Composites, Part B* **2017**, 110, 56.
- [31] W. Zhang, Q. Liu, L. Guo, P. Wang, S. Liu, J. Chen, Z. Lei, *J. Environ. Chem. Eng.* **2021**, 9, 106689.
- [32] H. Chen, Z. Liu, Xu Chen, Y. Chen, Z. Dong, X. Wang, H. Yang, *Bioresour. Technol.* **2020**, 310, 123498.
- [33] I. Benito-González, A. López-Rubio, A. Martínez-Abad, A. R. Ballester, I. Falcó, L. González-Candelas, G. Sánchez, J. Lozano-Sánchez, I. Borrás-Linares, A. Segura-Carretero, M. Martínez-Sanz, *Mar. Drugs* **2019**, 17, 409.
- [34] D. N. Raba, D. R. Chambre, D.-M. Copolovici, C. Moldovan, L. O. Copolovici, *PLoS One* **2018**, 7, 13.
- [35] R. L. Scalzo, G. Bianchi, A. Genna, C. Summa, *Food Chem.* **2007**, 100, 1019.
- [36] H. Potvin, M. H. Back, *Can. J. Chem.* **1973**, 51, 183.
- [37] M. Wada, J. Sugiyama, T. Okano, *J. Appl. Polym. Sci.* **1993**, 49, 1491.
- [38] Y. Nakamura, Y. Ono, T. Saito, A. Isogai, *Cellulose* **2019**, 26, 6529.
- [39] I. Benito-González, M. del M. Ortiz-Gimeno, A. López-Rubio, A. Martínez-Abad, A. Garrido-Fernández, M. Martínez-Sanz, *Food Bioprod. Process.* **2022**.
- [40] R. J. Viëtor, A. G. J. Voragen, S. Angelino, *J. Inst. Brew.* **1993**, 99, 243.
- [41] L. Heath, W. Thielemans, *Green Chem.* **2010**, 12, 1448.
- [42] N. Pircher, S. Veigel, N. Aigner, J. M. Nedelec, T. Rosenau, F. Liebner, *Carbohydr. Polym.* **2014**, 111, 505.
- [43] O. Aykanat, M. Ermeydan, *J. Innovative Sci. Eng.* **2020**, 4, 1.
- [44] F. Villain, J. Coudane, M. Vert, *Polym. Degrad. Stab.* **1994**, 43, 431.
- [45] C. Barreneche, A. I. Fernández, L. F. Cabeza, R. Cuypers, *Appl. Energy* **2015**, 137, 726.
- [46] S. Xiang, L. Feng, X. Bian, G. Li, X. Chen, *Polym. Test.* **2020**, 81, 106211.
- [47] D. Ciftci, A. Ubeyitogullari, R. R. Huerta, O. N. Ciftci, R. A. Flores, M. D. A. Saldana, *J. Supercrit. Fluids* **2017**, 127, 137.
- [48] M. J. Nine, M. Ayub, A. C. Zander, D. N. H. Tran, B. S. Cazzolato, D. Losic, *Adv. Funct. Mater.* **2017**, 27, 1703820.
- [49] L. Shen, H. Zhang, Y. Lei, Y. Chen, M. Liang, H. Zou, *Carbohydr. Polym.* **2021**, 255, 117405.
- [50] T. Tappi, *TAPPI test methods T* **1993**, 211, 64.
- [51] P. G. Wiles, I. K. Gray, R. C. Kissling, *J. AOAC Int.* **1998**, 81, 620.
- [52] M. Martínez-Sanz, I. Benito-González, A. López-Rubio, *Procedimiento Para La Preparación de Aerogels Hidrofóbicos*, **2021**.
- [53] J. F. Saeman, *Ind. Eng. Chem.* **1945**, 37, 43.
- [54] M. Martínez-Sanz, P. Lopez-Sanchez, M. J. Gidley, E. P. Gilbert, *Cellulose* **2015**, 22, 1541.
- [55] N. Wang, E. Ding, R. Cheng, *Polymer* **2007**, 48, 3486.
- [56] Acoustics — Determination of sound absorption coefficient and impedance in impedance tubes — Part 2: Transfer-function method **1998**.
- [57] A. Farina, *Audio Engineering Society Convention* **2000**, 108.