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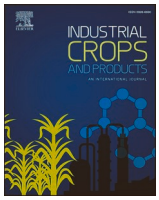

Microwave heating for sustainable valorization of almond hull towards high-added-value chemicals

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ABSTRACT

Microwave (MW) treatment promotes homogeneous heating compared to conventional methods, thus increasing the recovery of high-added-value compounds and leading to a considerably lower amount of both by-products and side reactions. Therefore, the main goal of this work is to valorize almond hull (AH) via microwave (MW)-assisted radiation (0–200 W, 0–300 psi, 100–190 °C, 10–40 min). In this context, two different pathways were evaluated. Firstly, the transformation of AH into levulinic acid (LA), one of the major bio-based chemicals obtained from lignocellulosic biomass. The so-called almond hull extractives-free biomass (AH-EFB) led to the best results after using both Lewis ($AlCl_3$·6 H_2O, 1 mol/L, 87 % molar yield) and Brønsted (*p*-toluenesulfonic (*p*-TsOH), 0.25 mol/L, 91 % molar yield) acids, at 190 °C for 20 min. This latter not only provides a sustainable system in contrast to mineral acids such as H_2SO_4 or HCl, but also the possibility of being recovered and recycled for further transformations. In a parallel secondary experiment, the recovery of biologically active compounds (BACs) was studied separately. For this purpose, antioxidant assays and phenolic profiling were carried out, which demonstrated that MW was more efficient than traditional methods (i.e. soaking) based on obtained values in terms of scavenging activity and polyphenols. Overall, this valorization approach involves most of the Green Chemistry principles, thus contributing to the development of almond biorefineries.

1. Introduction

Lignocellulosic biomass is emerging as an alternative, renewable and endless feedstock to obtain high-added-value products compared to petroleum-based ones (Banerjee et al., 2017; Lorente et al., 2020; Lucas-Torres et al., 2016; Mechnou et al., 2021), mainly due to its high carbon content, thus facilitating its transformation towards fine chemicals. Particularly, agro-industrial wastes coming from the almond industry are an interesting target matrix to be valorized due to the several issues of many factories, being needed to manage them.

Almond tree (*Prunus dulcis (Mill.)*) is one of the most popular crops around the world. Based on the International Nut and Dried Fruit Council data (NDFC, Nuts and dried fruits. Statistical year book, 2019), a growing increase in almond production has been observed over the last decade. For instance, during the 2019–2020 season, the maximum value of almond production was achieved, reaching up to 1.36 million metric tons, counting for an increase of up to 7 % from the previous season and 26 % above the previous ten-year average. The USA is the dominant almond-producing country, generating around 80 %, whereas Spain ranks third, accounting for an estimated 6 % of annual worldwide production. During almond processing, the main wastes and by-products generated are almond skin, shell and hull.

Almond hull (AH) is the most external shell of almonds and is considered the heaviest material in the almond fruit. The composition of the hulls, as well as of the rest of by-products and kernel differs according to environmental conditions, the agrochemical management and almond variety (Aktas et al., 2015; Holtman et al., 2015; Prgomet et al., 2017; Salgado-Ramos et al., 2022b).

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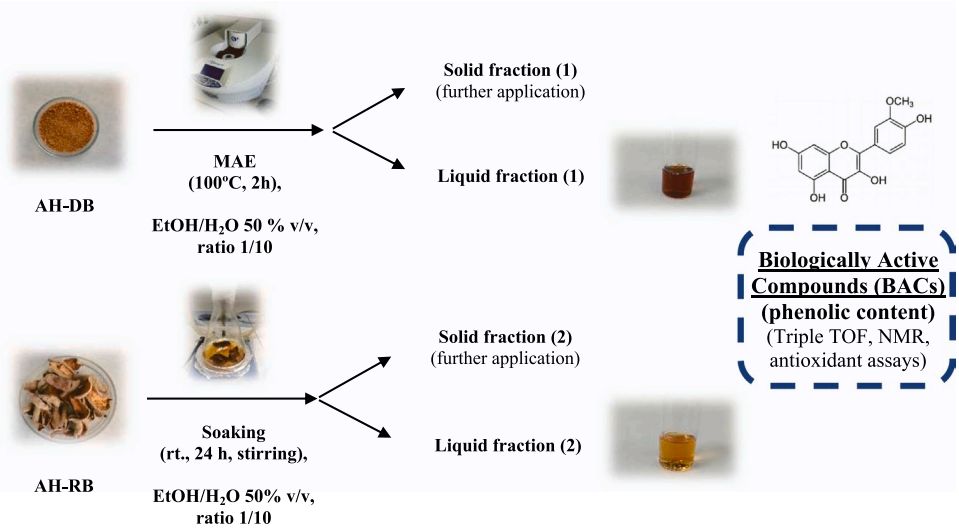

Fig. 1. Schematic representation for the exploitation of almond hull (AH) as source of biologically active compounds (BACs) via microwave-assisted extraction (MAE) and conventional treatment (soaking). Derived solids AH-dried biomass (AH-DB) and AH-raw biomass (AH-RB).

Both chemical properties and composition of AH suggest feasible valorization pathways for this matrix. For instance, AH is an interesting source of some bio-based valuable compounds such as polyphenols. Polyphenols are antioxidant compounds which have been demonstrated to be useful in the prevention of some noncommunicable diseases, mainly those associated with oxidative stress, such as cancer or aging, as well as autoimmune, cardiovascular, or neurodegenerative (Freyssin et al., 2018, 2020; Silva et al., 2019). Furthermore, non-conventional methodologies and techniques which enable improved efficiency are increasingly being developed and adopted for more efficient recovery of polyphenols from biomass or foods compared to conventional methods, which involve harsh conditions in terms of temperature, time and organic solvent (Khawli et al., 2021; Kokkali et al., 2020; Sahin et al., 2017). The antioxidant activity of AH has already been demonstrated by some authors (Kahlaoui et al., 2019; Prgomet et al., 2017, 2019), as well as the application of some of these non-conventional techniques in this matrix for polyphenolic recovery, such as pulsed electric fields (PEF) (Salgado-Ramos et al., 2022b) and ultrasound-assisted extraction (UAE) (Kahlaoui et al., 2019).

On the other hand, AH can be both energetically and chemically exploited to produce some platform and fine chemicals, like levulinic acid (LA). Levulinic acid (also known as 4-oxopentanoic acid) is considered one of the most valuable chemicals obtained from biomass, according to the US Department of Energy (Werpy et al., 2004). It should be noted the wide range of applications for LA, ranging from pesticides, solvents or pharmaceuticals, to food additives and cosmetics (Mika et al., 2018). Moreover, LA shows key characteristics for promoting utility in green chemistry, since it provides a highly functional character due to the presence of carboxylic and carbonyl groups. This fact enables it to be a versatile biobased building block to produce multiple high-end products, which can be applied as solvents, plasticizers, or fuels, as well as in coatings, electronics, lubricants, or photography. Some examples of the high-added-value chemicals obtained from LA are 2-methyltetrahydrofuran, succinic acid, δ-aminolevulin acid, valeric acid or acetyl acrylic acid (Antonetti et al., 2016; Mika et al., 2018), and notably γ-valerolactone (GVL), obtained by hydrogenation of LA, is one of the most valuable compounds due to its current applications as green solvent and biofuel additive (Osatiashtiani et al., 2017).

This work reports for the first time the improved valorization of AH via MW heating towards both chemical and energetic pathways, as well as its exploitation as an antioxidant source, to the best of our knowledge. The sustainability of MW lies in its high atomic economy for each process, thus leading to a decrease in terms of both side reactions and undesired by-products. This fact allows MW to exhibit excellent energy efficiency compared to conventional heating, providing better yields as well as shorter reaction times (Bouras et al., 2015; Koubaa et al., 2016). This effect by microwave radiation is due to a combination of thermal effects and the selective absorption of radiation by polar molecules, resulting in a homogeneous heating mechanism in contrast to conventional treatments, where the heat is transferred by convection from the flask walls to the flask contents (de la Hoz et al., 2005; Lucas-Torres et al., 2016). MW radiation has several applications in chemistry, from biomass treatment to organic synthesis and medicinal chemistry (Cravotto and Carnaroglio, 2017). Herein, the use of MW as a heating method for both catalytic conversion to LA and polyphenol recovery considerably facilitates mass transfer between the solid feedstock and the aqueous solution. Furthermore, considering the obtention of LA, the high-available temperatures promote the digestion of the dilute acid, thus leading to a synergistic effect in terms of improved product yield. The fact that the valorization of AH by microwaves has not been reported to date, in addition to the use of both environmentally sustainable catalysts and solvents according to Green Chemistry principles, make this work a valuable and worthwhile contribution to research in this field, not only for AH byproducts but also for any kind of lignocellulosic biomass.

2. Material and methods

2.1. Chemicals

p-Toluenesulfonic acid (>98.5 %, CAS No. 6192-52-5), trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) (CAS No. 53188-07-1), potassium bromide (CAS No. 7758-02-3), potassium persulfate ($K_2S_2O_8$) (CAS No. 7727-21-1), $AlCl_3 \cdot 6H_2O$ (CAS No. 7784-13-6), 2,2′-Azino-Bis-3-Ethylbenzothiazoline-6-Sulfonic Acid (ABTS) (CAS No. 30931-67-0), 3-(trimethylsilyl) propionic-2,2,3,3-d_4 acid sodium salt (98 atom % D, CAS No. 24493-21-8), gallic acid (CAS No. 149-91-7), fluorescein (CAS No. 2321-07-5), 2,2'-Azobis(2-amidinopropane) dihydrochloride (AAPH) (CAS No. 2997-92-4) and Folin–Ciocalteu reagent were bought from Sigma-Aldrich (Steinheim, Baden-Württemberg, Germany). Deuterium oxide (99.96 % atom D, CAS No. 7789-20-0), dimethyl sulfoxide (DMSO) (CAS No. 67-68-5), ethanol (CAS No. 64-17-5), sodium phosphate (Na_2HPO_4) (CAS No. 7601-54-9), sodium carbonate (Na_2CO_3) (CAS No. 497-19-8) and potassium phosphate

(KH_2PO_4) (CAS No. 7 778-77-0) were acquired from VWR (Saint-Prix, France). Maleic acid (CAS No. 110-16-7) was obtained from Fluka. Ethyl acetate (CAS No. 141-78-6) was supplied from Scharlab.

2.2. Feedstock treatment and characterization

Almond hull raw biomass (AH-RB) was collected in Toledo (Spain), in the region of Los Yébenes, at the first stage of the 2016/2017 season. Firstly, AH-RB was lyophilized to remove moisture (11.72 ± 0.54 %) in a Telstar LyoQuest-85 PLUS freeze dryer (Telstar Technologies, Terrassa, Spain). Then, it was blade-milled using a Fritsch Pulverisette 14 (Fritsch, Idar-Oberstein, Germany) working at 20,000 rpm for 1 min, thus obtaining the namely dried-powdered almond hull dried biomass (AH-DB). The so-called solids almond hull polar extract (AH-PE) and almond hull extractives-free biomass (AH-EFB) were obtained from AH-DB (Salgado-Ramos et al., 2022b).

2.3. Recovery of polyphenols from AH

The liquid extracts for the antioxidant determinations were obtained after MW heating and soaking (Fig. 1). For the first sample, 1 g of the solid AH-DB was introduced into 35 mL microwave glass reactor along with 10 mL of a EtOH:H_2O mixture (50 % v/v). Then, the reactor was closed and put in a CEM Discover monomode microwave-reactor (CEM Discover SP, Matthews, NC, USA), in which temperature management was checked using an infrared sensor at 100 °C for 2 h. The reactor worked in a closed mode, allowing to control both pressure (from 0 to 300 psi) and power (from 0 to 200 W). After the reaction, the mixture was filtered under vacuum, washing the crude with an EtOH:H_2O mixture. The obtained solid was retained for future application. The liquid fraction was kept safe for further antioxidant assays.

Soaking was carried out in an Erlenmeyer flask, which was charged with 10 g of the solid AH-RB and 100 mL of a mixture EtOH:H_2O (50 % v/v). The reaction took place at room temperature under stirring for 24 h, according to the work previously reported for some winemaking wastes (Lapornik et al., 2005). The workup for the recovery of the liquid fraction was the same as MW heating.

2.4. Antioxidant assays and LC-MS analysis

Total phenolic content (TPC) was determined following the Folin-Ciocalteu method, as previously described (Martí-Quijal et al., 2021; Salgado-Ramos et al., 2022b). Briefly, 100 μL of sample were mixed with 3 mL of Na_2CO_3 2 % (w/v) and 100 μL of Folin Ciocalteu reagent and incubated for 1 h at room temperature in darkness. Then, the absorbance was measured at 765 nm in a Perkin-Elmer UV/Vis Lambda 2 spectrophotometer (Perkin-Elmer, Jügesheim, Germany). A standard curve was prepared using different concentrations of gallic acid. The results were expressed as mg Gallic Acid Equivalents / g dry weight (mg GAE / g DW).

The phenolic profile characterization and quantification was performed considering previously described method (Rosello-Soto et al., 2019), using a Agilent 1260 Infinity (Agilent, Waldbronn, Germany) with a Waters UPLC C18 column 1.7 μm (2.1 ×50 mm) Acquity UPLC BEH.C18 (Waters, Cerdanyola del Vallès, Spain) for the separation of the main phenolic compounds in the samples, and a TripleTOF™ 5600 LC/MS/MS system (AB SCIEX, Foster City, CA, USA) for the identification. An external calibration curve was used for the quantification, choosing a representative polyphenol of each group of phenolic compounds potentially found in the samples. The selected polyphenols were: genistein (for isoflavonoids), gallic acid (as representative compound from phenolic acids), hydroxytyrosol (for phenylethanoids), resveratrol (for stilbenes) and apigenin (flavones), naringenin (flavanones), kaempferol (flavonols) and catechin (flavanols) as representative compounds of flavonoids.

Regarding antioxidant assays, Trolox Equivalent Antioxidant Capacity (TEAC) and Oxygen Radical Absorbance Capacity (ORAC) were carried out, according to a previous work (Salgado-Ramos et al., 2022b). Results were expressed as μmol Trolox Equivalent / g dry weight (μmol TE / g DW).

2.5. General procedure for LA obtention

All reactions were carried out in a CEM Discover monomode MW-reactor (CEM Discover SP, Matthews, NC, USA) in which temperature management was checked using an infrared sensor for the required time. The reactor allowed us to control both pressure (from 0 to 300 psi) and power (from 0 to 300 W). The experiments were performed by duplicate.

In a typical assay, 0.10 g of the selected sample were loaded in a 10 mL microwave glass reactor in addition to 2 mL of the acidic aqueous solution (*p*-toluenesulfonic acid (*p*-TsOH) or $AlCl_3{\cdot}6\ H_2O$) at the required concentration. KBr was previously added as a co-catalyst in order to improve LA yields, according to the reported literature (Marcotullio and de Jong, 2010, 2011). After MW heating, the mixture was filtered, and then the crude reaction was washed for several times with deionized water. The aqueous liquid fraction was subsequently extracted by liquid-liquid extraction using ethyl acetate. Both aqueous and organic phase were separately evaporated under vacuum, and the dried obtained crudes analyzed by NMR. Quantitative conversions were obtained for all experiments.

2.6. NMR analysis

All reaction crudes were analyzed by Nuclear Magnetic Resonance (NMR) spectroscopy, with quantitative purposes (qNMR). 600 μL of D_2O (regarding LA experiments) or MeOD (sugar quantification) were used as solvent. The ^{1}H NMR spectra were recorded on a Bruker Ascend™ 500 spectrometer (Bruker Corporation, Billerica, MA, USA) at 500.16 MHz for the ^{1}H nucleus. Quantitative parameters were considered: acquisition time: 2.723 min; scans number: 16; pulse: 90 °(8 μs); relaxation delay (D1): 5 s. Chemical shifts were referred at 0 ppm by means of 3-(trimethylsilyl) propionic-2,2,3,3-d_4 acid sodium salt (TSP) solution (1.5 %wt. D_2O, 20 μL). qNMR was applied based on previous studies in the available literature (Lucas-Torres et al., 2016; Salgado-Ramos et al., 2022a), by addition of 50 μL of maleic acid 0.1 mol/L as an internal standard, according to Eq. (1):

$$m(x) = \frac{I(x)}{I(IS)} \bullet \frac{N(IS)}{N(x)} \bullet n(IS) \bullet M(x) \quad (1)$$

I(x) and I(IS) refer to the integral value for one signal or nucleus (N) of the compound x (N(x)) and internal standard (IS) (N(IS)), respectively; M(x) is the molecular weight of the compound x and n (IS) the number of mmol of IS added to the sample.

Regarding LA experiments, the number of hexoses in each sample were considered, therefore the overall absolute mass value can be transformed into LA molar percentage values using Eq. (2).

$$\%\ \text{molar}\ yield(\text{LA}) = \frac{\text{mol (LA)}}{\text{mol(hexoses) in starting}\ solid} \text{x}100 \quad (2)$$

2.7. FT-IR and SEM analyses

FT-IR spectra for the target solids were recorded in an IRAffinity-1S FT-IR instrument (Shimazdu, Kioto, Japan), equipped with a media work infrared lamp and DTGS Standard Detector. The analyses were carried out at 4 cm^{-1} of resolution and 45 scans per sample, and the frequency range collected from 500 to 4000 cm^{-1} in transmittance mode.

SEM images were taken in a ZEISS Gemini500 high resolution scanning electron microscopy (HRSEM, ZEISS, Oberkochen, Germany), with an Oxford EDS 80 mm^2 detector operating from 3 pA to 20 nA for electrical current intensity and 0.02–30 kV for voltage.

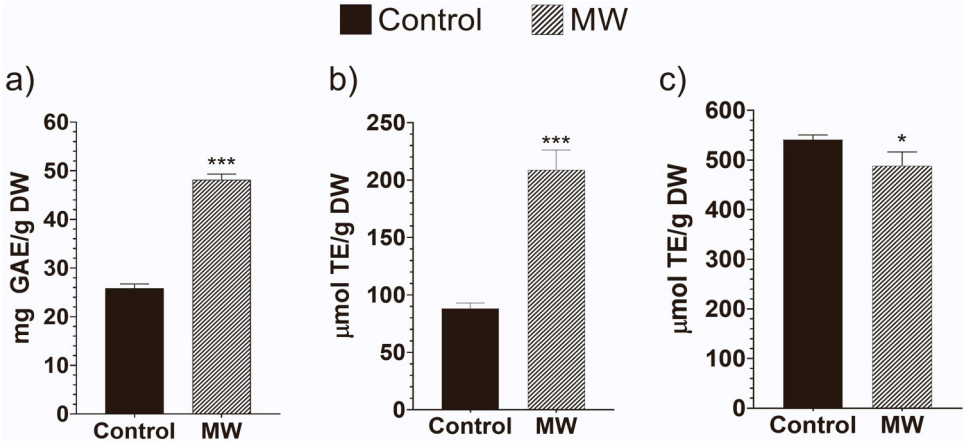

Fig. 2. Analysis of a) Total phenolic content (TPC), b) Trolox equivalent antioxidant capacity (TEAC) and c) Oxygen radical antioxidant capacity (ORAC) assays measured in almond hulls extracts obtained after a microwaves (MW) treatment, using the maceration process as control. * ** = $p < 0.001$; * = $p < 0.05$ vs. Control.

Table 1
Main polyphenols detected by HPLC-MS for the antioxidant liquid fraction obtained by microwave-assisted extraction (MAE) from almond hull (AH) biomass.

Compound	Formula	Intensity	RT[a] (min)	ppm
3-hydroxyphloretin	$C_{15}H_{14}O_6$	851,345	6.76	159.27
(+,-)-Catechin	$C_{15}H_{14}O_6$	851,345	6.76	159.27
(+,-)-Epicatechin	$C_{15}H_{14}O_6$	851,345	6.76	159.27
Kaempferol 3,7-O-diglucoside	$C_{27}H_{30}O_{16}$	545,210	10.82	102.02
Kaempferol 3-O-galactoside-7-O-rhamnoside	$C_{27}H_{30}O_{15}$	491,061	11.73	91.87
Procyanidin dimer (B1-B7)	$C_{30}H_{26}O_{12}$	389,496	7.54	72.87
Caffeoylquinic acids	$C_{16}H_{18}O_9$	252,233	7.60	47.20

[a]RT: retention time.

Table 2
Concentration of glucose and sucrose by quantitative NMR (qNMR) in the liquid extracts obtained by soaking and microwave-assisted extraction (MAE) from almond hull (AH).

Sugar	Chemical shift (ppm)	Soaking (mg/mL)[a]	MAE (mg/mL)[a]
Sucrose	5.39	2.75	4.13
α-glucose	5.11	5.95	4.82
β-glucose	4.48	7.70	7.82
Total		16.40	16.77

[a]mg calculated according to Eq. (1) in 600 µL of sample.

2.8. Statistical analysis

Concerning the results of antioxidants assays (TPC, TEAC and ORAC), a t-test was used to compare treated samples by MW with their control obtained by maceration. The results of LA yield for AH-PE, AH-DB, and AH-EFB were analyzed using an ANOVA test followed by Tukey post-test. The results were expressed as mean ± standard deviation, and it was considered significant when p-value was lower than 0.05. The GraphPad Prism 8.0.2 software (GraphPad Software, San Diego, CA, USA) was used to perform all statistical analysis.

3. Results and discussion

3.1. Microwave-assisted recovery of bioactive compounds

Microwave-assisted extraction (MAE) allows the extraction of intracellular compounds through the evaporation of intracellular water, causing an increase of pressure and thus promoting cell membrane disruption (Bodoira and Maestri, 2020; Mariatti et al., 2021). As can be observed in Fig. 2, microwave treatment clearly enhanced phenolics´ extraction compared to control, increasing the total phenolic content (TPC) value from 25.83 up to 48.11 mg GAE/g dry matter (DM). Moreover, the antioxidant capacity measured by the TEAC assay was also improved from 88.20 up to 208.75 µmol TE / g DW, which represents a 2.3-fold increase in the values. In addition, a strong positive correlation was found (r: 0.9816; $p < 0.001$) between the TPC values and TEAC results. This suggests the increase of antioxidant capacity probably due to the release of phenolic compounds, which have antioxidant activity (Bouras et al., 2015). Finally, as the opposite as occurs for TPC and TEAC, the activity observed by ORAC was significantly higher for soaking compared to MAE ($p < 0.05$). This fact could be attributed to the high sensibility of this assay respect to other BACs. Despite of that, it should be again remarkable the antioxidant capacity by MW (487.95 µmol TE / g DW), since only 2h were used in contrast to the 24h employed by soaking to only get to up to 540.78 µmol TE / g DW.

These results are in agreement with those reported in the existing literature. In this sense, Valdés et al. (2015) obtained a range of TPC from 62 up to 119 mg quercetin equivalent (QE)/g after MAE of skin from different almond varieties. Moreover, Dailey and Vuong obtained similar values for the TPC assay after the microwave treatment of macadamia nuts (Dailey and Vuong, 2016). Specifically, after applying 360 W for 4.5 min to 5 g of sample in 100 mL of water, they obtained a TPC value of 44.75 mg GAE/g. In addition, these authors also reported a TEAC value of 361.60 µM TE/g. Regarding antioxidant capacity, Ballard et al. (2010), reported an ORAC value of 2.79 mmol TE/g after MAE of peanut skins (855 W, 150 s). Moreover, the same authors reported a maximum TPC of 143.6 mg GAE/g when applied 855 W for 30 s to 1.5 g of peanut skins.

Further, the phenolic profile of the liquid crude fraction obtained after MAE was also analyzed. As can be observed in Table 1, the main present polyphenols were flavonoids (3-hydroxyphloretin), flavanols (catechin, epicatechin), as well as some hydroxycinnamic acids, such as caffeoylquinic acids, which are related to the available literature (Prgomet et. al, 2017). Moreover, it should be noted the presence of dimers, such as procyanidins B1-B7, and glycosylated polyphenols (kaempferol 3,7-O-diglucoside or kaempferol 3-O-galactoside-7-O-rhamnoside).

The presence of these glycosylated polyphenols in AH are also in agreement with the literature (Prgomet et al., 2017). This glycosylation in the hydroxyl groups (OH) present in the aromatic rings of polyphenols may have a negative effect in the scavenging activity, since these groups are involved in the inhibition step of free radicals (Cyboran-Mikolajczyk et al., 2018, 2019). This fact could explain the lower activity for MW crudes compared to soaking´ by ORAC assay.

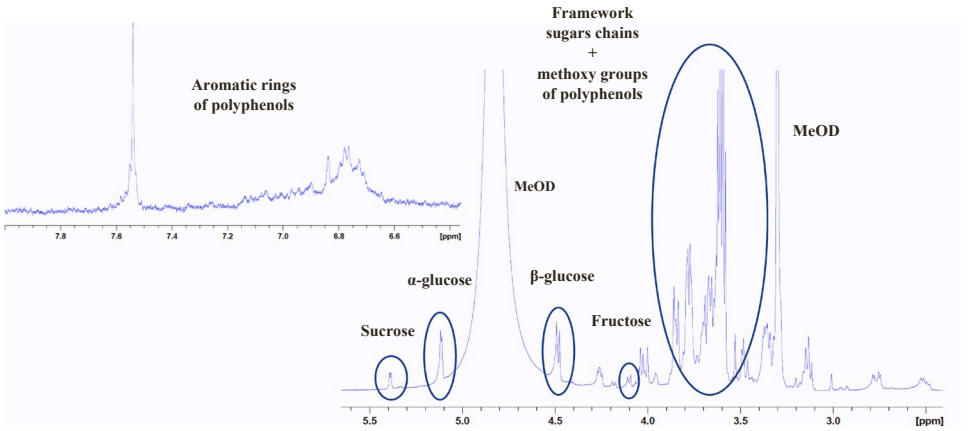

Fig. 3. Main identified sugars by ^{1}H NMR (MeOD, 500 MHz) in the liquid fraction obtained by soaking and microwave (MW)-assisted extraction (MAE) from almond hull (AH) biomass.

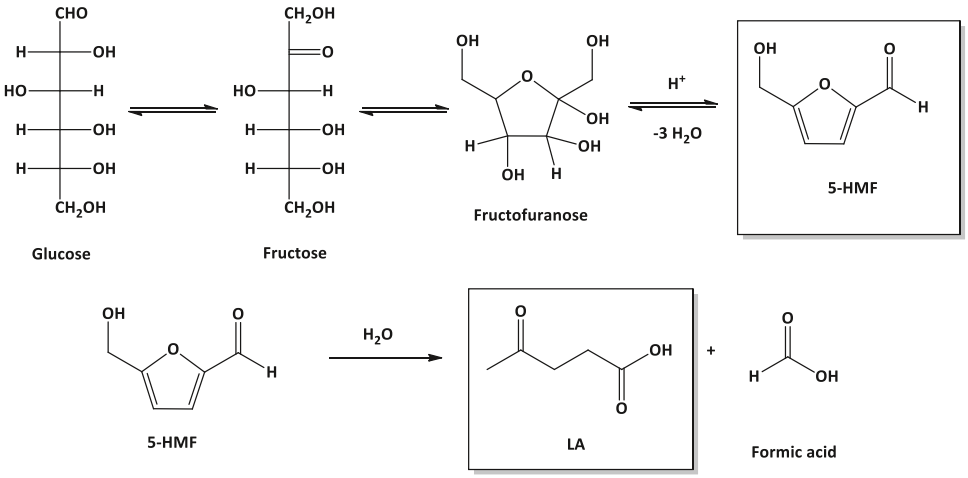

Fig. 4. General chemical path from cellulose to levulinic acid (LA) via 5-hydroxymethylfurfural (5-HMF).

Concurrently, owing to similar polarities, the extraction of BACs usually involves the recovery of sugars from the matrix, as detected by NMR (Fig. 3). These compounds are also considered as high-added-value compounds because of their direct application in the food sector, as well as being a valuable feedstock to obtain other fine chemicals, such as LA. In this way, quantitative NMR (qNMR) allowed us to determine the concentration of sugars (mainly glucose and sucrose) present in the liquid crudes after both MAE and soaking (Table 2). Once again, MW was demonstrated to be a more efficient approach for sugar recovery compared to soaking as well, since despite the same amount of glucose and sucrose detected, the obtention of MW crudes only took 2 h compared to 24 h for conventional systems, as mentioned.

3.2. Valorization of almond hull (AH) towards levulinic acid (LA)

Levulinic acid (LA) production from lignocellulosic biomass usually involves two steps: the first one consists of the hydrolysis of the cellulose fraction into glucose and the second step is based on the dehydration of these glucose units into LA (Fig. 4). Both hydrolysis and dehydration take place under acidic conditions. For this purpose, it is commonly accepted to employ the use of mineral acids, such as H_2SO_4 or HCl, which have already been demonstrated to be useful for LA obtention from different biomass sources, with high relative yields (≈40–50 %), under MW treatment too (Galletti et al., 2012; Szabolcs et al., 2013; Tukacs et al., 2017).

Nonetheless, this work was focused on the use of sustainable and reusable acidic catalysts, such as *p*-toluenesulfonic acid (*p*-TsOH), which has been already reported for the synthesis of LA from glucose (Kang et al., 2017). The significance of this catalyst lies in its high acidity, like other mineral acids such as H_2SO_4, in relation to their pKa values (−2.8 *versus* −3 for H_2SO_4), as well as its recovery and reusability from the reaction crude. On the other hand, the effectiveness of a sustainable Lewis acid such as $AlCl_3$•6 H_2O, which has been already reported for 5-HMF and LA (Jiang et al., 2015; Li et al., 2014), was also tested.

For this transformation, the employment of biphasic systems is commonly used (Dutta et al., 2022; Mellmer et al., 2014). Therefore, the organic green solvent would serve as storage for LA after being formed in the aqueous phase, thus avoiding further decomposition. Some ideal properties for these solvents would be, for instance, no volatility, high affinity for the desired compounds as well as facilitated recovery from the organic phase, and finally green properties. However, for this work, an aqueous monophasic system was employed. The reason was to try to drive the reaction directly to LA by the hydration of 5-HMF, which can only be isolated with the use of a biphasic system. Thus, this intermediate step towards the generation of LA would not take place, thus ensuring a subsequent reduction in terms of total yield of said intermediate compound. Moreover, the use of water as solvent would also pave the way for a more sustainable system.

For the experiments, three different AH-derived products were considered: i) almond hull dried biomass (AH-DB), composed of fibers

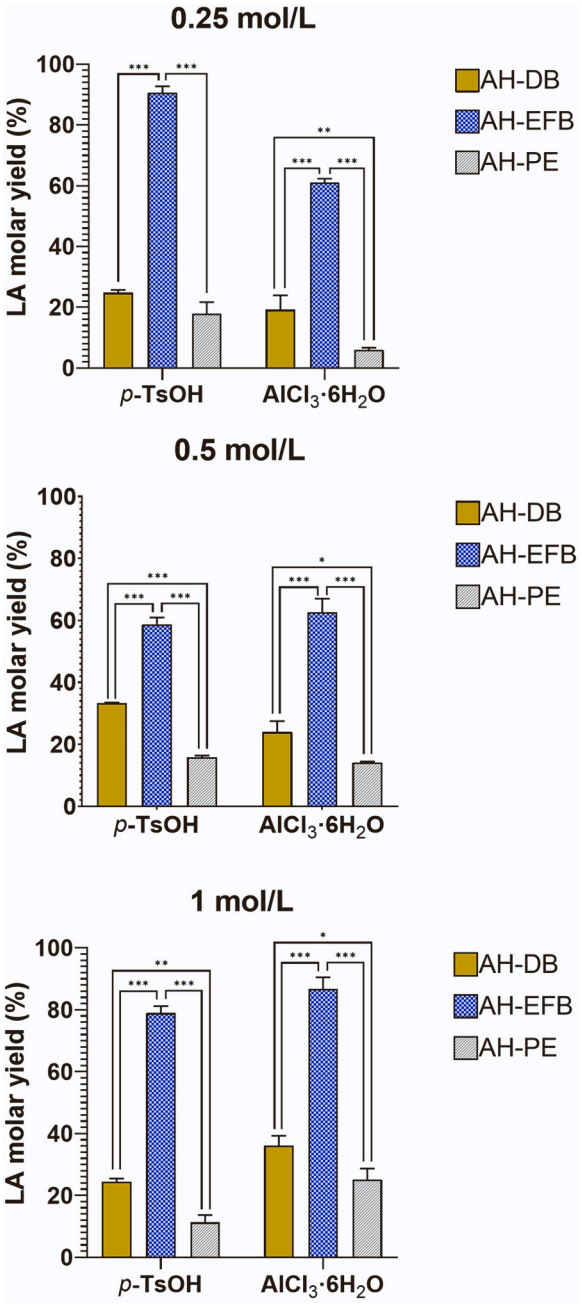

Fig. 5. Transformation towards levulinic acid (LA) from the almond hull (AH) derived dried biomass (DB), extractives-free biomass (EFB) and polar extract (PE): a) 0.25 mol/L of catalyst, b) 0.5 mol/L of catalyst and c) 1 mol/L of catalyst. Reaction conditions: AH-derived: 0.10 g; catalyst: *p*-toluenesulfonic acid (*p*-TsOH) or $AlCl_3$•6 H_2O (2 mL of acidic solution); co-catalyst: KBr (0.35 g). 190 °C, 20 min. Microwave (MW)-assisted radiation. * = $p < 0.05$; * * = $p < 0.01$; * ** = $p < 0.001$.

(cellulose, hemicellulose and lignin) and extractives (mainly freely accessible mono- and disaccharides); ii) almond hull extractives-free biomass (AH-EFB), solely composed of fibers and iii) almond hull polar extract (AH-PE), mainly composed of freely accessible mono- and disaccharides (Salgado-Ramos et al., 2022b), all of them being a hexose rich fraction.

Despite some works in the available literature report the development of LA from xylose or even hemicellulose (Chamnankid et al., 2014; Gurbuz et al., 2012), the established reaction conditions in terms of temperature (190 °C) could favor their fast decomposition into undesired products, since it has been reported that temperatures above 170 °C would trigger side reactions from these matrices (Guenic et al., 2015; Lopes et al., 2017). Thus, the hemicellulose fraction, which is present in quantities ~9 % in AH (Salgado-Ramos et al., 2022b), was ruled out for LA production in this work, with LA production being limited to only cellulose (7.44 %) and freely accessible mono- and disaccharides (36.25 %).

Therefore, Fig. 5 shows the obtained results after the use of both Brønsted (*p*-TsOH) and Lewis acids ($AlCl_3$•6 H_2O) at 0.25, 0.5 and 1 mol/L, which were effective for the hydrolysis of cellulose to LA.

Firstly, as mentioned, the role of KBr (in general for halide salts) is to accelerate dehydration step towards desired products. Both the nucleophilicity and basicity of the anion, as well as the atomic ratio for cation strongly influence the process (Enslow and Bell, 2015a). Based on previous studies in our group, KBr was the optimal choice for monophasic system to obtain LA as well, thus being selected for this work.

Furthermore, from Fig. 5a it can be seen that AH-EFB led to the best LA molar yield, with its values being significantly higher when compared to those obtained for AH-DB and AH-PE ($p < 0.001$). It should be noted that the reaction conditions used here were reported in our previous studies for the transformation of microcrystalline cellulose to LA (Lorente, 2019), involving both hydrolysis and dehydration steps. AH-EFB is only composed of cellulose, hemicellulose and lignin, without any free carbohydrates, therefore these conditions can be considered as optimal, achieving yields near to 90 % and above 60 % in terms of LA for *p*-TsOH and $AlCl_3$•6 H_2O, respectively (Fig. 5a). In addition, LA yields were not significantly different for AH-DB and AH-PE for the former (25 % vs. 18 %, $p > 0.05$) in contrast to $AlCl_3$•6 H_2O experiments (20 % vs. 6 %, $p < 0.01$).

Compared to AH-EFB, which is rich in cellulose, both AH-DB and AH-PE are mainly comprised of free sugars (Salgado-Ramos et al., 2022b). While the studied conditions are optimal for cellulose conversion, it may be too harsh for sugars and trigger side reactions. This fact might be attributed to the low activation energy found for side reactions (decomposition, polymerization, etc) in contrast to the energy required to obtain the desired product by dehydration step, as occurs in some of these kinds of reactions (Weingarten et al., 2010).

Therefore, despite the engaging achieved yields for both *p*-TsOH and $AlCl_3$•6 H_2O after using AH-EFB as starting material, the subsequent experiments for AH-DB and AH-PE led to unpromising results. For that reason, the effect of the catalyst load was studied, increasing the acid concentration until 0.5 and 1 mol/L, with the rest of parameters remaining constant. Results are shown in Fig. 5b and c.

Firstly, considering the activity of the stronger acid catalyst (*p*-TsOH), it was observed that after using the higher *p*-TsOH loads, the lowest LA yields were obtained, except for AH-DB. According to the literature (Hu et al., 2015), excessive acidity resulting from Brønsted acids can lead to undesirable side reactions, such as polymerization between sugars and derivatives. Thus, an increase in terms of *p*-TsOH load from 0.25 to 0.5 mol/L led to LA yields from 91 % to 59 % in AH-EFB (Fig. 5a and b). Despite of that, a significance difference was still found respect to both AH-DB and AH-PE ($p < 0.001$). Further, it should be noted that Brønsted acids are considered useful for enhancing cellulose hydrolysis by attacking the C-O-C glycosidic bond, as well as for initiating the conversion of fructose into 5-HMF, based on Fig. 4 (Román-Leshkov and Davis, 2011; Weingarten et al., 2013). This last finding could explain the fact that LA yield in AH-PE did not decrease and remained almost unchanged (18 % vs. 16 % at 0.25 and 0.5 mol/L, respectively), whereas AH-DB lead to a slight improvement in terms of LA, from 25 % to 33 %, mainly due to the cellulose fraction, in contrast to AH-PE, in which only free carbohydrates are present. Moreover, this increase for AH-DB led to significantly higher yields when compared to AH-PE at 0.5 mol/L ($p < 0.001$).

On the other hand, Lewis acids mainly promote the isomerization of glucose into fructose (Yu et al., 2016), which could improve the LA yield. Furthermore, it has been also reported that Lewis's acids can be

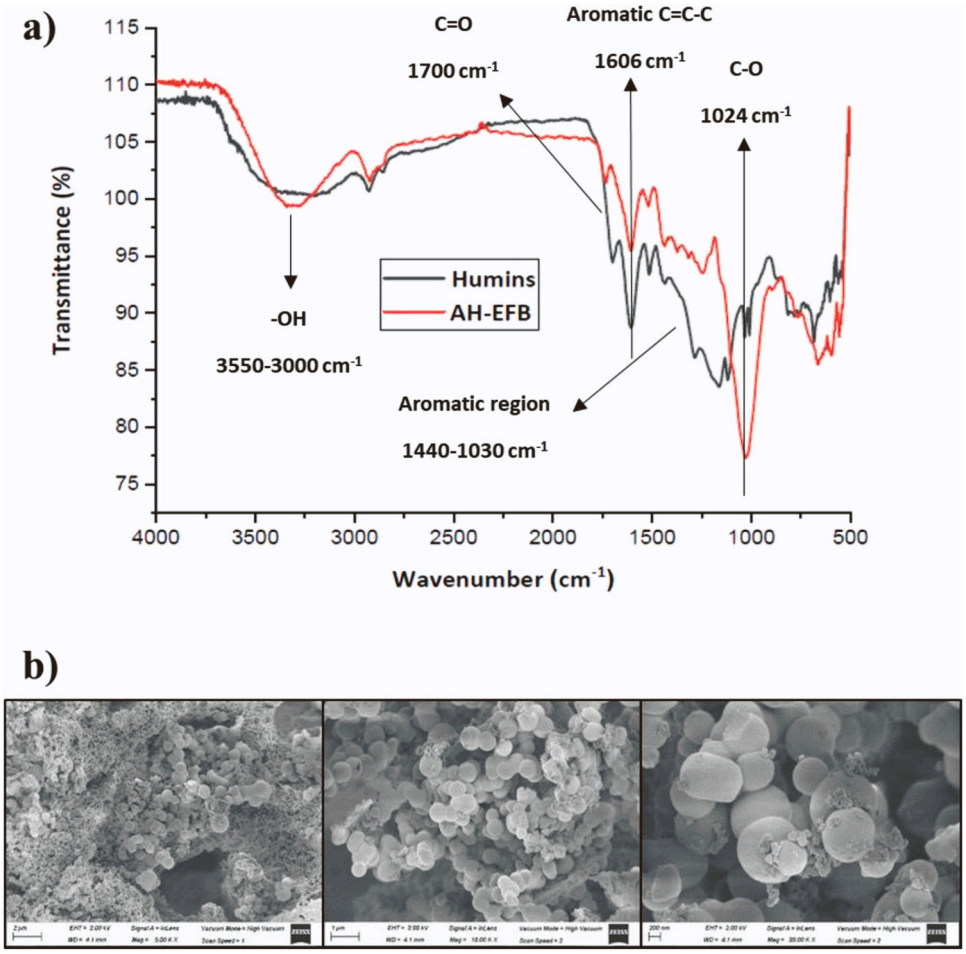

Fig. 6. a) FT-IR spectra for almond hull extractives-free biomass (AH-EFB) (red) and humins derived from AH-EFB for experiments at 0.25 mol/L of *p*-toluenesulfonic acid (*p*-TsOH) (black) and b) SEM images at different magnifications for humins derived from AH-EFB experiments at 0.25 mol/L of *p*-toluenesulfonic acid (*p*-TsOH).

Table 3
Generation of levulinic acid (LA) from almond hull polar extract (AH-PE). Reaction conditions: AH-PE: 0.10 g; catalyst: 2 mL of aqueous acidic solution; co-catalyst: KBr (0.35 g). Microwave (MW)-assisted radiation.

	Catalyst	Catalyst load (mol/L)	Temperature (°C)	Time (min)	LA molar yield (%)
1	*p*-TsOH	0.10	190	20	8.06 ± 0.76
2	*p*-TsOH	0.25	190	10	8.61 ± 1.15
3	*p*-TsOH	0.25	150	20	5.81 ± 2.02
4	*p*-TsOH	0.25	150	40	8.15 ± 0.67
5	$AlCl_3 \cdot 6H_2O$	0.10	190	20	5.29 ± 1.24
6	$AlCl_3 \cdot 6H_2O$	2.00	190	20	12.70 ± 2.12
7	$AlCl_3 \cdot 6H_2O$	1.00	190	40	10.54 ± 0.32
8	$AlCl_3 \cdot 6H_2O$	1.00	150	40	10.27 ± 5.06

hydrolyzed, with the subsequent H^+ ion release in aqueous media (Choudhary et al., 2013; Enslow and Bell, 2015b), thus providing both Brønsted and Lewis acidity. These released protons could strongly contribute to the effective hydrolysis of cellulose and the further dehydration of fructose to 5-HMF previously mentioned, as well as to the rehydration of 5-HMF into LA. In that case, the higher $AlCl_3 \bullet 6\ H_2O$ loads employed, the higher LA yields obtained for the three tested solids, being AH-EFB again the best material towards LA obtention (63 % molar yield) compared to AH-DB and AH-PE (24 % and 14 %, respectively, $p < 0.001$) (Fig. 5b) at 0.5 mol/L, mainly again due to the highest proportion of cellulose.

Finally, a similar trend was also observed at 1 mol/L as well (Fig. 5c). In this way, the yield for AH-DB and AH-PE with this catalyst decreased largely due to the highly acidic conditions at this load, thus leading towards humin production. Moreover, as occurred at 0.5 mol/L, these two solids led to significant differences in terms of LA ($p < 0.01$), possibly due to the certain presence of cellulose in the former.

On the other hand, for these solids as well, an improvement in terms of LA with respect to both $AlCl_3 \cdot 6\ H_2O$ 0.5 mol/L and 0.25 mol/L using $AlCl_3 \cdot 6\ H_2O$ 1 mol/L was observed, although the obtained yields were not promising (Fig. 5). In this line, some authors reported that Lewis acids have a high rate of glucose decomposition, although the selectivity to LA is not remarkable, thus corroborating that most of the glucose could be transformed into humins within a pure Lewis acid catalytic system (Li et al., 2014; Wang et al., 2015). Furthermore Choudhary et al. (2013) also reported that Lewis's acid mainly facilitates the conversion of fructose and furans (5-HMF) to humins. This fact could thus explain why LA molar yields above 36 % were not obtained for AH-DB and 25 % for AH-PE despite the high glucose and fructose content, as it was discussed above. This difference was again significant ($p < 0.05$), attributed to the cellulose fraction in AH-DB as well. Finally, it should be noted once more the high LA yield observed for AH-EFB with the increasing of $AlCl_3 \cdot 6\ H_2O$ load, achieving above 80 % for 1 mol/L (Fig. 5c), significantly higher compared to both AH-DB and AH-PE ($p < 0.001$).

In parallel, humins derived from LA obtained under the best reaction conditions (AH-EFB, *p*-TsOH 0.25 mol/L) were analyzed by FT-IR and SEM to the best of our knowledge, thus evaluating their main properties

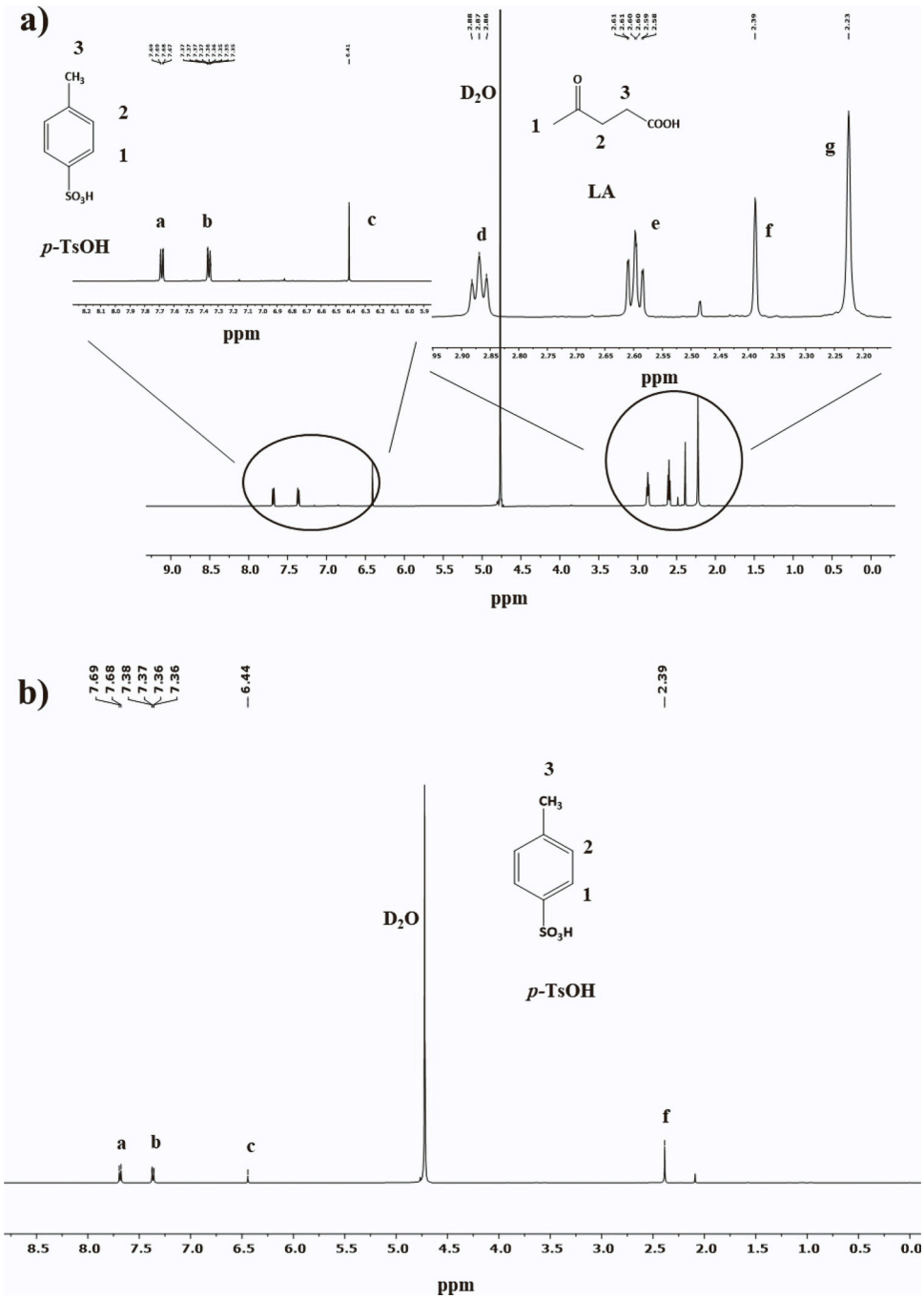

Fig. 7. ^{1}H NMR spectrum (D_2O, 500 MHz) of the organic crudes (OC) (a) and aqueous phase (AP) (b) for levulinic acid (LA) obtention after experiments with *p*-toluenesulfonic acid (*p*-TsOH).

Table 4
Chemical shifts regarding to the above ^{1}H NMR spectra (Fig. 7).

Signal	Chemical shift (ppm)	Multiplicity	Assignment	Identified
a	7.69	Doublet	H_1 (*p*-TsOH)	OC / AP
b	7.37	Doublet	H_2 (*p*-TsOH)	OC / AP
c	6.41	Singlet	IS[a]	OC / AP
d	2.88–2.86	Triplet	H_3 (LA)	OC
e	2.61–2.58	Triplet	H_2 (LA)	OC
f	2.39	Singlet	H_3 (*p*-TsOH)	OC / AP
g	2.23	Singlet	H_3 (LA)	OC

[a]IS: Internal standard; OC: Organic crude; AP: Aqueous phase.

in terms of composition and morphology. Concerning these materials, they are dark compounds, and tarry to solid and insoluble polymeric structures promoted under the decomposition or fragmentation of LA, as well as by the condensation of these products with the initial glucose, thus promoting a decrease in terms of LA (Filiciotto et al., 2018; van-Zandvoort et al., 2013). Results for these analyses are shown in Fig. 6.

The FT-IR spectra (Fig. 6a) suggests the presence of aromatics structures in the humins, as it is possible to observe mainly by the C=C-C vibration (1606 cm^{-1}) band. Furthermore, this aromaticity could be particularly marked for the bands between 1440 and 1030 cm^{-1}, related to the C-H and C-O bonds of the aromatic rings (Sevilla et al., 2011; Xiao et al., 2014). On the whole, the decrease observed for humins in the C-O band at 1024 cm^{-1}, mainly related to C-O-C stretch for primary alcohols

in cellulose, along with the increasing in terms of aromaticity compared to the solid AH-EFB, confirms the progressive depolymerization of cellulose from this solid into LA (Lorente et al., 2020), thus augmenting the aromatic moiety in the obtained humins after reaction.

This aromaticity could be also proposed considering the SEM images (Fig. 6b). For instance, as it can be seen in the figure, there are plenty of clustered microspheres, which could be associated with furan structures according to some authors (Filiciotto et al., 2018; vanZandvoort et al., 2013).

Therefore, when higher *p*-TsOH loads are used, lower LA molar yields are obtained, this catalyst being useful at low concentrations (0.25 mol/l), especially for AH-EFB (approximately 90 %). In contrast, the lower acidity of $AlCl_3{\cdot}6\ H_2O$ compared to *p*-TsOH could explain that, in order to achieve molar yields above 80% from AH-EFB as well, higher catalyst loads (1 mol/L) would be required. Overall, the application of enabling, green technologies, such as MW radiation, along with both the use of reusable catalysts such as *p*-TsOH and the avoidance of organic solvents, would pave the way to the first, sustainable upgrading of AH towards LA, to the best of our knowledge, fully adhering to Green Chemistry.

Finally, as previously discussed, the presence of free carbohydrates in AH-PE might require milder conditions to achieve higher yields, since the depolymerization step of cellulose is not required. Bearing this in mind, and in order to improve LA yields, further reactions from AH-PE were carried out. For that purpose, reaction conditions were softened in terms of acid concentration, reaction time or temperature. Despite this effort, no improvement was observed (Table 3).

For all reactions from AH-DB, AH-EFB and AH-PE, qNMR was applied for LA molar yields, considering the integral value for LA signals (Eqs. 1–2). Fig. 7a shows a ^{1}H NMR spectrum for organic crudes (OC) from the experiments with *p*-TsOH, being possible to observe LA and *p*-TsOH signals. Despite there being trace amounts in the OC, *p*-TsOH can be recycled from aqueous phase (AP) (Fig. 7b), being useful for further transformations and corroborating its sustainability. The main chemical shifts and multiplicity of these signals are detailed in Table 4.

4. Conclusions

In this work, a sustainable, efficient valorization via microwave (MW)-assisted radiation for the lignocellulosic waste of almond hull (AH) has been developed for the first time, to the best of our knowledge. It has been noted the transformation of the AH towards levulinic acid (LA) production, an interesting platform chemical, under green conditions after using sustainable Lewis ($AlCl_3{\bullet}6\ H_2O$) and Brønsted (*p*-toluenesulfonic (*p*-TsOH)) acidic catalysts. From a sustainability perspective, the reaction system by these two catalysts shows remarkable advantages, such as less corrosion or the recyclability of *p*-TsOH compared to the use of the mineral acids H_2SO_4 and HCl. The so-called solid almond hull extractives-free biomass (AH-EFB) led to promising results, achieving near to 90 % with the employment of *p*-TsOH 0.25 mol/L and $AlCl_3{\bullet}6\ H_2O$ 1 mol/L. In contrast, from the almond hull polar extract (AH-PE) and derived almond hull dried biomass (AH-DB) non-significant results compared to AH-EFB were achieved, largely due to the high amount of free carbohydrates present in these solids which could enhance side reactions towards humins. Nonetheless, it is worthy to note the suitable exploitation of these humins derived for LA transformation for biobased materials, catalysis or CO_2 capture, suggesting another pathway for valorization, close to the desired zero-waste, and therefore, to sustainability.

In a parallel experiment, the valorization of AH as a source of antioxidants was carried out. In this context, the results obtained demonstrated the efficiency of MW heating as a useful tool to recover biologically active compounds (polyphenols) compared to conventional methods (i.e., soaking). Moreover, the mild conditions in terms of temperature and time demonstrate MW to be an interesting tool for polyphenol recovery from AH.

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CRediT authorship contribution statement

Manuel Salgado-Ramos: Methodology, Formal analysis, Writing – original draft, Writing – review & editing. **Francisco J. Martí-Quijal:** Methodology, Formal analysis, Writing – original draft, Writing – review & editing. **Alberto J. Huertas-Alonso:** Methodology, Formal analysis. **M. Prado Sánchez-Verdú:** Conceptualization, Resources, Funding acquisition, Project administration, Supervision, Writing - review & editing. **Francisco J. Barba:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Andrés Moreno:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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