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Country report

Ultrasounds application for nut and coffee wastes valorisation via biomolecules solubilisation and methane production

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ABSTRACT

Lignocellulosic materials (LMs) are abundant feedstocks with excellent potential for biofuels and biocommodities production. In particular, nut and coffee wastes are rich in biomolecules, e.g. sugars and polyphenols, the valorisation of which still has to be fully disclosed. This study investigated the effectiveness of ultrasounds coupled with hydrothermal (i.e. ambient temperature *vs* 80 °C) and methanol (MeOH)-based pretreatments for polyphenols and sugar solubilisation from hazelnut skin (HS), almond shell (AS), and spent coffee grounds (SCG). The liquid fraction obtained from the pretreated HS was the most promising in terms of biomolecules solubilisation. The highest polyphenols, i.e. 123.9 (±2.3) mg/g TS, and sugar, i.e. 146.0 (±3.4) mg/g TS, solubilisation was obtained using the MeOH-based medium. However, the MeOH-based media were not suitable for direct anaerobic digestion (AD) due to the MeOH inhibition during AD. The water-based liquors obtained from pretreated AS and SCG exhibited a higher methane potential, i.e. 434.2 (±25.1) and 685.5 (±39.5) mL CH_4/g $glucose_{in}$, respectively, than the HS liquors despite having a lower sugar concentration. The solid residues recovered after ultrasounds pretreatment were used as substrates for AD as well. Regardless the pretreatment condition, the methane potential of the ultrasounds pretreated HS, AS, and SCG was not improved, achieving maximally 255.4 (±7.4), 42.8 (±3.3), and 366.2 (±4.2) mL CH_4/g VS, respectively. Hence, the solid and liquid fractions obtained from HS, AS, and SCG showed great potential either as substrates for AD or, in perspective, for biomolecules recovery in a biorefinery context.

1. Introduction

The search for alternative sources of energy is a crucial aspect to guarantee the sustainable development of human activities. In this perspective, recovery and valorisation of waste materials, e.g. lignocellulosic materials (LMs), offers a great opportunity (Velvizhi et al., 2022). LMs are abundant wastes produced during agricultural, municipal and industrial activities (Koupaie et al., 2019). LMs are mainly composed of cellulose, hemicellulose, and lignin linked together in a complex structure that hinders their decomposition and valorisation. In particular, the presence of lignin creates a physical barrier around cellulose and hemicellulose sugars (Xu et al., 2019). Apart from those three main biopolymers, depending on the specific characteristics of the LM, these substrates can be rich in valuable biomolecules, such as polyphenols, low molecular sugars, protein, and oils (Mirmohamadsadeghi et al., 2021).

Nuts and coffee wastes, in particular, are emerging as a new source of valuable products besides having a high methane potential (Battista et al., 2021; Oliva et al., 2021; Shen et al., 2018). The cultivation of nut trees is mainly located in USA, Turkey and China. Nevertheless, nuts are exported worldwide, either with or without the shell (International Nut and Dried Fruit Council Foundation, 2021 Nut and Dried Fruit Council Foundation, 2021). The edible part of nuts only represents a small portion compared to the amount of wastes, i.e. shells, leaves, husks, and skins, generated during the harvesting season (Shen et al., 2018). Coffee trees are mainly cultivated in Africa, South and Central America (International Coffee Organization, 2020). A considerable amount of waste is produced along the coffee production chain. Firstly, the outer skin, pulp, parchment, and silver skin are removed from the coffee beans, generally in the production country. After that, coffee is exported worldwide generally as green beans. Coffee beans are usually roasted and ground *in loco* before being packed to be sold (Murthy and Naidu, 2012). The waste production behind a cup of coffee continues with the beverage production. The spent coffee grounds generation amounts to

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roughly 6 million tons per year (Battista et al., 2021).

Anaerobic digestion (AD) is an advantageous and widely explored process for LMs valorisation. During the first stage of AD, carbohydrates, proteins and lipids are hydrolysed into sugars, amino acids, and long-chain fatty acids (Bianco et al., 2021a). The hydrolysis stage is considered the limiting step for AD of LMs due to recalcitrance caused by lignin protection and the complex bonds among cellulose, hemicellulose and lignin (Sawatdeenarunat et al., 2015). In the second stage, i.e. acidogenesis, the soluble monomers are fermented into alcohols, volatile fatty acids, and hydrogen before being converted into acetate, carbon dioxide and hydrogen during the acetogenic stage. During the fourth and last phase, archaea utilise acetic acid and hydrogen to produce methane (Li et al., 2019).

The need to enhance the methane production from LMs has led to the development of several pretreatment methods that focus, in the first place, on removing the most recalcitrant components, but also on obtaining selected liquid or solid streams that can be further valorised following other patterns than AD (Oliva et al., 2022a). In this perspective, the use of ultrasounds is a promising pretreatment technique. Ultrasounds have been widely used to enhance the methane potential of sludge, digestate and manure (Garoma and Pappaterra, 2018; Ormaechea et al., 2018). In addition, this technique has been recently tested on LMs (Korai and Li, 2020; Zou et al., 2016b). Ultrasonic waves generate cavitation phenomena in the liquid medium that affect the lignocellulosic structure by removing part of the lignin and reducing the crystallinity and degree of polymerisation of cellulose. On the other hand, a partial sugar hydrolysis can occur (Bundhoo and Mohee, 2018). In addition, an ultrasounds pretreatment can be easily combined with other techniques, combining the effect of chemical and physical pretreatments (Oliva et al., 2022a).

This study investigated for the first time the combination of ultrasounds with thermal and methanol (MeOH)-based pretreatment on nut and coffee residues, i.e. hazelnut skin (HS), almond shell (AS), and spent coffee grounds (SCG). The ultrasounds pretreatment was performed at ambient temperature (T_{amb}) and 80 °C, and the influence of different media, i.e. distilled water and a 50% (*v/v*) MeOH solution catalysed by sulfuric acid, on the chemical composition of the solid residues and the compounds released in the liquid fraction was studied. Several studies focused on obtaining methane via AD from the slurry obtained after a pretreatment. In contrast, this study aimed to disclose the optimal route for each solid and liquid fraction recovered after the pretreatment of HS, AS, and SCG, based on their specific composition. The liquid fraction obtained after ultrasounds pretreatment was characterised in terms of sugar and polyphenolic compounds before undergoing AD. The optimal pathway to valorise the liquid fraction obtained in the various pretreatment conditions was discussed depending on the specific characteristics of the liquor. Raw and pretreated solid residues were subjected to AD as well to understand the correlation between the various pretreatment conditions and the methane potential of the solid residues.

2. Materials and methods

2.1. Substrates and inoculum

The three substrates selected for the present study, i.e. HS, AS, and SCG, were obtained, prepared, and stored according to Oliva et al. (2021) before undergoing AD. Digestate from buffalo manure (DBM) was collected from a full-scale AD plant and degassed before being used as the inoculum for the experimental activities. The total (TS) and volatile (VS) solid content of the inoculum and raw LMs is shown in Table 1.

2.2. Ultrasounds pretreatment

The ultrasounds pretreatment was performed using a DL 510H ultrasonic bath (Bandelin, Berlin, Germany) with frequency, nominal power, and amplitude of 35 kHz, 160 W, and 100%, respectively. Two different media were tested for ultrasonic waves diffusion, i.e. distilled water and 50% (*v/v*) water-MeOH solution catalysed by 0.1% (*w/v*) sulfuric acid (MeOH-based). The pretreatment was performed in 250 mL Duran bottles filled with 15 g of LM and 150 mL of medium. Four bottles at a time were placed in the ultrasonic bath. The ultrasounds pretreatment was performed for 1 h at T_{amb} and 80 °C. The bottles containing the LMs were shaken manually every 10 min during the pretreatment. The energy density (E_d) was calculated following Eq. (1), as reported by Zou et al. (2016):

$$E_d = \frac{P \bullet t}{m \bullet TS_0} \quad (1)$$

where P (W) is the nominal ultrasonic power, t (min) is the pretreatment time exposure, m (kg) is the mass of LMs undergoing the pretreatment, and TS_0 (g/g) is the total solid content of the LMs before the pretreatment.

After the pretreatment, the solid residues were separated from the liquor using a textile cloth, washed with abundant distilled water, and dried at 40 °C before being used as the substrate for AD. The liquor was taken for characterisation and stored at − 20 °C until evaluation of the methane potential.

Table 1
Characterisation of the inoculum, i.e. digestate from buffalo manure (DBM), and raw substrates, i.e. hazelnut skin (HS), almond shell (AS), and spent coffee grounds (SCG), in terms of total (TS) and volatile (VS) solid content.

	DBM	HS	AS	SCG
TS [a] (%)	5.8 ± 0.0	90.5 ± 0.1	90.2 ± 0.1	90.1 ± 0.2
VS [a] (%)	4.0 ± 0.0	87.9 ± 0.1	87.1 ± 0.8	88.5 ± 0.2
VS/TS (g/g)	0.70	0.97	0.96	0.98

[a] TS and VS are based on g/100 g wet matter.

2.3. Methane potential assessment

The methane potential of raw and pretreated LMs, as well as the liquors obtained under the various pretreatment conditions, was evaluated by performing batch biochemical methane potential (BMP) tests in 250 mL serum bottles (OCHS, Bovenden, Germany). The bottles were kept under mesophilic, i.e. 37 (±1) °C, conditions. The anaerobic conditions were ensured by flushing the reactors with Argon gas.

The first set of experiments aimed to evaluate the methane potential of raw and the solid fraction of pretreated LMs. Each bottle was loaded with 1 g VS from raw or pretreated LMs (liquid phase decanted) and 1.5 g VS from DBM. A final solid content of 2.1% TS was achieved by adding demineralised water, reaching the final working volume of 150 mL. The second set of experiments evaluated the methane potential of the liquor obtained after the pretreatment. Each bottle was filled with 30 mL of the liquor upon completion of the ultrasounds pretreatment, 1.5 g VS from DBM, i.e. 37.2 g, and an amount of demineralised water calculated to reach the same moisture as in the first set of experiments, i.e. 2.1% TS, regardless the working volume. Control biochemical tests were simultaneously carried out to evaluate the methane potential of the inoculum. In the second experimental set, the methane potential of the media was evaluated to account for the presence of MeOH during batch assays. All experiments were performed in triplicate, and the bottles were shaken manually once per day.

2.4. Analytical methods and calculations

The TS and VS content of the inoculum and raw and pretreated LMs was measured according to the standard methods (APHA, AWWA, WEF, 2005). The chemical composition, i.e. total extractives, structural sugars, lignin, and ashes, of raw and pretreated substrates was determined by Celignis Limited (Limerick, Ireland), as previously described by Oliva et al. (2021).

The substrate solubilisation was calculated by comparing the amount of TS from raw and pretreated substrates following Eq. (2).

$$Substratesolubilisation(\%) = \frac{TS_{raw} - TS_{pretreated}}{TS_{raw}} \bullet 100 \quad (2)$$

where TS_{raw} and $TS_{pretreated}$ is the amount (g) of TS from each substrate before and after the ultrasounds pretreatment.

A mass balance assessment was performed considering the percentage of substrate solubilised and the chemical composition measured before and after each pretreatment. The balance returns the amount (g) of each lignocellulosic component present in the raw substrate and the solid fraction recovered after the ultrasounds pretreatment.

The liquor obtained from the ultrasounds pretreatment was collected for pH measurements and determination of soluble polyphenols and sugar concentration. The pH of the liquor was measured with a HI-98103 pH meter (Hanna Instruments, Woonsocket, USA). The concentration of soluble polyphenols was determined following the Folin-Ciocalteu (F-C) method, according to Cubero-Cardoso et al. (2020). The absorbance was read at 655 nm using a V-530 UV/VIS spectrophotometer (Jasco, Tokyo, Japan). The total sugar concentration was measured according to the Dubois method (Dubois et al., 1956) using a 7600 UV–Vis spectrophotometer (Xylem, Weilheim, Germany) to read the absorbance at 492 nm. The polyphenols and sugar concentrations were determined using phenol crystals (C_6H_6O) and glucose ($C_6H_{12}O_6$) as the standards for the calibration curve, respectively.

The methane production from the first set of experiments was quantified volumetrically using a water displacement apparatus consisting of a Drechsel bottle and a glass cylinder (Glass Studio, Naples, Italy) connected by a capillary tube, as described by Papirio (2020). The Drechsel bottle was filled with a 12% NaOH solution used for carbon dioxide sequestration. The glass cylinder was used to measure the volume of water displaced by the methane that surpassed the carbon dioxide trap. The water displaced corresponds to the amount (mL) of methane produced between two measuring points (Filer et al., 2019). In the second set of experiments, a different method was used to measure the methane production from the liquor obtained after the ultrasounds pretreatment. The biogas production was evaluated manometrically, as described by Oliva et al. (2021). The gas composition was determined with a HPR-20 RD mass spectrometer (Hiden Analytical, Warrington, UK) equipped with a capillary tube heated at 140 °C and capable of analysing 0.8 mL/min of the gas mixture accumulated in the headspace of the serum bottles.

The net cumulative methane production from the two sets of experiments was calculated as the average of the biological triplicates after subtracting the average methane production of the controls. The methane potential of the raw LMs and the solid residues recovered after ultrasounds pretreatment was expressed as mL CH_4/g VS, whereas the methane production from the liquors was reported as mL CH_4/100 mL liquor. The methane potential of the liquors was also calculated per grams of initial glucose (i.e. mL CH_4/g $glucose_{in}$) for a better understanding of the efficiency of the substrate utilisation during AD. Methane production was recorded regularly until the daily accumulation was below the negligible threshold in all bottles, i.e. 1% of the cumulative production (Holliger et al., 2016).

2.5. Model fitting

The experimental data obtained from the BMP tests digesting raw LMs and the solid residues recovered after the ultrasounds pretreatment were compared with a modified Gompertz model (Mancini et al., 2018). The kinetics of methane production were estimated following Eq. (3):

$$G(t) = G_m \bullet \exp\left\{ -exp\left[\frac{R_m \bullet e}{G_m} \bullet (\lambda - t) + 1\right]\right\} \quad (3)$$

where G_m (mL CH_4/g VS) and R_m (mL CH_4/g VS/d) are, respectively, the maximum specific methane potential and rate assessed with the model, λ (d) is the lag phase time, t (d) is the time of the AD process, G(t) (mL CH_4/g VS) is the cumulative specific methane production achieved at t (d), and e = exp (1).

The model fitting was conducted using the Origin2018 software (OriginLab Corporation, Northampton, USA). The correlation coefficient (r^2) between experimental and model data was obtained with the Excel 2016 software (Microsoft Corporation, Redmond, USA).

2.6. Statistical comparison

The significance of the changes in methane potential, chemical composition, as well as polyphenols and sugar solubilised, among the various pretreatment conditions was evaluated using Minitab 17 Statistical Software (Minitab LCC, USA). A one-way analysis of variance (ANOVA) followed by the Tukey post hoc test was performed. The difference was considered statistically significant when the p-value was below 0.05.

3. Results

3.1. Polyphenols and sugar solubilisation using ultrasounds

Table 2 shows that HS solubilisation increased with ultrasounds temperature and was higher when using the MeOH-based medium. The maximum solubilisation (i.e. 23.5%) was achieved when applying ultrasounds at 80 °C in the MeOH-based medium. In contrast, the application of ultrasounds did not affect AS solubilisation (Table 2). The highest solubilisation for AS was 6.4%. Regarding SCG (Table 2), increasing the pretreatment temperature enhanced the substrate solubilisation by 35 and 26% in water and MeOH-based medium, respectively. On the contrary, the medium composition had only a minor impact on SCG. The maximum SCG solubilisation (i.e. 20.8%) was obtained at 80 °C in water. The pH of the liquors obtained after applying ultrasounds is reported in Table 2.

The HS liquor showed the highest concentration of released polyphenols and sugar. In particular, 11.48 (±0.07) and 11.21 (±0.21) g polyphenol/L were measured in the liquor when using the MeOH-based medium at T_{amb} and 80 °C, respectively. On the other hand, the pretreatment temperature enhanced polyphenols solubilisation when using H_2O as the medium. The polyphenols concentration was 4.83 (±0.02) g/L after ultrasounds at T_{amb}, whereas it increased to 7.24 (±0.11) g/L when the temperature was 80 °C. The sugar concentration measured in the liquor followed the same trend as polyphenols. Using the MeOH-based medium, ultrasounds solubilised 12.91 (±0.23) and 13.22 (±0.30) g sugar/L at T_{amb} and 80 °C, respectively. Water was less effective than the MeOH-based medium, resulting in 6.49 (±0.81) and 9.89 (±0.33) g sugar/L at T_{amb} and 80 °C, respectively.

Polyphenols solubilisation from AS was greatly influenced by the pretreatment temperature and medium composition, yet significantly lower than what achieved with HS ($p < 0.05$) (Table 2). The highest polyphenols concentration, i.e. 0.45 (±0.01) g/L, was measured in the MeOH-based liquor obtained at 80 °C. At the same temperature, the water medium enabled to solubilise only 0.24 (±0.01) g polyphenols/L from AS. A lower impact of the ultrasounds conditions was observed on the sugar solubilisation from AS (Table 2). The use of the MeOH-based medium at 80 °C was the most performing condition, resulting in 2.94 (±0.08) g sugar/L, whereas water at T_{amb} solubilised 1.96 (±0.17) g sugar/L.

Polyphenols and sugar solubilisation from SCG was influenced by the temperature and medium during the ultrasounds pretreatment (Table 2). Similarly to AS, the use of the MeOH-based medium at 80 °C resulted in the highest polyphenols concentration in the liquor, i.e. 0.78 (±0.02). On the contrary, using water at 80 °C was the most effective condition for sugar solubilisation from SCG, i.e. 2.72 (±0.07) g sugar/L. The pretreatment temperature greatly influenced the solubilisation of polyphenols and sugar from SCG when using water as the medium,

Table 2
Substrate solubilisation efficiency after ultrasounds, pH of the liquor, and polyphenols and sugars solubilised through ultrasounds using different media, i.e. distilled water and a 50% (*v/v*) methanol (MeOH) solution catalysed by 0.1% (*w/v*) sulfuric acid, at different temperatures, i.e. ambient temperature (T_{amb}) and 80 °C. The polyphenols and sugars are expressed as concentration measured in the liquor and as milligrams of biomolecule solubilised per gram of dry lignocellulosic material undergoing ultrasounds pretreatment.

Substrate	Pretreatment condition	Substrate solubilisation (%)	pH	Polyphenols (g/L)	Polyphenols (mg/g TS)	Statistical information [a]	Sugars (g glucose/L)	Sugars (mg glucose/g TS)	Statistical information [a]
Hazelnut skin	H_2O T_{amb}	14.6 ± 1.4	5.4	4.83 ± 0.02	53.4 ± 0.2	c	6.49 ± 0.81	71.7 ± 9.0	c
	H_2O 80 °C	17.2 ± 0.2	5.1	7.24 ± 0.11	80.0 ± 1.2	b	9.89 ± 0.33	109.3 ± 3.7	b
	MeOH T_{amb}	19.3 ± 0.1	3.7	11.48 ± 0.07	126.9 ± 0.7	a	12.91 ± 0.23	142.6 ± 2.5	a
	MeOH 80 °C	23.5 ± 0.4	4	11.21 ± 0.21	123.9 ± 2.3	a	13.22 ± 0.30	146.0 ± 3.4	a
Almond shell	H_2O T_{amb}	5.7 ± 0.2	5.1	0.07 ± 0.00	0.7 ± 0.0	d	1.96 ± 0.17	21.7 ± 1.8	c
	H_2O 80 °C	5.6 ± 0.0	4.9	0.19 ± 0.00	2.1 ± 0.0	c	2.47 ± 0.06	27.3 ± 0.6	b
	MeOH T_{amb}	5.6 ± 0.0	2.4	0.24 ± 0.01	2.7 ± 0.1	b	2.04 ± 0.04	22.6 ± 0.5	c
	MeOH 80 °C	6.4 ± 0.1	2.5	0.45 ± 0.01	5.0 ± 0.1	a	2.94 ± 0.08	32.6 ± 0.8	a
Spent coffee grounds	H_2O T_{amb}	15.4 ± 0.2	5.2	0.34 ± 0.02	3.8 ± 0.2	d	1.50 ± 0.08	16.7 ± 0.9	c
	H_2O 80 °C	20.8 ± 0.3	4.6	0.57 ± 0.02	6.3 ± 0.2	c	2.72 ± 0.07	30.2 ± 0.8	a
	MeOH T_{amb}	15.1 ± 0.5	3.3	0.65 ± 0.01	7.2 ± 0.1	b	1.72 ± 0.07	19.1 ± 0.7	b
	MeOH 80 °C	19.1 ± 0.1	3.2	0.78 ± 0.02	8.6 ± 0.2	a	1.89 ± 0.07	21.0 ± 0.8	b

[a] Significant difference, i.e. $p < 0.05$, occurs when two conditions do not share letters.

whereas it had a lower impact in the case of the MeOH-based medium (Table 2).

3.2. Liquor valorisation through anaerobic digestion

The liquor recovered after the ultrasounds pretreatment was used as the substrate for AD. Despite the low pH of the liquors (Table 2), once mixed with the inoculum, all BMP tests started at a pH ranging between 7.7 and 8.0 (Table S1). The gas compositional analysis revealed that only methane and carbon dioxide were produced during AD (data not shown). The methane potential of water-based liquors significantly increased with the pretreatment temperature ($p < 0.05$) for AS and SCG, whereas no significant difference for HS ($p > 0.05$) was observed (Table S1). The water-based liquors recovered after the HS pretreatment produced 85.3 (±12.2) and 79.9 (±5.6) mL CH_4/100 mL liquor when the ultrasounds pretreatment was performed at T_{amb} and 80 °C, respectively (Fig. 1). The water-based liquors obtained from AS and SCG showed an increased methane potential by 27 and 56% when the pretreatment occurred at 80 °C, achieving 107.0 (±6.2) and 160.9 (±16.6) mL CH_4/100 mL liquor, respectively (Fig. 1). The cumulative production

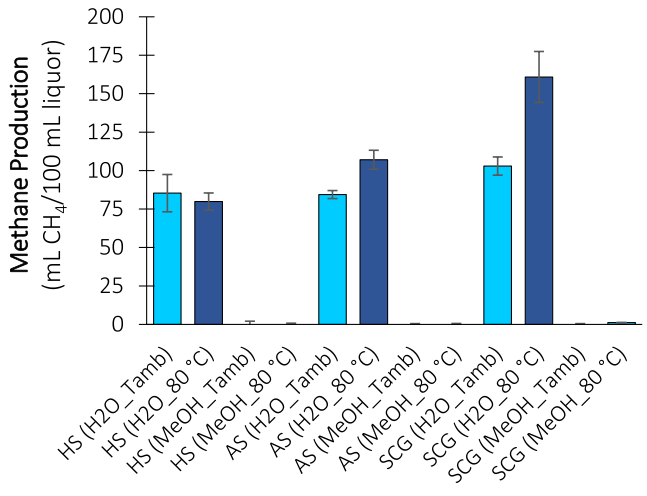

Fig. 1. Methane potential of the liquor recovered after the ultrasounds pretreatment of hazelnut skin (HS), almond shell (AS), and spent coffee grounds (SCG) performed at ambient temperature (T_{amb}) and 80 °C using different media, i.e. distilled water and a 50% (*v/v*) methanol (MeOH) solution catalysed by 0.1% (*w/v*) sulfuric acid.

(Fig. 1) showed that no methane was produced when the MeOH-based medium was used for ultrasounds diffusion, regardless the LM and the temperature used during the ultrasounds pretreatment (Fig. 1).

3.3. Impact of ultrasounds on the chemical composition of hazelnut skin, almond shell and spent coffee grounds solid residues

The compositional analysis (Table 3) revealed that, among the three untreated LMs, HS and AS have the highest lignin content, i.e. 39.7 (±0.1) and 37.0 (±0.4) g/100 g TS, respectively, whereas SCG has a lignin content of 18.7 (±0.4) g/100 g TS. On the other hand, the untreated SCG is rich in structural sugars, i.e. 43.2 (±0.1) g/100 g TS, with mannan (i.e. 54.4%), glucan (i.e. 21.8%), and galactan (i.e. 19.9%) being the most abundant. The overall sugar content of AS is 41.2 (±0.1) g/100 g TS. The sugar speciation showed that xylan (i.e. 63.8%) is dominant in AS, and glucan (i.e. 31.3%) is the second most abundant sugar. The untreated HS has only 13.7 (±0.1) g/100 g TS of structural sugars, mainly glucan (i.e. 74.5%). Apart from lignin and structural sugars, the total extractives represent 35.0 (±0.0) and 29.0 (±0.5) g/100 g TS of the overall dry matter of untreated HS and SCG, respectively. On the contrary, the total extractives content of untreated AS is 7.5 (±0.1) g/100 g TS.

The ultrasounds pretreatment removed up to 13.1% of the total extractives from HS (Table 3). The increase in the pretreatment temperature enhanced the removal of total extractives from HS ($p < 0.05$), regardless the medium. The lignin content in the pretreated HS decreased ($p < 0.05$) up to 10.5%. Consequently, the content of structural sugars increased ($p < 0.05$) up to 17.1 (±0.1) g/100 g TS after ultrasounds pretreatment of HS at 80 °C (Table S3). The mass balance assessment (Table S2) confirmed the solubilisation of extractives and lignin from HS under all the pretreatment conditions tested in this study. On the other hand, the solubilisation of structural sugars from HS was observed only at T_{amb}.

Regarding AS and SCG (Table 3), the ultrasounds pretreatment removed up to 50.7 ($p < 0.05$) and 18.6% ($p < 0.05$) of the extractives, respectively (Table S3). On the other hand, structural sugars and lignin concentrations measured in the pretreated AS and SCG were higher ($p < 0.05$) or comparable ($p > 0.05$) with the raw substrates, regardless the pretreatment condition (Table S3). The mass balance assessment (Table S2) showed that the lignin removal from AS and SCG was minimal compared to HS. In contrast, all pretreatment conditions enabled the removal of total extractives from AS and SCG. The solubilisation of structural sugars from SCG increased with the pretreatment temperature and was higher when using the MeOH-based medium. On the other

Table 3
Chemical composition of untreated and ultrasounds pretreated substrates expressed as total extractives, total structural sugars (i.e. glucan, xylan, mannan, arabinan, galactan, and rhamnan), total lignin, and ashes content. HS: hazelnut skin, AS: almond shell, and SCG: spent coffee grounds. Pretreatment media: distilled water and a 50% (*v/v*) methanol (MeOH) solution catalysed by 0.1% (*w/v*) sulfuric acid. Pretreatment temperature: ambient temperature (T_{amb}) and 80 °C.

Substrate	Pretreatment condition	Total Extractives (g/100 g TS)	Total Structural Sugars [a] (g/100 g TS)	Total Lignin [b] (g/100 g TS)	Ashes (g/100 g TS)	Unknown [c] (g/100 g TS)	Structural sugars speciation					
							Glucan (g/100 g TS)	Xylan (g/100 g TS)	Mannan (g/100 g TS)	Arabinan (g/100 g TS)	Galactan (g/100 g TS)	Rhamnan (g/100 g TS)
HS	untreated	35.0 ± 0.0	13.7 ± 0.1	39.7 ± 0.1	2.7 ± 0.1	8.9 ± 0.1	10.2 ± 0.1	1.0 ± 0.0	0.3 ± 0.0	0.7 ± 0.0	0.9 ± 0.0	0.7 ± 0.0
	H_2O T_{amb}	34.0 ± 0.0	14.0 ± 0.5	35.6 ± 0.2	2.1 ± 0.1	14.4 ± 0.14	10.6 ± 0.2	0.7 ± 0.0	0.2 ± 0.0	0.7 ± 0.1	1.0 ± 0.0	0.8 ± 0.1
	H_2O 80 °C	32.3 ± 0.5	17.1 ± 0.5	38.5 ± 0.4	1.6 ± 0.1	10.5 ± 0.6	11.4 ± 0.2	1.9 ± 0.2	0.4 ± 0.0	1.2 ± 0.0	1.2 ± 0.0	1.0 ± 0.1
	MeOH T_{amb}	33.8 ± 0.2	14.5 ± 0.6	36.2 ± 0.6	1.5 ± 0.0	14.1 ± 0.7	11.0 ± 0.4	0.8 ± 0.1	0.2 ± 0.0	0.7 ± 0.1	1.0 ± 0.0	0.8 ± 0.0
	MeOH 80 °C	30.4 ± 0.2	17.1 ± 0.1	36.4 ± 0.4	1.6 ± 0.1	14.5 ± 0.5	12.8 ± 0.1	1.0 ± 0.1	0.3 ± 0.1	0.8 ± 0.0	1.2 ± 0.1	0.9 ± 0.1
AS	untreated	7.5 ± 0.1	41.2 ± 0.1	37.0 ± 0.4	1.6 ± 0.1	12.6 ± 0.7	12.9 ± 0.2	26.3 ± 0.5	0.1 ± 0.0	0.7 ± 0.1	1.1 ± 0.1	0.2 ± 0.0
	H_2O T_{amb}	3.8 ± 0.1	40.6 ± 0.3	41.9 ± 0.3	0.5 ± 0.2	13.2 ± 0.4	12.4 ± 0.2	25.4 ± 0.1	0.0 ± 0.0	0.9 ± 0.0	1.3 ± 0.0	0.6 ± 0.0
	H_2O 80 °C	6.5 ± 0.5	43.4 ± 0.2	39.0 ± 0.2	0.1 ± 0.0	10.9 ± 0.6	16.2 ± 0.1	24.1 ± 0.0	0.0 ± 0.0	1.3 ± 0.0	1.4 ± 0.0	0.5 ± 0.0
	MeOH T_{amb}	3.7 ± 0.2	44.5 ± 0.3	41.1 ± 0.7	0.6 ± 0.2	10.2 ± 0.7	14.7 ± 0.1	27.4 ± 0.4	0.0 ± 0.0	0.9 ± 0.0	1.3 ± 0.0	0.3 ± 0.0
	MeOH 80 °C	4.0 ± 0.3	40.3 ± 0.1	41.8 ± 0.2	0.3 ± 0.1	13.7 ± 0.5	13.5 ± 0.1	24.9 ± 0.1	0.0 ± 0.0	0.6 ± 0.0	1.0 ± 0.0	0.3 ± 0.1
SCG	untreated	29.0 ± 0.5	43.2 ± 0.1	18.7 ± 0.4	1.4 ± 0.2	7.7 ± 0.7	9.4 ± 0.1	0.3 ± 0.1	23.5 ± 0.2	1.5 ± 0.0	8.6 ± 0.0	0.0 ± 0.0
	H_2O T_{amb}	24.5 ± 0.4	47.1 ± 0.2	21.6 ± 0.3	1.0 ± 0.1	5.9 ± 0.5	9.5 ± 0.0	0.1 ± 0.0	26.0 ± 0.2	1.7 ± 0.0	9.8 ± 0.0	0.0 ± 0.0
	H_2O 80 °C	26.2 ± 0.2	43.5 ± 0.3	20.9 ± 0.4	0.6 ± 0.0	8.9 ± 0.5	9.2 ± 0.1	0.1 ± 0.0	23.8 ± 0.2	1.4 ± 0.1	9.0 ± 0.0	0.0 ± 0.0
	MeOH T_{amb}	23.6 ± 0.0	48.6 ± 0.1	21.1 ± 0.3	0.1 ± 0.0	6.6 ± 0.5	9.6 ± 0.3	0.1 ± 0.0	26.8 ± 0.2	1.8 ± 0.0	10.2 ± 0.2	0.1 ± 0.0
	MeOH 80 °C	24.6 ± 0.1	46.0 ± 0.0	20.5 ± 0.0	0.1 ± 0.0	8.9 ± 0.6	9.8 ± 0.0	0.2 ± 0.1	25.3 ± 0.1	1.6 ± 0.0	9.1 ± 0.1	0.0 ± 0.0

[a] Total structural sugars are obtained as the sum of glucan, xylan, mannan, arabinan, galactan, and rhamnan.
[b] Total lignin is calculated as the sum of acid soluble lignin and Klason lignin (Sluiter et al., 2008).
[c] The unknown matter is calculated as the complement to 100 of the other components.

hand, the trend for the solubilisation of structural sugars from AS was not clearly identified.

3.4. Methane potential of the substrates before and after ultrasounds pretreatment

The solid residues obtained after the ultrasounds pretreatment were used as the substrates for AD and compared with the raw LMs. The pretreated HS showed a lower methane potential than raw HS (Fig. 2A). Raw HS produced 255.5 (±2.8) mL CH_4/g VS. The HS pretreated using water as the medium for the ultrasounds pretreatment at T_{amb} and 80 °C lost ($p < 0.05$) 10 and 9% of the methane potential, achieving 228.9 (±8.4) and 232.6 (±6.4) mL CH_4/g VS, respectively. On the other hand, the ultrasounds pretreatment in the MeOH-based medium did not significantly ($p > 0.05$) affect the methane potential of HS. The AD kinetic parameters did not improve after the applied ultrasounds pretreatment, being comparable to or worse than those obtained with the raw HS (Table 4).

The highest methane production from AS was obtained from the raw substrate, i.e. 50.6 (±0.2) mL CH_4/g VS (Fig. 2B). The AS residues after the ultrasounds pretreatment showed a significantly lower ($p < 0.05$) methane potential than the raw substrate. No significant difference ($p > 0.05$) in the residual methane potential from AS among the ultrasounds pretreatment conditions was observed, showing a decrease ranging from 15 to 22%. All kinetic parameters were negatively affected by the ultrasounds pretreatment. In particular, λ was considerably higher than for raw AS (Table 4).

The SCG was the only solid residue in this study that benefited from the ultrasounds pretreatment. The highest methane production, i.e. 366.2 (±4.2) mL CH_4/g VS, was measured from the SCG pretreated with ultrasounds in water at T_{amb} (Fig. 2C). Although the statistical comparison revealed that the difference in methane potential was not significant ($p > 0.05$), the kinetic parameters showed an increase in the methane production rate from 9 to 13%, depending on the specific pretreatment condition (Table 4).

4. Discussion

4.1. Biomass solubilisation during ultrasounds pretreatment

This study showed for the first time a novel approach to valorise nut and coffee wastes through ultrasounds pretreatment. The available studies in the literature used the sonicated slurry (i.e. the mixture of the liquid and solid fractions) from ultrasound pretreatment of LMs as the substrate for methane production (Korai and Li, 2020; Qi et al., 2021). This approach can lead to the waste of valuable compounds that can be better valorised than via AD. Also, some of these compounds, e.g. polyphenols, can inhibit the AD process (Balasundaram et al., 2022). With the strategy here proposed, the optimal path for each fraction can be chosen by either using the solid and liquid fractions as the substrate for AD separately or, as a suggestion for future studies, using the liquid fraction for biomolecules recovery.

Ultrasound has been reported to be an effective technique for biomolecules extraction from algae, plants and fruit residues (Bhushan

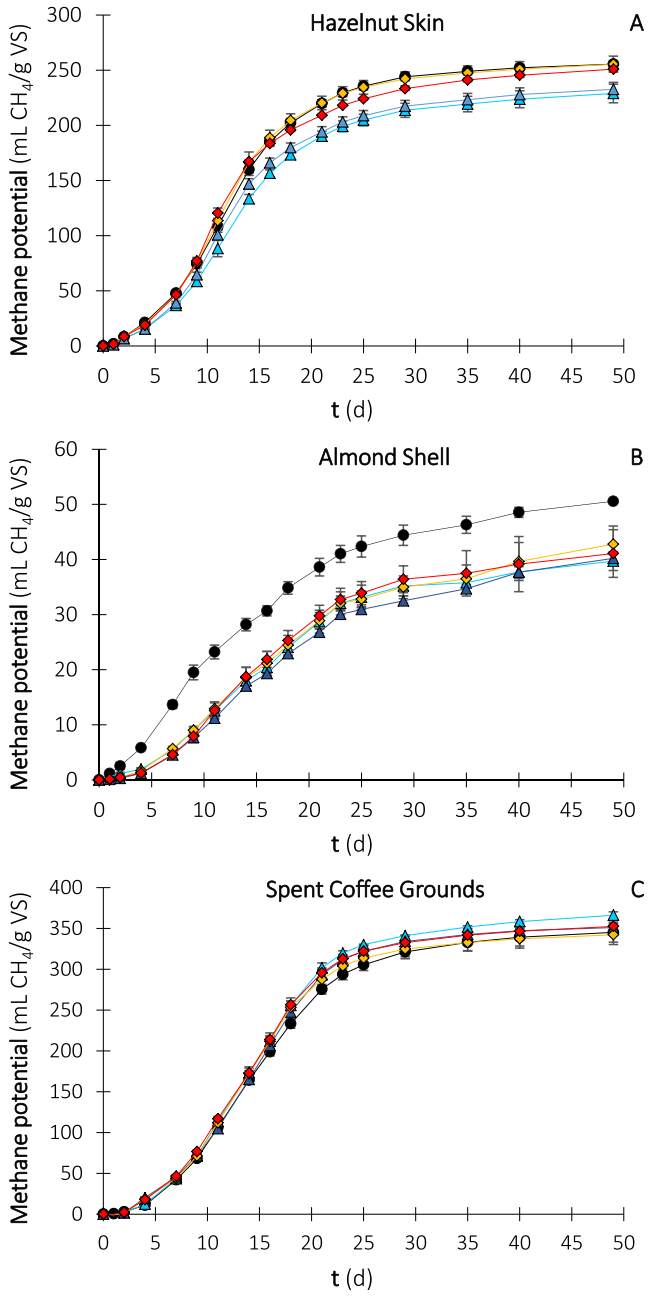

Fig. 2. Cumulative methane production obtained from the anaerobic digestion of raw and ultrasounds pretreated hazelnut skin (A), almond shell (B), and spent coffee grounds (C): raw (●), H_2O at T_{amb} (▲), H_2O at 80 °C (▲), MeOH-based medium at T_{amb} (◆), MeOH-based medium at 80 °C (◆).

et al., 2020; de Sousa e Silva et al., 2017). In this study, the polyphenols and sugar solubilised from LMs through the ultrasounds pretreatment were quantified (Table 2). Polyphenols are generated from lignin disruption during the pretreatment (Covarrubias-García and Arriaga, 2022). The sugar solubilised through ultrasounds mainly comes from the hemicellulose hydrolysis, whereas the cellulosic component of the biomass is generally unaffected by ultrasonic waves (Perrone et al. (2016)). In addition, polyphenols and sugars are present in the non-bound matter of LMs, i.e. the extractives (Tajmirriahi et al., 2021).

4.1.1. Polyphenols solubilisation

HS is particularly rich in total extractives, i.e. 35.0% (Table 3). A considerable amount of the HS extractives are polyphenols, being mainly monomeric and oligomeric flavan-3-ols (Spagnuolo et al., 2021). The high polyphenols and lignin content resulted in 53.4 – 126.9 mg polyphenols/g TS solubilised from HS (Table 2), depending on the ultrasounds condition. The highest amount of polyphenols solubilised in this study is above the HS polyphenols content reported by Ivanović et al. (2020), i.e. 70 mg/g TS, indicating that part of the polyphenols measured come from the lignin disruption achieved during the ultrasounds pretreatment (Table S2). Similarly, polyphenols are the most abundant components of AS extractives (Queirós et al., 2020). However, the low total extractives content of AS (i.e. 7.5%) observed in this study (Table 3) and the scarce lignin removal (Table S2) resulted in a significantly lower polyphenols solubilisation from AS than HS ($p < 0.05$), i.e. 0.7 – 5.0 mg/g TS (Table 2). On the contrary, despite the high total extractives content (i.e. 29.0%) of SCG (Table 3), polyphenols only represent a minor portion of the extractives in SCG (Sant'Anna et al., 2017). Therefore, considering the slight lignin removal during the pretreatment (Table S2), the polyphenols solubilised from SCG, i.e. 3.8 – 8.6 mg/g TS, were significantly lower than what was observed for HS ($p < 0.05$) (Table 2).

The capability of obtaining biomolecules from LMs depends on the chemical and physical properties of the substrate (Ibrahim et al., 2019). Oliva et al. (2021) showed that despite the recalcitrance caused by the high lignin content, HS is easily dented by solvent-based pretreatments due to its high porosity. On the other hand, the compact external surface and low porosity of AS made this LM particularly resistant to pretreatments (Oliva et al. (2021)). In the present study, the pretreatment temperature was a key parameter for polyphenols solubilisation when distilled water was the medium for the ultrasounds pretreatment. Similarly, Tanase et al. (2018) reported an increment in polyphenols solubilisation when increasing the temperature of the medium during ultrasounds pretreatment from 40 to 60 °C. Ultrasounds generate hot spots due to bubble collapse, increasing the temperature of the medium (Bundhoo and Mohee, 2018). This facilitates cavitation phenomena, likely being the reason for the increased polyphenols solubilisation from all LMs here investigated (Table 2).

The impact of the pretreatment temperature on polyphenols solubilisation was lower when using the MeOH-based medium. An increase in the pretreatment temperature during ultrasounds pretreatment facilitates cavitation phenomena but may lower the power of bubble collapse. The vapour generation increases with the temperature of the solvent and fills the cavitation bubbles, reducing the energy released once collapsing (Bussemaker and Zhang, 2013). Therefore, the optimal pretreatment temperature depends on the given system. The boiling point of MeOH is lower than that of distilled water. Therefore, at 80 °C, the vapour production from the MeOH-based medium is expected to be greater than that from water, and to have a greater negative impact on the ultrasounds pretreatment. On the other hand, using low polarity liquids, such as organic solvents, offers the opportunity to combine the effects of organosolv and ultrasounds pretreatment. Juttuporn et al. (2018) investigated polyphenols removal from sugarcane bagasse using ultrasounds, showing that the ethanol (EtOH)-based medium was more efficient than water. MeOH and EtOH-based solutions are the most employed organic solvents for polyphenols removal through ultrasounds (Dzah et al., 2020). In addition, MeOH may have a better impact than EtOH on lignin solubilisation (Sameni et al., 2017).

4.1.2. Sugar solubilisation

The pretreated HS solid residues had a higher content of structural sugars and lower lignin and total extractives content than the raw LM (Table 3). However, the sugar analysis showed that the liquor recovered after the ultrasounds pretreatment of HS had the highest sugar concentration among the LMs investigated (up to 146.0 mg/g TS). The sugar speciation (Table 3) showed that the main sugar in HS is glucan, which is associated with the cellulosic component of the biomass (Bulmer et al., 2021). On the contrary, the hemicellulose sugars are minor components of the HS. After the ultrasounds pretreatment, the glucan content slightly increased, indicating that mainly other components of HS were

Table 4
Experimental methane potential followed by statistical information and kinetic parameters, i.e. maximum methane potential (G_m), maximum methane rate (R_m), lag phase (λ), and correlation coefficient (r^2), obtained from the anaerobic digestion of raw and ultrasounds pretreated substrates using water (H_2O) and a 50% (*v/v*) methanol (MeOH) solution catalysed by 0.1% (*w/v*) sulfuric acid as the pretreatment media. HS: hazelnut skin, AS: almond shell, and SCG: spent coffee grounds. Pretreatment temperature: ambient temperature (T_{amb}) and 80 °C.

Substrate	Experimental methane potential (mL CH_4/g VS)	Statistical information [a]	G_m [b] (mL CH_4/g VS)	R_m [b] (mL CH_4/g VS•d)	λ [b] (d)	r^2 [c]
HS raw	255.5 ± 2.8	a	254.3	15.76	3.9	0.9989
HS H_2O T_{amb}	228.9 ± 8.4	b	227.2	12.95	4.1	0.9982
HS H_2O 80 °C	232.6 ± 6.4	b	230.8	13.35	3.9	0.9967
HS MeOH T_{amb}	255.4 ± 7.4	a	253.4	15.61	3.7	0.9979
HS MeOH 80 °C	250.9 ± 1.9	a	248.9	14.15	3.5	0.9939
AS raw	50.6 ± 0.2	a	49.4	2.32	1.9	0.9945
AS H_2O T_{amb}	39.7 ± 1.7	b	39.0	1.90	4.5	0.9980
AS H_2O 80 °C	40.2 ± 1.1	b	39.2	1.73	4.9	0.9966
AS MeOH T_{amb}	42.8 ± 3.3	b	41.5	1.82	4.4	0.9962
AS MeOH 80 °C	41.1 ± 4.3	b	40.3	2.07	5.3	0.9990
SCG raw	345.1 ± 11.8	ab	345.1	19.61	5.6	0.9996
SCG H_2O T_{amb}	366.2 ± 4.2	a	365.1	21.31	5.6	0.9987
SCG H_2O 80 °C	351.0 ± 4.9	ab	350.6	22.13	5.7	0.9972
SCG MeOH T_{amb}	342.3 ± 12.1	b	341.2	21.36	5.4	0.9987
SCG MeOH 80 °C	352.5 ± 6.8	ab	351.3	21.49	5.4	0.9986

[a] Not sharing letters means that the condition was significantly different ($p < 0.05$) than the compared condition.
[b] Predicted by fitting the experimental data with a modified Gompertz model.
[c] Correlation coefficient between experimental and model data.

removed (Table S2). Therefore, the sugars present in the HS liquor were likely solubilised from the non-bound matter, i.e. extractives. Frankó et al. (2018) previously reported the presence of free sugars in the water-soluble extractives of LMs, i.e. spruce and pine softwood. Apart from the structural sugars, HS is rich in galacturonic acid, generated from pectin degradation during the roasting process (Košťálová and Hromádková, 2019).

The pretreatment temperature was a key parameter to enhance the sugar solubilisation from HS in water (Table 2). On the other hand, the MeOH-based medium at T_{amb} was effective enough to remove all soluble sugars from HS under the ultrasounds conditions tested in this study. Therefore, no significant effect of the temperature was observed during the MeOH-based pretreatment. The importance of the temperature for sugar solubilisation in water was previously reported by da Silva Donadone et al. (2020) for peach palm residue. On the other hand, to the best of the authors' knowledge, the impact of the temperature on ultrasound-assisted solubilisation of sugar from LMs in the MeOH-based media has never been investigated before.

Similarly to other nut shells, AS showed a low free sugar content (Shen et al., 2018), in line with the low amount of sugar solubilised in the ultrasound liquors (Table 2). The highest pretreatment temperature increased the sugar removal. The highest sugar solubilisation, i.e. 32.6 mg/g TS, from AS was achieved at 80 °C in the MeOH-based medium. The amount of sugar here solubilised corresponded to over 90% of the overall non-structural sugar content of AS reported by Shen et al. (2018), suggesting that the extra potential for sugar solubilisation from AS is limited. Moreover, no significant change in sugar speciation was observed in the pretreated AS (Table 3), suggesting that the sugars are mainly solubilised from the non-bound matter (Table S2).

The sugar solubilised from SCG at T_{amb} in water (i.e. 16.7 mg/g TS) and MeOH-based medium (i.e. 19.1 mg/g TS) was slightly lower than that achieved by Ballesteros et al. (2015) via alkaline pretreatment at 25 °C, i.e. 23.8 mg/g TS. In this study, the ultrasound-assisted solubilisation lasted only 1 h, whereas Ballesteros et al. (2015) performed the alkaline pretreatment overnight. In addition, increasing the pretreatment temperature allowed the solubilisation of up to 30.2 mg sugars/g TS (Table 2). Contrary to HS and AS, the MeOH-based medium did not enhance the sugar solubilisation from SCG (Table 2). The sugar speciation of the pretreated SCG was similar to that of the raw SCG, and the lignin content barely changed after pretreatment (Table 3). In contrast, the total extractives content was lower (up to 19%) upon pretreatment (Table 3). The solubilisation of extractives was higher when using the MeOH-based medium, following the trend of polyphenols solubilisation, as discussed in Section 4.1.1. On the other hand, the solubilisation of polyphenols and sugar does not fully justify the high solubilisation percentage observed, i.e. 15 – 21%. Apart from the components investigated in this study, SCG is an oil-rich LM (Goh et al., 2020), likely being solubilised during the ultrasounds pretreatment as well, and accounting for the solubilisation percentage here observed. In particular, MeOH has been widely used for oil extraction from SCG (Battista et al., 2021), which can explain the higher solubilisation percentage observed when using the MeOH-based medium for ultrasounds pretreatment.

4.2. Valorisation of ultrasounds pretreatment fractions via anaerobic digestion

4.2.1. Ultrasounds-resulting liquors

The liquor from pretreated HS was rich in sugars, likely coming from the easily biodegradable non-bound matter (Table S2). The highest methane production, i.e. 85.3 (±12.2) mL CH_4/100 mL liquor, was obtained from the water-based liquor at T_{amb} (Fig. 1). The water-based liquor obtained from the ultrasounds pretreatment at 80 °C showed a higher sugar content, i.e. 9.9 g/L, than at T_{amb}, i.e. 6.5 g/L, but gave a similar methane production (Fig. 1). The failure to increase the methane potential is likely attributed to the higher polyphenols concentration that may have partially inhibited the AD process (Balasundaram et al., 2022; Oliva et al., 2022b). The liquid fraction from the ultrasounds pretreated AS and SCG exhibited a similar performance as substrates for AD, with the liquors recovered after ultrasounds at 80 °C producing more methane (Fig. 1). Contrary to HS, the sugars solubilised in the liquors from AS and SCG were significantly higher than the polyphenols (Table 2), resulting in a higher methane potential than the HS liquors despite the overall lower sugar concentration (Table 3). Xue et al. (2018) reported that increasing the concentration of phenolic compounds solubilised from LMs resulted in a lower sugar degradation in the fermentation of sugar-rich liquid substrates, which likely occurred in the AD of the HS liquors.

The lower polyphenols concentration in the liquid fractions resulted in a higher methane yield per gram of sugar added in the AD process (Table S1). The water-based liquors recovered from SCG pretreatment at T_{amb} and 80 °C showed the highest methane yield among the LMs investigated, producing 685.5 (±39.5) and 590.5 (±60.8) mL CH_4/g $glucose_{in}$, respectively (Table S1). The water-based liquors recovered from the ultrasounds pretreatment of AS at T_{amb} and 80 °C produced 431.6 (±13.2) and 434.2 (±25.1) mL CH_4/g $glucose_{in}$, respectively (Table S1). On the other hand, the inhibitory effect of polyphenols at

high concentrations was confirmed by the low methane yield achieved from the HS liquor, i.e. 131.5 (±18.7) and 80.8 (±5.6) mL CH_4/g $glucose_{in}$, respectively (Table S1). The MeOH present in the liquors completely inhibited methane production, regardless the LM used (Fig. 1). At moderate concentrations, MeOH is beneficial for the AD process, being a direct methanogenic substrate for methylotrophic methanogens (Feng et al., 2021). Nevertheless, higher MeOH concentrations without a proper microbial acclimation can hinder the methanogenic activity. Mancini et al. (2021) reported that 14.3 g VS/L is the half-maximal inhibitory concentration for methane production from MeOH-rich (i.e. 694 g MeOH/L) wastewater. Therefore, when using MeOH-based media for ultrasounds pretreatment, the recovery of the organic solvent is suggested to avoid AD inhibition and reduce the overall costs of the process. On the contrary, water-based liquors can be immediately subjected to AD.

4.2.2. Ultrasounds pretreated solid substrates

The solid HS residues after the ultrasounds pretreatment showed a high methane potential (Table 4), despite the loss of sugar and polyphenols. The methane potential of raw HS, i.e. 255.5 (±2.8) mL CH_4/g VS, is comparable with previous studies (Mancini et al., 2016). The pretreated HS showed an increased structural sugar percentage while a lower lignin concentration was observed (Table 3). Nevertheless, the methane potential of the HS obtained after the ultrasounds pretreatment in water was slightly lower than that of raw HS (Fig. 2A). This can be attributed to the loss of non-structural sugars during ultrasounds, as discussed in Section 4.1.2. On the other hand, for the HS pretreated in the MeOH-based medium, the higher polyphenols removal (Table 2) balanced the loss of fermentable sugars and returned a methane potential similar to the raw HS (Table 4). The overall content of structural sugars measured in HS was significantly lower than that of other nut residues (Bianco et al., 2021b; Shen et al., 2018), reaching a maximum of 17.1% after the ultrasounds pretreatment. The high methane production compared to the low sugar content can be explained by the high porosity of the HS, which allows a proper substrate-microorganism contact during AD (Oliva et al., 2021). In addition, the extractives of HS are reported to have a high protein and lipid content, i.e. 7.4 and 12.0 g/100 g TS (Ivanović et al., 2020), being additional substrates for methane production (Cheng and Brewer, 2021).

AS was the most recalcitrant among the LMs investigated in this study, and the ultrasounds pretreatment further lowered the AS methane potential (Fig. 2B). Contrary to HS, the physical properties limit the biodegradation of AS, having low porosity and compact external surface (Oliva et al., 2021). The methane potential of raw AS, i.e. 50.6 (±0.2) mL CH_4/g VS, is comparable with that reported by Shen et al. (2018). Generally, the AD of nut shells leads to a lower methane production than other nut residues due to their coriaceous structure used to protect the edible fruit from grazers and the environment (Shen et al., 2018; Xiao et al., 2020). The ultrasounds pretreatment removed part of the extractives, whereas the structural components were barely touched (Table 3), resulting in a slight reduction of the methane potential and a longer lag phase (Table 4), as previously observed when removing the extractives from AS by organosolv pretreatment (Oliva et al., 2021). The main structural sugars present in AS are xylan and glucan (Table 3), which are reported to be the most important substrate for AD of LMs (Zhong et al., 2015). Nevertheless, the high lignin content and the compact external surface strongly limit the hydrolysis of structural sugars from LMs (Xu et al., 2019).

The AD of SCG residues after ultrasounds showed a higher methane production rate than raw SCG (Table 4). The main changes in the chemical composition were the loss of extractives and the increment in mannan and lignin content (Table 3). The lower lignin content and increased contact surface, due to the powdery nature of the SCG, resulted in the highest methane potential among the LMs investigated, i.e. 345.1 (±11.8) mL CH_4/g VS (Fig. 2C). Other authors reported a lower methane production from raw SCG (Battista et al., 2021). This difference in methane potential can be attributed to the diversity in the coffee species, as well as in torrefaction and coffee brewing procedures.

4.3. Perspectives of ultrasounds applications for lignocellulosic materials valorisation

The optimal methodology for ultrasounds application is still debated. Recent studies showed an enhanced methane potential using the sonicated slurry obtained after the ultrasounds pretreatment of corn stover (Hassan et al., 2017) and cannabis straw (Qi et al., 2021) as the substrates for AD. In contrast, this study evaluated separately the methane potential of the liquid (Fig. 1) and solid (Fig. 2) fractions. Alternatively, Zou et al. (2016a, 2016b) pretreated dairy manure and wheat straw with ultrasounds before digesting the slurry. Therefore, the contribution in terms of the extra methane produced from the sole LM was thus far not fully disclosed in the literature.

The energy density used for ultrasounds pretreatment ranges between 500 and 50000 kJ/kg TS (Boni et al., 2021). Nevertheless, some authors also applied a higher energy density in their work (Hassan et al., 2017). An energy density of 6000 kJ/kg TS enhanced the biogas production from food waste by 59% (Rasapoor et al., 2019), while 2500 kJ/kg TS enabled to increase the methane production from fruit and vegetable wastes by 80% (Zeynali et al., 2017). The failure in increasing the methane potential of the solid residues in this study using an E_d value of 10600 kJ/kg/TS (calculated using Eq. (1)) could be due to the high recalcitrance and hard external surface of the substrates here investigated. Hassan et al. (2017) used a significantly higher E_d, i.e. 88500 kJ/kg VS, to increase the methane potential of corn stover by 43%, using the sonicated slurry as the substrate. On the other hand, in this study, the ultrasounds pretreatment was carried out to improve the release of biomolecules present in LMs, which could be a further valorisation of the HS, AS, and SCG with a multi-product biorefinery approach.

This work demonstrated the viability of releasing high-value bioproducts while maintaining the high methane potential of the solid residues. Organic agroindustrial wastes have been widely explored for biofuels production. Nevertheless, the interest in specific biomolecules recovery is recently increasing (Jain et al., 2022). In this perspective, ultrasounds pretreatment is a promising strategy offering several possibilities to regulate and optimise the process, e.g. temperature control, medium of diffusion, and energy density applied (Oliva et al., 2022a). The future developments for ultrasounds applications seem to head toward the coupling with specific solvents to promote either the release of biomolecules or an increment of the methane potential from the solid residues. Apart from the organic solvent investigated in this study, i.e. MeOH, ultrasounds were employed to assist alkaline pretreatment (Korai and Li, 2020) and dilute acid hydrolysis (Ríos-González et al., 2021) of LMs. A further suggestion may be to investigate ultrasounds assistance to other solvent-based pretreatments that do not require high temperature, i.e. over 100 °C, to activate the reaction, e.g. deep eutectic solvents (Wang and Lee, 2021). Nevertheless, investigating and optimising the valorisation of the liquid and solid fractions independently seems to be a more attractive approach, especially for the LMs rich in valuable bioproducts such as polyphenols, protein, and oils.

5. Conclusion

The liquid and solid fractions obtained from HS, AS, and SCG after ultrasounds pretreatment (using water and a MeOH-based medium at T_{amb} and 80 °C) were investigated to determine their potential in terms of methane production and solubilisation of polyphenols and sugar. HS has the greatest potential for biomolecules solubilisation among the LMs investigated, achieving up to 126.9 and 146.0 mg/g TS of polyphenols and sugar solubilised, respectively. The liquors obtained from HS would benefit from further studies to investigate the selective recovery of specific biomolecules. On the other hand, the methane potential of the HS liquors was limited compared to the amount of sugar solubilised.

Polyphenols and sugar solubilised from AS and SCG were significantly lower than those obtained from HS, but the AS and SCG liquors showed a higher methane potential. Thus, the water-based liquors from AS and SCG are suitable for direct AD, producing up to 107.0 and 160.9 mL CH_4/100 mL liquor, respectively. In contrast, the liquid fractions obtained using the MeOH-based medium would need a further step of MeOH removal to avoid the inhibition of methanogenesis. Apart from the liquid fractions, the solid residues obtained after the ultrasounds pretreatment showed a great potential for methane production for the three LMs investigated, although in most cases being comparable with the raw LMs.

CRediT authorship contribution statement

A. Oliva: Conceptualization, Data curation, Formal analysis, Investigation, Validation, Visualization, Writing – original draft, Writing – review & editing. **S. Papirio:** Conceptualization, Supervision, Resources, Writing – review & editing. **G. Esposito:** Supervision, Resources, Writing – review & editing. **P.N.L. Lens:** Supervision, Resources, Writing – review & editing, 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.

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Appendix A. Supplementary data

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