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Integration of extraction and acid hydrolysis processes as a strategy for better use and obtaining products from coffee residues

Integración de los procesos extracción e hidrólisis ácida como estrategia para mayor aprovechamiento y obtención de productos de residuos de café

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Abstract
The present study used a mixture of coffee processing residues to develop integrated processing for extracting high-value compounds with solvents and acid hydrolysis. The waste mixture comprised 55% bagasse, 40% husk, and 5% parchment. The physicochemical characterization showed 9.39 ± 0.37% of soluble fraction, and 90.61 ± 0.37% of the insoluble fraction, of which 60.41 ± 0.67% was cellulose, 6.44 ± 1.32% was hemicellulose and 23.21 ± 0.29% was lignin. In the first stage, the treatments of Organosolv and Organosolv assisted with ultrasonic (OAU) were applied at three particle sizes. The maximum yields of polyphenols were obtained with the smallest particle size and were 11.32 ± 0.63 mg GAE (gallic acid equivalents)/g DW (dry weight) for Organosolv and 10.12 ± 0.55 mg GAE/g DW for OAU. The best results for carbohydrate release were obtained with acid hydrolysis (0.5 % H_2SO_4) and OAU pretreatment. Principal component analysis indicated that the OAU treatment with hydrolysis at 15 psi was the best to obtain polyphenols, arabinose, and xylose.
Keywords: Carbohydrates, Acid hydrolysis, Integration processes, Coffee wastes, Organosolv.

Resumen
En el presente trabajo se utilizó una mezcla de residuos del beneficio del café con el fin de desarrollar un procesamiento integrado por la extracción de compuestos de alto valor con solventes e hidrólisis ácida. La mezcla de residuos estuvo compuesta de 55 % de bagazo, 40 % de cascarilla y 5 % de pergamino. La caracterización fisicoquímica mostró 9.39 ± 0.37 % de fracción soluble y 90.61 ± 0.37 % de fracción insoluble de la cual, 60.41 ± 0.67 % fue celulosa, 6.44 ± 1.32 % fue hemicelulosa y 23.21 ± 0.29 % fue lignina. En la primera etapa se aplicaron tratamientos Organosolv y Organosolv asistido con ultrasonicación (OAU) a tres tamaños de partícula. Los máximos rendimientos de polifenoles se obtuvieron con el menor tamaño de particula y fueron de 11.32 ± 0.63 mg GAE (equivalentes de ácido gálico) /g DW (peso seco) para Organosolv y 10.12 ± 0.55 mg GAE/g DW para OAU. Los mejores resultados para la liberación de carbohidratos se obtuvieron con hidrólisis ácida (0.5 % de H_2SO_4) y pretratamiento OAU. El análisis de componentes principales indicó que el tratamiento OAU con la hidrólisis a 15 psi fue el mejor para obtener polifenoles, arabinosa y xilosa.
Palabras clave: Carbohidratos, Hidrólisis acida, Procesos integrados, Organosolv, Residuos de café.

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1 Introduction

Since the publication of the 2030 Agenda for Sustainable Development (United Nations, 2018), the public and private sectors have focused their efforts on implementing methodologies in compliance with the Sustainable Development Goals (SDG). Among the methodological implementations, applying biorefinery principles for polluting plant residues is a viable way to fulfill the SDGs. Specifically, the waste generated from the processing of coffee, whose activity generates more than 7,900 t/year of waste (International Coffee Organization, 2020), its poor disposal causes serious contamination problems in soils, rivers, and aquifers due to high concentrations of phenolic compounds (Ramírez-Velasco *et al*., 2016). On the other hand, it is documented that the natural degradation of these residues increases the greenhouse effect due to the generation of gases from the fermentation of cellulose, hemicellulose, and lignin (Mussatto *et al*., 2011; Ballesteros *et al*., 2014). Harvesting strategies focus on obtaining easily accessible molecules, known as non-structural components, and on hydrolyzing complex molecules, which give structure and rigidity to residues and are known as structural components (Hikichi *et al*., 2017; Janissen and Huynh, 2018). Non-structural compounds can be obtained from extraction methods such as Organosolv (Banu *et al*., 2020), using ethanol as a solvent and low concentrations of acid facilitates the removal of recalcitrant components and molecules such as polyphenols. (Zhao *et al*., 2009; Thoresen *et al*., 2020) and as a complement to the extraction process, innovative techniques such as ultrasound are used since the formation of cavitations is induced on the surface of the residue, destabilizing the lignocellulose matrix, increasing the contact surface with the solvent (Soria *et al*., 2012), this process facilitates the solubilization of molecules according to the polarity of the solvent used (Ravindran *et al*., 2017a). The non-structural components, which is the residual solid fraction, are mainly composed of cellulose, hemicellulose, and minimal concentrations of lignin (Katzen and Schell, 2008), which through chemical hydrolysis processes allows obtaining oligomers or monosaccharides of great industrial importance (Stoklosa and Hodge, 2014; Jeong and Lee, 2015).

Therefore, it is possible to generate continuous processes to take advantage of the components of coffee residues under the concept of integration of processes that allow the use of organic matter, generating value-added molecules as well as contributing to the reduction of its polluting effect, fulfilling with the SDGs of the 2030 Agenda. This study aimed to integrate two physicochemical processes (extraction-hydrolysis) to obtain products of industrial interest and make the most of coffee residues.

2 Material and methods

2.1 Collection and conditioning

The coffee residues came from the wet mill. They were collected in Amixtlán, located in the Sierra Norte de Puebla, Mexico (20°02'53.1" N, 97°47'56.1" W), between 400 and 1,700 meters above sea level with warm sub-humid climate and rain all year round. The residues were dried in a convection oven at 60°C until reaching a moisture percentage of less than 10 % (w/w) (Hames *et al*., 2008); The dry residues were ground and sieved, collecting three particle sizes: PS1, PS2, and PS3, whose mean sizes were ≥ 2.38 mm (#8 mesh, large), between 2.37 and 1.68 mm (#12 mesh, medium) and ≥ 1.00 mm (#16 mesh, minor) respectively. The fractions obtained were stored in plastic bags at room temperature until analysis (Ballesteros *et al*., 2014).

2.2 Residues coffee classification

The residues were collected from the same site in a mixture of bagasse, husk, and parchment. The mixture was dried in an oven at 60°C for 24 h, homogenized, a random sample was taken, weighed, and the fractions in the mix were manually separated (bagasse, husk, and parchment). Finally, each sample fraction was considered, and the present percentage of each fraction in the total mixture was obtained.

2.3 Characterization of the mixture

The methodology described by Sluiter *et al*. (2008) was followed to characterize the waste mixture. To obtain the aqueous extracts fractions (AEF), the Soxhlet system was used, adding 10 g of the residue mixture and 100 mL of distilled water at a reflux rate of 4 cycles/hour for 13 hours. To obtain the ethanolic extract fractions (EEF), the residues resulting from AEF were used by adding 100 mL of absolute ethanol at a reflux rate of 5 cycles/hour for 7 hours. Both extracts were frozen until analysis.

The extractive-free residual fraction (EFRF) resulting from the previous stage was used to determine holocellulose and cellulose. The methodology described by Álvarez Rodriguez *et al*. (2012) was used. Two grams of EFRF in a 250 mL flask with 150 mL of water, 0.2 mL of acetic acid, and 1 g of sodium chlorite was mixed and covered with a watch glass and placed in a water bath at 70-80ºC, stirring constantly; every 30 minutes, 0.22 mL of acetic acid and 1 g of sodium chlorite were added until the white sample was observed. Subsequently, it was placed in a cold bath until it reached 10ºC, filtered with Whatman paper (GF/A grade), and the retained solids were washed with 50 mL of water. Finally, the biomass contained in Whatman paper was dried in an oven at 105ºC for 24 h until dry weight. The percentage of holocellulose was calculated by relating

the weight retained with that of EFRF by 100 %. After the determination of holocellulose, the retained biomass was used to determine cellulose; 1 g of biomass was placed in a 100 mL flask, and 10 mL of 17.5 % NaOH solution was added slowly, and in a water bath at 25ºC it was mixed and kept resting for 5 minutes. Another 5 mL of 17.5 % NaOH solution was added, mixed, and rested for 30 minutes, then 30 mL of water was added, mixed, and rested for 60 minutes. The mixture in the flask was filtered through Whatman paper (GF/A grade); the biomass retained on the filter was washed with 25 mL of 17.5% NaOH solution and 30 mL of H_2O, then washed with 30 mL of water. Subsequently, the vacuum pump was turned off, and 15 mL of 10 % acetic acid was added to the washed biomass and settled for 3 minutes; before turning on the vacuum pump, 50 mL of H_2O was added. The retained material was dried at 105ºC for 24 h until dry weight, and the retained biomass was again related to the EFRF mass by 100 % to calculate cellulose. The difference in the amount of holocellulose and cellulose determined the hemicellulose content (in percentage).

Lignin was determined following the methodology described by AIDER (2013), 1 g of EFRF was placed in a 50 mL flask, and 15 mL of 72 % H_2SO_4 solution was added slowly, stirring daily; it was kept to stand for 2 hours a water bath at 25°C, then the mixture was transferred to a 1000 mL flask, and 255 mL of water were added, covered with a watch glass and boiled gently for 4 hours. During that time, the volume of the solution was maintained by adding water. Finally, the mixture was kept at rest overnight; after this time, it was filtered, washed with hot water, and placed in an oven at 105°C for 24 h until dry weight. The weight ratio of biomass retained with the weight of the EFRF multiplied by 100 indicated the percentage of lignin.

2.4 Extractions

For this stage, a completely randomized block experimental design was used. Two treatments were considered; Organosolv (ORGAN) and Organosolv assisted with ultrasonication (OAU). Two blanks, Organosolv blank (BORGAN) and blank of Organosolv assisted with ultrasonication (BOAU) and three particle sizes (PS1, PS2, and PS3). The organosolv solution was prepared at 68 % ethanol and 1.5 % H_2SO_4, and a 1:10 (solid: solution) ratio was used for all particle sizes. For the ORGAN treatment, it was incubated for 45 min at 51°C (Ravindran *et al*., 2018). The OAU treatment was incubated for 40 min at 40°C in an AquaWave 9380 50/60 Hz ultrasonic bath. (Al-Dhabi *et al*., 2017; Ravindran *et al*., 2017a). The organosolv solution was replaced by water in the preparation of the blanks.

Subsequently, the extraction mixture was filtered through filter paper, and the solids retained (solid fraction, SF) were washed at 23ºC with two volumes of ethanol: water (8:2) solution, dried in an oven at 65ºC for 15 hours, they were weighed and stored at -5ºC for later analysis. On the other hand, the extracts (liquid fraction, LF) were concentrated by a rotary evaporator to remove the ethanol. Three volumes of water were added to the remaining volume and frozen for analysis.

2.5 Physicochemical hydrolysis

The SFs resulting from the extraction with organosolv were subjected to acid hydrolysis treatments. The experimental design considered three treatment conditions (T1 = 28°C for 24 h at 150 rpm, T2 = 28ºC for 36 h at 150 rpm, and T3 = 15 psi for 10 min without stirring) with 0.5 % H_2SO_4 solution and water as blank. The reaction mixture was in a 1:10 solid: liquid (g: mL) ratio. After the procedures, the mixtures were centrifuged (Beckman Coulter, 22R Centrifuge) at 14,000 rpm for 5 min. Two fractions were obtained; hydrolysis liquid fraction (HLF), which was stored at -5°C, and the residual solid fraction (RSF), which was dried at 65°C for 15 hours, weighed and stored for later analysis.

2.6 Analysis of liquid fractions

The total content of polyphenols (TCP) was measured according to Geremu *et al*. (2016) with modifications in volume. Two-hundred microliters of the sample, 1 mL of Folin-Ciocalteu commercial solution diluted ten times, and 800 μL of 7.5% Na2CO3 were placed in 2 mL amber Eppendorf tubes, mixed, and kept settling for 30 minutes in the dark. Samples were read at 765 nm using gallic acid as a standard and reported as mg GAE (gallic acid equivalents)/g DW (dry weight).

Reducing sugars were measured using the 3,5-dinitrosalicylic acid method according to Ávila-Núñez *et al*. (2012) using D-glucose as a standard and reported as mg Glucose/g DW.

For the detection and quantification of monosaccharides, the liquid fractions (AEF, EEF, LF, and HLF) were centrifuged at 14,000 rpm for 15 minutes at 23ºC; the supernatant was filtered twice through 0.20 μm nylon membranes and analyzed by UHPLC (UltiMate 3000, Thermo Scientific). A 10 μL injection volume was used with a HyperREZ XP Carbohydrate H+ (Phenomenex) column at 65°C in the oven; water was used as the mobile phase at a flow rate of 0.6 mL/min and with a refractive index detector (RefractoMax 520). Arabinose, galactose, glucose, mannose, and xylose were used as monosaccharide standards (Chem Service) at concentrations of 0.3125 %, 0.625 %, 1.25 %, 2.5 %, and 5 %, respectively. Both for the detection of polyphenols and reducing sugars, spectrophotometric methods (Thermo Scientific, Biomate 3) were used.

2.7 Monitoring of matrix wear by FTIR spectroscopy

The SF and Residual Solid Fractions (RSF) were crushed until a particle size of less than 0.149 mm was obtained.

They were analyzed in an Agilent model (CARY 630) Fourier Transform Infrared Spectrophotometer (FTIR), data collection was performed in the spectral range from 4000 to 600 cm^{-1}, with a resolution of 100 scans, and the analyzes were performed in triplicate.

2.8 Statistical analysis

All experiments performed in the present study were run in triplicate. Significant differences between extractions and hydrolysis were evaluated using analysis of variance (ANOVA). Duncan test was used to differentiate between means considering an alpha value equal to 0.05. To perform the principal component analysis (PCA), the R software, open access version 4.2.1, was used (Wickham, 2016; R Core Team, 2022; Wickham *et al*., 2022).

3 Results

3.1 Collected waste

The collection point is a site intended to dump residues from the wet mill without any classification or separation; for this reason, it was necessary to know the composition of the collected mixture, the appearance of the residue obtained is shown in Fig. 1, and the composition it was 55 % bagasse, 40 % husk, and 5 % parchment. The results of the characterization of the residue mixture were 9.39 ± 0.37 % of soluble fraction and 90.61 ± 0.37 % of the insoluble fraction. In the AEF, 72.08 ± 4.57 mg/g DW of reducing sugars, 15.21 ± 0.92 mg GAE/g DW of total polyphenols, 0.27 ± 0.10 mg/g DW of glucose, 0.17 ± 0.00 mg/g DW of galactose and 0.11 ± 0.02 mg/g DW arabinose were quantified; in EEF, 70.96 ± 1.35 mg/g DW of reducing sugars, 2.97 ± 0.47 mg GAE/g DW of total polyphenols, and 0.05 ± 0.02 mg/g DW of galactose were quantified. In the EFRF, 60.41 ± 0.67 % of cellulose, 6.44 ± 1.32 % of hemicellulose, and 23.21 ± 0.29 % of lignin were quantified (Table 1).

3.2 Stage 1: Extraction of soluble compounds (non-structural)

The soluble compounds in coffee residues can be obtained from extraction processes directed towards specific components; in this first stage, the extraction process was directed towards phenolic compounds. In Fig. 2, the total content of polyphenols extracted by the treatments and their blanks is shown; in all cases, the phenolic content was higher with smaller particle size, obtaining 11.32 ± 0.63 mg GAE/g DW in ORGAN, 10.12 ± 0.55 mg GAE/g DW in OAU, 9.76 ± 1.15 mg/g DW in BORGAN and 9.19 ± 0.54 mg/g DW in BOAU.

Simultaneously, sugars and reducing agents, and monosaccharides were quantified. The amount of reducing sugars in the extracts was higher in the treatments with smaller PS. Fig. 3 shows the yields of each treatment and its target at the three particle sizes, highlighting the BOAU treatments with 39.03 ± 1.27 mg/g DW and OAU with 36.82 ± 0.70 mg/g DW. Regarding monosaccharides present in the extracts, glucose, xylose, galactose, and arabinose were detected. In Fig. 4, each monosaccharide obtained by each treatment at each particle size is distinguished. Glucose was detected in OAU at all three particle sizes (Fig. 4A), showing a maximum concentration of 2.82 ± 0.94 mg/g DW at PS2; arabinose was detected in the treatment targets at PS2 and PS3 (Fig. 4B), presenting more content in BOAU with 14.45 ± 0.94 mg/g DW with PS3 and 14.35 ± 0.46 mg/g DW at PS2. In comparison, xylose was detected in the two blanks and OAU at the three particle sizes (Fig. 4C), showing a higher concentration in BOAU with 9.36 ± 0.23 mg/g DW at PS3. Finally, galactose was detected in all treatments and all particle sizes. (Fig. 4D), showing the maximum contents in the BOAU treatment in the three particle sizes: 19.70 ± 1.22 mg/g DW for PS3, 19.92 ± 0.07 mg/g DW for PS2, and 18.94 ± 1.41 mg/g DW for PS1.

PS1 ≤ 2.38 mm (mesh #8)

PS2 between 2.37 and 1.68 mm (mesh #12)

PS3 ≥ 1.00 mm (mesh #16)

Figure 1. An aspect of each particle size retained by # 8 mesh (large-PS1), # 12 mesh (medium-PS2), and # 16 mesh (smaller-PS3).

Table 1. Comparison of the content of components in the coffee residues in the mixture (husk, pulp and bagasse).

Component	Media ± DS	Husk[1]	Pulp[2]	Bagasse[2]
Aqueous Extracts Fractions (AEF)				
Total phenols (mg GAE/g DW)	15.21 ± 0.92	ND	ND	ND
Reducing sugars (mg/g DW)	72.08 ± 4.57	ND	ND	ND
Glucose (mg/g DW)	0.27 ± 0.10	ND	ND	ND
Galactose (mg/g DW)	0.17 ± 0.00	ND	ND	ND
Arabinose (mg/g DW)	0.11 ± 0.02	ND	ND	ND
Ethanolic Extracts Fractions (EEF)				
Total phenols (mg GAE/g DW)	2.97 ± 0.47	ND	ND	ND
Reducing sugars (mg/g DW)	70.96 ± 1.35	ND	ND	ND
Glucose (mg/g DW)	ND	ND	ND	ND
Galactose (mg/g DW)	0.05 ± 0.02	ND	ND	ND
Arabinose (mg/g DW)	ND	ND	ND	ND
Extractive Free Residual Fraction (EFRF)				
Cellulose (%)	60.41 ± 0.67	23.77±0.09	63.0 ± 2.5	43.0 ± 8.0
Hemicellulose (%)	6.44 ± 1.32	16.68±1.30	2.3 ± 1.0	7.0 ± 3.0
Lignin (%)	23.21 ± 0.29	28.58±0.46	17.5 ± 2.2	9.0 ± 1.6

[1]Ballesteros *et al*., (2014); [2]Murthy & Madhava Naidu, (2012).

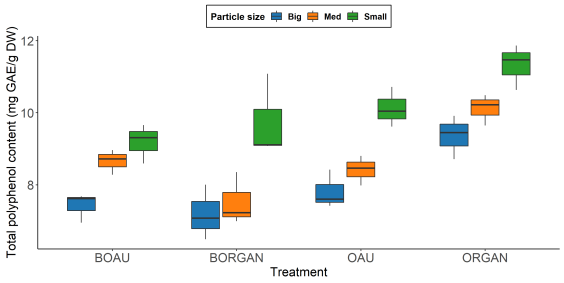

Figure 2. Yields of total polyphenols obtained by extraction treatment with ORGAN, UAO and their targets at three particle sizes (n=3).

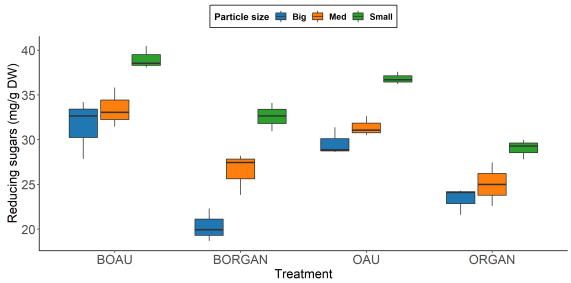

Figure 3. Reducing sugars extracted by treatment with ORGAN, UAO, and their targets at three particle sizes (n=3).

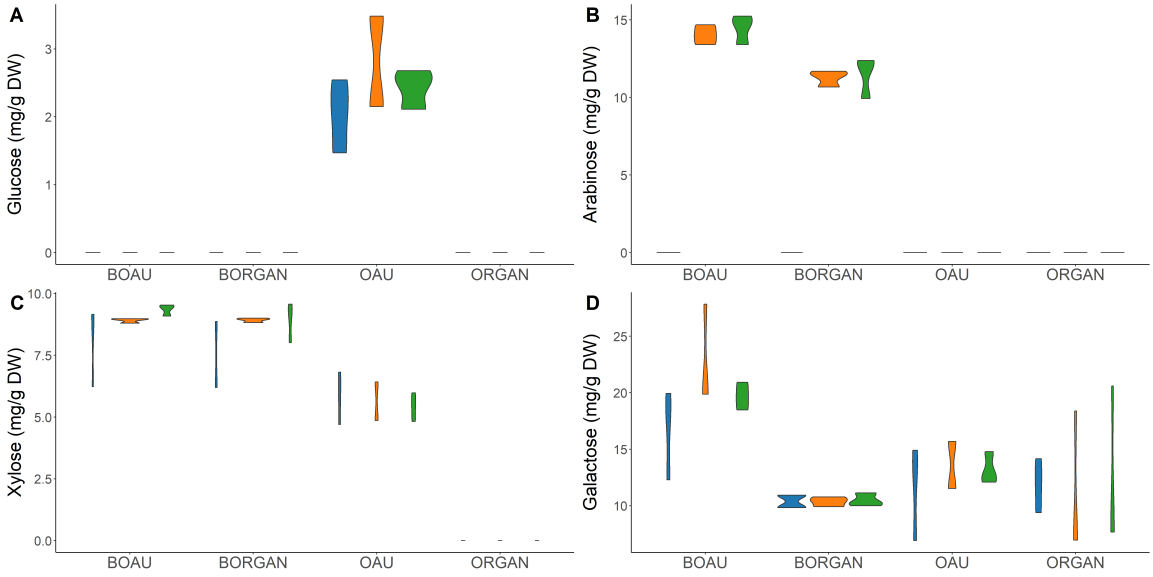

Figure 4. Monosaccharides detected in extraction treatments at three particles; PS1 (■), PS2 (■), and PS3 (■) (n=3).

Table 2. Spectral regions in the mid-IR region for lignocellulosic samples *.

Spectral region (cm^{-1})	Functional group	Vibrational mode	Corresponding molecule
3500-3200	γ (O-H)	Elongation	Cellulose/lignin
3000-2850	C-H	Elongation	Cellulose/hemicellulose
1750-1710	C=O	Elongation	Free aldehydes/ketones/esters of lignin and hemicellulose
1680-1600	C=C; C-O aromático	Asymmetric elongation	Lignin/aromatic
1500-1475	C=C; N-H	Elongation in a plane	Aromatic lignin/phenolics/proteins
1470-1426; 1371	C-C; C-O	Elongation/ deformation	Carboxylates/carboxylic acids/lignin
1265-1215	C-O-C	Asymmetric elongation	Residual aromatic ring of lignin and cellulose (β-Glucopyranose)
1080-1030	C-O; C=H; C-C-O	Elongation	Polysaccharides
1115-900	C-O	Elongation	Hydroxyl groups/sugar ethers
835	CH	Elongation	Breaking of lignin, hemicellulose and cellulose rings

* Table built with information from (Zara *et al*., 2017; de Carvalho Oliveira *et al*., 2018; Jorge Montalvo *et al*., 2019; Gabhane *et al*., 2020; Ahmed & Choi, 2021; Volli *et al*., 2021).

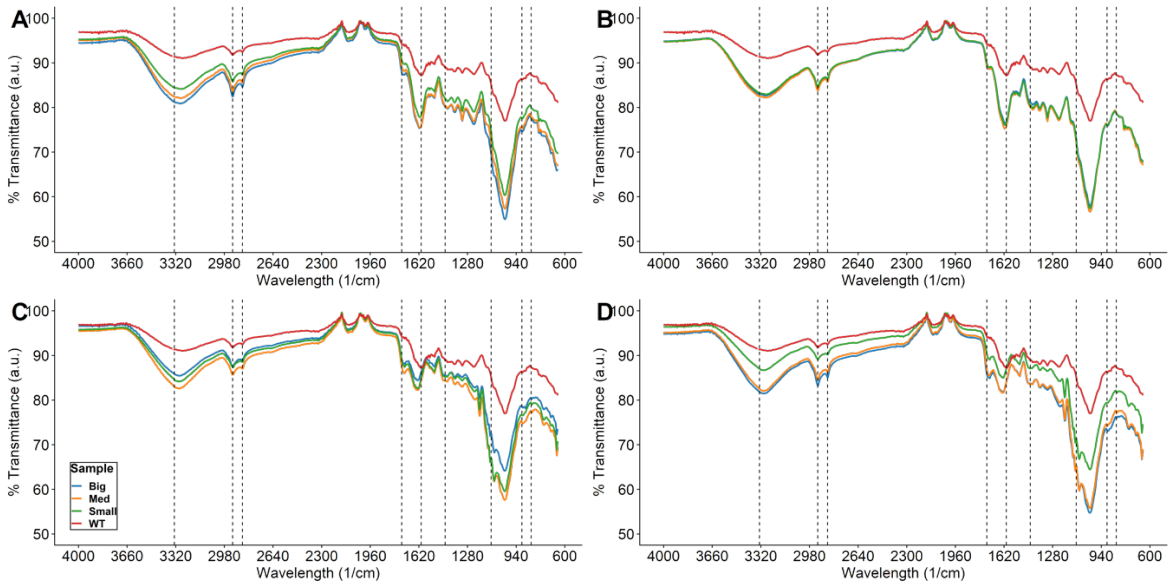

Figure 5. FTIR spectra of solid fraction after extraction treatment A) BOAU, B) BORGAN, C) OAU, and D) ORGAN for the three particle sizes contrasting with residue without treatment (WT).

After extraction, the residual matrix showed changes in its functional groups, visible by FTIR spectroscopy. In the FTIR spectra of Fig. 5, regions or wavelengths corresponding to functional groups of hemicellulose, cellulose and lignin are indicated (Table 2); these functional groups were compared in the residue before and after the extraction treatments. The spectrum of the BOAU derived from SF (Fig. 5A) does not present new peaks in the regions of interest but does show the elongation of other peaks. On the other hand, the BORGAN treatment derived from SF (Fig. 5B) does not differ in all the treatments; only a difference is observed with the untreated residue since specific signals are defined and lengthened. Regarding the SF of the ORGAN and OAU treatments (Fig. 5C and 5D), changes in %T are observed, highlighting a peak attached to the main one between 1115 and 900 cm^{-1}. In addition, at 835 cm^{-1}, the %T is reduced. On the other hand, two peaks appear, one at 1740 cm^{-1} and another between 1604 and 1437 cm^{-1}.

Table 3. Percentage of matter available after the extraction process.

Particle size	BUAO	BORGAN	UAO	ORGAN
PS1 (> 2.38 mm)	86.58 ± 0.55 % a	85.41 ± 1.14 %^{a}	93.77 ± 0.06 %^{a}	91.88 ± 0.07 %^{a}
PS2 (2.37 < PS < 1.68 mm)	84.55 ± 0.64 %^{b}	85.93 ± 0.40 %^{a}	93.34 ± 0.16 %^{b}	91.06 ± 0.24 %^{b}
PS3 (1.67 < PS < 1.00 mm)	83.07 ± 0.08 %^{c}	82.31 ± 0.63 %^{b}	90.86 ± 0.15 %^{c}	89.24 ± 0.21 %^{c}

Different letter in the same column is significant.

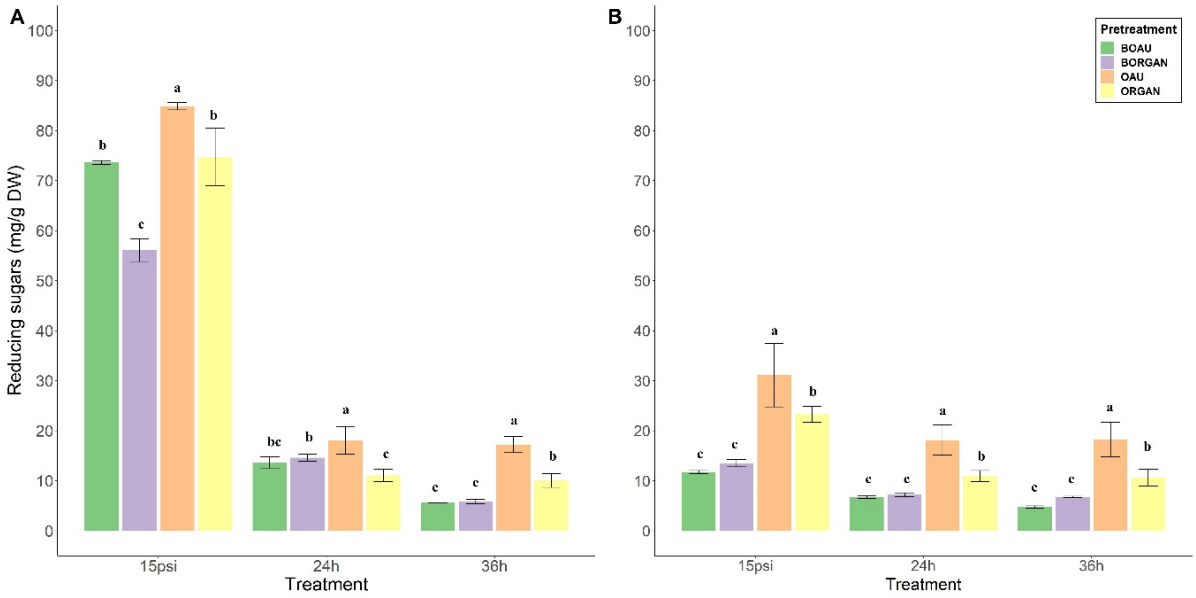

Figure 6. Reducing sugars obtained by hydrolysis with A) acid solution and with B) water as blank at 15 psi-10 min, 24 h-28 ºC-150 rpm, and 36 h-28 ºC-150 rpm, different letter in the same treatment is significant (n=3).

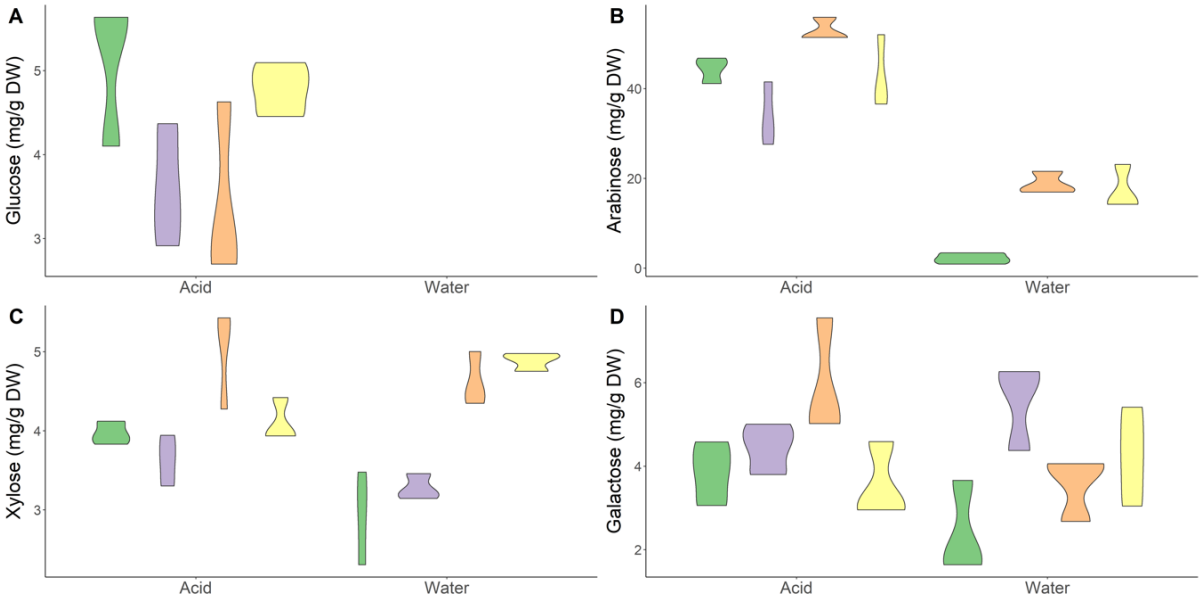

Figure 7. Concentration of monosaccharides obtained from hydrolysis with water and acid solution at 15 psi-10 min of the SF of the pretreatments (■) BOAU, (■) BORGAN, (■) OAU, and (■) ORGAN (n=3).

After extraction, the percentage of the residual matter was calculated. Table 3 shows the value in percentage of the three particle sizes. An inversely proportional relationship between wear and particle size was observed. The results indicated less wear at a larger particle size and greater wear at a smaller particle size, which show 89.24 ± 0.21 % of available mass after ORGAN, 90.86 ± 0.15 % after OAU, 82.31 ± 0.63 % after BORGAN and 83.07 ± 0.08 % after BOAU.

3.3 Stage 2: Modification of structural compounds

The waste utilization strategy in stage two focused on degrading its structural components, such as cellulose and hemicellulose, through acid hydrolysis. The ANOVA analysis and comparison between means (Duncan's test) allowed differentiating between the treatments (Table 3). The treatment with the smallest particle size was chosen. The SFs were hydrolyzed under three processing conditions with a 0.5 % H_2SO_4 acid solution and water as the reaction blank. The hydrolysates (HFL) were analyzed, and sugars (reducing sugars), monosaccharides, and total polyphenols were quantified.

In Figure 6, the reducing sugars released by the processing conditions are shown regarding the conditions 24 h and 36 h. The obtained hydrolysate (HFL) of FS treatment of OAU and ORGAN does not differ in its content when 0.5 % acid or water is used. On the other hand, comparing the acid condition at 15 psi with its hydrolysis blank, the four SF showed high sugar content, and the SF of OAU had the highest content of released sugars (84.85 ± 0.71 mg/g DW). This fraction was chosen for analysis by UHPLC to identify the monosaccharides and their concentration in the hydrolysates.

The monosaccharides detected and identified in HLF were glucose, arabinose, xylose, and galactose (Fig. 7). Glucose was only detected in the SF subjected to acid treatment, presenting the highest concentration in the HLF of SF from BOAU treatment with 5.12 ± 0.88 mg/g DW (Fig. 7A). Arabinose (Fig. 7B) was detected in the four hydrolysates with acid treatment, whereas with water it was not observed in HLF of FS of BORGAN treatment; the best values were with acid treatment, and the highest content was presented by the hydrolysate of OAU treatment of SF, releasing 52.93 ± 2.58 mg/g DW. On the other hand, xylose was detected in all SF subjected to hydrolysis under acid conditions and in the hydrolysis blank. Comparing the amount of xylose released in reaction with acid and its blank, similar values are observed between both conditions of the OAU treatment of SF and BORGAN treatment (Fig. 7C). In contrast, hydrolysate of OAU treatment of the SF presented 5.00 ± 0.63 mg/g DW. Finally, galactose was detected in all hydrolysates of SF at both conditions; the highest content of galactose was observed in the acid hydrolysate of OAU treatment of SF with 5.94 ± 1.94 mg/g DW (Fig. 7D).

During hydrolysis, phenolic compounds could be released from residual lignin in addition to sugars. Although the organosolv extraction treatment focused on removing total polyphenols, lignin was also removed, leaving a lower percentage in the SF. Figure 8 presents the results obtained from the total polyphenol content of the HLF are presented. More polyphenols were detected in the three treatment conditions (Fig. 8B) from BOAU and BORGAN of SF, while the OAU and ORGAN of SF did not differ between treatments at 24 h and 36 h, only the treatment with 15 psi showed significant differences concerning the other treatments. On the other hand, in acid conditions (Fig. 8A) for 24 h and 36 h, the four SF did not show differences among themselves. At 15 psi, the contents of polyphenols are higher.

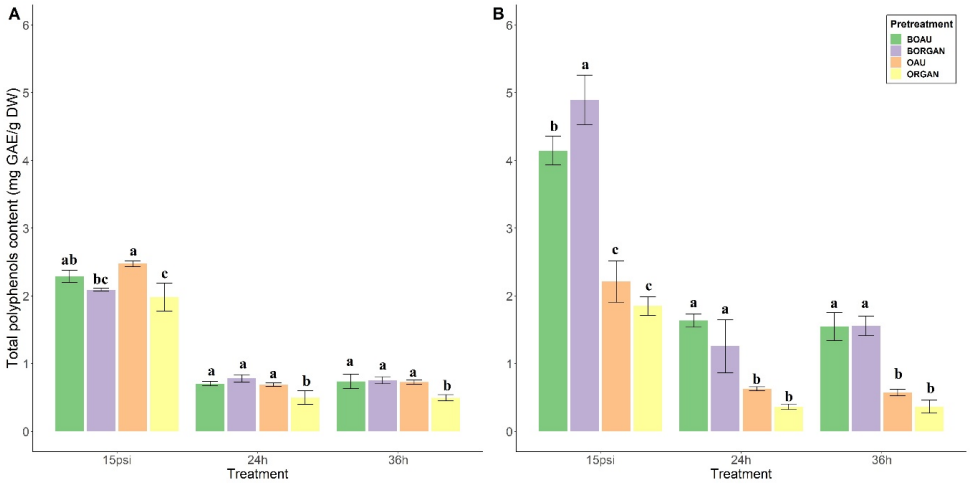

Figure 8. Total content of polyphenols obtained in hydrolysates with A) acid solution and with B) water as blank at 15 psi-10 min, 24 h-28 ºC-150 rpm, and 36 h-28 ºC-150 rpm, different letter in the same treatment is significant (n=3).

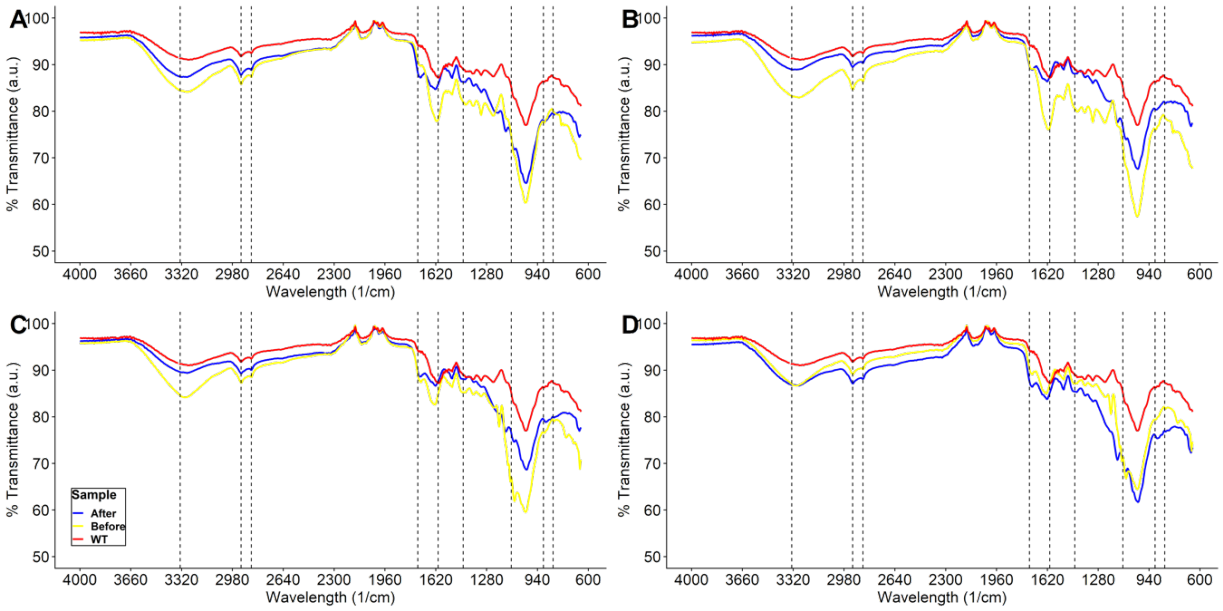

Figure 9. FTIR spectra of residual solid fraction obtained after acid hydrolysis treatment at 15 psi-10 min compared against the residual fraction of each extraction treatment A) BOAU, B) BORGAN, C) OAU, and D) ORGAN and residue without treatment (WT).

Table 4. Matrix of main components by processing stage.

Variables	Stage 1: extraction		Stage 2: hydrolysis	
	PC1	PC2	PC1	PC2
Residual mass	0.493	-0.296	0.088	0.664
Polyphenols	0.159	-0.087	0.405	-0.142
Reducing sugars	-0.304	-0.583	0.469	0.174
Glucose	0.217	-0.671	-0.01	0.637
Arabinose	-0.506	0.073	0.488	0.061
Xilose	-0.479	-0.139	0.478	0.025
Galactose	-0.327	-0.3	0.375	-0.313

PC = Principal Components.

After the hydrolysis treatments, RSF of acid treatment at 15 psi was subjected to FTIR analysis and compared with the spectrum of each SF and with the residue without treatment (WT). The RSF from BOAU and BORGAN (Fig. 9A and 9B) show changes in the region from 1400 to 1100 cm^{-1} due to the disappearance and decrease of peaks; in contrast, in RSF of OAU and ORGAN (9C and 9D) peaks disappear. On the other hand, an increase in %T is distinguished at 3330 cm^{-1}, 2922 cm^{-1}, and 2854 cm^{-1} signal regions of functional groups O-H and C-H of oligosaccharide fragments. In this second process, the matter was weighed after acid hydrolysis at 15 psi, and the percentage of residual dough was determined concerning dry weight. The rate of wear for FS of ORGAN treatment was 72.01 ± 0.56 %; for OAU treatment was 71.65 ± 0.52 %; for BORGAN treatment of 71.41 ± 0.65 % and BOAU treatment 72.60 ± 0.13 %.

3.4 Principal Component Analysis (PCA)

A principal component analysis (PCA) was used due to the number of variables quantified in both processes. Figures 10 and 11 show the behaviors with two principal components (PC). The highest percentage of variance was observed in the evaluated data set; for stage one, the two PC describe 65.76% of the variance, and in stage two, 77.37 % (Fig 10A and Fig 11A).

As a result of the PCA, the weights of each variable in each component were also obtained and are shown in Table 4; the sign indicates the effect on the component, positive or negative. In stage 1, PC1 has a mostly positive relationship with residual mass and a negative relationship with arabinose, xylose, and galactose. On the other hand, PC2 is negatively affected by reducing sugars and glucose. For stage 2, PC1 is further positively influenced by reducing sugars in addition to arabinose, xylose, and galactose. Regarding PC2, the residual mass and glucose variables positively affect more than the other variables. The PCA can also be used to group and differentiate the evaluated population. In this study, a scatter plot was applied to group the treatments in both stages, thus, in Fig. 10B and Fig. 11B, PC1 vs. PC2 is shown, and OAU was differentiated from the other treatments.

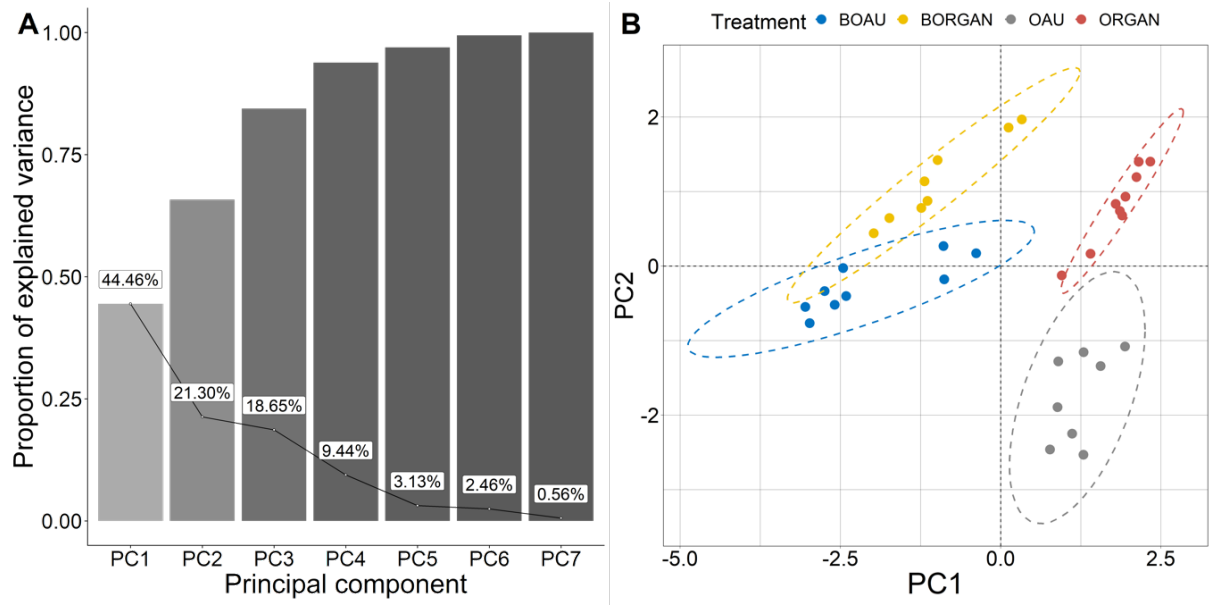

Figure 10. Proportion of accumulated variance explained by each PC (A) and the relationship between variable residual mass and reducing sugars to group the treatments (B) after applying PCA to the first processing.

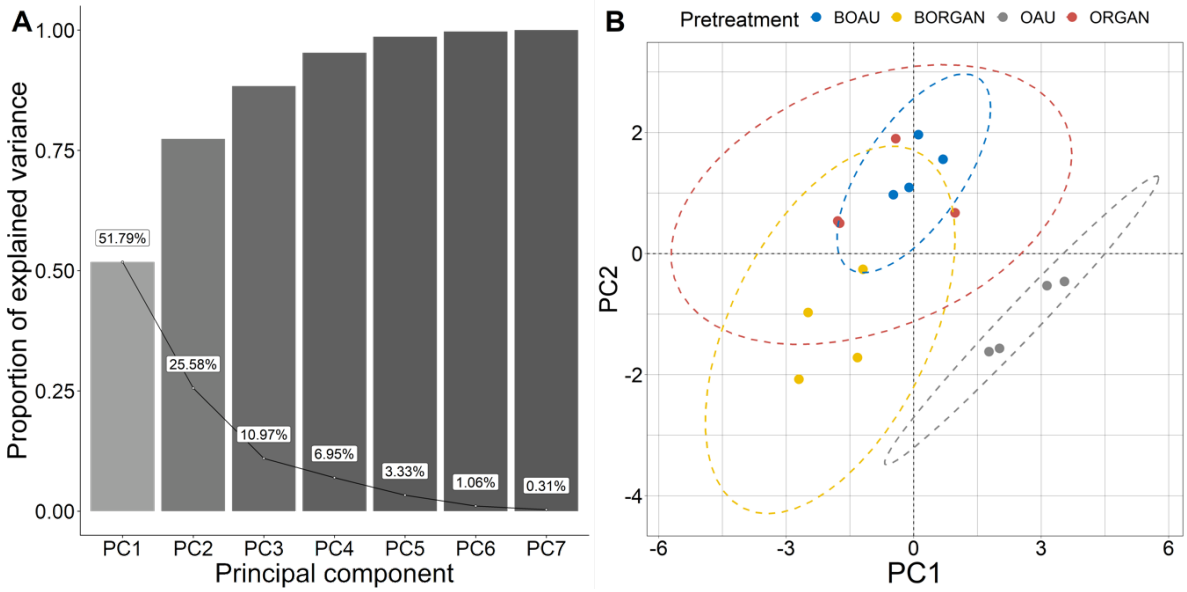

Figure 11. Proportion of cumulative variance of the eight components obtained from PCA (A) considering PC1 and PC2 to evaluate the data structure and highlight the SF of the pretreatments in the second processing stage (B).

4 Discussion

The present study decided to study with a mixture of residues and processes that showed a better possibility of using and obtaining products based on the characteristics of coffee residues.

The mixture of residues was chosen for two reasons: at the collection point or place of final disposal, the producers indistinctly placed the residues of bagasse, husk, and parchment. Table 1 shows the possible advantage of working with a mixture of residues than with the individual fractions because, in the case of the structural components, such as cellulose, hemicellulose, and lignin, there is a greater quantity in the mixture, this can be explained if the structural

components are considered as part of an extensive property that turns out to be additive when mixed (Chang, 2010). Therefore, the values of the structural components in the mixture show better than individually, which leads to an increase in the use of the mixture components.

On the other hand, coffee wastes can be valuable for their soluble non-structural components, such as polyphenols, since they can be easily extracted due to their polar nature and arrangement in the matrix. During the characterization of the mixture (Table 1), water and ethanol were evaluated as solvents, which helped to know the nature of the non-structural components, focusing the study on the polyphenol content and the amount and type of soluble sugars. The highest percentage of non-structural sugars was found in AEF as well as polyphenols, allowing us to consider the nature of the polyphenols in the residues as glycoside flavonoids, which are formed by a flavonoid attached to a sugar or a large number of hydroxyl groups making them more soluble in water than in ethanol due to their amphiphilic nature (Guo *et al*., 2021; Pérez-Nájera *et al*., 2013), also considering the polarity of water against that of ethanol it was reasonable to find a higher amount of sugars and polyphenols in AEF than in EEF (Sluiter *et al*., 2008).

4.1 Products of the first process

Coffee residues have a high content of phenolic compounds that can be used to generate high-value products; however, these residues are rarely used and are toxic to the environment due to poor disposal. Therefore, for better use of waste, the first stage of the integrated process focused on removing polyphenols and other recalcitrant compounds, obtaining two types of products, an extract rich in polyphenols and lignin and a solid fraction formed by structural components available for hydrolysis.

From the diversity of processes used for removing polyphenols and lignin, the ORGAN and OAU treatments were selected for two reasons, firstly because of the reagents used, water, ethanol, and acid, which, considering future scaling, are accessible, profitable, and less expensive (Thoresen *et al*., 2020); and second, because it represents the application of innovative technologies allowing greater removal.

The extraction conditions with ORGAN were taken from Ravindran *et al*. (2018), resulting in the mixture of polyphenols of 11.32 ± 0.63 mg GAE/g DW similar amount as those obtained by worn coffee beans (11.2 mg GAE/ g DW); therefore these conditions can be considered reproducible with the mixture and these extracts can be used to purify phenolic compounds such as gallic, coumaric, ferulic, cinnamic, chlorogenic and caffeine acid (Manasa *et al*., 2020).

On the other hand, considering the presence of residual lignin in SF after the extractions, polyphenols were found in the hydrolysates since it is known that lignin is composed of monomers linked with very diverse chemical bonds (Lu and Ralph, 2010). When lignin is hydrolyzed, mixtures of polyphenols are released; therefore, the values obtained in the hydrolysates respond to a low percentage of residual lignin present in SF after treatment since the content of polyphenols in SF of ORGAN and OAU were low (Fig. 8). The results suggest that the ORGAN and OAU processes facilitate the extraction of this type of compound.

In the first stage of the process, sugars with a concentration of 36.82 ± 0.70 mg/g DW with OAU were also obtained, which is an amount higher than that reported by Ravindran *et al*. (2018) who detected 29.05 mg/g DW of carbohydrates by enzymatic hydrolysis of coffee residues. The greater amount of sugars obtained is likely due to the presence of bagasse in the mixture since it is made up of 14.8 ± 5.3 % of sugars (Pleissner *et al*., 2016).

The monosaccharides glucose, mannose, galactose, and arabinose are very common for coffee residue because they are part of the hemicellulose and mucilage (Nguyen *et al*., 2019; Ravindran *et al*., 2017b); most of these sugars were detected in the extracts, is highlighted that only in the extracts obtained by OAU it was possible to detect glucose, this probably due to the generation of microcavities formed by the action of ultrasound exposing the internal layers of the residue to the action of the solvent (Chandrasekara, 2018); therefore, the cellulose fibers are more exposed to acid hydrolysis, releasing a greater amount of glucose. It should be noted that xylose was also detected, coming from the residual hemicellulose adhered to the cellulose fibers. Has been described that coffee contains hemicelluloses, mainly of xylan and arabinogalactan, which are the source of xylose, arabinose, and galactose (Heinen *et al*., 2019; Ho *et al*., 2011) that were also detected in this process. This first intervention not only served to extract polyphenols and remove lignin, but it is also possible to obtain carbohydrates from hemicellulose, mucilage, and cellulose.

4.2 Hydrolysis of structural components

The results obtained in the acid hydrolysis (Fig. 6) indicate similar concentrations of sugars for the SF, OAU, and ORGAN treatments; this allows us to deduce that the first stage is necessary since it exposes the cellulose fibers (structural component) to the action of acid. The results indicated a sugar content of 84.85 ± 0.71 mg/g DW at 15 psi. In another study, with characteristics like those of the present study, a greater quantity of sugars was quantified due to the use of a pretreatment applied of the residues of coffee using the organosolv method, followed by enzymatic hydrolysis obtaining a maximum of 350.12 mg/g DW (Ravindran *et al*., 2017b). It is important to note that the method used in this study presented a low concentration of polyphenols (less than 5 mg /mL), which probably has a minimal inhibitory effect on the development of some bacteria and yeasts (Pérez-Cadena *et al*., 2018; Ma *et al*., 2021).

On the other hand, the monosaccharides detected in this stage reinforce the idea of hemicellulose made up of

xylan and arabinogalactan and allow us to assume a greater richness of hemicelluloses in the residue matrix since the xylose quantified in the first stage is higher than the second stage. According to the results obtained in the second stage of the process, it is probable that the arabinogalactan is bound to the cellulose fibers and that when the latter is hydrolyzed, the arabinogalactan is released and hydrolyzed by the acid conditions tested. And consequently, the highest concentration of arabinose was detected, leaving galactose as part of xylan and arabinogalactan. The hydrolysis of this mixture of residues allowed an excellent yield of arabinose, if it is considered what was mentioned by Mayanga-Torres *et al*., (2017), who used coffee beans in a hydrolysis system with subcritical water reaching a maximum of 13.32 mg/g DW of arabinose, in addition to glucose (2.44 mg/g DW), xylose (1.93 mg/g DW) and cellobiose (44 mg/g DW), on the other hand, Ravindran *et al*. (2017a) applied treatment with ultrasonication and potassium permanganate on worn coffee residues obtaining high concentrations of glucose (62.4 ± 0.6 mg/g DW), galactose (33.7 ± 1.5 mg/g DW) and mannose (16.01 ± 0.3 mg/g DW), in addition to 45.6 ± 0.1 mg/g DW of arabinose, which in less than those obtained in the present work, what was of 78.70 ± 3.66 % of arabinose, therefore, can be considered to apply this system to generate mainly this monosaccharide, since it is essential for the pharmaceutical, chemical and food industry because it serves as a precursor for vaccines and other biomolecules or as an ingredient in functional foods (Fehér, 2018).

4.3 Matrix changes visible by FTIR

There are several ways to demonstrate the changes suffered by the residue matrix, including combined spectroscopic techniques such as FTIR-ATR (Zara *et al*., 2017; Mondragón-Cortez *et al*., 2022) or individual. Due to their speed, the FTIR spectra are chosen to monitor the wear of lignocellulosic residues (Zara *et al*., 2017; Montalvo *et al*., 2019).

After this first processing, the residue mixture was worn down not only by the removal of non-structural components but also by the solubilization of a fraction of hemicellulose and lignin, made visible in the detected monosaccharides and supported by the FTIR spectra, since comparing them with residues without treatment, in regions of functional groups of hemicellulose and lignin, new peaks or reductions in the percentage of transmittance (%T) can be seen. The peak observed in the region 1115 to 900 cm^{-1} corresponds to hydroxyl groups and sugar ethers that may indicate a higher exposure of matrix polysaccharides. The appearance of two peaks, one at 1740 cm^{-1}, corresponds to aldehydes, ketones, or free esters derived from the hydrolysis of lignin and hemicellulose; the peaks between 1604 and 1437 cm^{-1} correspond to the presence of C=C, C-C and N-H groups that derive from aromatic rings from lignin hydrolysis or phenolics (Zara *et al*., 2017; Ravindran *et al*., 2018; Volli *et al*., 2021).

On the other hand, the FTIR spectra performed at the RSF indicated greater wear of the sample since the changes in the spectrum in the region from 1400 to 1110 cm^{-1} are due to carboxylic and β-Glucopyranose groups, exposed by the denaturation/solubilization of cellulose and hemicellulose fractions. The increases in %T at 3330 cm^{-1}, 2922 cm^{-1}, and 2854 cm^{-1} correspond to cellulose functional groups exposed by polysaccharide hydrolysis. The spectra of residual fractions showed similarity with spectra of pure cellulose (Zara *et al*., 2017), which are characterized by presenting peaks of marked intensity at 3326 cm^{-1} (stretching of the -OH group), 2933 and 2854 cm^{-1} (stretching of C-H bonds) and 1714 cm^{-1} (stretching of C=O), highlighting the new arrangement of the matrix. Finally, since the organic matter is not completely worn away, it can be considered viable to continue processing the residual solid fraction, perhaps to synthesize activated carbon (Chiang *et al*., 2020; Kang *et al*., 2020) or more monosaccharides such as glucose to produce second-generation fuels (Laca *et al*., 2019).

4.4 Description of processes for integration

The objective of applying a PCA was to reduce the dimensionality of the data set for future cases, a condition that implies fewer variables and a description of the processes involved (Bartholomew, 2010; Syms, 2018) since the PCA can be used as a technique of generation of hypotheses that aims to describe patterns, instead of testing formal statistical hypotheses (Syms, 2018), was possible reducing the set of variables evaluated to two PCs allowed acquiring the loadings of each stage for a better understanding.

Each loading indicates an effect on the PC, but together they make it possible to give meaning and weight to the variables in each PC, better summarizing the data set (Geladi and Linderholm, 2020). PC1 and PC2 of stage 1 describe the essential variables to select the treatment that wears the material the most and eliminates the greatest amount of polyphenols, leaving aside the monosaccharides arabinose, xylose, and galactose as products of interest. For stage 2, PC1 describes the production of arabinose and xylose, quantified as reducing sugars, and PC2 describes how hydrolysis affects the residual mass and disposes of the matrix to continue hydrolyzing. The information provided by the PCA clarifies how both processes would be integrated and the products to focus on to better use this mixture of waste. It is recommended as a first intervention to apply to a particle size retained in mesh #16 the OAU treatment for greater extraction of polyphenols, later, to the SF use hydrolysis at 15 psi-10 min to produce arabinose and xylose, and thus allow better material wear and high yields of products of interest.

Conclusions

The integrated process of the coffee residues applied in the present study consists in using as a first stage an extraction with Organosolv assisted with ultrasonication that solubilizes part of the lignin and other non-structural components, obtaining mainly phenolic compounds and non-structural carbohydrates and later, a second stage, which consisted of acid hydrolysis at 15 psi-10 min that facilitates the hydrolysis of cellulose where carbohydrates are primarily obtained in the form of monosaccharides and oligosaccharides. This integrated process allows better use of organic matter to get phenolic compounds as products of interest and carbohydrates such as arabinose, glucose, and xylose.

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