



Integrated processes applied to cocoa bean hulls to obtain phenolic compounds and cellulose

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Abstract

The cocoa bean hull is one of the main residues generated by the cocoa industry, accounting for approximately 10–20% of the total bean weight and resulting in large amounts of discarded biomass, which is rich in valuable components, including phenolic compounds (PC) and cellulose. This study aimed to valorize cocoa bean hull through the extraction of PC and cellulose using an eco-friendly approach and to propose the utilization of this residue by integrated processes resulting in value-added biobased products. For PC extraction, raw cocoa bean hulls (RCBH) and autoclave pretreated cocoa hulls (PTH) were subjected to a heat-assisted extraction (HAE) with water and to an ultrasound-assisted extraction (UAE) with water or 50% ethanol, while cellulose-rich materials were obtained by peracetic acid treatment. HAE applied to RCBH provided the highest PC content (16.67 mg GAE/g db) and antioxidant capacity, reaching 48 mg TE/g db by DPPH and 156 mg TE/g db by ABTS. Peracetic acid treatment promoted substantial delignification, increasing cellulose contents from 25.06 to 40.48% in the starting materials to 46.87–69.20% in the corresponding cellulose-rich fractions. The extracted materials exhibited increased crystallinity, reaching 74.4%. Overall, the results support further investigation of cocoa bean hull as a feedstock for integrated recovery of PC and cellulose, although process scalability, environmental impacts, economic feasibility, and valorization of the remaining fractions require further evaluation.

Keywords Lignocellulosic residue · Heat-assisted extraction · Ultrasound-assisted extraction · Peracetic acid

1 Introduction

The transformation of agroindustrial residues has been increasingly studied, with growing interest from both the academic community and civil society, aligning with the concepts of circular economy and biorefinery, in which different chemical, biochemical and thermochemical processes are applied in the transformation of agroindustrial, forestry and organic residues, resulting in value-added biobased products [1, 2]. Additionally, a particular political and social pressure has been applied to industries to reduce the amount of residues generated from their manufacturing activities,

aiming at a zero-waste goal by minimizing residue generation, maximizing their use and valorization [3].

Cocoa (*Theobroma cacao* L.) is an important commodity across major tropical growing regions worldwide, with an annual production of almost 5 million tons of dry cocoa beans [4, 5]. According to the International Cocoa Organization [5], West Africa dominate the global supply, led by Côte d'Ivoire and Ghana as the first and second largest producing nations, respectively, followed by Nigeria and Cameroon. In Latin America, Ecuador stands out as the third-largest producer globally and the leading supplier of fine-flavor cocoa, with Brazil, Peru, the Dominican Republic. Across all producing regions, cocoa processing generates substantial volumes of residues, reinforcing the need for sustainable valorization strategies to convert them into high-value biobased products.

The main residues generated during cocoa processing are the cocoa fruit hull and the cocoa bean hull. The cocoa bean hull corresponds to the outer fraction responsible for coating the cocoa bean, representing approximately 10–20%

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of the total fruit weight [3, 4, 6]. It is composed of carbohydrates, proteins, lipids, phenolic compounds (PC), and dietary fibers, showing itself to be a potential raw material for use in different industrial sectors [4, 6–8].

PC are molecules derived from secondary metabolism of plants and act in maintaining organisms homeostasis, exhibiting antioxidant and antimicrobial activities. These compounds are highly valued in various sectors, including the food and pharmaceutical industries. Therefore, the improper disposal of cocoa bean hulls leads to the loss of these bioactive compounds, highlighting the need for technological strategies for their recovery and valorization [4, 8]. For example, in the food industry, PC can be used as natural food preservatives to inhibit lipid oxidation in meat products, replacing synthetic antioxidants; in pharmaceutical sector, they can be used in anti-aging topical creams.

Cellulose is a biopolymer that can be obtained from microbial, animal, or plant origins. This biopolymer is a linear homopolysaccharide composed of glucose monomers linked by β -1,4 glycosidic bonds [9]. Cellulose is a semicrystalline polysaccharide, containing regions with higher molecular organization, called crystalline regions, and others with lower organization, referred to as amorphous regions [10]. In plants, cellulose is present in the cell wall, where it performs a structural role and forms the lignocellulosic complex in association with hemicellulose and lignin molecules. Cellulose is of great commercial interest, and it is employed in several industrial sectors, including paper, packaging, food, pharmaceuticals, and cosmetics. Agroindustrial residues are considered potential sources for cellulose extraction, representing an alternative source to cellulose obtained from wood [11, 12].

The conventional processes employed for the extraction of both PC and cellulose are generally carried out in aqueous medium and involve the use of large amounts of reagents, resulting in the generation of substantial volumes of effluents. Alternatives for PC extraction are already being explored, among which heat-assisted extraction (HAE) and ultrasound-assisted extraction (UAE) stand out. HAE is based on exposing the sample to heat and agitation in a liquid medium, while UAE is a non-thermal process in which the sample is subjected to acoustic cavitation, and in both cases, the processes can be conducted in the absence of chemical reagents, using water or renewable solvents, reducing effluents generation [8, 13].

For extraction of cellulose from lignocellulosic residues, the main challenge results from disrupting the lignocellulosic complex. Bleaching conventional methods rely on chlorinated solvents, which generate environmental impacts, making the use of alternative processes imperative. Peracetic acid has been increasingly explored for cellulose delignification in lignocellulosic residues [11, 12, 14–16].

This solvent is composed of acetic acid and hydrogen peroxide, which is characterized by its high oxidative activity [17]. According to Paiva et al. [12], peracetic acid promotes the oxidative degradation of lignin through the hydroxylation of aromatic structures, reducing the molecular weight and increasing the hydrophilicity of lignin, which makes it more easily removed from the lignocellulosic complex, preserving the cellulose structure. Lignin can be converted into various high value-added products through thermal depolymerization, microbial conversion or chemical processing via oxidation and reduction reactions, with applications in pharmaceutical and cosmetic sectors, between others [2].

Despite extensive literature addressing biorefinery principles, the development of feasible technological systems still needs to be more explored. To achieve a viable valorization/transformation pathway, this study proposes an integrated approach based on the structural architecture of the lignocellulosic complex. Considering that PC are entrapped within the complex lignocellulosic network of cellulose, hemicellulose, and lignin, PC extraction as the initial step can maximize the recovery of these bioactive molecules before they undergo degradation during the harsher chemical or thermal treatments typically required for cell wall disruption. Thus, this study aimed to present some technological alternatives for the extraction of PC and cellulose from cocoa bean hulls, using an ecofriendly approach, and to propose a full utilization of this residue by integrated processes resulting in value-added biobased products.

2 Materials and methods

2.1 Materials

Cocoa bean hull was provided by ECOM Agroindustrial Corp. Limited (Veracruz, Mexico). The residue was dried at 50 °C for 24 h in an air circulation oven (Marconi MA 415, Brasil) and then milled using a knife mill Marconi MA-680 (Brazil). The milled residue was sieved through a 48-mesh sieve (0.297 mm) to obtain a homogeneous particle size. The resulting material was stored in sealed plastic containers at room temperature until further use. All reagents used in this study were of analytical grade PA (pure for analysis); ethanol absolute, acetic acid, hydrogen peroxide 200 V, NaOH, sulfuric acid, cetyltrimethylammonium bromide, sodium lauryl sulfate, ethylenediamine tetraacetic acid, sodium borate, anhydrous sodium dihydrogen phosphate and monoethylene glycol were purchased from Synth (São Paulo, SP, Brazil). DPPH (2,2-diphenyl-1-picrylhydrazyl), ABTS (2,2'-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid), Trolox, and gallic acid were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2 Methods

The sequence of analyses carried out in this study is presented in Fig. 1. Two starting materials were employed for both the extraction of PC and cellulose: RCBH (raw cocoa bean hulls) – obtained from the raw residue after milling, and PTH (pretreated cocoa hulls) – obtained from RCBH pretreated in an autoclave as described below.

As observed in Fig. 1, RCBH and PTH were subjected to parallel PC and cellulose extraction to compare how the autoclave pretreatment affected efficiency of extractions. PC extraction was carried out from both RCBH and PTH by two methods: HAE (Heat-Assisted Extraction), and UAE (Ultrasound-Assisted Extraction) using two different solvents - pure water (UAE-H₂O) and a 50% ethanol mixture (UAE-Ethanol50%).

Finally, the solid fraction remaining specifically after the RCBH undergo PC extraction by HAE was collected and designated as RHPC (Residual Hull from PC Extraction by HAE); from this material cellulose was also extracted. As the results with HAE were more promising for PC extraction from RCBH, only this sample was used for a further round of cellulose extraction and characterization.

For each sample (PTH, RHPC, CE-RCBH, CE-PTH, and CE-RHPC), the solid fraction yield was calculated and expressed as g/ 100 g of RCBH. Cellulose recovery was calculated as the ratio of recovered cellulose to the initial cellulose content of RCBH and expressed as a percentage.

2.2.1 Pretreatment of RCBH to obtain PTH by autoclave

RCBH was subjected to a pretreatment by autoclaving [9] resulting in the PTH (Fig. 1). RCBH was placed in Erlenmeyer flasks, maintaining a 1:25 ratio (RCBH: water), and the sample was then autoclaved for 40 min at 121 °C and 2 atm (Primatec, Brazil). After this process, the sample was filtered using synthetic polyester fabric as the filter. The resulting solid material labeled as PTH was dried for 24 h at 45 °C in an air circulation oven (Marconi MA 035, Brazil) and stored in plastic containers at room temperature. Autoclave pretreatment was applied to remove pectic substances and other interfering gums, aiming for a more efficient extraction of PC and cellulose [9].

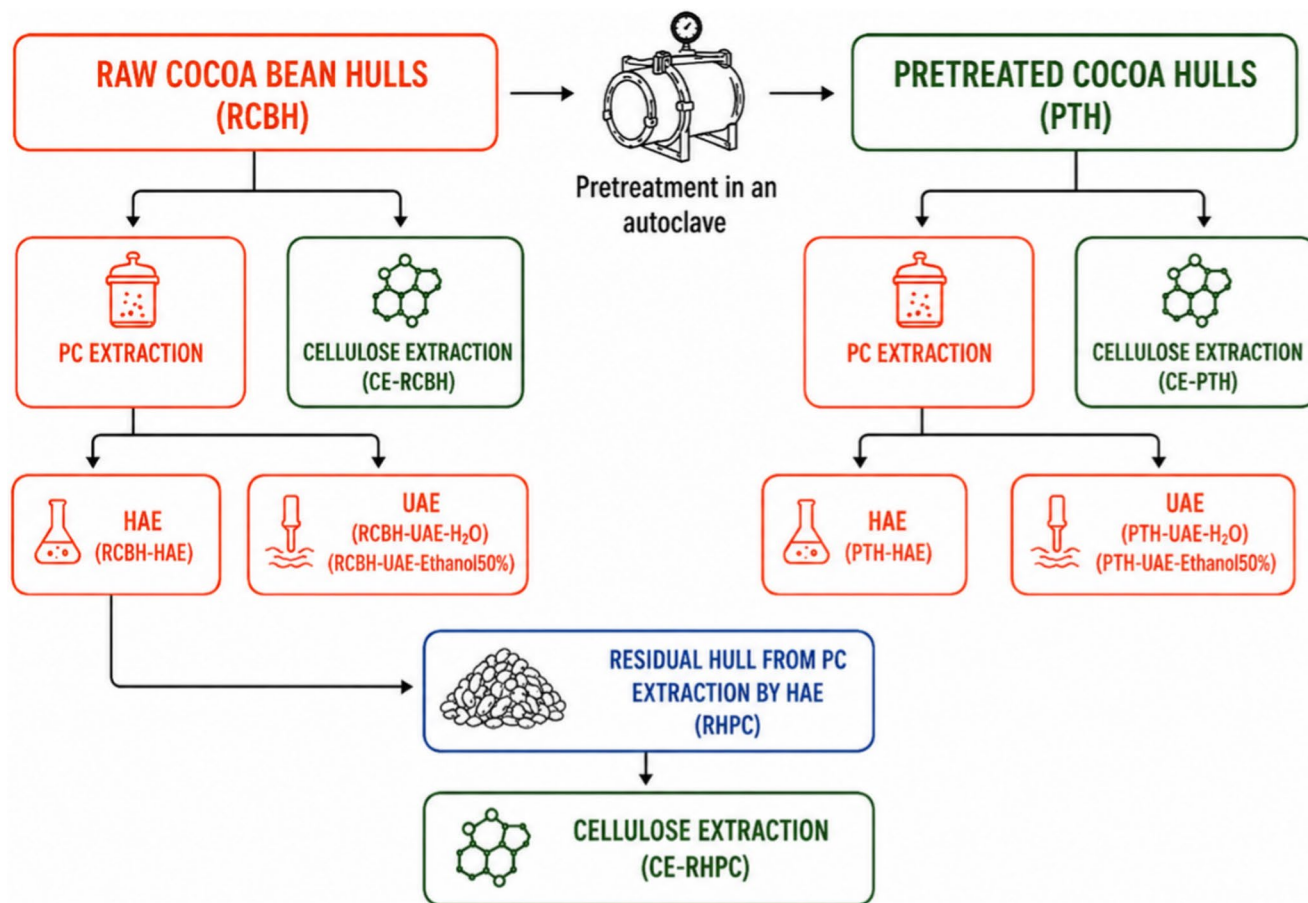


Fig. 1 Flow chart of processes performed on RCBH

2.2.2 Heat-Assisted Extraction (HAE) of PC from RCBH and PTH

HAE was performed according to the methodology of Rebollo-Hernanz et al. [8], with modifications. Each sample (RCBH and PTH) was mixed with water at a concentration of 0.02 g/mL in an Erlenmeyer flask and subjected to a temperature of 100 °C in a Dubnoff water bath (Tecnal, TE-053, SP Brazil) under continuous agitation for 50 min. Once the extraction was completed, the samples were stored at -6 °C (Elux Refrigerator, RDE37, Brazil) until further analyses. The material obtained from RCBH and PTH was named RCBH-HAE and PTH-HAE.

The solid fraction remaining after the RCBH undergo PC extraction by HAE is collected and designated as RHPC and it was stored for future cellulose extraction.

2.2.3 Ultrasound-Assisted Extraction (UAE) of PC from RCBH and PTH

UAE was carried out according to Jafari et al. [18], with modifications. Approximately 10 g of each sample were added to 170 mL of distilled water or 50% ethanol solution. The material was subjected to ultrasonication (QSonics Q700, United States) at 40 °C for 30 min (the system was coupled to a percolation bath at a constant temperature), at a frequency of 20 kHz, power of 700 W, and amplitude of 60%, using a cylindrical probe with a diameter of 19.1 mm (QSonica, United States). The samples were filtered through a synthetic polyester fabric, and the extract was frozen at -6 °C (Elux Refrigerator, RDE37, Brazil) for further analyses. The material obtained from RCBH and PTH, using water as solvent, was named RCBH-UAE-H₂O and PTH-UAE-H₂O, respectively; and the material obtained from RCBH and PTH, using 50% ethanol solution, was named RCBH-UAE-Ethanol50% and RCBH-UAE-Ethanol50%, respectively.

2.2.4 Extraction of cellulose from RCBH, PTH, and RHPC

Cellulose was extracted [19] from RCBH, PTH, RHPC by HAE. Approximately 100 g of each sample (RCBH, PTH, and RHPC) were added to 2.5 L of peracetic acid solution (50% acetic acid, 38% hydrogen peroxide and 12% distilled water), which was kept under agitation in a magnetic stirrer (IKA C-MAGHS 7, Germany) for 24 h at 70 °C. After the procedure, the extract was filtered and washed with 1.0 mol/L NaOH, ensuring a pH range between 5.0 and 6.0. The cellulose-rich material resulting from this process was dried in an air circulation oven (Marconi MA 035, Brazil) at 40 °C for subsequent characterization. The material obtained from RCBH, PTH, and RHPC was named CE-RCBH, CE-PTH, and CE-RHPC, respectively.

2.3 Analytical methods

2.3.1 Cellulose, hemicellulose and lignin contents

Cellulose and hemicellulose were determined in the RCBH and PTH materials using the Van Soest method [20], through the quantification of acid detergent fibers (ADF) (sulfuric acid and cetyltrimethylammonium bromide) and neutral detergent fibers (NDF) (sodium lauryl sulfate, ethylenediamine tetraacetic acid, sodium borate, anhydrous sodium dihydrogen phosphate and monoethylene glycol). Briefly, 0.5 g of each sample was placed in a 100 mL Erlenmeyer flask containing 50 mL of the respective reagent. The flasks were sealed and heated in a boiling water bath for 1 h. Subsequently, the samples were filtered and washed with water, followed by a final wash with 40 mL of acetone. The residues were dried in an oven at 60 °C for 24 h and then weighed. The NDF and ADF contents were calculated using Eqs. (1) and (2), respectively:

$$\% \text{ NDF} = \frac{\text{final sample weight}}{\text{initial sample weight (dry basis)}} \times 100 \quad (1)$$

$$\% \text{ ADF} = \frac{\text{final sample weight}}{\text{initial sample weight (dry basis)}} \times 100 \quad (2)$$

The hemicellulose content was calculated by subtracting the NDF (%) from the ADF (%), and the cellulose content by subtracting the ADF (%) from the lignin content (%).

The lignin content in the RCBH and PTH materials was determined using the method of the Technical Association of the Pulp and Paper Industry (TAPPI T222 om-88) [21]. Lignin content was determined as acid-insoluble lignin. Each sample was treated with 72% sulfuric acid to hydrolyze carbohydrates, followed by dilution and further hydrolysis under heating. The remaining insoluble residue was filtered, washed, dried to constant weight, and quantified gravimetrically as lignin. The analyses were performed in triplicate.

2.3.2 Water and oil absorption capacities

Water and oil absorption capacities were determined for the RCBH and PTH materials following the methodology described by Benítez et al. [22], with modifications. In a Falcon tube, 30 mL of distilled water (or sunflower oil) and 1.0000 g of sample were added. The mixture was vortexed for 1 min and then allowed to stand for 24 h. After this period, the material was centrifuged for 20 min at 3000 rpm (Eppendorf 5804, Germany), the supernatant was discarded, and the residue was weighed. The analysis was performed in triplicate. Water absorption capacity was expressed as g H₂O / g sample, and oil absorption capacity was expressed as g oil / g sample. The analyses were performed in triplicate.

2.3.3 Swelling capacity

The swelling capacity was determined for both the RCBH and the PTH. A total of 250 mg of each sample and 5 mL of distilled water were added to a graduated cylinder, in triplicate. The material was shaken for 30 min at 150 rpm on an orbital shaker (MA 140 CFT, Brazil) to eliminate air bubbles. After shaking, the graduated cylinders were left to stand for 24 h [23]. The analyses were performed in triplicate. The swelling capacity (mL/g) was expressed according to Eq. 3 below:

$$\text{Swelling Capacity} = \frac{\text{mL occupied by the sample}}{\text{g of sample}} \quad (3)$$

2.3.4 Emulsifying activity

Emulsifying activity was determined for the RCBH and PTH materials according to Seibel & Beléia [24]. In a Falcon tube, 1.0000 g of sample was added to 10 mL of distilled water and 10 mL of sunflower oil. The total volume was measured, and the mixture was homogenized using a Turrax disperser (Turratec TE-102, Tecnal, Brazil) for 1 min at 16,000 rpm. The sample was then centrifuged (Eppendorf 5804 R, Germany) at 1500 rpm for 5 min at 15 °C, and the volume of the emulsified layer was measured. The analyses were performed in triplicate. Emulsifying activity was expressed according to the following equation:

$$\text{Emulsifying Activity (\%)} = \frac{\text{Volume of the emulsified layer}}{\text{Total volume of the tube}} \times 100 \quad (4)$$

2.3.5 Apparent density

The apparent density was determined by adding 10 g of RCBH or PTH sample to a 10 mL graduated cylinder. The cylinder was gently tapped 15 times, and the occupied volume was measured. The density (g/mL) was calculated as the ratio between the mass and the volume of the sample [24]. The analyses were performed in triplicate.

2.3.6 Quantification of Phenolic Compounds (PC)

The modified Folin–Ciocalteu method was used for PC determination in the RCBH and PTH materials [25]. Five-point analytical curves were performed in triplicate measurements with a known concentration of gallic acid (5–50 µmol/L). The results were expressed as grams of gallic acid per milligram of dry solids (mg GAE/g db). The analyses were performed in triplicate.

2.3.7 Determination of antioxidant activity

The antioxidant activity was determined in the RCBH and PTH materials using the DPPH (2,2-diphenyl-1-picrylhydrazyl) and ABTS (2,2'-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid) methods. According to the DPPH method [26, 27], the antioxidant capacity was determined using a Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) analytical curve (2–5 mmol/L), and the result was expressed as mg Trolox equivalent/100 g of sample (mg TE/100 g). Samples absorbance was measured at 517 nm (Biochrom Libra S22 UV/Vis, United States). For the ABTS assay, the calibration curve consisted of a standard Trolox solution (1–8 mmol/L), read in a spectrophotometer at 730 nm (Biochrom Libra S22 UV/Vis, United States) [28]. Results were expressed as mg TE/g of dry solids (mg TE/g db). The analyses were performed in triplicate.

2.3.8 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was conducted on RCBH, PTH, RHPC, and on the cellulose-rich materials extracted from each sample (CE-RCBH, CE-PTH, and CE-RHPC). The samples were pulverized in a benchtop analytical mill (IKA A10, Germany) and homogenized with potassium bromide (KBr) to be compressed into pellets. KBr pellets with a thickness of 1 mm were prepared, and the samples were used at a concentration of 1% relative to the weight of the KBr. The analyses were performed using a Shimadzu FTIR-8300 spectrometer (Japan), operating at a spectral resolution of 4 cm^{−1} and a spectral range of 4,000–500 cm^{−1} [16].

2.3.9 X-ray Diffraction (XRD)

The crystallinity of each sample (RCBH, PTH, RHPC, CE-RCBH, CE-PTH, and CE-RHPC) was investigated by XRD. The samples were pulverized using a benchtop analytical mill (IKA A10, Germany), and the analyses were performed using a Panalytical X'Pert PRO MPD diffractometer (Netherlands), with copper Kα radiation (λ = 1.5418 Å), operating at 40 kV and 30 mA, ramp rate of 1°/min. The relative crystallinity index (CrI) was calculated according to Eq. 5, as described by Segal et al. [29].

$$\text{CrI (\%)} = \left[\frac{I_{200} - I_{am}}{I_{200}} \right] \times 100 \quad (5)$$

Where I_{200} is the maximum intensity of the diffraction peak corresponding to the crystalline lattice at $2\theta = 22^\circ\text{--}23^\circ$, and I_{am} is the minimum intensity of the diffraction peak associated with the amorphous region at $2\theta = 18^\circ\text{--}19^\circ$ [11].

2.3.10 Scanning Electron Microscopy (SEM)

SEM was performed on RCBH, PTH, RHPC, and the cellulose-rich material extracted from each sample (CE-RCBH, CE-PTH, and CE-RHPC). The samples were dried in an air circulation oven (Marconi MA 035, Brazil) at 60 °C for 3 h and subsequently stored in desiccators containing anhydrous calcium chloride for 7 days. The dried samples were mounted on bronze supports using double-sided adhesive tape. Subsequently, the samples were covered with a thin gold layer (40–50 nm) and analyzed at magnifications ranging from 200 to 6,000 times using a scanning electron microscope (FEI Quanta 200, United States), operating at an accelerating voltage of 30 kV for all samples [16].

2.3.11 Thermogravimetric Analysis (TGA)

TGA was performed on RCBH, PTH, RHPC, and the cellulose-rich material extracted from each sample (CE-RCBH, CE-PTH, and CE-RHPC). The scans were performed in a Shimadzu TGA-50 thermogravimetric analyzer (Japan), from room temperature up to 600 °C, at a heating rate of 20 °C/min under a nitrogen flow of 20 mL/min [16].

2.4 Statistical analysis

Statistical analyses were performed using SigmaPlot 11.0 (Systat Software Inc., 2008, San Jose, CA, USA). The data were submitted to the Student's t-test for comparison of means between two samples, or to the Tukey's test for comparisons between three or more samples, with 5% significance ($p \leq 0.05$).

3 Results and discussion

3.1 Pretreatment of RCBH to obtain PTH by autoclave

The material yield after the autoclaving pretreatment of RCBH was 64.24% $\pm$ 3.93%, therefore, for every 100 g of RCBH, 64.24 g of PTH were obtained. PTH was expected to present improved accessibility of the cell wall matrix, thereby facilitating the recovery of both PC and cellulose [9, 30].

3.2 Cellulose, hemicellulose and lignin contents of RCBH and PTH

Table 1 presents RCBH and PTH cellulose, hemicellulose, and lignin contents. RCBH presented 25.06, 4.81, and 31.14% of cellulose, hemicellulose, and lignin,

Table 1 Cellulose, hemicellulose and lignin contents of RCBH and PTH

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)
RCBH	25.06 $\pm$ 0.44 ^b	4.81 $\pm$ 3.46 ^a	31.14 $\pm$ 0.9 ^b
PTH	40.48 $\pm$ 0.98 ^a	0.33 $\pm$ 1.99 ^b	44.42 $\pm$ 0.7 ^a

Means $\pm$ standard deviation. Different letters within the same column indicate significant differences according to t- test ($p \leq 0.05$)

respectively. In comparison, Souza et al. [31] reported similar values for cellulose (26.66%), higher values for hemicellulose (9.50%), and lower values for lignin (20.27%) for cocoa bean hulls. Possible, these differences may be attributed to several factors, including cocoa variety, geographical origin, cultivation conditions, fruit maturity, post-harvest processing (particularly fermentation, drying, and roasting), as well as differences in the analytical methods used to determine lignocellulosic composition. The residue used in this study originated from an agroindustrial facility in Mexico, and was derived from raw material from the same country, whereas Souza et al. [31] used residue from Brazil.

It was observed that the pretreatment in the autoclave resulted in significant increases in cellulose content from 25.06 to 40.48%, and in lignin content from 31.14 to 44.42% (Table 1). It can be observed that, as discussed in Sect. 3.1, for every 100 g of RCBH, 64.24 g of PTH were obtained, which means that 100% of the cellulose was recovered from RCBH. Furthermore, considering that the cellulose content of RCBH was 25.06% (Table 1), and that in the PTH sample 40.48% corresponds to cellulose, it can be said that there was an enrichment in the cellulose content resulting from the removal of soluble compounds, including pectins, gums, and other compounds extracted in hot water.

This effect has been reported in previous studies. According to Dimawarnita et al. [9], autoclave pretreatment of cocoa residues promotes the removal of pectic substances and other impurities, facilitating subsequent processing. Pinkaew et al. [30] reported that an autoclave pretreatment is effective for extracting pectin from cocoa hulls by promoting plant cell rupture. Mantovan et al. [15] analyzed the cellulose content of *in natura* and depectinized orange bagasse subjected to a heat treatment in a hydrochloride acid solvent bath (HCl 0.05 M) under continuous stirring at 80 °C for 60 min. They reported values of 12% and 27% cellulose, respectively, for *in natura* and depectinized samples, indicating that pretreatment can promote pectin removal and enhance cellulose extraction; these authors reported 100% of cellulose recovery from the raw material, and also reported a cellulose enrichment resulted from removal of soluble sugars, gums, aqueous extractives, and other non-fibrous components during acid pectin extraction.

3.3 Techno-functional properties of RCBH and PTH

Table 2 presents the results of the techno-functional properties analysis of the RCBH and PTH samples. In this study, significant differences were observed between the samples for all properties, indicating that exposure to high temperatures after pretreatment of RCBH to obtain PTH affected its techno-functional properties.

When compared with the RCBH sample, PTH exhibited higher water and oil absorption capacities (Table 1), and lower swelling and emulsifying capacities. These effects may be associated with heat exposure, which promotes morphological changes in the residue, such as the formation of surface pores that increase the contact area between the material and water or oil, thereby facilitating water and oil retention. In addition, exposure to high temperatures may lead to protein denaturation, interfering with emulsifying activity [32].

Water absorption and swelling capacities can provide relevant information on the potential application of the residues in the development of new food products, allowing their characterization as hydration agents and functional ingredients, capable of improving texture and moisture retention in solid foods or functional beverages. Additionally, oil absorption capacity can influence sensory attributes such as palatability, flavor retention, and mouthfeel [7].

Delgado-Ospina et al. [32] reported lower values of water and oil absorption capacities for cocoa bean hulls, namely 4.6 g H₂O/g for water absorption and 1.30 g oil/g for oil absorption. However, a greater emulsifying capacity was observed by them, with a value of 45%. Salvatore et al. [33] also reported lower water (3.57 g/g) and oil (2.38 g/g) absorption values for cocoa bean hull than values observed in this study for RCBH and PTH.

Furthermore, when compared with other lignocellulosic residues investigated by Silva et al. [34], such as coffee hull, oat hull, and soybean hull, both RCBH and PTH exhibited high water absorption and swelling capacities. PTH also showed a higher oil absorption capacity. These results indicate that cocoa bean hull can be considered a promising raw material for the exploration and development of novel food products.

3.4 Extraction of PC and antioxidant activity

In this study, two methods were employed for the extraction of PC, HAE and UAE, using water (UAE-H₂O) and 50% ethanol (UAE-50% ethanol) as solvents. The efficiency of PC extraction was affected by both the extraction technique and the solvent system. HAE resulted in the maximum PC content of 16.67 mg GAE/g db between RCBH samples (Table 3). For PTH samples, HAE yielded 6.56 mg GAE/g

Table 2 Techno-functional properties of raw cocoa hull (RCBH) and pretreated cocoa hull (PTH)

Property	RCBH	PTH
Water Absorption Capacity (g H ₂ O/g)	7.05±0.57 ^a	9.40±0.14 ^b
Oil Absorption Capacity (g oil /g)	2.86±0.18 ^a	5.10±0.22 ^b
Swelling Capacity (mL/g)	12.09±0.51 ^a	8.53±0.23 ^b
Emulsifying Activity (%)	18.00±2.0 ^a	0.17±0.29 ^b
Apparent Density (g/mL)	0.51±0.01 ^a	0.25±0.00 ^b

Means±standard deviation. Different letters in the same row indicate a significant difference according to the t-test ($p \leq 0.05$)

Table 3 Phenolic compounds (PC) in extracts obtained by HAE and UAE from RCBH and PTH

Sample	PC (mg GAE/ g db)	DPPH (mg TE/ g db)	ABTS (mg TE/ g db)
RCBH-HAE	16.67±0.39 ^a	48±0.02 ^a	156±8.20 ^a
RCBH-UAE - H ₂ O	5.68±0.25 ^b	14±0.20 ^d	57±7.40 ^c
RCBH-UAE-Ethanol50%	11.97±0.48 ^c	16±0.40 ^c	97±11.90 ^b
PTH-HAE	6.56±0.12 ^d	34±0.40 ^b	40±2.20 ^d
PTH-UAE - H ₂ O	3.03±0.25 ^e	11±0.10 ^e	18±9.70 ^e
PTH-UAE - Ethanol 50%	8.02±0.58 ^f	16±0.20 ^c	29±1.00 ^e

Means±standard deviation. Different letters within the same column indicate significant differences according to the t-test ($p \leq 0.05$)

db, and when UAE was applied to these samples, a solvent-dependent effect was observed; extraction with water resulted in 3.03 mg GAE/g db, while the use of 50% ethanol increased the PC content to 8.02 mg GAE/g db. Thus, HAE was more effective than UAE for RCBH samples, but for PTH, the use of 50% ethanol in UAE resulted in greater PC recovery. Therefore, the differences observed cannot be attributed exclusively to the energy source applied during extraction.

Garcia-Oliveira et al. [35] reported that HAE is more effective than UAE-ethanol (0-100%). These authors reported that HAE (40 °C/60 min) facilitated the extraction of approximately 26% more PC compared to UAE (20 °C/20 min/400 W). According to these authors, differences in the amounts of PC recovered by HAE and UAE may be related to the distinct mechanisms by which energy is delivered during extraction. In HAE, thermal energy facilitates the release and transport of PC, whereas UAE primarily relies on acoustic cavitation, which was performed at room temperature. Although both approaches are recognized as effective for the recovery of PC, their results suggested that cavitation under non-heated conditions was less efficient than thermal treatment, since increasing temperature can decrease solvent viscosity and surface tension, improving solvent penetration, molecular diffusion, and mass transfer from the lignocellulosic matrix to the extraction medium.

PTH exhibited the lowest levels of PC, regardless of the extraction method employed (Table 3). These results may reflect alterations induced by the autoclave pretreatment,

which could have solubilized or degraded the easily extractable phenolic fraction or modified the interactions between the phenolic compounds and the lignocellulosic matrix.

Previous studies have investigated the extraction of PC from different raw materials subjected to high temperatures and reported an increase in PC concentration as a function of temperature elevation [4, 8, 35]. This increase in PC concentration in samples exposed to high temperatures is associated both with enhanced compound solubility and with the release of intracellular contents due to heat-induced cell lysis, as well as with the liberation of PC bound to other substances as a result of their degradation [36], such as lignin degradation.

In addition to yielding higher PC contents, the HAE presents greater industrial applicability due to its low cost and ease of process modification. Rebollo-Hernanz et al. [8] stated that HAE can be used to obtain phenolic-rich extracts from cocoa bean hulls using water as the only extracting agent, resulting in new food ingredients with potential antioxidant and health-promoting properties. In their study, they reported maximum values of 7.33 mg GAE/g, which are lower than those obtained in this study.

In another study, researchers extracted PC from cocoa bean hull by autoclaving at 135 °C, 2 bar by 3 to 13 min, under different pH conditions (2–10), resulting in a maximum PC value of 14.5 mg GAE/g [7], which is comparable to this present study. Conversely, Švarc-Gajić et al. [37] quantified PC extracted from cocoa bean hull using subcritical water extraction, in which the sample was subjected to pressurization (30 bars) at 150 °C for 30 min, and obtained maximum values of 45 mg GAE/g, this behavior was attributed to temperature-induced modifications in water properties, including lower viscosity and surface tension, as well as a reduced dielectric constant. Together, these changes enhance mass transfer and promote the recovery of bioactive constituents, including PC. In addition, subcritical water facilitates the hydrolysis of linkages between PC and the lignocellulosic matrix, increasing the release of bound PC.

In this study, the values obtained by UAE using 50% ethanol were 11.96 mg GAE/g db (RCBH-UAE-Ethanol50%), 8.02 mg GAE/g db (PTH-UAE-Ethanol50%), demonstrating higher efficiency compared to extraction using water alone (Table 3); although the use of ethanol 50% proved to be more efficient than water, it may increase extraction costs for certain applications, as an additional step is required for solvent removal.

Lopes et al. [38] reported higher PC values than those obtained in the present study, extracting approximately 25.70 mg GAE/g after exposure to heat at 45 °C for 30 min. In contrast, the extraction of PC from cocoa bean hull through pressurization (10 MPa) in the presence of ethanol

(99.8%) at 70 °C for 20 min that resulted in a maximum value of 9.6 mg GAE/g of sample [39], which is similar to the values found in this study.

Two methods were used to quantify antioxidant activity, DPPH and ABTS (Table 3), and the results show that higher PC values were generally associated with higher antioxidant activity, but the relationship was not strictly proportional across all samples. RCBH-HAE showed the highest values for all responses: 16.67 mg GAE/g db of PC, 48 mg TE/g db by DPPH, and 156 mg TE/g db by ABTS, while PTH-UAE-H₂O had the lowest PC content and antioxidant activity, with 3.03 mg GAE/g db, 11 mg TE/g db by DPPH, and 18 mg TE/g db by ABTS.

Higher PC contents in cocoa bean hulls have been positively associated with higher antioxidant activity measured by DPPH and ABTS assays [6, 35, 36]. This relationship has been attributed to the ability of phenolic compounds to donate electrons or hydrogen atoms and form resonance-stabilized phenoxyl radicals. However, PC are not the only compounds contributing to the antioxidant activity of this residue, as other bioactive constituents, including methylxanthines, may also contribute to its overall antioxidant capacity.

Mellinas et al. [36] evaluated the antioxidant activity of cocoa hull extracts using the ABTS assay after microwave-assisted extraction and reported maximum values of 28.6 mg TE/g and 25.9 mg TE/g. These values were higher than those obtained by conventional Soxhlet extraction (22.2 mg TE/g) but lower than those observed in the present study. In another study employing HAE for the extraction of PC from cocoa bean hull, the authors reported a maximum antioxidant activity of 19.45 mg TE/g using the ABTS method [8]. Additionally, Gil-Ramírez et al. [4] reported an antioxidant activity of 85 mg TE/g for cocoa bean hull determined by the ABTS assay using the same methodology as the present work; however, methanol was used as the solvent, reinforcing the notion that extract composition varies according to the extraction methodology employed. The observed differences in antioxidant activity may be attributed to several factors, including the extraction solvent and extraction conditions, which determine the recovery of PC according to their polarity and solubility. In addition, variations in the botanical source, geographical origin, cultivation conditions, and post-harvest processing can influence the measured antioxidant capacity, making sometimes direct comparisons among studies difficult [40].

Botella-Martínez et al. [6] reported lower antioxidant activity determined by the DPPH assay than that observed in the present study for extracts of *in natura* cocoa bean hull, with a maximum value of 5.53 mg TE/g. In the cited study, the sample of Ghanaian origin was subjected to PC extraction using different reagents in multiple steps. The

antioxidant activity of cocoa bean hull can be associated with the presence of PC, since, in this study, the sample that exhibited the highest antioxidant activity also showed the highest PC concentration.

Based on these results, it can be stated that HAE proved to be effective for obtaining materials with high antioxidant activity from RCBH, reaching 48 mg TE/g db and 156 mg TE/g db as determined by the DPPH and ABTS assays, respectively (Table 4). Therefore, the RCBH represents a promising option for the development of antioxidant products, such as teas, food ingredients, and cosmetic products.

3.5 Cellulose extraction

Table 4 summarizes the cellulose, hemicellulose, and lignin contents of RCBH, PTH, and RHPC before and after peracetic acid treatment, as well as their extraction yields (g/100 g RCBH) and cellulose recovery relative to the initial cellulose content of RCBH (25.06 g/100 g RCBH).

Initially, RCBH, PTH, and RHPC presented cellulose contents of 25.06%, 40.48%, and 38.13%, respectively. After peracetic acid treatment, the cellulose content increased to 46.87%, 69.20%, and 67.58% for the CE-RCBH, CE-PTH, and CE-RHPC samples, respectively (Table 4), in addition, a significant reduction in lignin content, ranging from 77% to 90%, was observed in the analyzed samples (Table 4). Thus, peracetic treatment resulted in cellulose rich-materials acting primarily as an oxidative delignifying agent that also degrades hemicellulose, leaving behind a cellulose-rich solid residue [9, 11, 12].

When comparing CE-RCBH with CE-PTH, a higher cellulose content was observed for pretreated sample, which was consistent with the results from RCBH and PTH (Table 4), which was attributed to the removal of pectin during this stage, resulting in an improved cellulose extraction, as discussed previously.

Dimawarnita et al. [9] used three concentrations of peracetic acid to isolate cellulose from heat-pretreated cocoa hull and obtained 69.39% cellulose. This result is similar to that found in the present study for the CE-PTH sample, which exhibited the highest cellulose content (69.2%).

Previous studies using peracetic acid have demonstrated the effectiveness of this bleaching agent for cellulose extraction. Mayta et al. [41] employed sodium hydroxide, sodium chlorite, hydrogen peroxide, and peracetic acid to extract cellulose from corn hull and they achieved the best results with the sample treated with peracetic acid, increasing the cellulose content from 25.7% to 75.1%. In another study, Paiva et al. [10] used peracetic acid to extract cellulose from oat hull and soybean hulls and reported significant increases in cellulose content of 473% and 108%, respectively.

Paiva et al. [12] reported the use of peracetic acid for cellulose extraction from coffee hull, highlighting the advantage of a single-step method in which cellulose content enhancement and material bleaching occur simultaneously, making the process faster and more cost-effective.

Regarding solid fraction yields and cellulose recovery, CE-RCBH showed a cellulose recovery of approximately 99% (Table 4), indicating that the chemical treatment effectively preserved most of the cellulose initially present in RCBH. In contrast, the apparent cellulose recoveries exceeding 100% for PTH and CE-PTH, should not be interpreted as an increase in the absolute amount of cellulose, but rather as an indication of cellulose enrichment after processing. For PTH, this apparent recovery may be associated with the preferential removal of non-cellulosic components during pretreatment, increasing the relative proportion of cellulose in the recovered material. A similar effect was observed for CE-PTH, in which the more extensive removal of lignin compared with the other samples further enriched the cellulose fraction. Moreover, recoveries slightly above 100% may arise from the propagation of experimental variability associated with gravimetric yield and compositional analyses. Overall, these findings indicate that the treatments promoted the selective removal of non-cellulosic components while largely preserving the cellulose fraction. This behavior is consistent with the recognized effectiveness of peracetic acid as a delignifying and bleaching agent, capable of promoting lignin removal while maintaining the integrity of cellulose-rich fibers [9, 12, 41]. Ayeni et al. [42] also reported cellulose recovery between 102 and 109% using hydrogen peroxide and lime based oxidative pretreatment

Table 4 Cellulose, hemicellulose and lignin contents of raw cocoa bean hull (RCBH); and cellulose, hemicellulose and lignin contents, solid fraction yield and cellulose recovery of pretreated cocoa bean hull (PTH); residual hull from phenolic compound extraction by HAE (RHPC); cellulose derived from RCBH (CE-RCBH); cellulose derived from PTH (CE-PTH); and cellulose derived from RHPC (CE-RHPC)¹

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Solid fraction yield (g/100 g RCBH)	Cellulose recovery (%)
RCBH	25.06±0.44 ^d	4.81±3.46 ^{ab}	31.14±0.90 ^a	-	
PTH	40.48±0.98 ^c	0.33±1.99 ^{ab}	44.42±0.70 ^b	64.24	104
RHPC	38.13±3.37 ^c	1.74±2.69 ^{ab}	40.11±1.60 ^c	40.50	62
CE-RCBH	46.87±2.17 ^b	7.23±0.28 ^a	3.27±0.90 ^d	53.08	99
CE-PTH	69.20±2.50 ^a	1.39±1.56 ^b	8.16±1.10 ^e	48.29	133
CE-RHPC	67.58±1.46 ^a	2.64±0.93 ^b	9.11±1.70 ^e	31.62	85

Different letters within the same column indicate significant differences according to Tukey's test ($p \leq 0.05$)

of wood waste to enhance enzymatic hydrolysis, and they reported this as a cellulose enrichment that was attributed to the removing of hemicellulose and lignin with negligible cellulose degradation.

3.6 Fourier Transform Infrared Spectroscopy (FTIR)

Regarding the FTIR spectra of cocoa bean hull, no differences were observed among RCBH, PTH, and RHPC (Fig. 2), indicating that autoclave pretreatment and PC extraction did not affect the main functional groups in these samples.

In the region around 3400 cm^{-1} , a broad band corresponding to hydrogen stretching of hydroxyl (OH) groups was observed, which are present in cellulose, hemicellulose, and lignin molecules. The bands observed at 2918 cm^{-1} and

2850 cm^{-1} are related to C–H stretching vibrations [9, 43, 44]. The bands located at 1629 cm^{-1} and 1417 cm^{-1} are associated with C = C double bonds [43].

The band observed at 1062 cm^{-1} represents the C–O–C bond and is associated with the β -(1 $\rightarrow$ 4)-glycosidic linkage between the glycosidic units that form cellulose [44], indicating the preservation of glycosidic linkages during the extraction process.

When comparing the FTIR spectra of the extracted cellulose samples (CE- RCBH, CE- PTH, and CE- RHPC) with those of RCBH, PTH, and RHPC, similar bands to those observed in the starting materials were detected at 3400 cm^{-1} , 2918 cm^{-1} , 2850 cm^{-1} , 1629 cm^{-1} , and 1062 cm^{-1} , as previously discussed (Fig. 2).

Some differences were observed between the spectra of the cellulose samples and the starting materials (RCBH,

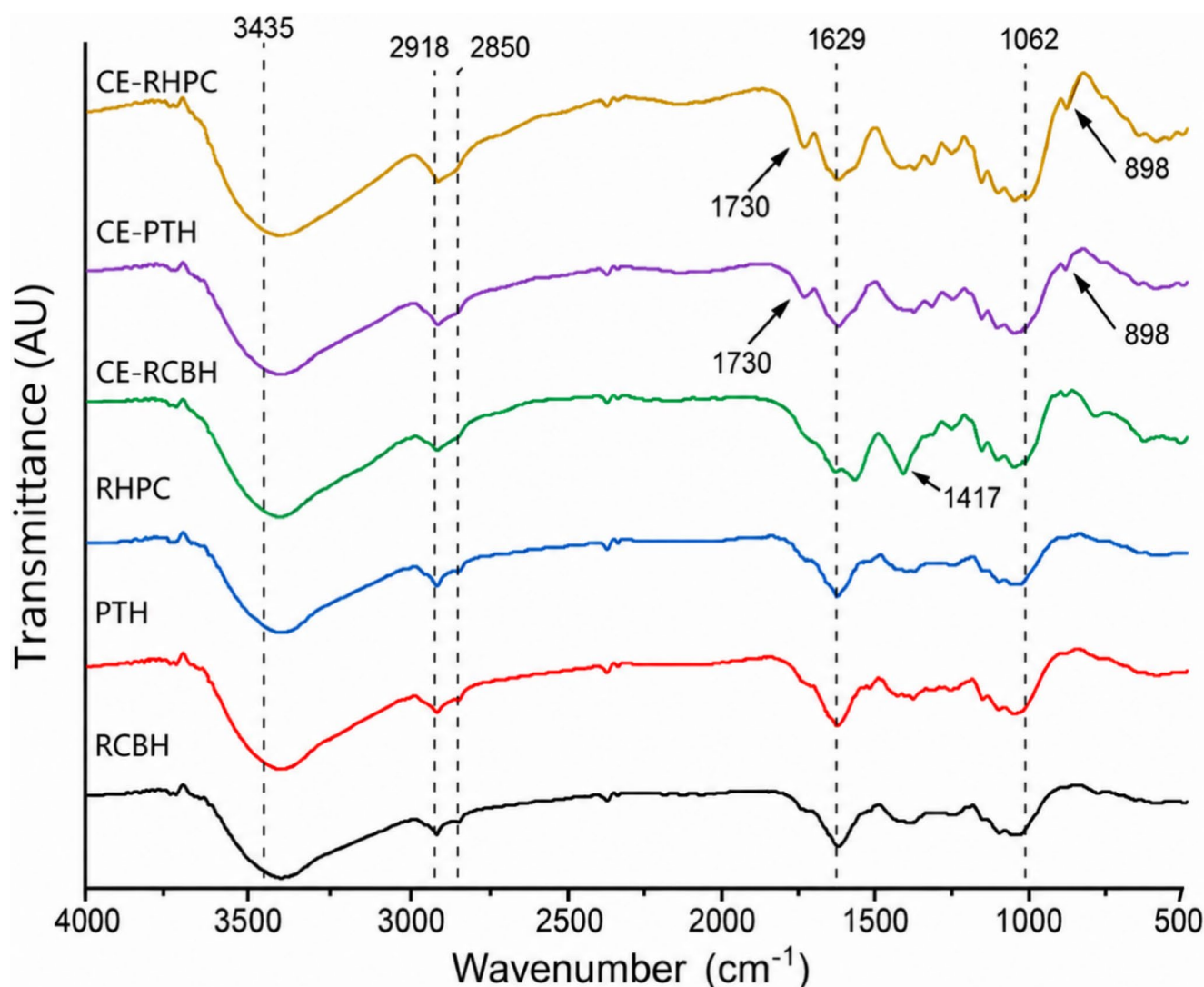


Fig. 2 FTIR spectra of raw cocoa bean hull (RCBH); pretreated cocoa bean hull (PTH); residual hull from phenolic compound extraction by HAE (RHPC); cellulose derived from RCBH (CE-RCBH); cellulose derived from PTH (CE-PTH); and cellulose derived from RHPC (CE-RHPC)

PTH, and RHPC). In the CE-PTH and CE-RHPC samples, a band in the region around 1730 cm^{-1} was observed that was not present in CE-RCBH, which may be associated with the oxidative action of peracetic acid on C–OH groups during cellulose extraction. This assignment is supported by previous studies using this bleaching agent, in which a band in the same region was also reported [11, 14, 16].

Another band observed only in samples CE-PTH and CE-RHPC is located at approximately 898 cm^{-1} , which is indicative of the β -glycosidic linkage of cellulose [14, 15], consistent with the higher cellulose contents in these samples (Table 4). In contrast, in the CE-RCBH sample, an intense band at around 1417 cm^{-1} was observed, associated with the presence of CH_2 and CH groups in hemicellulose, corroborating the fiber composition data, in which CE-RCBH exhibits a higher hemicellulose content (Table 4).

3.7 X-ray Diffraction (XRD)

The XRD analysis results are presented in Fig. 3, showing that all samples exhibited characteristics of a semicrystalline material, with both amorphous and crystalline regions. In the CE-RCBH, CE-PTH, and CE-RHPC samples, a main diffraction peak at $2\theta = 22.5^\circ$ was observed, and it was more pronounced when compared to the RCBH, PTH, and RHPC samples, indicating an increase in material crystallinity; these results are consistent with the material composition (Table 4). According to Debiagi et al. [14], an increase in cellulose content leads to an enhancement of the peaks in XRD diffractograms due to the reduction in hemicellulose and lignin contents, which are essentially amorphous.

Six additional diffraction events were observed at 11.57° , 16.97° , 19.12° , 28.27° , 29.87° , and 33.72° in the sample

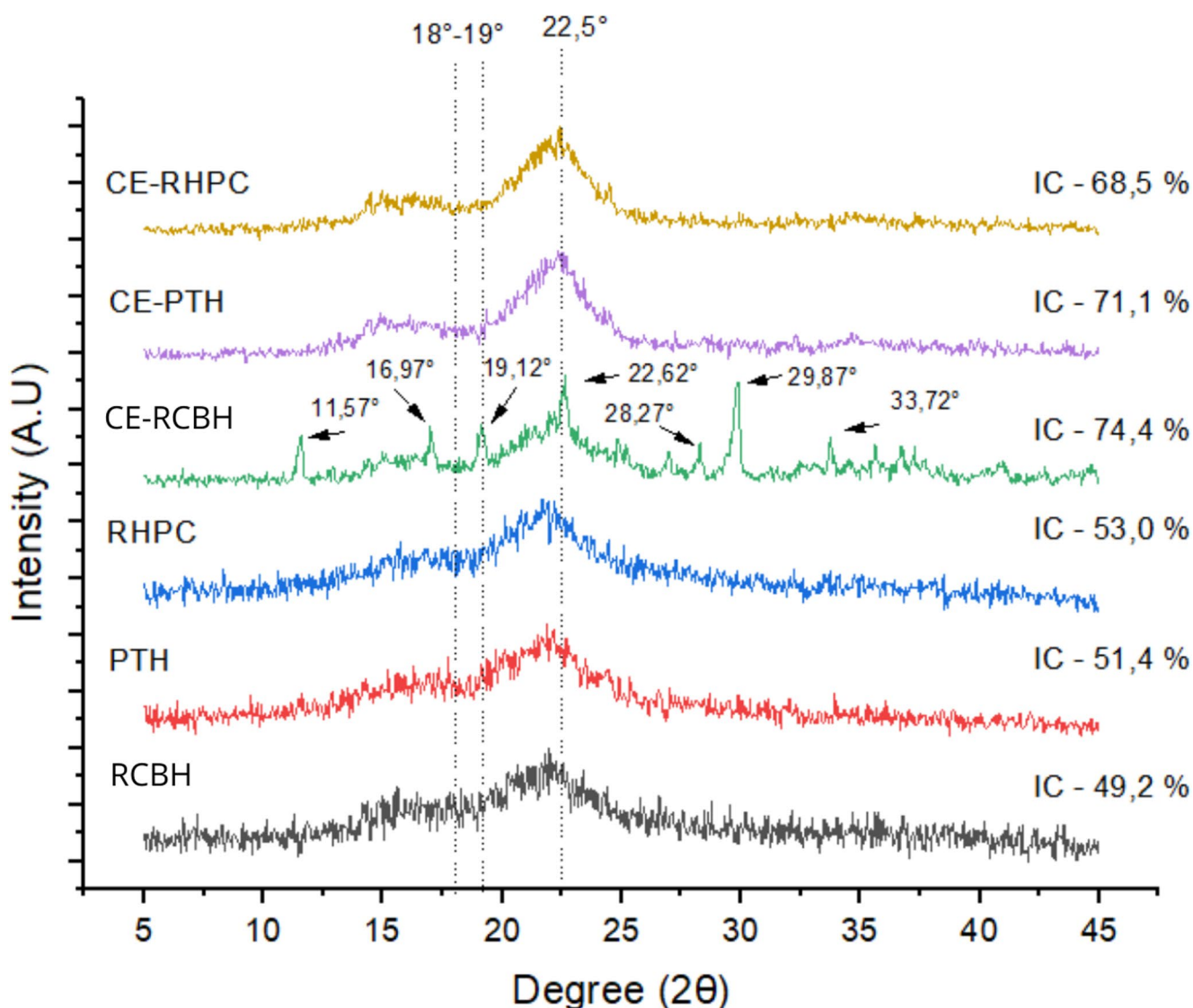


Fig. 3 XRD diffractograms of raw cocoa bean hull (RCBH); pretreated cocoa bean hull (PTH); residual hull from phenolic compound extraction by HAE (RHPC); cellulose derived from RCBH (CE-RCBH); cellulose derived from PTH (CE-PTH); and cellulose derived from RHPC (CE-RHPC)

CE- RCBH, indicating structural changes in the material. The peak at 16.97° is characteristic of cellulose type I, as is the peak at 22.5° ; however, the peak at 19.12° is associated with cellulose type II, revealing a hybrid structure composed of cellulose I and cellulose II [14–17, 44, 45]. The peak at 28.27° may represent pectin interference in the sample, as it has been detected in XRD patterns of commercial pectin [46].

The crystallinity indices (CI) of the samples are presented in Fig. 3. All cellulose samples exhibited higher CI values than their corresponding starting materials, indicating that the removal of amorphous substances, such as hemicellulose and lignin, resulted in increased crystallinity [14, 15]. The CE-RCBH sample showed the highest CI (74.4%), followed by CE-PTH (71.1%) and CE- RHPC (68.5%) (Fig. 3).

In this study, cellulose extraction using peracetic acid resulted in a material with a higher crystallinity index (CI) compared to previous studies. Marim et al. [47] used peracetic acid to obtain cellulose from orange bagasse and reported a maximum CI of 42%. When peracetic acid was combined with ultrasound-assisted extraction, the CI increased to 54%; however, this value remained lower than that observed in the present study. In another study using corn straw for cellulose extraction with peracetic acid, a

lower CI value (61.4%) was also reported for the extracted cellulose [41].

Cocoa industry residues have already been explored for cellulose extraction using peracetic acid; however, the literature reports the use of cocoa pod hull treated with peracetic acid in combination with other acids, yielding a material with a crystallinity index (CI) of 11.71%, which is considerably lower than that obtained in the present study [9].

The crystallinity of a material reflects the parallel organization of cellulose chains sustained by intra- and inter-molecular hydrogen bonds, and an increase in CI indicates enhanced molecular organization and hydrogen bonding, leading to improved material properties such as strength and rigidity, thereby enabling applications in different fields. The high degree of cellulose crystallinity allows its use in rubber reinforcement, filler materials, electronic materials, packaging materials, among others [48].

3.8 Scanning Electron Microscopy (SEM)

Figure 4 presents the morphological differences among the RCBH, PTH, RHPC, CE- RCBH, CE- PTH, and CE- RHPC samples observed by SEM. When compared to RCBH, PTH

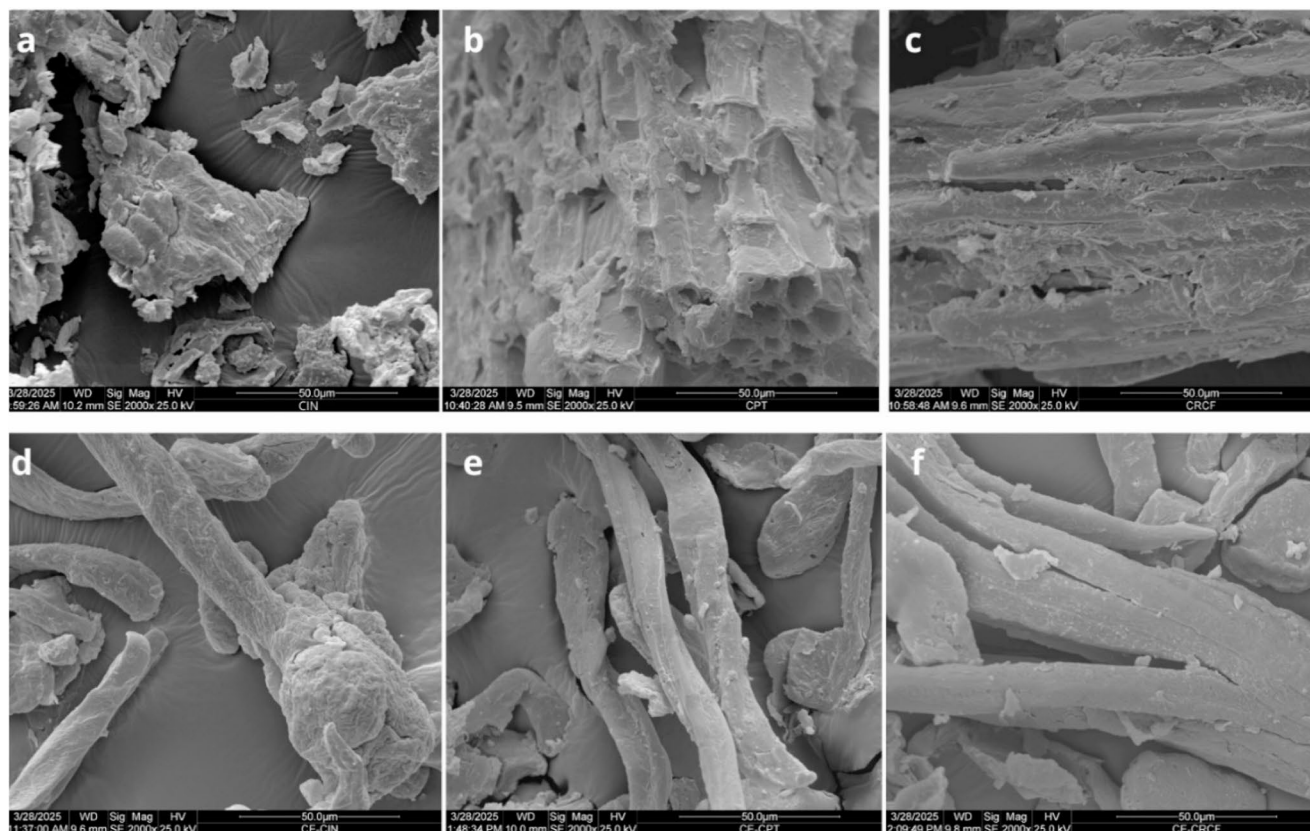


Fig. 4 Scanning Electron Microscopy (SEM) images: (a) raw cocoa bean hull (RCBH); (b) pretreated cocoa bean hull (PTH); (c) residual hull from phenolic compound extraction by HAE (RHPC); (d) cellu-

lose derived from RCBH (CE-RCBH); (e) cellulose derived from PTH (CE-PTH); and (f) cellulose derived from RHPC (CE-RHPC)

samples, which were subjected to heat treatment, exhibited pore-like structures, corroborating the results previously reported for water and oil absorption, in which PTH presented higher water and oil absorption values (Table 2). Exposure of lignocellulosic materials to heat leads to morphological modifications, promoting pore formation on the residue surface [32].

The cellulosic-rich materials extracted using peracetic acid exhibited a homogeneous surface (Fig. 3d–f), and cellulosic fibers appeared as individualized bundles, confirming the lignin and hemicellulose removal, a behavior that has also been reported in previous studies using peracetic acid for cellulose extraction [9, 12, 49].

3.9 Thermogravimetric Analysis (TGA)

Figure 5 presents the thermograms of the studied samples. It was observed that all samples exhibited a degradation event below 100 °C, which is characteristic of lignocellulosic residues and corresponds to either water evaporation from

the sample or the degradation of low-molecular-weight substances [14, 15, 44, 45].

In the samples RCBH, PTH, and RHPC, a second degradation event was observed. In the RCBH sample, the onset of degradation occurred at lower temperatures compared to PTH and RHPC, starting at 181 °C and reaching a maximum event at 289 °C, which may be associated with the presence of other substances in the sample [50], since RCBH exhibited a low crystallinity index, indicating the presence of additional compounds in the material. Another feature supporting this hypothesis is the presence of events observed exclusively in the RCBH sample at 393 °C and 462 °C, which have been previously associated with the thermal decomposition of pectin [51]. For the PTH and RHPC samples, degradation onset was observed at 250 °C, with a maximum event at 340 °C, a behavior previously reported for cocoa hull and attributed to the degradation of hemicellulose and cellulose [49, 52].

For the cellulose-rich material (CE-RCBH, CE-PTH, and CE-RHPC), a second degradation stage was observed

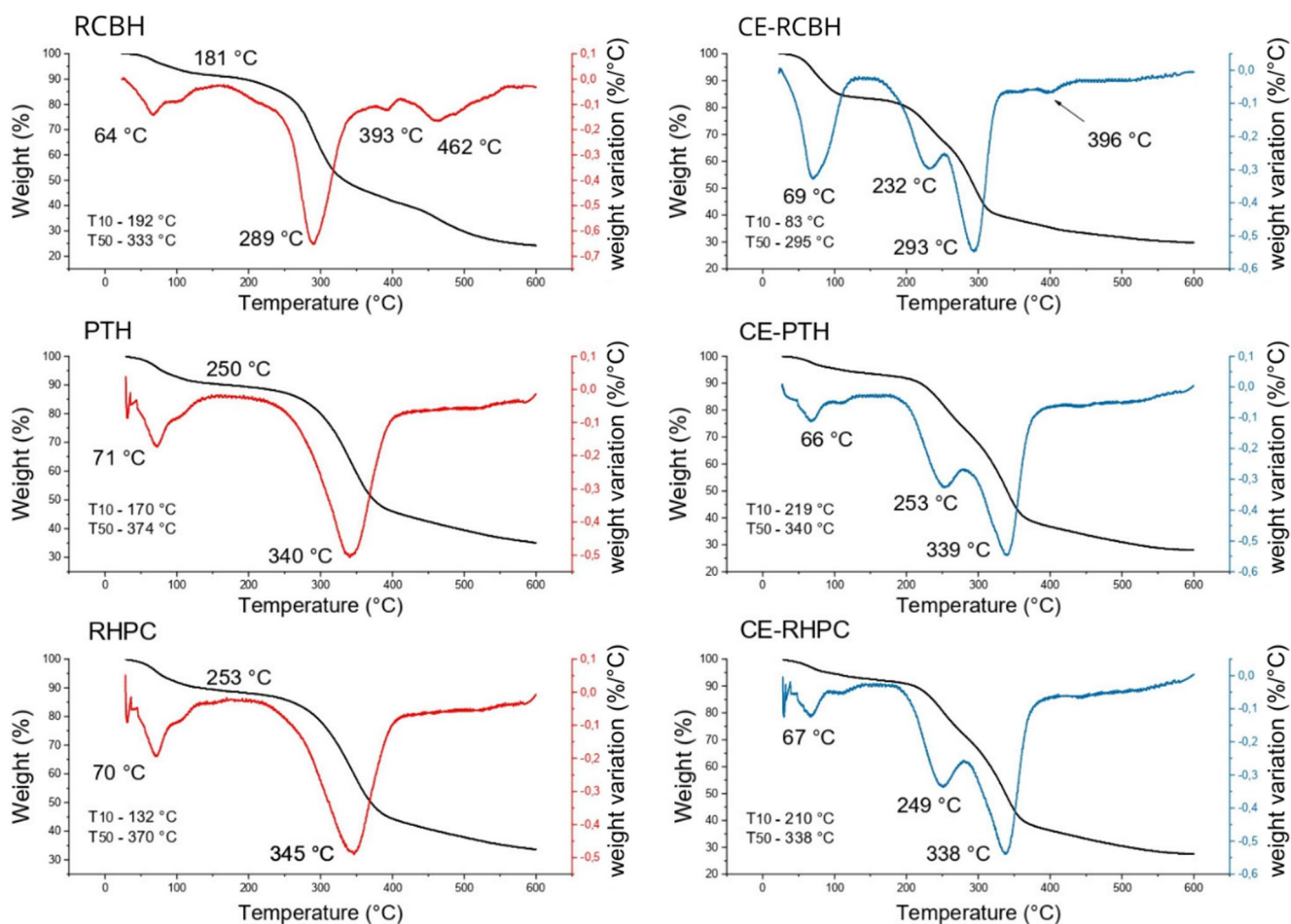


Fig. 5 TGA and DTG curves raw cocoa bean hull (RCBH); pretreated cocoa bean hull (PTH); residual hull from phenolic compound extraction by HAE (RHPC); cellulose derived from RCBH (CE-RCBH); cellulose derived from PTH (CE-PTH); and cellulose derived from RHPC (CE-RHPC)

as a double event, in which the first event, occurring between 232 °C and 253 °C, is associated with hemicellulose degradation, while the second event, occurring between 293 °C and 339 °C, is related to cellulose degradation.

Figure 5 shows the T_{10} and T_{50} values for each sample, representing the temperatures required for 10% and 50% mass loss of the material, respectively. When comparing the T_{50} values, it was observed that the materials subjected to thermal treatments, PTH and RHPC, resulted in higher thermal degradation resistance, requiring higher temperatures to achieve 50% mass loss. In addition, the derived celluloses, CE-PTH and CE-RHPC, also exhibited this behavior for both T_{50} and T_{10} .

4 Conclusions

This study indicates that cocoa bean hull has potential as an agroindustrial feedstock for the recovery of value-added components, particularly PC and cellulose, through an integrated processing approach. Among the extraction methods evaluated, HAE resulted in higher PC recovery for RCBH than UAE under the experimental conditions investigated. Peracetic acid treatment promoted the removal of non-cellulosic components, producing cellulose-enriched materials with higher crystallinity than the corresponding starting samples.

RCBH subjected to HAE resulted in the highest phenolic content (16.67 mg GAE/g db) and antioxidant capacity, reaching 48 mg TE/g db by DPPH and 156 mg TE/g db by ABTS. Following peracetic acid treatment, cellulose contents of up to 87% and a crystallinity index of 74.4% were obtained. These findings suggest that the investigated treatments can selectively recover PC and produce cellulose-enriched fractions from cocoa bean hull under the conditions evaluated.

The results provide a basis for further investigation of integrated strategies for cocoa bean hull valorization; however, the present study was conducted under laboratory-scale conditions, and the potential environmental and economic benefits of the proposed approach were not assessed. Therefore, conclusions regarding industrial feasibility, scalability, and overall sustainability cannot yet be established.

Moreover, although the proposed approach aimed at the integrated utilization of cocoa bean hull, the potential applications of all resulting fractions were not evaluated. Future studies should characterize and investigate the valorization of lignin and hemicellulose- and pectin-rich liquor streams, as well as assess process scalability, mass and energy requirements, environmental impacts, and economic feasibility. Such investigations are necessary to determine whether the proposed approach can support the effective and sustainable utilization of cocoa bean hull at an industrial scale.

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Data availability All data generated or analysed during this study are included in this published article.

Declarations

Competing interests The authors declare no competing interests.

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