Reactive extrusion process to obtain a multifunctional fiber-rich ingredient from coffee hull

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Abstract:
Brazil is a country with strong agricultural production, annually producing a large amount of lignocellulosic residues. The valorization of these residues as ingredients for the food industry aims at environmental, social, and economic sustainability. Coffee hull is a by-product generated by the coffee industry that can be used to produce new food ingredients with high added value. This study aimed to obtain a multifunctional fiber-rich ingredient from a coffee hull using a one-step process based on reactive extrusion with alkaline hydrogen peroxide or sulfuric acid. For this purpose, we submitted a coffee hull to extrusion with sulfuric (1% and 3%) acid or alkaline hydrogen peroxide (1% and 3%) in one-step processes. Then, the obtained materials were characterized through their physicochemical and techno-functional properties. All treated samples had an increase in their cellulose and insoluble dietary fiber contents and also presented an increase in their porosity as observed by scanning electron microscopy. The sample modified with 3% alkaline hydrogen peroxide (AHP3) had the highest cellulose content (45.17%), insoluble dietary fiber (78.20%), density (3.54), water absorption capacity (1.96 g/g), and oil absorption capacity (0.86 g/g). All samples had thermal stability from room temperature to 300 °C and in all samples, the crystallinity indexes decreased after treatment. Reactive extrusion was effective in modifying the coffee hull. Our study proposes a green route to obtain a higher value-added product from lignocellulosic waste, with some advantages including short reaction times, low reagents concentrations, little or no effluent generation, and the possibility of scaling to industrial scale.
Keywords: alkaline hydrogen peroxide; coffee hull; insoluble fibers; sulfuric acid.

Processo de extrusão reativa para obter um ingrediente multifuncional rico em fibras a partir da casca do café

Resumo:
O Brasil é um país com forte produção agrícola, produzindo anualmente uma grande quantidade de resíduos lignocelulósicos. A valorização desses resíduos como ingredientes para a indústria alimentícia visa à sustentabilidade ambiental, social e econômica. A casca de café é um subproduto gerado pela indústria cafeeira que pode ser utilizado para a produção de novos ingredientes alimentícios com alto valor agregado. O objetivo deste estudo foi obter um ingrediente multifuncional rico em fibras a partir da casca de café, utilizando um processo de uma etapa baseado na extrusão reativa com peróxido de hidrogénio alcalino ou ácido sulfúrico. Para isso, a casca de café foi submetida à extrusão com ácido sulfúrico (1% e 3%) ou peróxido de hidrogénio alcalino (1% e 3%) em processos de uma etapa. Em seguida, os materiais obtidos foram caracterizados através de suas propriedades físico-químicas e tecnofuncionais. Todas as amostras tratadas tiveram um aumento nos seus teores de celulose e fibra alimentar insolúvel, e também apresentaram um aumento na sua porosidade, como observado por microscopia eletrônica de varredura. A amostra modificada com peróxido de hidrogénio alcalino a 3% (AHP3) apresentou o maior teor de celulose (45,17%), fibra alimentar insolúvel (78,20%), densidade (3,54), capacidade de absorção de água (1,96 g/g) e

capacidade de absorção de óleo (0,86 g/g). Todas as amostras apresentaram estabilidade térmica desde a temperatura ambiente até 300 °C e em todas as amostras os índices de cristalinidade diminuíram após o tratamento. A extrusão reativa foi eficaz na modificação da casca de café. O estudo propõe uma rota verde para a obtenção de um produto de maior valor agregado a partir de resíduos lignocelulósicos, com algumas vantagens como tempos de reação curtos, baixas concentrações de reagentes, pouca ou nenhuma geração de efluentes e possibilidade de escalonamento para escala industrial.
Palavras-chave: *ácido sulfúrico; casca de café; fibras insolúveis; peróxido de hidrogénio alcalino.*

1 Introduction

Brazil is the largest coffee producer in the world, in 2022/2023 Brazil was expected to produce 62.6 million bags (60 kg), accounting for about one-third to half of the world's coffee production, and the worldwide production will reach approximately 167.5 million bags (60 kg) (Periyasamy *et al.,* 2022; USDA, 2023). Additionally, Brazil is the largest exporter of coffee in the world and it occupies the second position among the countries that consume the beverage (ABIC, 2022).

In the processing of coffee beans, the amount of residues constitutes approximately 30-50% of the production, which means that the amount of processed coffee can be similar to the amount of residues generated through processing (Peshev *et al.*, 2018). Coffee hulls are lignocellulosic material obtained from the dry processing of coffee that retains the outer peel, pulp, and parchment of the coffee berry (Arya *et al.*, 2022); its chemical composition includes lignin (38%), cellulose (28%), hemicellulose (25%), proteins (8-11%), ashes (3-7%), lipids (1-3%) and caffeine (1%) (Ávila; Martins; Goldbeck, 2020; Oliveira *et al.*, 2021; Pandey *et al.*, 2000; Periyasamy *et al.*, 2022).

According to Hassan, Williams and Jaiswal (2018), coffee hulls are mainly employed as compost, vermicompost, livestock feed, and household fuel. Sometimes it is being disposed of freely in the environment, being an interesting raw material to obtain fiber-rich ingredients for the food industry.

Usually, the physiological effects of coffee and coffee processing residues have been focused on its caffeine content, ignoring other components present in coffee, such as polysaccharides and dietary fibers, which have several beneficial physiological effects for health, including minimization of the risk of coronary heart disease, diabetes, and weight control (Santos; Silva; Pintado, 2022).

The introduction of these fiber-rich products in the food industry as flours or additives can be considered a promising strategy, allowing them to exert a multifunctional role, improving techno-functional properties as they can be used as thickeners, gelling agents, fillers, and water retainer agents. Additionally, incorporating these residues into a food product can contribute to the eco-sustainability of the coffee industry in a circular economy, minimizing negative environmental and economic impacts from a large amount of residue and by-products improperly discarded (Difonzo *et al.,* 2022; Iriondo-Dehond; Iriondo-Dehond; Del Castillo, 2020).

In recent years, several studies have reported the modification of agroindustrial residues by the use of chemical, physical, and enzymatic methods, or their combination, aiming at improving their nutritional and techno-functional properties, especially increasing dietary fiber contents and improving some technological characteristics, such as water absorption capacity (Galdeanol; Grossmann, 2006; Van Buggenhout *et al.,* 2015; Yoshida; Prudencio, 2020).

Alkaline peroxide has been reported as an efficient reagent for the modification of lignocellulosic residues, it acts as an effective agent in the delignification and solubilization of hemicellulose, increasing the cellulose content of samples. This is due to the hydroperoxide anion (HOO-) formation at alkaline pH, which is the main active species in the peroxide. In contrast, hydrogen peroxide is unstable under alkaline conditions and decomposes into hydroxyl (OH-) and superoxide (O2-) radicals. These radicals are responsible for oxidizing the lignin structure, which attacks the hydrophilic (carboxyl) groups, breaking some bonds and eventually dissolving lignin and hemicellulose (Yoshida; Prudencio, 2020). Schmitz *et al.* (2021) stressed that alkaline hydrogen peroxide is an interesting bleaching agent for retaining the composition of lignocellulosic materials making them suitable as food ingredients. Xia *et al.* (2022) reported the effect of an alkaline hydrogen peroxide treatment on the delignification of corn stalks; results showed that oxidative treatments could

be considered promising strategies for biomass utilization due to their excellent performance and economic costs.

Likewise, acid treatments can be used to obtain new materials from lignocellulosic residues, they act by hydrolyzing hemicelluloses and removing soluble lignin, resulting in increased cellulose contents (Pereira; Marim; Mali, 2022; Tu; Hallett, 2019). Acidic pretreatment can be performed with either a dilute acid at an elevated temperature or a concentrated acid at a lower temperature, being carried out with dilute acid typically involves adding (0.2-2.5%, w/w) of acid solution to the biomass with regular mixing at 120 to 210 °C (Periyasamy *et al.,* 2022).

Extrusion cooking combined with a chemical treatment can promote delignification of the material, as well as decrease the crystallinity of the cellulose by breaking the hydrogen bonds that maintain its supramolecular structure, resulting in materials with higher water absorption capacity and better sensory properties (Cardoso *et al.,* 2016; Vilela *et al.,* 2016; Yoshida; Prudencio, 2020).

Coffee hull is a raw material that has been little explored considering its promising character due to its structural composition and high availability. This reinforces the need for more studies and favorable conditions for use in biotechnological ways for better employability of this biomass. Thus, this study aimed to obtain a multifunctional fiber-rich ingredient from the coffee hull using a one-step process based on reactive extrusion with alkaline hydrogen peroxide or sulfuric acid.

This article is organized as follows: section 2 presents the materials and methods used to carry out the study; section 3 contains the results obtained, as well as a discussion of the results based on the relevant literature; finally, section 4 presents the conclusion.

2 Materials and methods

Section 2 contains the materials and methods used in the study. Section 2.1 contains information on obtaining and conditioning the waste (coffee hull) and the main reagents used to modify the waste. Item 2.2 describes the method used to modify the waste using extrusion. The subsequent items provide the methods for characterizing the materials obtained.

2.1 Materials

Coffee hull (CH) (*Coffea arabica*) was supplied by the Institute of Rural Development of Paraná – IDR (Londrina, Paraná State, Brazil), and the residue was dried in an air-circulating oven (Marconi MA 035, São Paulo, Brazil) for 12 hours at 45°C, and then ground and sieved (180 to 300 µm). During the analysis period, the material was kept at room temperature. The reagents used in this study (Sulfuric acid, and hydrogen peroxide and sodium hydroxide) have an analytical grade (Synthlab, Diadema, Brazil).

2.2 Modification of coffee hull by reactive extrusion

CH was modified by reactive extrusion in a single screw extruder (AX Plastics, Diadema, SP, Brazil) with a screw diameter of 1.6 cm and a screw length/diameter ratio (L/D) of 40, with four heating zones and a matrix of 0.8 cm in diameter. The temperature in all zones was 100 °C, and the screw speed was 60 rpm. Sulfuric acid (SA) and alkaline hydrogen peroxide (AHP) were used in different concentrations (1.0 and 3.0% g acid/100 g residue) as modifying agents. SA or AHP in different concentrations were dissolved in distilled water and mixed with the residue (100 g), resulting in a final moisture content of 32% (g water/100 g residue). Each mixture was slowly added to sealed plastic bags and equilibrated for 1 h before extrusion. A control sample was extruded without any reagent other than water, resulting in the same final moisture content of 32%.

To determine the initial moisture content, about 2 to 10 g of the sample was weighed into a pre-weighed metal capsule and heated for 105 °C until constant weight. Moisture (%) was calculated from the difference between the initial and final mass of the samples. The obtained extruded samples were washed three times using distilled water for neutralization; the final pH was determined using 1 g of each samples and 10 mL of water, and after 10 minutes the pH was measured employing a digital potentiometer (HI 3221, HANNA, Romania) previously calibrated with buffer solutions of pH 4.0 and 7.0. Then, samples were dried in an air-circulating oven (Marconi MA 035, São Paulo, Brazil) for 12-24 hours at 60°C, and milled to obtain particles ranging from 150 to 220 µm. The reactive extrusion parameters were based on a previous study by Pereira, Marim, and Mali (2022). Samples modified

with SA 1.0 and 3.0% were labeled as SA1 and SA3, and samples modified with AHP 1.0 and 3.0% were labeled as AHP1 and AHP3.

2.3 Determination of chemical composition

Proteins, ashes, and moisture were performed according to the official AOAC methodologies (AOAC, 2012). Nitrogen content was determined by the Kjeldahl method and protein content was calculated using a conversion factor of 6.25. Lipids were extracted and determined according to the methodology recommended by the IAL (2008). An aliquot of 2 g of each sample was used in a Soxhlet extractor, using petroleum ether as extracting solvent, for 8 hours.

Carbohydrate content was determined by difference, subtracting from 100 the sum of the values obtained for moisture, ash, proteins, and lipids.

Cellulose and hemicellulose were determined by the Van Soest (1965) method, and the lignin content by the Technical Association of the Pulp and Paper Industry (TAPPI, 1999) method.

2.4 Bulk density and pH

Bulk density (BD) was determined according to Benítez *et al.* (2011), using a graduated cylinder (10 mL) that was filled with the samples up to 10 mL by constant tapping, and bulk density was calculated as grams per cm^3 (g/cm^3). pH was determined using 1 g of each sample and 10 mL of water, and after 10 minutes the pH was measured employing a digital potentiometer (HI 3221, HANNA, Romania) previously calibrated with buffer solutions of pH 4.0 and 7.0.

2.5 Scanning electron microscopy (SEM)

The fibers were analyzed for their microstructure by scanning electron microscopy (SEM) using a microscope (FEI Quanta 200, Oregon, USA). The samples were ground into 15 to 20 nm particles, dried at 60 °C for 24 hours, and left in a desiccator with silica for 24 hours before analysis. Then, each sample was mounted on bronze stubs, the surfaces were coated with a gold layer (40-50 nm), and samples were observed using an accelerating voltage of 20 kV.

2.6 Fourier transform-infrared spectroscopy (FTIR)

The samples were dried in an oven at 60 °C for 24 hours and kept in a desiccator with silica for 24 hours. FTIR spectra were obtained with a spectrophotometer (Shimadzu FTIR-8300, Kyoto, Japan). The analyses were performed 4000 to 500 cm^{-1}, with 4 cm^{-1} of resolution. A total of 64 scans were performed on each sample.

2.7 X-ray diffraction (XRD)

XRD was performed using a Panalytical X'PERT PRO MPD diffractometer with copper k radiation (λ = 1.5418 Å) under 40 kV and 30 mA operating conditions. Scanning ranged from 2θ = 5 to 2θ = 45°, step -0.1, and speed 1° /min, equipped with a secondary graphite beam monochromator. The crystallinity index (CI) was calculated (Equation 1) by the method of Segal *et al.* (1959):

$$CI = \left(\frac{\mathrm{I002} - I_{am}}{I_{002}}\right) \times 100 \quad (1)$$

where, CI is the crystallinity index of the cellulose, I_{002} the peak intensity (002) (2θ = 20 – 22°), and I_{am} is the peak intensity corresponding to the peak at 2θ = 18°.

2.8 Differential scanning calorimetry (DSC)

DSC analysis were performed on a Shimadzu DSC 60 calorimeter (Kyoto, Japan). Samples were placed in aluminum containers and heated from room temperature to 300 °C, with a heating rate of 10 °C/min in a 50 mL/min nitrogen atmosphere.

2.9 Water absorption capacity (WAC)

WAC was determined according to Lu, Liu, and Li (2013). Exactly 2.000 g of the samples were weighed and 25 mL of distilled water was added to previously weighed Falcon tubes. The set was

placed under constant agitation at 150 x g for 30 minutes at room temperature in a Quimis orbital shaking incubator (Diadema, Brazil) and centrifuged for 10 minutes at 3500 x g (Hettich Centrifuge, Universal model 320R, Darmstadt, Germany). The supernatant was discarded and the tube containing the wet sediment was weighed. WAC was calculated as the ratio between the wet sediment weight (hydrated fiber) and the dry matter weight (dehydrated fiber), expressed in g of water absorbed per g of sample.

2.10 Oil absorption capacity (OAC)

OAC was determined according to Lu, Liu, and Li (2013). Exactly 2.000 grams of the samples were weighed and 25 mL of commercial soybean oil was added to previously weighed Falcon tubes. The set was placed under constant agitation at 150 x g for 30 minutes in a Quimis orbital shaking incubator (Diadema, Brazil) and then centrifuged for 10 minutes at 3500 x g. The supernatant was discarded and the tube containing the sample was weighed. OAC was calculated as the ratio between the final weight of the sediment and the weight of the dry matter, expressed in g of oil absorbed per g of sample.

2.11 Swelling capacity (SC)

Approximately about 1.000 g of each sample was weighed into a 25 mL test tube and 20 mL of distilled water was added. The mixture was constantly stirred for 2 hours on a shaker incubator (CT-712 Cientec, Brazil). After this procedure, the suspensions were left to rest for 18 hours until complete decantation. The swelling capacity was calculated by the ratio between the volume occupied by the sample (mL) and the sample weight (g).

2.12 Water adsorption isotherms

The samples (approximately 0.500 g) were conditioned in a desiccator with calcium chloride (UR ~ 0%) for 48 hours and then were placed in Aqua Sorp Isotherm Generator equipment (Decagon Devices, Pullman, WA, USA). The moisture content of the samples in equilibrium was expressed in g of water per g of dry matter. The analysis was carried out in triplicate and the adsorption curves were adjusted to the Guggenheim, Anderson, and De Bôer (GAB) model. The isotherm model of GAB (Bizot, 1984) can be expressed as follows (Equation 2):

$$M = \frac{m_0 C K a_w}{1 - K a_w}(1 - K a_w + C K a_w) \quad (2)$$

where M is the equilibrium moisture (g.water/100.g.solids), a_w is the water activity, m_0 is the monolayer value (g.water/100.g.solids), and C and K are GAB constants. Assays were performed in triplicate.

2.13 Glucose Adsorption (GA)

Glucose-adsorption capacity was determined according to the method described by Ou *et al.* (2001), with slight modifications. One gram of sample was mixed with 100 mL of glucose solution (500 mmol/L) and incubated at 37 °C for 1 hour. After 1 hour, samples were centrifuged (3500 x g, 15 minutes), and the final glucose content in the supernatant was determined by the di-nitrosalicylic acid (DNS) method (Miller, 1959).

2.14 Statistical analysis

Analyses of variance (ANOVA) and Tukey's mean comparison test ($p \leq 0.05$) were performed with R software (R Foundation for Statistical Computing, Vienna, Austria).

3 Results and discussions

Section 3 contains the results and discussion. The chemical composition of the samples, raw and modified waste, is presented in section 3.1. The results of the characterization of the materials are presented in separate items, 3.2 to 3.8. Each result presented is supported by a pertinent discussion based on the data obtained in this study and found in the literature.

3.1 Chemical composition

Table 1 shows the results of the composition of coffee hulls. The samples did not differ statistically in terms of moisture, lipids, and carbohydrates, while ash and protein contents differed from each other by the Tukey test ($p < 0.05$), in which there was a decrease for the samples that were subjected to the treatments under reactive extrusion.

Table 1 – Chemical composition of raw CH, control sample and samples modified with SA and AHP

Samples	Moisture (%)	Ash (%)	Protein (%)	Lipids (%)	Carbohydrates (%)
Raw CH	6.60^{a}	5.37^{b}	11.24^{a}	2.50^{a}	74.29^{a}
Control sample	6.25^{a}	6.16^{a}	11.10^{a}	1.29^{a}	75.20^{a}
SA1	5.67^{a}	3.20^{d}	10.14^{b}	1.06^{a}	79.93^{a}
SA3	5.61^{a}	2.81^{d}	9.45^{b}	1.06^{a}	81.07^{a}
AHP1	3.89^{a}	2.86^{d}	9.55^{b}	1.15^{a}	82.55^{a}
AHP3	4.31^{a}	3.60^{c}	10.53^{ab}	0.89^{a}	80.67^{a}

Means followed by different letters in the same column differ from each other according to the Tukey Test ($p \leq 0,05$)
Source: research data

Other studies carried out with raw coffee hulls found values ranging between 8-11% for proteins, 0.5-3% for lipids, and 58-85% for carbohydrates (Gouvea *et al*., 2009), which are consistent with the results found in this study. Some factors may contribute to variations in coffee hull composition, such as variations in processing, storage, transport, and processing conditions.

Table 2 shows the results obtained for hemicellulose, cellulose, and lignin content of samples, where it can be observed that there was no significant difference between the samples for hemicellulose and lignin before and after the treatments by reactive extrusion. There was observed a significant increase in cellulose content for the modified samples compared to raw coffee hull, the AHP3 sample was the one that presented the highest cellulose value. Similar results were found by Vilela *et al.* (2016), who reported that the physical properties of the fibers are altered in the chemical treatment with hydrogen peroxide, which acts by solubilizing part of the lignin and reducing the crystallinity of the cellulose, producing a material with improvement in some fiber characteristics, such as techno-functional properties.

Table 2 – Composition of the fiber of raw CH, control sample, and samples modified with SA and ASH

Samples	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Insoluble dietary fibers (%)*
Raw CH	27,92 ± 4,86^{c}	9,33 ± 2,02^{a}	28,72 ± 2,21^{a}	65.97 ± 3.04^{b}
Control sample	30,85 ± 1,87^{c}	11,06 ± 5,05^{a}	27,01 ± 1,59^{a}	68.92 ± 2.95^{b}
SA1	39,84 ± 1,41^{b}	11,27 ± 4,26^{a}	27,75 ± 2,13^{a}	78.86 ± 2.53^{a}
SA3	40,96 ± 0,54^{ab}	8,19 ± 0,66^{a}	28,02 ± 0,79^{a}	77.17 ± 0.88^{a}
AHP1	42,18 ± 0,09^{ab}	9,55 ± 1,19^{a}	25,58 ± 2,04^{a}	77.31 ± 0.97^{a}
AHP3	45,17 ± 1,55^{a}	8,46 ± 0,25^{a}	24,57 ± 1,95^{a}	78.20 ± 1.05^{a}

Means followed by different letters in the same column differ from each other according to the Tukey Test ($p \leq 0,05$).
* Values obtained from the sum of cellulose, hemicellulose, and lignin contents
Source: research data

Other authors mentioned in their studies that chemical treatments using an alkaline medium preserve cellulose structure (Chen; Zhao; Xia, 2009), and also that the addition of hydrogen peroxide can favor the removal of lignin and hemicellulose (Alvira *et al.,* 2010), which was not observed in this study. The reactive extrusion process employed in this study was performed in a short time, with samples remaining between 2 and 3 minutes inside the extruder, and this possibly did not favor lignin or hemicellulose removal. Additionally, SA and AHP were employed in lower concentrations at lower reaction times compared to other studies, Dutra *et al.* (2018) reported concentrations de AHP entre 0.5 and 7.4% for 1 to 24 hours of reaction for several lignocellulosic materials.

All treated samples had a higher content of insoluble fibers (Table 2), and this possibly occurred because protein, ashes, and lipids were removed during the reactive extrusion process. Insoluble fibers help to accelerate intestinal transit, increase fecal bulk, and slow down the hydrolysis of glucose, thus contributing to the reduction of some diseases in the colon (Santos; Silva; Pintado, 2022).

3.2 Bulk density and pH

The bulk density of raw coffee hull was 6.11, and for all treated samples the bulk density decreased (Table 3), including the control sample, with values ranging between 3.54 and 3.38, which means that the extrusion process affected the physical structure of the materials, possible by increasing their porosity, as observed by SEM. Yoshida and Prudêncio (2020) reported that a decrease in bulk density can be interesting in bakery applications; these authors also reported that fiber modification that results in higher porosity results in lower density values.

The pH values ranged from 5.47 and 6.20 (Table 3), which was expected because all samples were washed to remove unreacted SA or AHP, and also they were subjected to a neutralization step.

Table 3 – Bulk density and pH of raw CH, control sample, and samples modified with SA and AHP

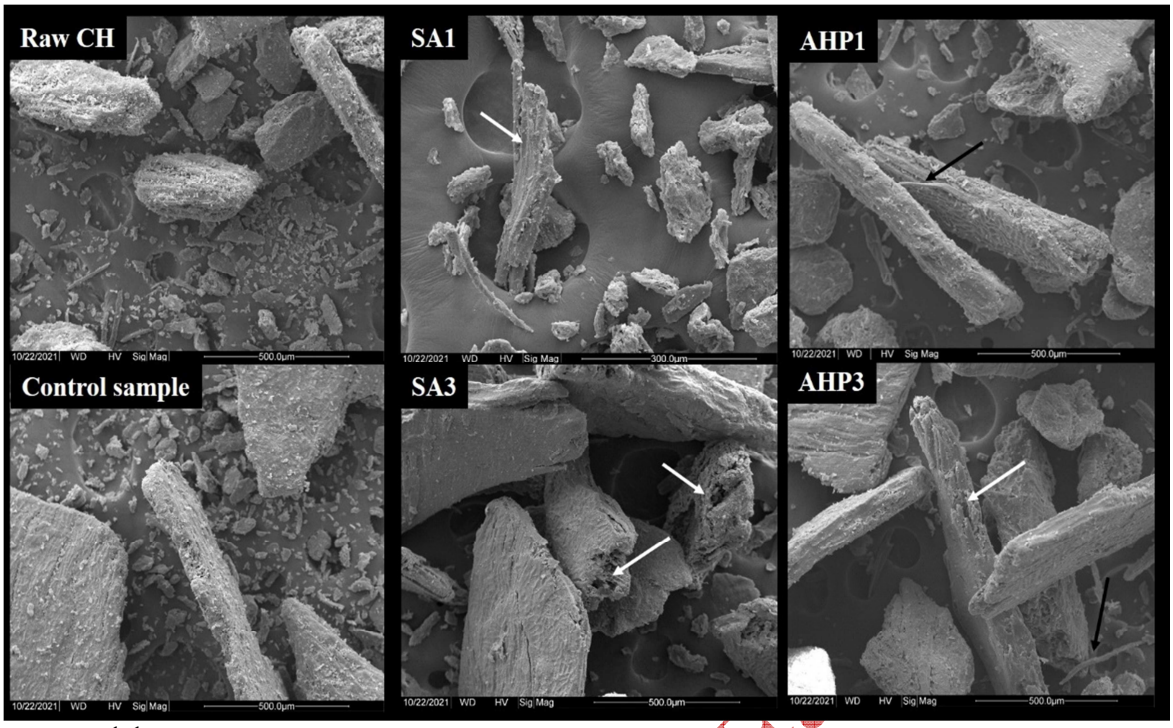
Samples	Bulk density (g/cm^3)	pH
Raw CH	6.1 ± 0.2^{a}	5.47 ± 0.02^{b}
Control sample	3.7 ± 0.1^{c}	5.58 ± 0.01^{b}
SA1	4.1 ± 0.1^{b}	5.19 ± 0.04^{b}
SA3	4.1 ± 0.1^{b}	5.20 ± 0.04^{b}
AHP1	4.3 ± 0.1^{b}	6.08 ± 0.12^{a}
AHP3	3.6 ± 0.1^{c}	6.20 ± 0.10^{a}

Means followed by different letters in the same column differ from each other according to the Tukey Test ($p \leq 0,05$)
Source: research data

3.3 Scanning electron microscopy (SEM)

Figure 1 shows the scanning electron microscopy images of the raw coffee hull and the samples that were modified by extrusion and their treatments. It can be seen that the images referring to the raw CH and the control sample form a compact structure due to non-cellulosic materials and waxes present on their surface.

Figure 1 – SEM images of raw CH, control sample, and samples modified with SA and ASH



Source: research data

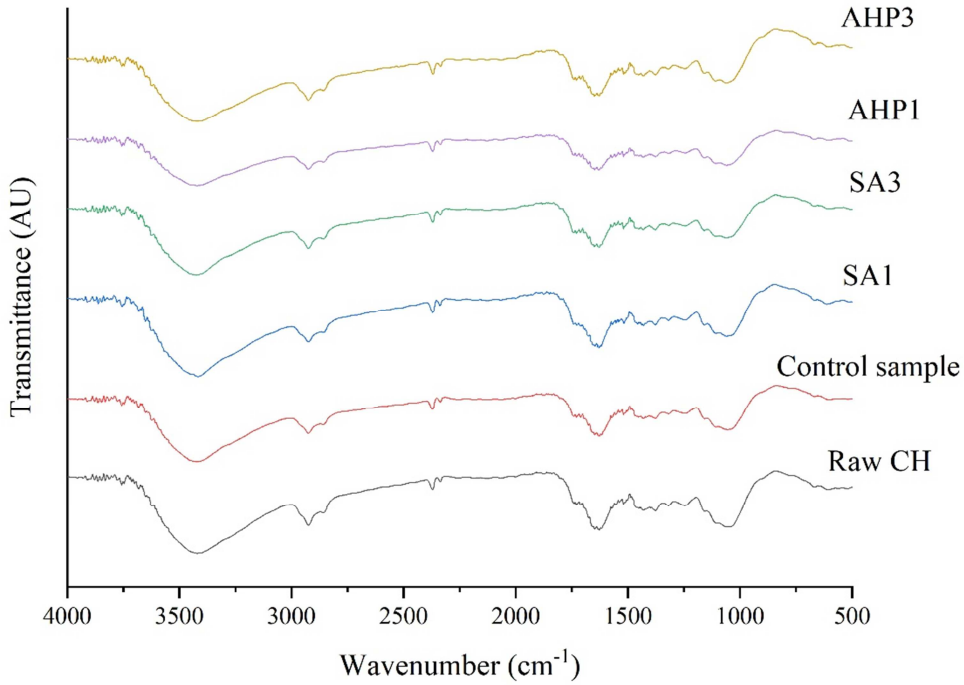
All treated samples presented pores in their surfaces, this effect was possibly caused by the extrusion plus the chemical treatment that contributed to the removal of wax and superficial fatty acids from the fibers' surfaces, which is consistent with bulk density results. Meng *et al.* (2022) obtained similar results for bamboo residues treated with AHP. Acid and/or alkaline hydrolysis have been reported in other studies as aligned in removing fatty acids and waxes from the surface and leaving the fibers exposed (Brígida *et al.,* 2010).

Acid-treated samples presented a rougher surface, due to the chemical treatment and the shear force, high temperatures, and pressure during the extrusion process (Figure 1). The samples treated with AHP presented more fiber bundles and deep valleys.

3.4 Fourier transform- infrared spectroscopy (FTIR)

Figure 2 represents the FTIR spectrum of the samples, it was found that there was no difference between the raw CH and the treat samples. In all samples bands at 3400 cm^{-1} were identified, which were attributed to the stretching of OH groups from cellulose, hemicellulose, lignin, proteins, and other components. Bands at 2920-2840 cm^{-1} were observed for all samples, and they corresponded to the CH stretching vibration of alkyl groups.

Figure 2 – FTIR spectra of raw CH, control sample, and samples modified with SA and ASH



Source: research data

At 2900 cm^{-1} was observed which can be attributed to the C=O group of hemicellulose and/or the ester bonds of the carboxyl groups present in hemicellulose and lignin.

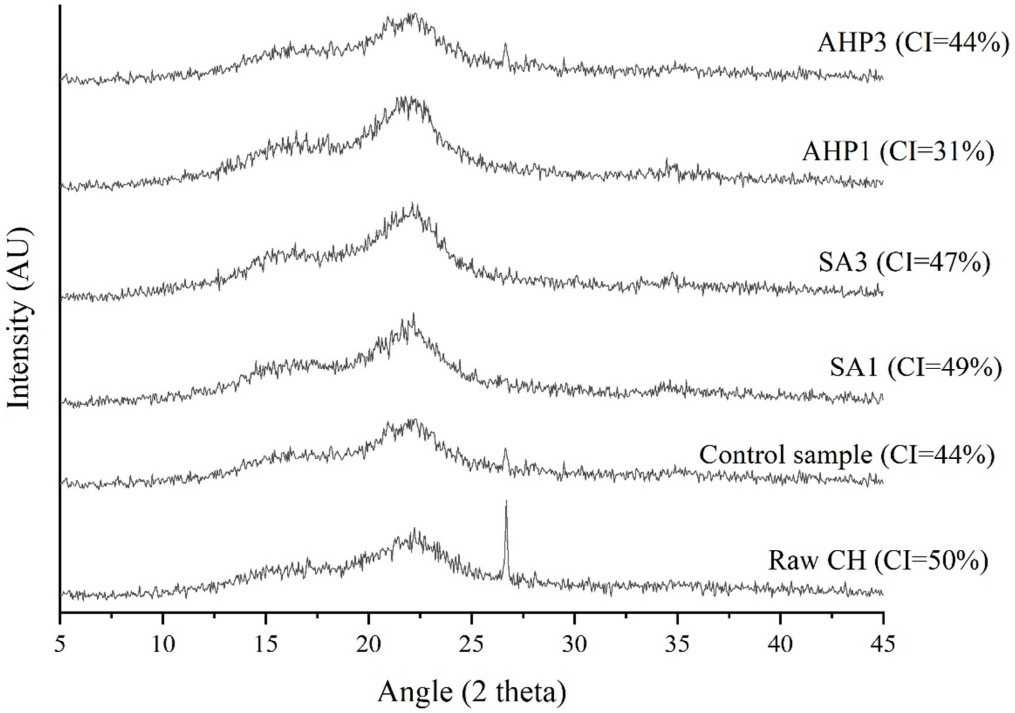
According to Cardoso *et al.* (2016), AHP may favor changes in hemicellulose and lignin. The C=O group present in the fiber can be increased by oxidation reactions or decreased by cyclization reactions, both of which are promoted by hydrogen peroxide. The bands between 1400 cm^{-1} to 1000 cm^{-1} are characteristic bands of fiber spectra (lignin, hemicellulose, and cellulose).

According to Meng *et al.* (2022), in their study, they obtained higher intensity bands from cellulose after chemical treatment of bamboo residues with acid and alkaline reagents, which was not observed in this study.

3.5 X-ray diffraction (XRD)

XRD patterns of raw CH, control sample, and samples modified with SA and ASH are shown in Figure 3, and also their respective relative crystallinity indexes. In the reactive extrusion process, the fibers were exposed to high temperature and high shear force, however, these conditions did not affect the crystallinity pattern of the modified samples, which presented a peak around $2\theta=22^{o}$, which can be attributed to cellulose I as reported by Gabriel *et al.* (2020). Other studies that have subjected cellulose extracted from oat hulls to modification by relative extrusion also report that this process did not affect the inherent crystalline structure of the sample. About the fact that chemical reagents make it difficult to enter the crystalline region of cellulose due to its stable structure (Oliveira *et al.,* 2017).

Figure 3 – XDR patterns and relative crystallinity indexes (CI) of raw CH, control sample, and samples modified with SA and ASH



Source: research data

Raw coffee hull had a crystallinity index of 50% (Figure 3), agreeing with the results of Gabriel *et al.* (2020), which reported a value of 55% for the CI of raw coffee hull. During the reactive extrusion, the samples were submitted to high temperature and high shear force however, the extrusion process did not affect the crystallinity pattern of the modified samples. Larrea *et al.* (1997) reported that no significant changes in the X-ray diffraction patterns were observed for rice hulls subjected to reactive extrusion with hydrogen peroxide.

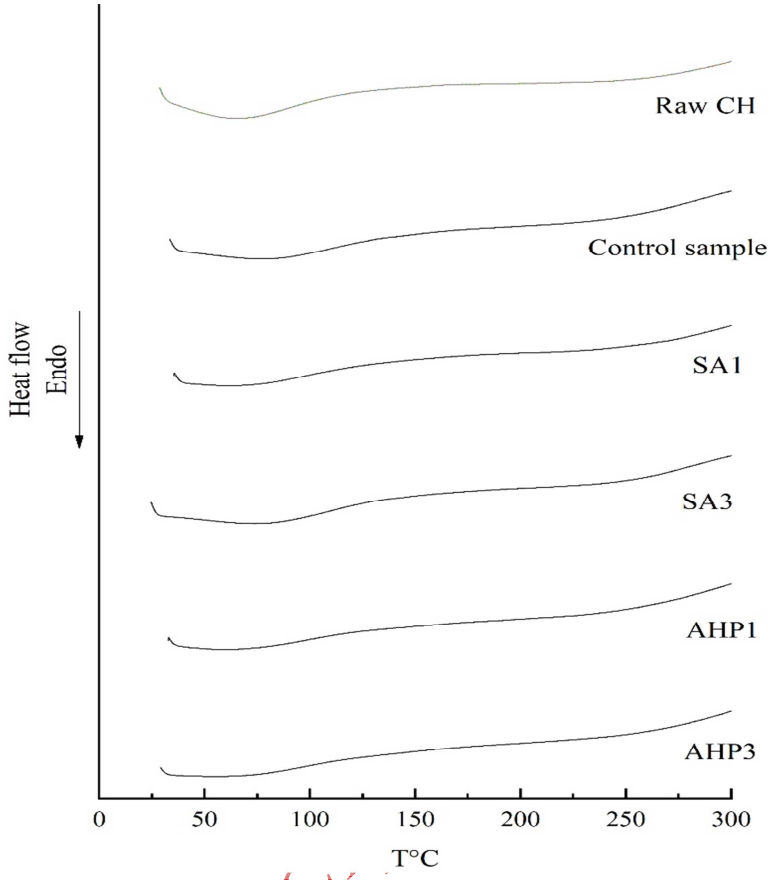
Crystallinity indexes (CI) of treated samples presented a decrease in their values (Figure 3) when compared to the raw coffee hull, and the AHP1 sample had a lower CI value. Vandenbossche *et al.* (2014) reported that blue agave bagasse presented a decrease in their CI after being subjected to an alkaline treatment by reactive extrusion. Oliva *et al.* (2017) reported that extrusion is a highly versatile process for the use of lignocellulosic residues, providing mixing, rapid heat transfer, and high shear stress, which promote defibrillation and reduce the crystallinity index and the degree of polymerization of cellulose.

Other authors reported an increase in the CI of residues after being subjected to chemical treatments. Gabriel *et al.* (2020) reported the use of NaOH (10%) in the pre-treatment of several lignocellulosic residues including coffee hull, and they obtained cellulose-rich materials with higher CI, and they attributed this effect to the removal of hemicellulose and lignin that exist in the amorphous regions, leading to the realignment of the cellulose molecules. Meng *et al.* (2022) also mentioned that bamboo residues presented increased crystallinity after the removal of some non-crystalline components such as lignin and hemicellulose.

3.6 Differential scanning calorimetry (DSC)

The DSC results (Figure 4) showed no difference between the samples, the samples did not undergo modification during the analysis, and it concluded that the samples have thermal stability against processing under this temperature range. All samples showed only small endothermic events can be observed between 50 a 100 ºC associated with water loss.

Figure 4 – DSC thermograms of raw CH, control sample, and samples modified with SA and ASH



Source: research data

3.7 Determination of techno-functional properties

The WAC evaluates the amount of water that fiber absorb this property is directly related to the content of soluble fibers present in the sample. As well, OAC measures the amount of lipids that fiber can absorb and relates to the fiber's ability to bind substances in the intestine, such as acids, bile salts, and cholesterol.

In this study, it was possible to observe an increase in the water and oil absorption capacity of the modified samples about the raw CH with a significant difference for WAC e OAC (Table 4). This increase is attributed to physical and structural changes, especially the increase of porosity in all treated samples that were observed by SEM, which left them more exposed to interactions. AHP3 samples had the highest WAC and OAC values of all samples (Table 4).

Table 4 – Technological functional properties of raw CH, control sample, and samples modified with SA and ASH

Samples	WAC (g/g)	OAC (g/g)	SC (mL/g)	GA(%)
Raw CH	1,33 ± 0,07^{b}	0,06 ± 0,05^{a}	13,90 ± 0,25^{a}	88 ± 0,13^{a}
Control sample	1,57 ± 0,07^{ab}	0,56 ± 0,01^{b}	13,25 ± 1,23^{a}	90 ± 0,01^{a}
SA1	1,58 ± 0,06^{ab}	0,68 ± 0,01^{ab}	14,50 ± 0,78^{a}	90 ± 0,02^{a}
SA3	1,56 ± 0,06^{ab}	0,69 ± 0,03^{ab}	14,86 ± 2,37^{a}	89 ± 0,06^{a}

AHP1	1,47± 0,06[ab]	0,52 ± 0,05[b]	15,45 ± 1,55[a]	91 ± 0,12[a]
AHP3	1,96± 0,10[a]	0,87 ± 0,10[a]	15,83 ± 0,49[a]	88 ± 0,13[a]

Mean values ± standard deviation (n = 3), Means followed by the same letter, in the same column, do not differ from each other, according to the Tukey Test with ($p < 0,05$).
WAC=Water absorption capacity, OAC=Oil absorption capacity, SC=Swelling capacity, GA=Glucose adsorption.
Source: research data

Vilela *et al.* (2016) observed an increase from 2.6 to 3.1 g/g in OAC when studying the modification of spent coffee grounds with 5–25% alkaline peroxide, which can explained by lower reagent concentrations that were employed in this study. Galdeanol and Grossmann (2006) evaluated the treatment with 7% hydrogen peroxide associated with extrusion on the hydration properties of oat hulls and obtained increases of 70% in water retention capacity and 55% in swelling volume. Moura *et al.* (2011) reported that low hydrogen peroxide concentrations (0.3–0.9%) have no effect on the oil absorption and holding capacity of fibers.

WAC values obtained in this study were lower than the values observed by Mantovan *et al.* (2021) for raw orange bagasse and for orange bagasse subjected to an alkaline treatment combined to autoclaving, they observed values of 4.56 and 3.10 g/g, respectively. Oats, soybean, and coffee hulls treated with alkaline hydrogen peroxide (2%, pH 11.5) combined with hydrothermal autoclave treatment had a significant increase in WAC values; raw coffee hull showed 4.5 g/g and 6.6 g/g after treatment (Silva *et al.,* 2022).

A product with a high OAC is of great importance to the industry, having several applications with, for example, improving the texture and shelf life of products through the control of polymorphism and the crystalline structure of fats and to promote the solubilization of flavors (Vilela *et al.,* 2016). Difonzo *et al.* (2022) reported that the use of appropriate technologies can transform lignocellulosic residues into innovative ingredients to be used in gluten free foods, including coffee by-products.

Swelling occurs due to a spontaneous fixation of water through the fibrous matrix by intermolecular forces, and this property was no affected by employed treatments, and SC ranged from 13.90 to 15.83 mL/g (Table 4). Larrea *et al.* (1997) used the pre-treatment process with alkaline hydrogen peroxide (1%) solution followed by the extrusion process to modify the rice hull fiber, and observed SC of 12.4 g/mL, and Benitez *et al.* (2019) reported SC of 3.8 g/mL for coffee parchment flour. SC values obtained in this study were higher than the values observed by Mantovan *et al.* (2021) for raw orange bagasse and for orange bagasse subjected to an alkaline treatment combined to autoclaving, they observed values of 8.83 and 8.43 g/g, respectively.

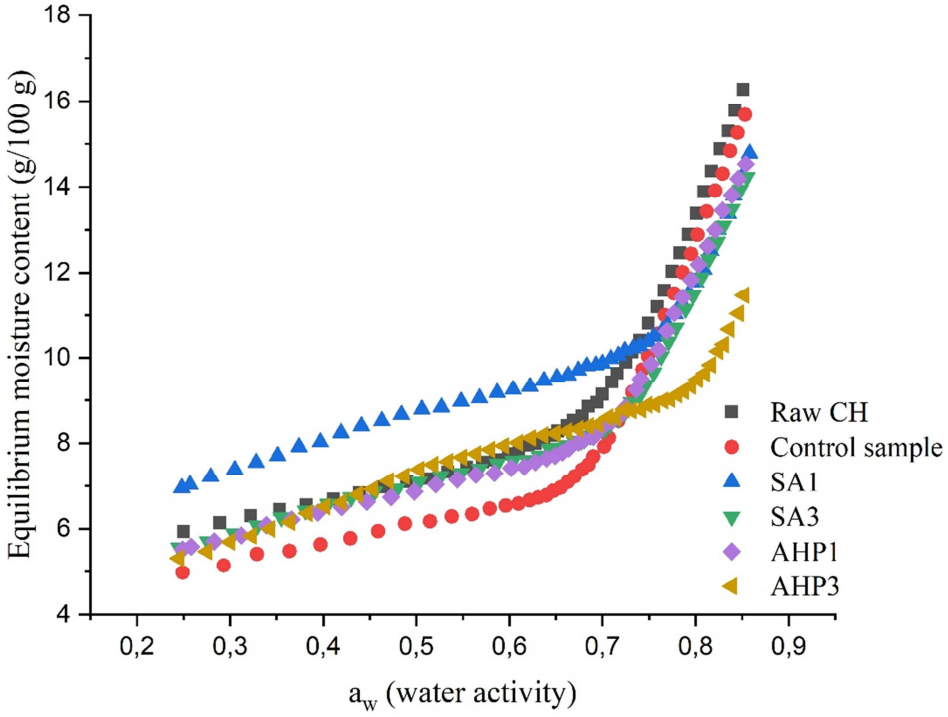
GA is measured by the amount of glucose that the fiber is able to absorb. Recent studies show that consumption of insoluble fiber has been associated with a decrease in the rate of diabetes and glucose absorption in the intestinal tract (Mello; Laaksonen, 2009). In studies carried out by Benitez *et al.* (2019), shows that the absorption of glucose is dependent on the glucose concentration, the higher its concentration, the higher the absorption rate. GA values were not affected by the different treatments in this study (Table 4), with values ranging from 88 to 91% (Table 4), indicating that the use of this residue can reduce the amount of glucose available in the intestinal lumen, consequently blunting the postprandial hyperglycemia, and according to Difonzo *et al.* (2022), fiber-rich ingredients can be interesting additives to improve the nutritional quality of bread, pasta, cake/muffins, biscuits and snacks, especially in gluten-free products, reducing the glycemic index of foods.

Through chemical composition, microbiological, aflatoxin, and acute toxicity analyses, Beltrán-Medina *et al.* (2020) showed that coffee silverskin presents a good food safety profile and can be employed for the manufacture of an extruded cereal-based food product as a ready-to-eat source of protein and fiber). The studies of the functional properties of agro-industrial by-products are extremely important for their viability as raw materials of higher added value for the food industry (Deepak; Jayadeep, 2022).

3.8 Water adsorption isotherms

Figure 5 presents the water adsorption isotherms of samples; it can be observed that all samples had an increase in their equilibrium moisture content that became more pronounced in a_w values higher than 0.65.

Figure 5 – Water adsorption isotherms of raw CH, control sample, and samples modified with SA and ASH



Source: research data

Table 5 presents the results of the adsorption isotherms where m_0 indicates the maximum amount of water that can be adsorbed in a single layer per gram of dry matter. Both chemical modification processes resulted in increased m_0 values. The sample that presented the highest value was the SA1, on the other hand, the control sample had the smallest m_0 value.

Table 5 – GAB model parameters of raw CH, control sample, and samples modified with SA and ASH

Samples	m_0	C	K	R^2
Raw CH	3,61	10000	0,9055	0,96
Control sample	2,82	10000	0,9634	0,96
SA1	5,56	10000	0,6685	0,90
SA3	3,80	10000	0,8353	0,93
AHP1	3,58	10000	0,8691	0,94
AHP3	5,16	56,262	0,6002	0,96

*GAB model: $M = (m_0CKaw)/(1-Ka_w)\times(1-Ka_w + CKa_w)$, M = equilibrium moisture (g water/100 g solids), a_w = water activity, m_0 = monolayer value (g.water/100 g.solids), C and K = GAB constants.
Source: research data

Mihranyan *et al.* (2004) stressed that the mechanisms of moisture sorption of cellulosic materials are complicated to understand, because of the complexity of their structure, and the water adsorption is affected by their composition and structural properties, such as surface area, pore volume, and crystallinity. Higher porosities and surface areas result in higher moisture adsorptions, while higher crystallinity indicates lower hydroxyl groups available to interact in the material surface, resulting in lower adsorption of water. According to Mantovan *et al.* (2021), samples with higher

crystallinity were less susceptible to adsorb water, and they also reported that the presence of pores can increase m_0 values of lignocellulosic materials.

4 Conclusions

The sample modified with 3% alkaline hydrogen peroxide (AHP3) had the highest cellulose content (45.17%), insoluble dietary fiber (78.20%), density (3.54), water absorption capacity (1.96 g/g), and oil absorption capacity (0.86 g/g), which results in a multifunctional ingredient, with nutritional, sensorial and techno-functional improvements, expanding the applications possibilities of this ingredient, for example in the composition of breads, pastas, cookies, snacks, and gluten-free products, reducing the glycemic index of foods.

All samples had thermal stability from room temperature to 300 °C and in all samples, the crystallinity indexes decreased after treatment. Reactive extrusion was effective in modifying the physical-chemical and techno-functional properties of the coffee hull, with some advantages including short reaction times, low reagent concentrations, little or no effluent generation, and the possibility of scaling to industrial scale.

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Conflict of interest

The authors declare that there is no conflict of interest in carrying out this work.

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