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Research article

Different novel extraction techniques on chemical and functional properties of sugar extracts from spent coffee grounds

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Abstract: Large amounts of solid wastes such as spent coffee grounds (SCGs) from brewing provide a valuable sugar source to investigate. The effects on the sugar properties of extraction factors were studied. Different solvent extractions using an autoclave showed distinguishable sugar contents and properties. Water extracted the highest total sugar content while alkali extracted the highest total phenolic content (TPC). The ultrasonic-water-bath-assisted extraction with water did not produce any significant content or TPC. Finally, the combination of ultrasonic-autoclave-assisted extraction with water at 40% amplitude for 10 min produced the highest total sugar content and TPC, similar to that found in samples from the autoclave extraction with water. The FT-IR spectra of SCGs sugar revealed both amorphous and crystalline structures. All sugar extracts from SCGs contained phosphorus, potassium and calcium as the main mineral elements. Thus, sugar extracts from SCGs can be considered as an alternative additive with a good TPC for food products.

Keywords: sugar extracts; spent coffee grounds; autoclave extraction; ultrasonic-autoclave-assisted extraction; ultrasonic-water-bath-assisted extraction

1. Introduction

Coffee is one of the most popular and consumed beverages in the world. The high consumption generates several by-products from coffee processing such as coffee silverskin, coffee pulp and spent

coffee grounds [1–3], which contain different organic compounds, including a source of bioactive compounds [3]. Therefore, coffee waste can be considered a sustainable and circular bio-economy resource. Spent coffee grounds (SCGs), as a by-product from the brewing process of coffee, create a massive amount of food solid waste that has a low cost. The SCGs have been utilized as a source of material for the production of fuel pellets and biodiesel [4], polysaccharides [5–7], bioactive compounds and prebiotic oligosaccharides [8]. Interestingly, SCGs contain several bioactive compounds such as caffeine, tannic acid, chlorogenic acid, antioxidant polysaccharides and melanoidins (a compound generated during coffee roasting) that could be a source of functional food ingredients [9]. The large amounts of organic compounds in SCGs, namely cellulose, hemicellulose, lignin, fatty acids, and other polysaccharides, can be exploited as a source of value-added food additives back into the food system [10]. Another study on the extraction of protein from SCGs identified alternative plant protein with functional properties [11] and the SCGs oil extract was investigated as an alternative to butter for healthier cookie products [12]. Carbohydrates (mainly cellulose and hemicellulose) represent about 50% of the water-insoluble fraction of coffee. However, water-soluble carbohydrates are also rich in the monosaccharides, such as arabinose, galactose, mannose and glucose, and oligosaccharides, such as raffinose, and stachyose [13,14]. Sugars in SCGs constituted approximately 45.3% (w/w dry basis) containing 46.8% mannose, 30.4% galactose, 19% glucose and 3.8% arabinose, with mannans being the major sugar component [5]. Differences in the chemical compositions of SCG are probably due to the coffee cultivar and process used during roasting and brewing.

There has been a great effort to extract polysaccharides presented in coffee and SCG was done with various extraction techniques. Oosterveld et al. [15] extracted sugars from green coffee with hot water at 170 °C providing higher yields of galactomannans and galactans. Later, Mussatto et al. [5] reported that the optimal extraction was achieved using dilute acid hydrolysis (100 mg H_2SO_4/g dry SCG matter) and 10 g/g liquid-to-solid ratio at 163 °C for 45 min with hydrolysis efficiency levels of 100%, 77.4%, 89.5% and 87.4% for galactan, mannan, arabinan and hemicellulose, respectively. Ballesteros et al. [7] studied an alkali pretreatment (4 M NaOH solution at 25 ℃) to extract polysaccharides from SCGs and found mostly galactose followed by arabinose, glucose and mannose, respectively, which showed thermostability and good antioxidant and antimicrobial activities. Microwave superheated water extraction at 1:10 of SCGs and water (g/mL) to extract polysaccharides from SCGs produced mainly galactomannans [6]. Using alkali extraction, the carbohydrate composition of used coffee waste was reduced to only two monomers: glucose and mannose [16]. Different approaches have been proposed for the extraction of sugar extracts from SCGs, mainly using water [17], diluted sulfuric acid [5], sodium hydroxide [7,18] or potassium hydroxide [17] as the solvent extraction. The current study verified the effectiveness of three types of solvents for sugar extraction from SCG based on previous reviews: water [6], acid (H_2SO_4) [5] and alkali (NaOH) [7]. Although the sugar extracts are rich in carbohydrate compositions, the main monosaccharides found in SCGs are glucose and mannose. Therefore, sugar extracts were expressed as glucose and mannose equivalents per gram of extract. Furthermore, sugar extracts in terms of monosaccharides (glucose and mannose) are used as indicators for food applications. For example, glucose has wide applications in the food industry, such as in energy drinks, and is used by diabetics to quickly raise their blood sugar levels in the event of uncomfortable or disabling hypoglycemia [19]. Mannose is a high-value sugar product that has an important role in human metabolism, especially in the glycosylation of certain proteins [20,21]. In addition, mannose has a wide range of applications in the food, beverage and pharmaceutical industries.

Three different extraction methods (autoclave, water bath and ultrasonic methods) for sugar from SCGs were investigated in the current study. Autoclave treatment has been proven to extract bioactive compounds more efficiently due to its high pressure and temperature [22]. Mild conditions occur in a water bath, in which material tissues are slowly heated to extract and release the inner components into the medium [23]. The advantage of water-bath heating is that the temperature can be accurately controlled so the reactants are heated evenly [24]. Nonetheless, ultrasonic extraction is an interesting recent technique that uses ultrasonic waves to intensify mass transfer, cell disruption and more enhanced penetration and to allow solvent penetration into the material cells resulting in the release of compounds [11,23]. High-intensity ultrasonication can accelerate heat and mass transport in a variety of food process operations and has been successfully used to improve drying, mixing, homogenization and extraction [25]. Samsalee and Sothornvit [11] reported that ultrasonic-assisted extraction was efficient to obtain protein extract from SCGs rich in antioxidant activity.

There has been no published study on the effects of autoclave extraction, ultrasonic, water bath-assisted or ultrasonic water bath assisted and ultrasonic, autoclave-assisted extraction on the properties of sugar extracts. We hypothesized that the combination of two extraction techniques would enhance the properties of sugar extracts from SCGs and provide better properties for the sugar extracts. Therefore, the extraction method, type of solvent extraction and extraction time are of interest to investigate the properties of sugar extracts from SCGs, such as sugar content, FT-IR spectra, X-ray diffraction and elemental analysis, as well as the total phenolic content.

2. Materials and methods

2.1. Materials

Spent coffee grounds (SCGs) were derived from a blend of Robusta (90%) and Arabica (10%) beans from a coffee shop in Nakhon Pathom province, Thailand. Petroleum ether was purchased from Fisher Scientific UK Ltd (Loughborough, UK). Folin-Ciocalteu reagent and sulphuric acid were obtained from Merck KGaA (Darmstadt, Germany). Gallic acid monohydrate and Trolox ((±)-6-hydroxy-2, 5, 7, 8-tetramethylchromane-2-carboxylic acid) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Sodium carbonate (Na_2CO_3) was purchased from Ajax Finechem Pty Ltd (Taren Point, NSW, Australia). D-mannose (99%) was obtained from Alfa Aesar (Heysham, UK). All chemicals and reagents used were analytical grade.

2.2. Methods

2.2.1. Spent coffee grounds

The SCGs were dried at 60 ℃ for 24 h in a hot-air oven (RedLINE RF 115, Tuttlingen, Germany). The moisture content of dried SCGs was 7.12 ± 0.89% dry basis. The SCGs were defatted with petroleum ether as solvent using an SCG:petroleum ether ratio of 50:500 g/mL in a shaking water bath (Memmert WNB 7–45, Schwabach, Germany) at 28 ℃ for 24 h. Then, the defatted SCGs were dried overnight under a fume hood at room temperature (28 ℃) and further dried in an oven at 60 ℃ for 1 h until constant weight was reached. The samples were kept in a polyethylene zip-lock bag and stored at room temperature for further analyses.

2.2.2. Sugar extraction of spent coffee grounds by different methods

2.2.2.1. Autoclave extraction

The autoclave extraction was done using an autoclave (HA-240M, Hirayama, Japan). Sugar extraction from defatted dried SCGs was performed according to the methods described by Mussato et al. [5], Passos and Coimbra [6] and Ballesteros et al. [7] with some modifications. Three different solvents were studied: distilled water, 0.25 M H_2SO_4 solution for acidic solvent and 4 M NaOH solution for alkaline solvent. In brief, the defatted dried SCGs were added to a flask containing a solvent solution at a solid-to-liquid ratio of 1:10 (w/v) to obtain a total volume of 540 mL in the flask. For extraction, the mixture was heated in an autoclave at 121 ℃ for 30 or 60 min and the mixture was cooled to 28 ℃. After that, the mixture was passed through filter paper (Whatman No. 1, Maidstone, UK) and centrifuged at 9,700 rpm and 4 ℃ for 15 min using a refrigerated centrifuge (Eppendorf centrifuge 5804R, Hamburg, Germany) to separate the supernatant solution and then adjusted the pH to 7. Sugar extract from the SCGs was recovered using ethanol precipitation [6]. An amount of 75% ethanol (v/v) was added in the extract solution and then centrifuged. The resulting precipitate was dried using a vacuum-drying oven (WTB Binder, Tuttlingen, Germany) at 60 ℃ for 12 h. Each sample was stored at room temperature (28 ℃) until further analyses. Each set of experiments was repeated three times and the values were reported on average. The selected solvent was used to further study the effect of the extraction method.

2.2.2.2. Ultrasonic-water-bath-assisted extraction

According to a previous study, distilled water was selected as an extraction solvent for ultrasonic-water-bath-assisted extraction because it was safe for humans and the environment compared to other solvents. The ultrasonic extraction equipment had a working frequency of 20 kHz and a full power output of 750 W with a 25 mm diameter stainless probe (VCX 750, Sonics & Materials, Inc., Newtown, CT, USA). The ratio of defatted dried SCGs-to-distilled water was 1:10 (w/v). The mixture was extracted using different ultrasonic amplitudes (40, 60 and 80%) and 30 min extraction time in the pulse duration mode (20 s on and 20 s off). After the ultrasonic pretreatment, the mixture was extracted using a water bath (Memmert WNB 7–45, Schwabach, Germany) at 95 ℃ for 30 or 60 min. Then, the mixture was cooled to 28 ℃ and was further extracted as described in section 2.2.2.1. for sugar extraction. The optimal ultrasonic amplitude level was selected for further sugar extraction.

2.2.2.3. Ultrasonic-autoclave-assisted extraction

Ultrasonic-autoclave-assisted extraction was evaluated as an alternative to the conventional extraction method for the sugars from SCGs. The defatted dried SCGs were weighed accurately and then transferred into a flask of distilled water (1:10 w/v). The mixture was extracted using an ultrasonic amplitude level of 40% (selected from section 2.2.2.2.) at different extraction times (10, 20 and 30 min) in the pulse duration mode (20 s on and 20 s off), placed into an autoclave at 121 ℃ for 30 min and then extracted as described in 2.2.2.1.

2.2.3. Properties of sugar extract from spent coffee grounds

To measure the pH, total sugars, reducing sugar and total phenolic content, the sugar extract was dissolved in distilled water to obtain a 0.01% sugar extract solution. The solution was vortexed for 1 min and centrifuged at 8,000 rpm for 10 min. Then, the supernatant solution was collected for further analysis.

2.2.3.1. Determination of color value

The sample color values (L*, a* and b*) in the CIE system (International Organization for Standardization, 2008) were measured using a Spectro-guide (BYK-Gardner GmbH; Geretsried, Germany). The L*, a* and b* values represented lightness (values from 0 to 100), redness (-)/greenness (+) and yellowness (-)/blueness (+), respectively.

2.2.3.2. Determination of pH value

The pH of the sugar solution was measured using a digital pH meter (PB11, Sartorius, Gottingen, Germany).

2.2.3.3. Determination of total sugars

The total sugar was determined using the phenol-sulfuric acid method [22]. A sample solution was prepared (1:10 dilution ratio). Two milliliters of sample solution were mixed with 0.05 mL of 80% phenol followed by 5 mL of sulfuric acid. The mixture was vortexed using a vortex mixer for 1 min and allowed to stand for 10 min. Then, it was shaken and placed in a water bath at 25 ℃ for 20 min before readings were taken. The absorbance of the characteristic yellow-orange color was measured at 490 nm using a spectrophotometer (Shimadzu UV–Visible 1800, Tokyo, Japan). Calibration curves were performed using glucose and mannose as standard solutions. The results obtained were expressed in milligrams of glucose equivalent per gram of extract (mg glucose/g extract) and milligrams of mannose equivalent per gram of extract (mg mannose/g extract).

2.2.3.4. Determination of reducing sugar

The reducing sugar was determined using the dinitrosalicylic acid (DNS) method [27]. Briefly, the procedure used a test tube with 3 mL of sample solution (100 μg/mL) added with 3 mL of the DNS reagent. The mixtures were stirred and heated at 80°C for 30 min in the water bath. Subsequently, the mixtures were allowed to cool for 20 min. The absorbance was measured at 575 nm using the spectrophotometer. The results obtained were expressed in milligrams of glucose equivalent per gram of extract (mg glucose/g extract) and milligrams of mannose equivalent per gram of extract (mg mannose/g extract).

2.2.3.5. Determination of total phenolic content

The total phenolic content (TPC) was determined according to the Folin-Ciocalteu assay. The

reaction mixture was prepared by adding 0.4 mL of the supernatant samples, 2 mL of 10% Folin-Ciocalteu reagent and 1.6 mL of 10% sodium carbonate. The mixtures were incubated at room temperature for 1 h. The absorbance of each sample was measured at 765 nm against a blank using the spectrophotometer. Gallic acid was used as a standard and the TPC was expressed as milligrams of gallic acid equivalent (GAE) per gram of extract (mg GAE/g extract).

2.2.3.6. Fourier transform infrared (FT-IR) spectra

The FT-IR spectra of samples were determined using a Spectrum 100 instrument (PerkinElmer Inc., Waltham, MA, USA) for the wavenumber range 4000–500 cm^{-1}, with the attenuated total reflectance technique. Spectra were recorded in absorbance mode based on 16 scans per spectrum at a resolution of 4 cm^{-1}. The interference of water and CO_2 from air was deducted during scanning.

2.2.3.7. X-ray diffraction analysis

The X-ray diffraction (XRD) patterns of samples were performed using an X-ray diffractometer (Aeris 600W, PANalytical, the Netherlands) operating at a CuKα wavelength of 0.154 nm. The samples were exposed to the X-ray beam with the X-ray generator running at 40 kV and 15 mA. Distribution patterns were obtained at 2Θ angles of 10–70° at 25 ℃ with a step size of 0.02°.

2.2.3.8. Micro X-ray fluorescence analysis

The elemental analysis of the sample was carried out using a micro X-ray fluorescence (μXRF) technique (M4 TORNADO Micro-XRF spectrometer, Bruker Nano GmbH, Berlin, Germany). The instrument was equipped with an X-Flash solid-state silicon drift detector, an Rh source (50 kV, 600 μA) and polycapillary optics (25 μm spot size). For mineral element identification and quantification using μXRF datasets, full X-ray spectra were evaluated and compared to a library of known characteristic XRF spectra. The final product represented elemental abundance in weight percentage for magnesium, silicon, phosphorus, sulfur, potassium, calcium, manganese, iron, copper, zinc, sodium, strontium and chlorine, which were normalized to 100% [28].

2.2.4. Statistical analyses

A completely randomized design was used. Three replications were used to determine each property. Data were subjected to analysis of variance and Duncan's multiple range test was used to determine significant differences at the 95% confidence interval. Analysis was performed using the SPSS package (SPSS 11.0 for Windows; SPSS Inc.; Chicago, IL, USA).

3. Results and discussion

3.1. Influence of different solvents and times on sugar extraction by autoclave technique

The pH value of sugar extract solution from SCGs was established in the range 6.95–7.78 (Table 1). Using water or acid as the solvent for different extraction times did not affect the pH value of the

samples. Conversely, the highest pH value was obtained in an alkaline solvent for 30 min of extraction. However, all sugar extract solutions had a pH value close to 7 (neutral pH) due to the pH adjustment in the sugar extraction process. The L*, a* and b* values of SCGs sugar extract are shown in Table 1. Different extraction solvents significantly affected the color values of SCGs sugar extract. Obviously, the acid extraction for 30 min significantly showed higher L* (lightness) and a* (redness) values (32.11 and 3.88, respectively) but lower b* (yellowness) value (8.74). Meanwhiles, the SCGs sugar extract samples using water and alkali extractions showed similar color parameter values. We hypothesize that the extraction at a low concentration of acid might not much change the color of sugar extracts, compared with a higher concentration of alkali.

Table 1. pH and color values of sugar extracts from SCGs using autoclave technique with different solvents (water, acid and alkali) and times (A) and same results using ultrasonic-water-bath-assisted extraction at 40, 60 and 80% amplitudes for 30 and 60 min (B).

A. Autoclave technique with different solvents and times

Solvent	Time (min)	pH	Color value		
			L*	a*	b*
Water	30	7.30 ± 0.03^{b}	9.32 ± 0.59^{a}	1.92 ± 0.16^{c}	12.62 ± 12.62^{cd}
	60	7.22 ± 0.06^{b}	8.26 ± 0.11^{a}	2.61 ± 0.11^{d}	11.91 ± 0.12^{c}
Acid	30	6.97 ± 0.10^{a}	32.11 ± 1.88^{c}	3.88 ± 0.13^{e}	8.74 ± 0.41^{a}
	60	6.95 ± 0.07^{a}	15.05 ± 1.36^{b}	0.85 ± 0.09^{a}	9.70 ± 0.30^{b}
Alkali	30	7.78 ± 0.03^{c}	9.10 ± 0.20^{a}	2.02 ± 0.02^{c}	12.63 ± 0.13^{cd}
	60	7.38 ± 0.06^{b}	10.75 ± 0.45^{b}	1.34 ± 0.11^{b}	12.88 ± 0.17^{d}

Data are mean ± standard deviation (n = 3).

Different superscript letters (a, b, c, d, e) in same column indicate significant ($p < 0.05$) differences in each property.

B. Ultrasonic-water-bath-assisted extraction with different amplitudes and times

Amplitude (%)	Time (min)	pH^{NS}	Color value		
			L^{*NS}	a^{*NS}	b^{*NS}
40	30	6.99 ± 0.11	11.68 ± 0.31	2.03 ± 0.14	14.12 ± 0.07
	60	6.96 ± 0.12	9.01 ± 0.66	2.32 ± 0.26	13.72 ± 0.29
60	30	7.01 ± 0.15	11.03 ± 1.95	1.88 ± 0.06	13.66 ± 1.09
	60	6.79 ± 0.35	9.38 ± 0.11	2.00 ± 0.11	13.19 ± 0.14
80	30	6.95 ± 0.04	9.08 ± 0.05	2.10 ± 0.19	13.07 ± 0.02
	60	6.97 ± 0.07	11.69 ± 0.36	2.06 ± 0.06	14.26 ± 0.00

Data are mean ± standard deviation (n = 3).

NS: not significant.

The total sugar and reduced sugar contents of the sugar extract are shown in Figure 1 (A). The water extraction presented the highest sugar content (glucose and mannose equivalent forms), followed by the alkali and acid extractions. Increasing the extraction time from 30 to 60 min did not significantly affect the total sugar content or the reduced sugar content for each solvent (Figure 1 (A)). However, the high temperature and pressure of autoclave extraction easily disrupted cell membranes and cell walls and also released substances from the SCGs. The lowest sugar content was recorded using the acid extraction, compared to the other solvents. The extraction time had no significant effect on the

sugar content. Undoubtedly, the acid extraction (0.25 M H_2SO_4) was not suitable for the extraction of sugars in SCGs. Mussatto et al. [5] reported that the major problem of acid hydrolysis was that the decomposition of monomeric sugars produced during the reaction takes place simultaneously with the hydrolysis of polysaccharides. Jin et al. [29] reported that alkaline pretreatment before enzymatic hydrolysis provided a better result for sugar production from SCGs compared to using acid pretreatment, as it was more effective in breaking the bonds between the lignocellulose.

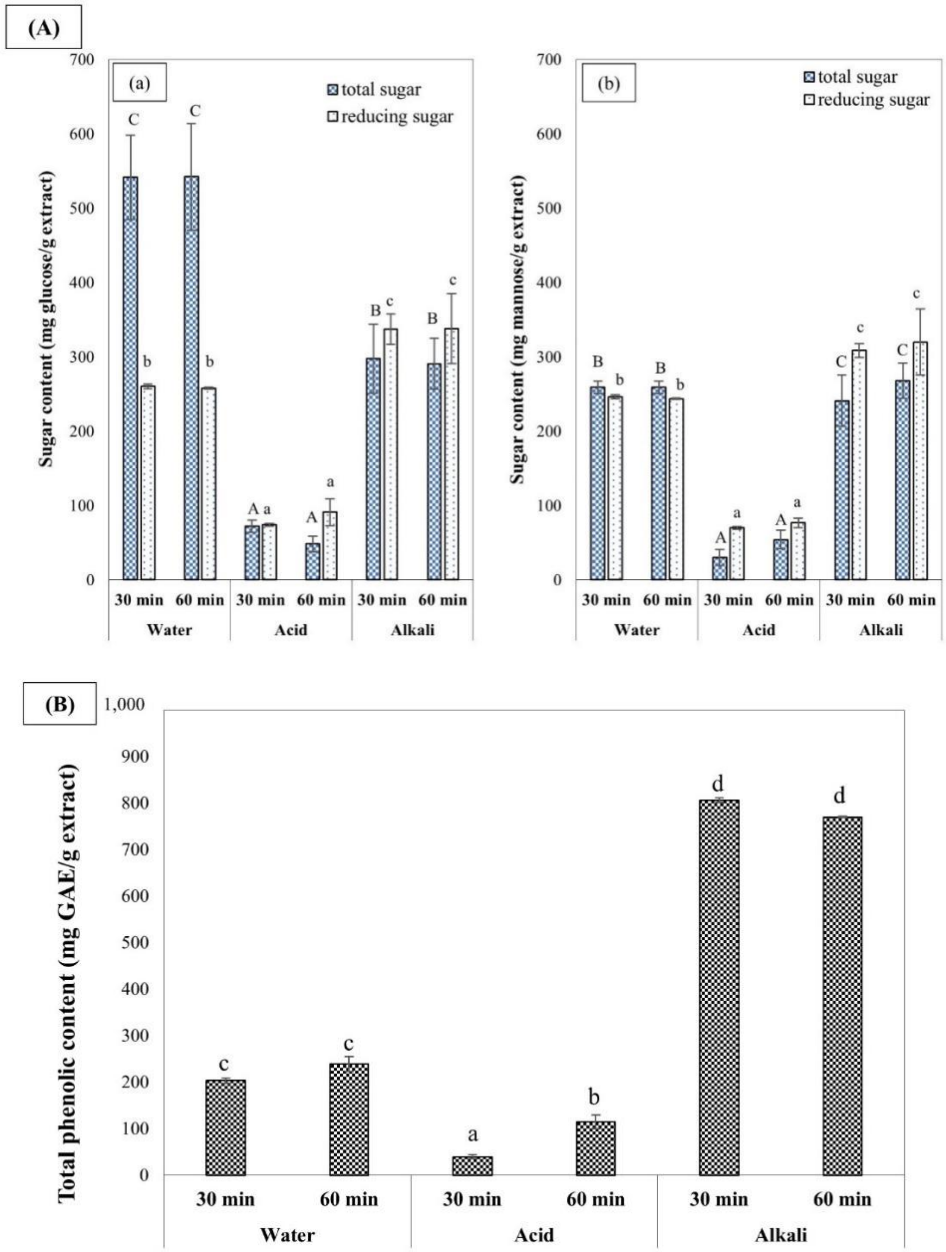

Figure 1. Total sugar and reducing sugar contents (A) and total phenolic content (B) of sugar extract from SCGs using autoclave technique with different solvents (water, acid and alkali) and times: with glucose (a) and mannose (b) as standard solutions. Data are mean ± standard deviation (n = 3). Different uppercase superscripts denote significant ($p < 0.05$) differences in total sugar content. Different lowercase superscripts denote significant ($p < 0.05$)

differences in reducing sugar content and total phenolic content.

From Figure 1 (A), the sugar contents of all sugar extract samples in the glucose-equivalent form were higher than the mannose equivalent form using the autoclave technique at 121 ℃. This was due to the high temperature leading to the release of glucose more easily than for mannose. Similar results were observed by Khuwijitjaru et al. [30] who reported that glucose was more easily released from a polymer structure than mannose at 100–150 ℃. In addition, the glucose content decreased at 175–200 ℃ and mannose became the major sugar product from subcritical water treatment of coconut meal. Similarly, coffee wastes had a higher glucose content (approximately 60%) than mannose content (approximately 40%) according to Pujol et al. [16]. Nonetheless, galactose and mannose were the most abundant sugars presented in the acid hydrolysis products of SCGs [5] and in subcritical water hydrolysis products using ultrasonic pretreatment of SCGs [31]. Overall, hydrolysis using water provided superior performance for sugar extraction in its glucose equivalent than either the acid or alkali extractions (Figure 1 (A)). Therefore, water was chosen as the solvent for further study. It is well known that water is a safe, inexpensive and environmental-friendly choice compared to organic solvents, such as sulfuric acid and sodium hydroxide. Furthermore, it is particularly advantageous in reducing costs in the sugar extraction process.

There was no significant difference in the total phenolic content of the sugar extract using water and alkali as solvents for different extraction times (Figure 1 (B)). The total phenolic content was higher in the sugar extract using an alkali extraction for 30 and 60 min (806.59 and 770.54 mg GAE/g extract, respectively) but no significant differences were observed. Sugar extraction using an acid solvent produced a lower total phenolic content than for the other solvents and the longer extraction time resulted in a significantly higher total phenolic content. Therefore, the type of extraction solvent affected the total phenolic content of the sugar extract. The results revealed that alkali extraction was an effective solvent for the extraction of the total phenolic content of sugar using an autoclave technique. The phenolic compounds from alkali extraction may possess more phenol groups than the phenolic compounds in the water and acid extraction. Similarly, Wu et al. [32] reported that alkaline hydrolysis released bound phenolics from seaweed more efficiently than acid hydrolysis. Based on the results for the total phenolic content, the best extracting solvent was alkali. However, the sugar extract using alkali extraction in this work was higher than the total phenolic content of 291.86 mg GAE/g reported by Bhaturiwala and Modi [33] for enzymatically hydrolyzed SCGs.

3.2. Influence of using ultrasonic-water-bath-assisted extraction for sugar extraction

We selected water as the solvent to study the effect of ultrasonic-water-bath-assisted extraction at different amplitude levels and extraction times in the water bath. The ultrasonic amplitude levels and extraction times did not significantly influence the pH or color parameters of any sugar extracts (Table 1). These results were in close agreement with the autoclave extraction method mentioned above. Moreover, there were no significant differences in color parameters (L*, a* and b*) of sugar extracts due to the effect of ultrasonic-water-bath-assisted extraction as shown in Table 1 (B). This might be a narrow range of ultrasonic amplitude levels to detect the change in the color of sugar extracts.

The ultrasonic amplitudes and extraction times (during the time in the water bath) influenced the sugar extraction from SCGs, as shown in Figure 2 (A). There was a significant decrease in the total

sugar content (glucose equivalent form) of sugar extract after receiving 40% and 80% amplitude for 60 min in the water bath compared to the extraction time for 30 min. In the case of the mannose equivalent form, the total sugar content was not significantly different, except for the 80% amplitude. The ultrasonic sound waves led to high shear forces which can disrupt cell walls and enable solvent penetration into plant cells, resulting in the release of constituents [34]. However, the current results suggested that increases in the ultrasonic amplitude level and extraction time tended to decrease both the total sugar and reduced sugar contents (expressed in terms of glucose and mannose). Ultrasonic treatment could enhance the release and diffusion of sugar content easily into the water solvent; however, a longer extraction time in the treatment may induce breakage and degradation of the sugar content. As reported, lowering the extraction temperature and lengthening the residence time slowed reducing sugar degradation [31].

There was no significant increase in the total phenolic content of the sugar extracts when the extraction time increased from 30 to 60 min, indicating that increasing the ultrasonic amplitude level did not necessarily improve the total phenolic content of sugar extracts. The total phenolic content of all SCGs sugar extracts using ultrasonic-water-bath-assisted extraction varied from 140.41 to 208.59 GAE/g extract (Figure 2 (B)) which was slightly lower compared to using the autoclave technique with water extraction (204.06 to 239.42 GAE/g extract).

An ultrasonic amplitude of 40% for 30 min extraction was chosen as the optimum level for further study using an ultrasonic- autoclave-assisted extraction because this combination produced the highest total sugar and reduced sugar content (525.13 and 290.77 mg glucose/extract, respectively); however, there was no significant difference in the total phenolic content compared to the other conditions. Furthermore, the condition mentioned above also increased the mannose-reducing sugar content (274.61 mg mannose/extract).

3.3. Influence of using ultrasonic-autoclave-assisted extraction for sugar extraction

At 30 min extraction, the ultrasonic amplitude levels did not show any differences in the sugar content of the SCGs extracts. A longer extraction time tended to lower the sugar content expressed as glucose equivalent. Therefore, an ultrasonic amplitude at 40% with 30 min extraction time was chosen as the optimal conditions for extraction for further study.

Different extraction times at 40% amplitude of ultrasonic (10, 20 and 30 min) combined with autoclave extraction were used to extract the sugar. The results indicated that increasing the extraction time reduced the sugar content (both total sugar and reduced sugar content) and that the extraction time significantly affected the total sugar and reduced sugar contents of the SCGs sugar extracts (Figure 3 (A)). It can be seen from Figure 3 (A) that there were maxima at 529.25 mg glucose/g extract (a) and 361.25 mg mannose/g extract (b) for the extraction of sugar using the ultrasonic-autoclave-assisted extraction at 40% amplitude for 10 min. Thus, the observed low sugar content might have resulted from the longer residence time in the ultrasonic-autoclave-assisted extraction due to heat generation during the ultrasonic process resulting in the degradation of the sugar content.

Longer extraction times led to lower total phenolic contents in the SCGs sugar extract, probably due to degradation of the phenolic compounds (Figure 3 (B)). Consequently, 10 min was chosen as the optimum extraction time for both the sugar and total phenolic contents. It was observed that the effect of extraction time on the sugar content was similar to that on the total phenolic content. Similarly, the results were in agreement with the decrease in the total sugar and reduced sugar contents.

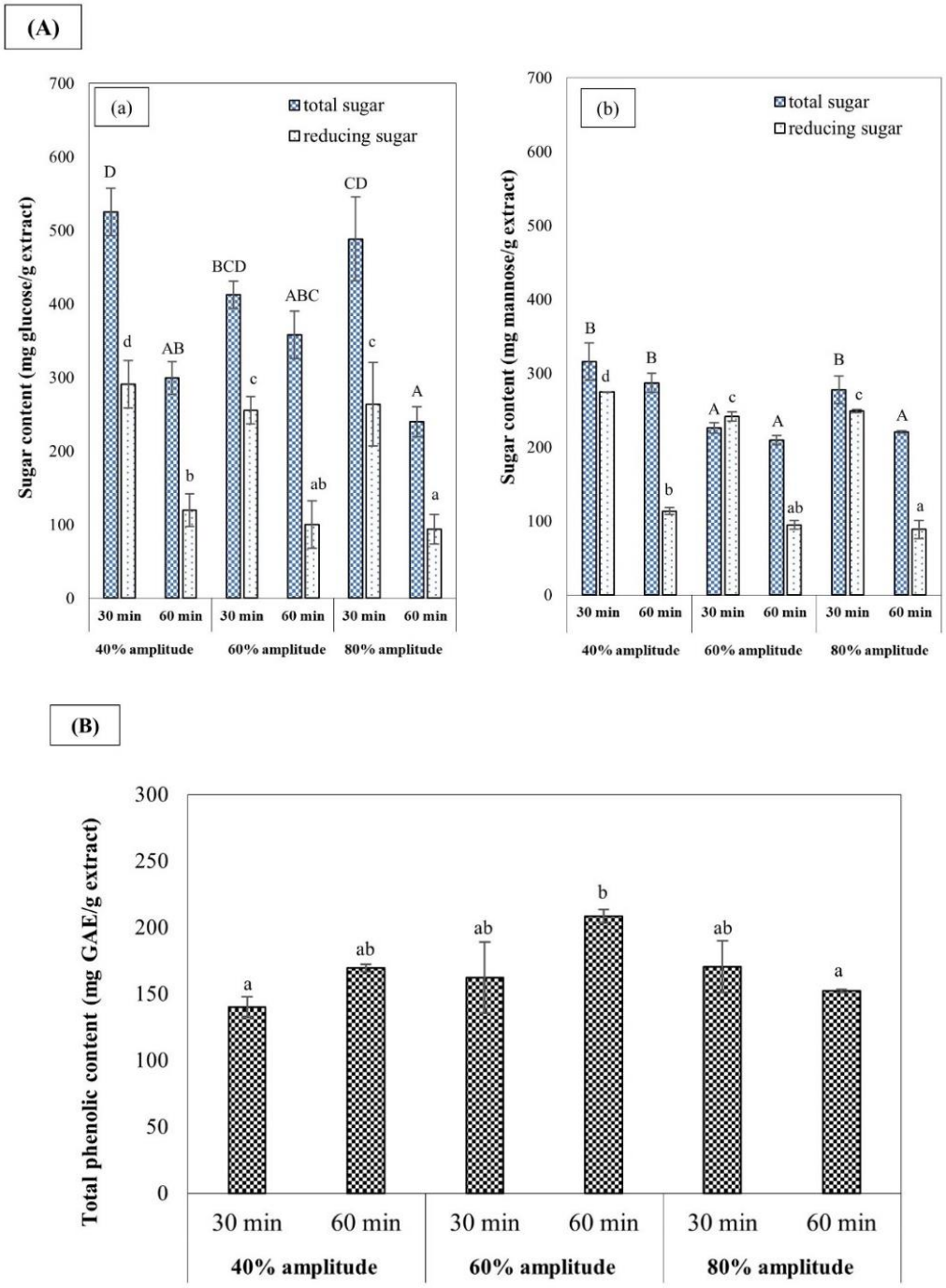

Figure 2. Total sugar and reducing sugar contents (A) and total phenolic content (B) of sugar extracts from SCGs using ultrasonic-water-bath-assisted extraction at 40, 60 and 80% amplitudes for 30 and 60 min: with glucose (a) and mannose (b) as standard solutions. Data are mean ± standard deviation (n = 3). Different uppercase superscripts denote significant ($p < 0.05$) differences in total sugar content. Different lowercase superscripts denote significant ($p < 0.05$) differences in reducing sugar content and total phenolic content.

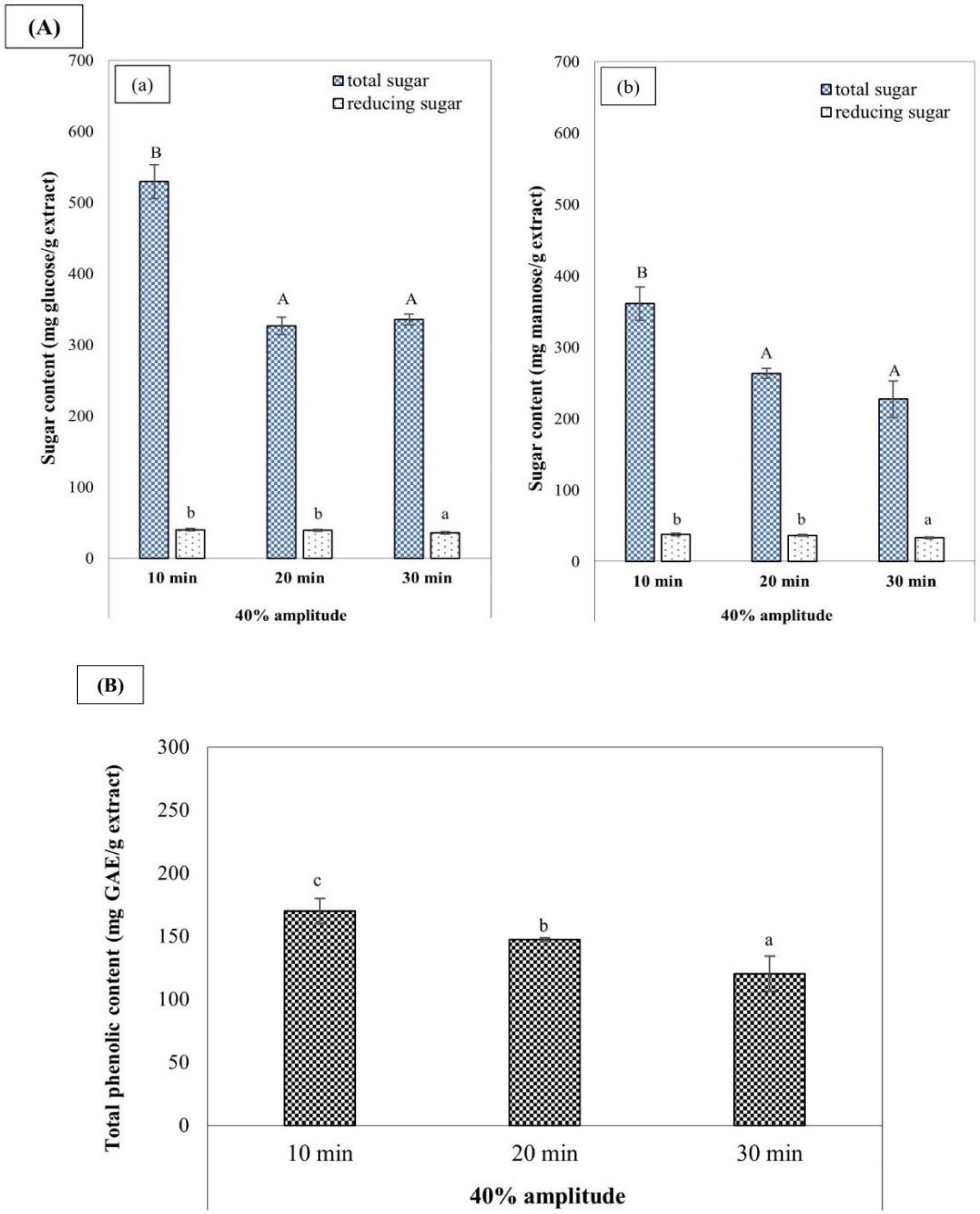

Figure 3. Total sugar and reducing sugar contents (A) and total phenolic content (B) of sugar extracts from SCGs using ultrasonic-autoclave-assisted extraction at 40% amplitude for 10, 20 and 30 min followed by autoclaving at 121 ℃ for 30 min: with glucose (a) and mannose (b) as standard solutions. Data are mean ± standard deviation (n = 3). Different uppercase superscripts denote significant ($p < 0.05$) differences in total sugar content. Different lowercase superscripts denote significant ($p < 0.05$) differences in reducing sugar content and total phenolic content.

Figure 4 (A) shows the FT-IR spectra of the SCGs sugar extracts with water as the extraction solvent for various extraction methods (autoclave extraction for 30 min, ultrasonic-autoclave-assisted extraction at 40% amplitude for 30 min and ultrasonic-water-bath-assisted extraction at 40% amplitude for 30 min). The major bands of all SCG sugar extracts were approximately at wavenumbers of 3306–3370 cm^{-1}, 2915–2925 cm^{-1}, 2850–2856 cm^{-1}, 1731–1738 cm^{-1}, 1369–1371 cm^{-1}, 1070–1078 cm^{-1},

1000–1001 cm^{-1}, 861–878 cm^{-1} and 798–800 cm^{-1}. The 1500–800 cm^{-1} region corresponded to the absorption zones of glucose, fructose and sucrose [35]. In the anomeric region, adsorption peaks at approximately 950–700 cm^{-1} exhibited the existence of mannose [36]. Hua et al. [37] reported that mannose and glucose units were assigned from characteristic peaks at about 814 and 873 cm^{-1}, respectively, which were close to those reported in the current study. This corresponded to the bending vibration of the C-H group. The bands between 1700 and 1500 cm^{-1} were associated with symmetrical stretching and asymmetrical vibrations of the C-O group [31]. Wavenumbers at 2915–2925 cm^{-1} and 2850–2856 cm^{-1} were attributed to asymmetrical and symmetrical stretching of C-H bonds in the aliphatic chains due to the presence of methyl and methylene groups [16]. Clearly, a strong absorption at wavenumber 3327 cm^{-1} was attributed to the stretching of the hydroxyl groups [38] which could be attributed to the polysaccharide. These hydroxyl groups were a functional group of the polyphenol or antioxidant compounds found in SCGs [39]. All FT-IR spectra demonstrated that the sugar extracts from the SCGs were mainly composed of polysaccharides.

Figure 4 (B) shows the XRD patterns for the SCGs sugar extracts with water as the solvent using different extraction methods. Samples of the SCGs sugar extracts from ultrasonic-autoclave-assisted extraction and ultrasonic-water-bath-assisted extraction had similar major intensities of diffraction peaks at 16°, 31.6°, 45.5° and 56° (2Θ). Conversely, the sample from autoclave extraction showed only main peak intensities at 16° and 20° (2Θ). The presence of a peak (2Θ) at around 16° and 20° represented the amorphous and crystalline fractions of lignocellulose, respectively [40]. Thus, the SCGs sugar extracts in the current study showed a structure of glucose with both crystalline and amorphous regions [7]. The peak intensity at 31.6° of the SCGs sugar extract was related to the diffraction of the sample as a semi-crystalline polymer [41]. Arab et al. [42] reported that most polysaccharides had an amorphous or semi-crystalline structure in which the intermolecular bonds were weaker in the amorphous regions than in the crystalline regions and the solubility and water uptake were higher in the amorphous polysaccharides. Therefore, the current results suggested that the extraction method resulted in different XRD patterns of the SCGs sugar extracts.

The sugar extracts from SCGs using autoclave extraction, ultrasonic-autoclave-assisted extraction and ultrasonic-water-bath-assisted extraction all using water as the solvent were investigated for mineral elements using μXRF, as shown in Table 2. There were 13 mineral elements identified and quantified: magnesium, silicon, phosphorus, sulfur, potassium, calcium, manganese, iron, copper, zinc, sodium, strontium and chlorine. The mineral elements of the SCGs were the same as those in defatted SCGs. Potassium was the most abundant element in both the SCGs and defatted SCGs, followed by calcium, sulfur, phosphorus and magnesium. Potassium was prominent in the SCGs, similar to the reports of Mussatto et al. [5], Ballesteros et al. [43] and Scully et al. [44]. However, three elements (sodium, strontium and chlorine) were not detected in either the SCGs or the defatted SCGs raw materials in the current study. Additionally, all sugar extracts from the SCGs had a clear increase in calcium, phosphorus, magnesium and manganese compared to the initial SCGs. After the extraction process, minor elements, such as sodium, strontium and chlorine, were found in the sugar extracts; however, silicon was not detected. Nonetheless, the sugar extracts from the three extraction techniques had the same mineral elements with similar compositions. The most important detected minerals were micronutrients essential for human health to regulate multiple metabolic and physiological functions [43]. Therefore, the SCGs sugar extract could be used as a nutrient source in fortified healthy food products.

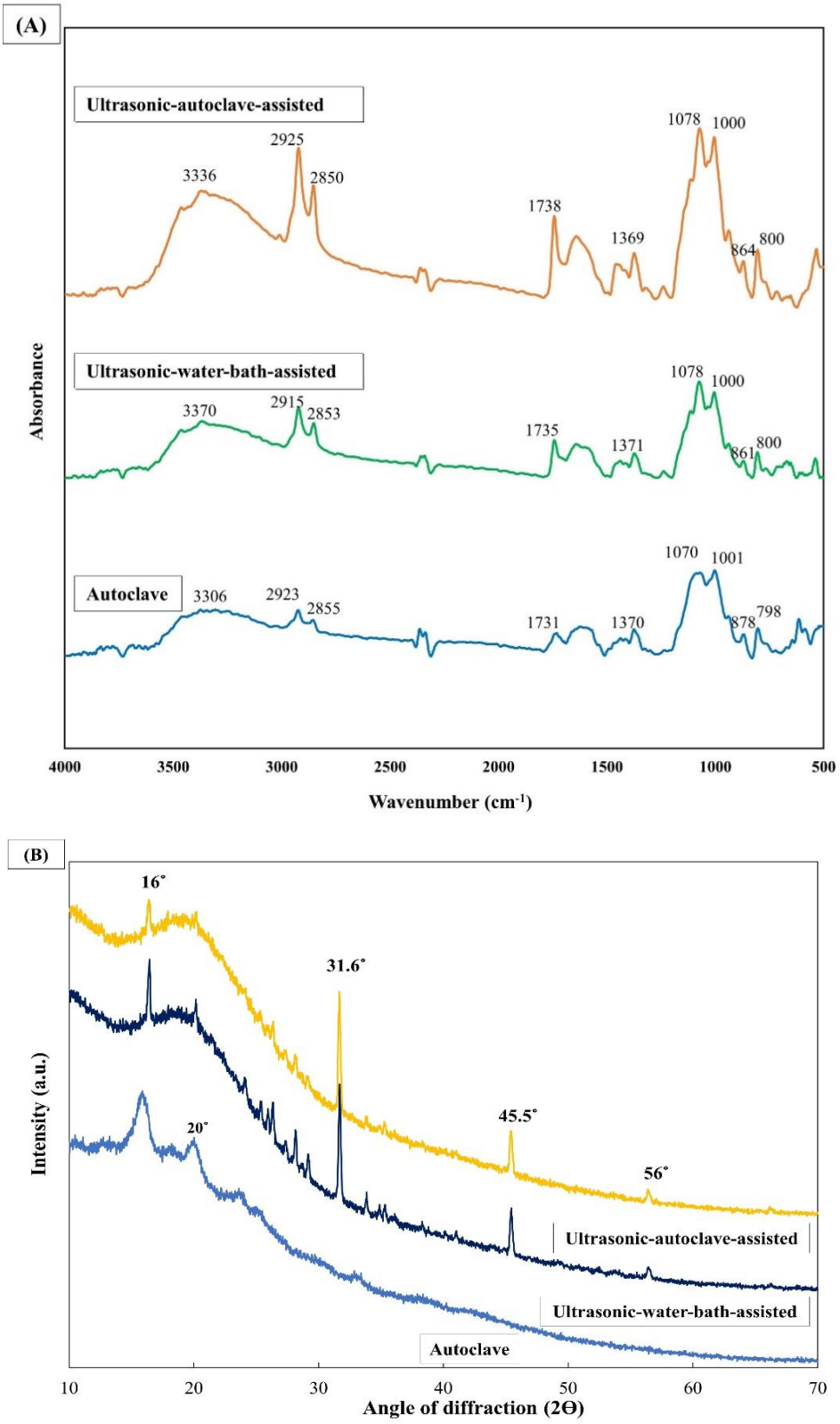

Figure 4. FT-IR spectra (A) and XRD diffractograms (B) of sugar extracts from SCGs using autoclave extraction for 30 min, ultrasonic-water-bath-assisted extraction at 40% amplitude for 30 min and ultrasonic autoclave-assisted extraction at 40% amplitude for 30 min with water as solvent.

Table 2. Mineral composition of spent coffee grounds, defatted spent coffee grounds and sugar extracts using different extraction methods.

Mineral element	Composition (wt. %)				
	SCGs	Defatted SCGs	Sugar extraction method		
			Autoclave	Ultrasonic-autoclave-assisted	Ultrasonic-water-bath-assisted
Magnesium	6.19	6.90	9.12	9.22	8.13
Silicon	0.11	0.04	nd	nd	nd
Phosphorus	6.36	6.42	24.92	25.43	21.04
Sulfur	8.71	9.41	0.44	0.39	0.38
Potassium	53.21	51.49	32.52	26.39	26.53
Calcium	23.96	24.28	28.90	34.25	38.20
Manganese	0.38	0.40	1.76	2.00	1.69
Iron	0.83	0.82	0.22	0.16	0.09
Copper	0.18	0.16	0.03	0.06	0.02
Zinc	0.07	0.08	0.11	0.10	0.08
Sodium	nd	nd	0.69	0.27	1.13
Strontium	nd	nd	0.09	0.08	0.09
Chlorine	nd	nd	1.19	1.64	2.60
Total (wt. %)	100.00	100.00	100.00	100.00	100.00

Note: Autoclave extraction for 30 min using water as solvent; Ultrasonic-autoclave-assisted extraction at 40% amplitude for 30 min using water as solvent. Ultrasonic-water-bath-assisted extraction at 40% amplitude for 30 min using water as solvent. nd: not detected.

4. Conclusions

The sugar extracts from SCGs were rich in total sugar content, reducing sugar content, total phenolic content and mineral elements. Water extraction using an autoclave technique at 121 °C produced the highest total sugar content while alkali extraction produced the highest total phenolic content. Water, a safe, inexpensive and environmental-friendly compound, was chosen as the solvent for sugar extraction using ultrasonic-water-bath-assisted and ultrasonic-autoclave-assisted extractions. Different ultrasonic amplitude levels (40, 60 and 80%) in ultrasonic-water-bath-assisted extraction for the same extraction times (30 and 60 min) made no significant differences to the sugar content (glucose equivalent) and total phenolic content. Finally, using ultrasonic-autoclave-assisted extraction at 40% amplitude for 10 min extraction time produced the best results of the highest total sugar content and highest total phenolic content. Glucose was the main sugar obtained from the SCGs sugar extract with both amorphous and crystalline structures. Phosphorus, potassium and calcium were the most abundant elements in the SCGs sugar extract. However, the autoclave method alone showed sufficient potential to be used for SCGs sugar extraction. Therefore, the sugar extract from SCGs could be used as an alternative food additive or as a functional food ingredient in a food system. Thus, this work identified an alternative process for the waste valorization of SCGs.

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Conflict of interest

The authors have no conflicts of interest to declare.

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