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Impact of microwave-assisted extraction on roasted coffee carbohydrates, caffeine, chlorogenic acids and coloured compounds

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ABSTRACT

Microwave-assisted extraction (MAE) allows to quickly achieve soluble compounds from solid matrices due to the promotion of temperatures higher than the solvent (atmospheric) boiling point, once a closed-vessel system is used for operating at high pressure. In this study, the feasibility of MAE for producing high yield coffee extracts with properties that allow their commercial application was tested through a quality by design approach. It was studied the influence of time of extraction (1, 5.5, 10 min), temperature (120, 150, 180 °C) and the mass-to-volume (m/V) ratio (2, 4, 6 g/60 mL) in the overall extraction yield (24–47%, w/w), carbohydrates content (18–43%, w/w), sugars composition, caffeine (4–7%, w/w), 5-caffeoylquinic acid (1–2%, w/w), colour and antioxidant activity of the extracts. FTIR analysis was used to study the resemblance of coffee extracts and commercial instant coffee. MAE allowed overall extraction yields considerably higher than the home brewing methods, mainly when performed at 180 °C, with a substantial increase in arabinogalactans (AG) extraction associated to higher temperatures. Temperature exerted a crucial role in coffee extracts differentiation, although time and m/V ratio also lead to different values in the responses. Under a circular economy concept, MAE was able to produce extracts that can be used as defined food/brew ingredients and provides a galactomannan and cellulose rich residue that can also be valued as a source of dietary fibre.

1. Introduction

Coffee is a well-studied food matrix used to prepare different types of brews known for their health effects, with different physicochemical properties due to distinct operational parameters used for their extraction (Gloess et al., 2013; Petracco, 2001). Roasted coffee composition depends on coffee species and the roasting degree affecting the brews properties (Farah, 2012; Illy & Viani, 2005). Roasted coffee compounds (*e.g.* caffeine, carbohydrates, melanoidins, chlorogenic acids) exhibit great structural diversity that confers different chemical, sensorial and biological properties to the brews (Farah, 2012; Ferreira et al., 2018; Gloess et al., 2013). Carbohydrates are a considerable fraction of coffee brews, representing up to 40% of the content of instant coffee, with important properties (*e.g.* viscosity, foamability). Chlorogenic acids are associated to the astringency, bitterness and acidity perceived through the ingestion of the coffee brews, besides their biological properties, and caffeine is the most studied coffee molecule mainly due to its stimulating effects.

Microwave-assisted extraction (MAE) presents advantages compared to conventional methods as the reduction of extraction time, improved yield and/or better accuracy (Ameer, Shahbaz, & Kwon, 2017; Delazar, Nahar, Hamedeyazdan, & Sarker, 2012). The MAE may be conducted in open or closed-vessel systems. The later ones allow higher temperatures and pressures, while avoiding the loss of volatile substances and extraction solvent. In these systems, the temperature and pressure of extraction are controlled, while radiated microwaves interact with the sample, with turntables (multimode system) used to ensure an equal energy distribution (Ameer et al., 2017; Delazar et al., 2012). In MAE occurs the penetration of microwave energy through the sample resulting in the heating of the solution due to the molecular friction between the rotating molecules through dipole reorientation under the influence of the changing or alternating electric field or via the conductive migration of dissolved ions (Lam & Chase, 2012; Rodriguez-Jasso, Mussatto, Pastrana, Aguilar, & Teixeira, 2011).

MAE was already tested for the reuse of antioxidants and carbohydrates from the coffee residues, the spent coffee grounds (SCG), that remain after coffee brews preparation (Passos & Coimbra, 2013; Passos et al., 2019; Passos, Moreira, Domingues, Evtuguin, & Coimbra, 2014;

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Pettinato, Casazza, Ferrari, Palombo, & Perego, 2019; Ranic et al., 2014). SCG comprise a different and organoleptically poorer matrix when compared to roasted coffee, as some compounds were already greatly extracted to the brew. Although MAE offers extraction conditions significantly different to those achieved with conventional methods of coffee extraction, to the best of our knowledge, its application directly to the roasted coffee matrix has only been reported using ethanol in a modified domestic microwave oven, not reaching pressurized conditions (Borja, Uy, Lim, Ong, & Ros, 2014). In this work, it was tested the hypothesis that MAE can be used as a quick methodology to produce coffee extracts with varied composition able to be used as food ingredients, studying the influence of time of extraction, temperature and mass-to-volume ratio.

2. Material and methods

2.1. Coffee samples and chemicals

A commercial blend of roasted coffee beans Delta® *Lote Chávena* was grinded (Flama −1231, particle profile in Fig. S1) and the powder used to perform the coffee extraction experiments. A commercially available instant coffee (I.C., Café Solúvel Delta®) was used as reference product.

2.2. MAE coffee experiments

The MAE experiments were conducted in 100 mL reactors able to endure high temperatures and pressures (up to 250 °C and 55 bar, respectively) placed on a multimode microwave oven - MicroSYNTH Labstation (maximum output: 1 kW, 2.45 GHz; Milestone Srl, Sorisole (BG), Italy). The device allows to monitor and control the vessel inner temperature in real-time as described in Passos and Coimbra (2013), with the content stirred continuously with a magnetic bar. Roasted coffee powder beans were grounded before the experiments and the powder placed on the reactor with 60 mL of distilled water. The experiments were performed in duplicate (two reactors in the apparatus). Microwave power was continuously adjusted by the system to attain the desired temperature in 2 min and maintained it during the experiment (Supplementary Material Fig. S2). Preliminary tests showed that overpressure occurs using high m/V ratios during prolonged times (10 min), data used for delimiting the extreme levels in the experimental design. After the MAE, the reactors were cooled down to room temperature and their content was vacuum filtrated (1.2 μm glass microfiber filter), frozen and freeze-dried, giving the overall extraction yield, and the insoluble residue oven dried (105 °C, 24 h). It was also performed a MAE at 80 °C (2 min, 2 g/60 mL) and a solid-liquid extraction (1 g/30 mL of distilled water in a covered Erlenmeyer flask) maintained at 80 °C in a water-bath with magnetic agitation (30 min). The solution content was vacuum filtrated (1.2 μm glass microfiber filter) and the retained material was washed with 30 mL of water. The filtrate was frozen and freeze-dried. The amount of freeze-dried solids in relation to the amount of ground coffee used (2, 4, or 6 g) gives the extraction yield (Y_1, %, w/w) (Eq. (1)):

$$Extraction\ \ yield\ \ (\%, w/w) = \frac{freeze-dried\ \ solids\ \ (g)}{ground\ \ coffee\ \ (g)} \quad (1)$$

2.2.1. Experimental design

The conditions used in each experiment were established according to a Box-Behnken design (BBD) with three independent factors - time (X_1, min), temperature (X_2, °C) and m/V ratio (X_3, g/60 mL) - and 3 levels - low, intermediate, and high coded (−1), (0) and (+1), respectively (Table 1). All experiments were performed in duplicate (two microwave reactors) comprising the design a 30-run experiment with six replicates of the centre point. The data obtained were adjusted to a second-order surface model represented by the Eq. (2):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j \quad (2)$$

where Y is the response observed in the dependent factor of interest, β_0, β_i, β_{ii} and β_{ij} terms represent the constant, linear, quadratic, and two-factor interaction regression coefficients, respectively, while x_i represents the independent variables (time, temperature, m/V ratio) in a dimensionless coded form. The dependent variables were: extraction yield (Y_1, %, w/w), carbohydrates (Y_2, %, w/w), galactomannans (Y_3, %, w/w) and arabinogalactans (Y_4, %, w/w) content in the extract. The different coefficients (main effects, interactions, and high-order effects) were found by analysis of variance using 95% significance level (p-value). The experimental data was statistically analysed using Statistica v12 and Minitab v17 software programs.

2.3. Extracts characterization

All freeze-dried extracts and residues obtained were analysed for the carbohydrates content and composition. Carbohydrates content was evaluated through the sum of the amount of the individual sugars achieved after acid hydrolysis and derivatization to alditol acetates (Lopes et al., 2016). The samples were incubated with 72% H_2SO_4 and hydrolysed with 2 M H_2SO_4 for 1 h at 120 °C. $NaBH_4$ (15% in NH_3 3 M, 1 h, 30 °C) was used to reduce the sugars released, which were acetylated with acetic anhydride (3 mL) at 30 °C during 30 min in the presence of 1-methylimidazole (450 μL). After washes with dichloromethane, the alditol acetate derivatives were analysed in a Perkin Elmer - Clarus 400 chromatograph equipped with a FID detector and a DB-225 column (30 m × 0.25 mm and 0.15 μm of film thickness) using 2-deoxyglucose as internal standard.

The determination of caffeine and free 5-caffeoylquinic acid (5-CQA) was performed based on Nunes, Cruz, and Coimbra (2012). Briefly, runs with coffee extracts solutions (10 mg mL^{-1}, filtrated with 0.22 μm filters) were performed on a HPLC-DAD apparatus equipped with a C18 column, eluted with formic acid 5% and methanol at a flow rate of 0.8 mL min^{-1}. Caffeine was detected at 280 nm and 5-CQA at 325 nm, with respective calibration curves prepared.

The specific extinction coefficient at 405 nm ($K_{mix,\ 405nm}$) was determined as the slope of absorbance in relation to concentration obtained with several dilutions (0–1 mg mL^{-1} in distilled water) of the freeze-dried coffee extracts placed in a microplate reader (Bekedam, Schols, van Boekel, & Smit, 2006; Lopes, Passos, Rodrigues, Teixeira, & Coimbra, 2019). Simultaneously, the measure was performed at 280 and 325 nm allowing to determine the $K_{mix,\ 280nm}$ and $K_{mix,\ 325nm}$.

The antioxidant activity of the MAE coffee extracts was determined through DPPH assay. The reaction mixture consists of 50 μL of extract (0.1 mg mL^{-1}) and 250 μL of DPPH solution (8.6 × 10^{-5} M in ethanol) placed in a 96-well microplate that stands for 30 min in darkness at 30 °C prior to the spectrophotometric measurement (517 nm). Water with DPPH was used as a control solution. DPPH scavenging activity was calculated according to Eq. (3):

$$Inhibition\ (\%) = \left[\frac{A_0 - (A - A_b)}{A_0}\right] \times 100 \quad (3)$$

representing A_0 the control (DPPH without sample), A the absorbance of the sample with DPPH and A_b the sample without DPPH (blank sample) (Souza et al., 2012)

Fourier-transform infrared spectroscopy (FTIR) analysis was performed in an infrared spectrometer (Bruker Alpha Platinum-ATR) in the mid-infrared region (4000–400 cm^{-1}) with a resolution of 4 cm^{-1} and 32 scans, operated in a room with controlled temperature (25 °C) and humidity (35%). The samples were placed on the crystal of the attenuated total reflectance accessory (ATR) and five replicates spectra were randomly obtained for each sample, cleaning the surface of the apparatus with ethanol (70%) between measurements. The FTIR

Table 1
Resume of coffee MAE settled according to a Box-Behnken design with three levels and three independent factors.

Run Order	Process Variables[a]			Extr. Yield[b]	Sugars[c]	Rha	Ara	Man	Gal	Glc	Caffeine[c]	5-CQA[c]	$K_{mix,\ 405nm}$
	Time	Temperature	m/V ratio										
	(X_1, min)	(X_2, °C)	(X_3, g/60 mL)	(Y_1, %, w/w)	(Y_2, %, w/w)			mol%			(%, w/w)	(%, w/w)	(mL mg^{-1} cm^{-1})
1-a	10.0 (+1)	180 (+1)	4 (0)	47.0	43.1 ± 3.2	1.1 ± 0.1	12.1 ± 0.2	26.3 ± 0.6	58.6 ± 0.6	1.8 ± 0.1	3.8	1.1	0.3974
1-b	10.0 (+1)	180 (+1)	4 (0)	45.5	42.3 ± 2.2	1.1 ± 0.0	11.9 ± 0.1	25.1 ± 0.5	60.2 ± 0.7	1.7 ± 0.0	4.9	1.4	0.3600
2-a	5.5 (0)	180 (+1)	6 (+1)	42.5	42.7 ± 4.0	1.3 ± 0.0	12.4 ± 0.4	33.1 ± 1.2	51.1 ± 0.9	2.1 ± 0.1	4.1	1.1	0.3300
2-b	5.5 (0)	180 (+1)	6 (+1)	39.3	38.0 ± 4.0	1.5 ± 0.4	12.0 ± 0.1	33.3 ± 0.4	51.3 ± 0.6	1.9 ± 0.3	4.8	1.4	0.3574
3-a	5.5 (0)	120 (-1)	2 (-1)	29.1	26.2 ± 3.2	3.2 ± 0.1	12.1 ± 1.0	55.7 ± 2.6	25.6 ± 0.9	3.3 ± 0.7	6.5	1.8	0.5705
3-b	5.5 (0)	120 (-1)	2 (-1)	29.0	25.8 ± 0.4	3.5 ± 0.1	12.7 ± 0.2	54.4 ± 1.2	25.7 ± 1.6	3.5 ± 0.0	6.6	1.8	0.5957
4-a	1.0 (-1)	150 (0)	2 (-1)	31.5	29.7 ± 1.6	2.6 ± 0.1	11.7 ± 0.8	56.8 ± 0.4	25.8 ± 0.4	3.2 ± 0.2	5.9	1.7	0.5587
4-b	1.0 (-1)	150 (0)	2 (-1)	30.8	29.7 ± 2.9	2.4 ± 0.0	11.1 ± 0.5	57.0 ± 2.3	25.9 ± 1.1	3.5 ± 0.6	5.9	1.7	0.6435
5-a	1.0 (-1)	180 (+1)	4 (0)	37.3	36.4 ± 1.2	1.9 ± 0.1	13.7 ± 0.4	41.1 ± 0.5	40.8 ± 0.4	2.5 ± 0.2	5.0	1.4	0.4385
5-b	1.0 (-1)	180 (+1)	4 (0)	39.3	34.9 ± 0.3	1.9 ± 0.1	14.2 ± 0.3	37.3 ± 1.1	44.5 ± 0.7	2.2 ± 0.1	5.9	1.6	0.4679
6-a	5.5 (0)	150 (0)	4 (0)	30.0	25.3 ± 2.0	3.1 ± 0.1	13.7 ± 0.1	48.5 ± 0.3	31.3 ± 0.9	3.5 ± 0.3	6.2	1.7	0.4893
6-b	5.5 (0)	150 (0)	4 (0)	31.9	29.1 ± 1.1	2.8 ± 0.1	14.0 ± 0.1	47.3 ± 0.7	32.5 ± 0.8	3.3 ± 0.2	6.0	1.6	0.4891
7-a	10.0 (+1)	120 (-1)	4 (0)	27.9	20.7 ± 3.1	3.5 ± 0.7	15.1 ± 2.1	44.5 ± 7.4	32.7 ± 4.0	4.3 ± 0.9	6.2	1.8	0.4819
7-b	10.0 (+1)	120 (-1)	4 (0)	28.1	24.6 ± 1.0	3.2 ± 0.3	13.2 ± 0.5	51.9 ± 1.8	27.8 ± 1.2	3.9 ± 0.3	6.4	1.9	0.5242
8-a	5.5 (0)	150 (0)	4 (0)	29.3	25.3 ± 0.6	3.1 ± 0.3	12.7 ± 0.1	53.3 ± 1.4	27.2 ± 1.1	3.8 ± 0.1	6.7	1.7	0.5201
8-b	5.5 (0)	150 (0)	4 (0)	32.6	28.5 ± 0.4	2.5 ± 0.1	12.6 ± 0.4	51.3 ± 2.6	30.5 ± 1.9	3.2 ± 0.1	6.1	1.6	0.5093
9-a	10.0 (+1)	150 (0)	2 (-1)	30.4	27.2 ± 1.8	3.1 ± 0.1	12.7 ± 0.1	54.5 ± 2.4	26.3 ± 1.8	3.5 ± 0.6	5.8	1.6	0.5644
9-b	10.0 (+1)	150 (0)	2 (-1)	33.4	28.9 ± 5.6	2.2 ± 0.2	13.3 ± 1.3	48.2 ± 1.5	33.0 ± 0.5	3.2 ± 0.6	5.4	1.5	0.5394
10-a	5.5 (0)	120 (-1)	6 (+1)	24.2	17.8 ± 1.1	4.4 ± 0.1	18.6 ± 1.0	33.4 ± 1.5	38.5 ± 0.7	5.1 ± 0.3	7.3	1.9	0.5320
10-b	5.5 (0)	120 (-1)	6 (+1)	24.9	18.8 ± 1.2	4.5 ± 0.1	17.4 ± 0.2	38.7 ± 0.2	35.0 ± 0.0	4.4 ± 0.1	7.3	2.1	0.5495
11-a	10.0 (+1)	150 (0)	6 (+1)	35.1	35.8 ± 4.5	1.7 ± 0.2	15.3 ± 0.9	27.4 ± 4.6	53.5 ± 3.4	2.0 ± 0.4	5.3	1.5	0.3554
11-b	10.0 (+1)	150 (0)	6 (+1)	28.5	28.3 ± 4.1	2.6 ± 0.7	15.8 ± 4.1	38.6 ± 10.2	39.8 ± 5.7	3.3 ± 0.6	6.2	1.7	0.4595
12-a	5.5 (0)	150 (0)	4 (0)	33.9	26.3 ± 0.8	2.7 ± 0.1	15.6 ± 0.5	43.0 ± 0.5	36.0 ± 0.4	2.8 ± 0.4	5.8	1.6	0.4348
12-b	5.5 (0)	150 (0)	4 (0)	30.1	23.3 ± 1.0	3.3 ± 0.2	15.7 ± 0.2	43.8 ± 0.4	33.3 ± 0.6	3.9 ± 0.2	5.9	1.7	0.4849
13-a	1.0 (-1)	120 (-1)	4 (0)	27.9	21.9 ± 0.6	3.3 ± 0.0	12.3 ± 0.3	55.0 ± 1.0	25.8 ± 0.8	3.6 ± 0.0	6.6	1.9	0.4834
13-b	1.0 (-1)	120 (-1)	4 (0)	26.4	21.7 ± 2.0	3.8 ± 0.1	14.9 ± 0.9	50.2 ± 0.0	27.0 ± 0.6	4.1 ± 0.4	6.9	2.1	0.5515
14-a	1.0 (-1)	150 (0)	6 (+1)	33.5	29.9 ± 2.3	2.3 ± 0.1	13.8 ± 0.9	45.3 ± 4.5	35.8 ± 3.4	2.7 ± 0.0	6.3	1.7	0.4613
14-b	1.0 (-1)	150 (0)	6 (+1)	28.5	25.1 ± 1.0	3.1 ± 0.1	13.5 ± 0.1	49.8 ± 0.2	30.2 ± 0.0	3.4 ± 0.4	7.0	1.8	0.5769
15-a	5.5 (0)	180 (+1)	2 (-1)	46.9	39.8 ± 0.4	1.3 ± 0.2	13.6 ± 0.2	26.5 ± 0.0	56.7 ± 0.5	1.8 ± 0.1	3.7	1.1	0.4130
15-b	5.5 (0)	180 (+1)	2 (-1)	43.8	43.4 ± 1.3	1.1 ± 0.0	12.1 ± 0.9	29.0 ± 0.8	56.0 ± 1.7	1.7 ± 0.0	3.8	1.1	0.4390

[a] The process variables are shown in real and (coded) values.
[b] Mass of freeze-dried coffee compared to the mass of roasted coffee prior to the extraction process.
[c] Mass of compound present in the freeze-dried extract.

spectra were baseline and SNV (standard normal deviate) corrected.

3. Results and discussion

3.1. Extraction yield

The coffee MAE shows a 2-fold variation (24.2–47.0%, w/w) throughout the conditions tested: 1.0, 5.5, and 10.0 min of extraction, 120, 150, and 180 °C, and 2, 4, and 6 g/60 mL (Table 1), respectively lower, intermediate and higher levels for the factors tested. The time considered was only the time at the defined temperature level. This excluded the 2 min required to achieve the desired temperature. This time was equal for all experiments. For comparison purposes, an experiment testing an infusion methodology and MAE with milder extraction conditions (80 °C) related to conventional coffee brews were performed (Table S1). Usually, the temperatures achieved in coffee brew methods are limited to the atmospheric water boiling point (1 atm or 1.01325 bar, 100 °C) or little more, when moka pot is used (Illy & Viani, 2005; Navarini, Nobile, Pinto, Scheri, & Suggi-Liverani, 2009; Petracco, 2001). The extraction performed at 80 °C showed that the yield for both infusion (26.6 ± 0.3%, w/w) and MAE method (26.0 ± 0.2%, w/w) were similar. These values are within the values reported for household coffee brewing methods (< 32%) even promoting a wide variation in operational parameters (Gloess et al., 2013; Lopes et al., 2019; Petracco, 2001). It seems that the radiation *per se* does not induce substantial differences compared to conventional coffee brew methods, or that there is no clear difference between conductive and microwave heating considering overall extraction yield, as already reported (Damm & Kappe, 2011). Table 1 shows that MAE was able to clearly improve the extraction yield in some of the conditions tested comparing to household methods. The closed vessels used promoted a fast increase of the water temperature to above the atmospheric boiling point, attempting to simulate what occurs in the instant coffee facilities. The MAE system used allowed to achieve the desired high temperatures within short times (2 min), which was maintained along the experiments (Fig. 1).

The box plots in Fig. 2a highlight the temperature as the most preponderant effect for the differentiation in coffee overall extraction yield, when compared with time and m/V ratio, evidencing a non-linear behaviour. The grouping of the results by temperature showed distinct ranges for the three levels tested: 24.2–29.1 (120 °C), 28.5–35.1 (150 °C), and 37.3–47.0% (w/w) (180 °C). Thus, using 120 °C does not result in an increment comparing to conventional system, while at 150 °C similar or higher values were attained depending on conditions tested and, at 180 °C, the extraction yield was always considerably higher than home brewing methods. The use of more drastic conditions (> 150 °C) should lead to the occurrence of solubilisation of the formerly unextractable compounds, namely with conventional brewing methods. The grouping of results by the variables time and m/V ratio showed a wide variation in the three levels tested but suggested that longer time of extraction and lower m/V ratio slightly increased the extraction yield, as observed with infusion methods (Lopes et al., 2019).

The temperature (X_2) exerted clearly the main preponderance with both linear (L) and quadratic (Q) terms exhibiting significant influence (78.0% and 7.6% of the results variability, respectively). The linear term for time is also significant, while the m/V ratio presented marginal significance ($p = 0.0574$), and the quadratic terms were non-significant. After removing the non-significant effects, the data fitted a reduced but significant ($p < 0.0001$) model, with high determination coefficient ($R^2 = 0.92$) and non-significant lack-of-fit (Table 2), represented by response surface plots (Fig. 3a-c). The interaction between time and temperature ($X_1.X_2$) was also significant, with the effect of temperature more noticeable when extraction time was longer (Fig. 2a).

Considering the total solids obtained after freeze-drying process, and assuming 60 mL as the volume after coffee extraction, it may be inferred that the coffee solutions contain 10–42 g L^{-1} of extracted total solids, values in accordance with different household coffee brewing methods (Lopes et al., 2016, 2019; Maeztu et al., 2001; Petracco, 2001).

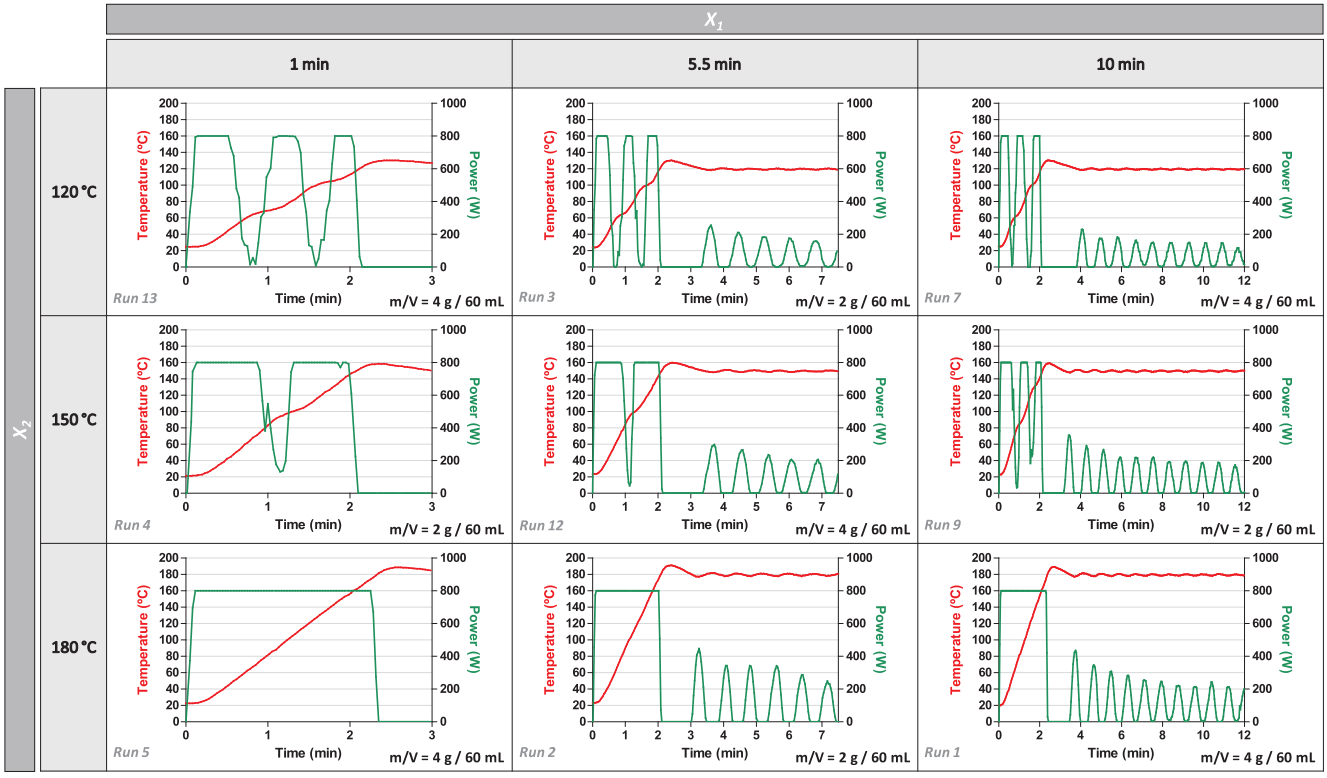

Fig. 1. Examples of the MAE experiment profile showing the measured temperature (—, °C) and power (—, W), according to two of the independent variables tested: time (X_1, min) and temperature (X_2, °C). The profile for all runs is presented in Fig. S2 in Supplementary Material.

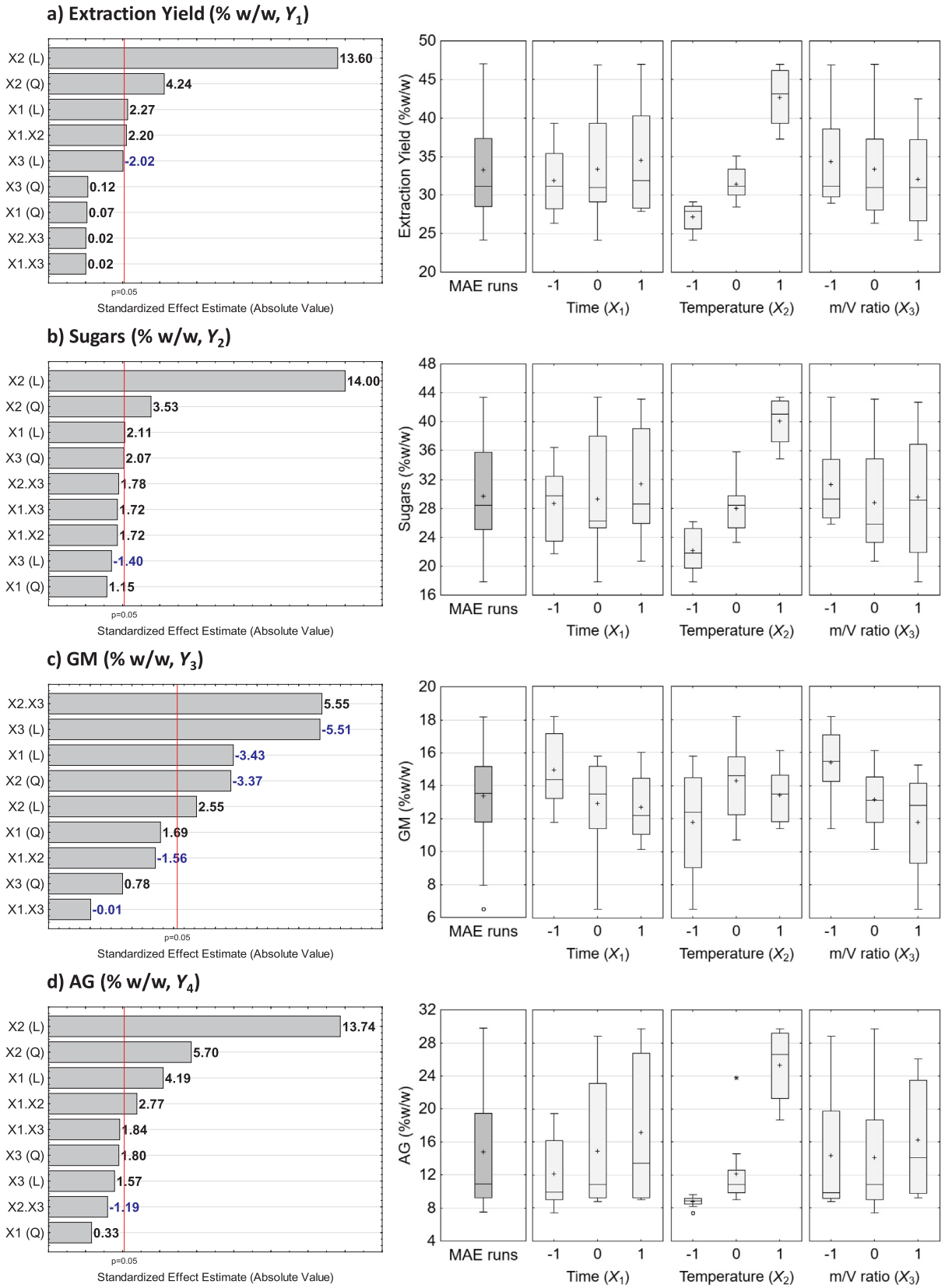

Fig. 2. Pareto chart (left) and box plot (right) showing the effects of time (X_1), temperature (X_2), and m/V ratio (X_3) during the MAE coffee experiments on the (a) extraction yield (Y_1, %, w/w), (b) sugars content in the extract (Y_2, %, w/w), (c) galactomannans (Y_3, %, w/w), and (d) arabinogalactans (Y_4, %, w/w) contents in the coffee extract. In the Pareto chart, the negative and positive effects are highlighted in blue and black, respectively. L and Q represent the linear and quadratic effects, respectively. The region (right side) of statistical significance (95% confidence level) is defined by the vertical line. In the box plot is represented the distribution of the raw data, containing the box the interquartile range and limiting the whisker the non-outlier range, with the median represented as (−) and the mean as ($^+$), while outliers (coeff. 1.5) are represented as (^{o}) and extremes (coeff. 3) as (*).

Table 2
Models developed for the description of the variation in dependent variables (Y_1 - extraction yield, Y_2 - sugars, Y_3 - galactomannans (GM) and Y_4 - arabinogalactans (AG)) as function of the parameters studied (X_1 - time, X_2 - temperature, X_3 - m/V ratio) with the corresponding coefficients of determination (R^2). The models are expressed in terms of coded values ((-1), (0), (+1)).

Response	Model Equation	R^2
Extr. Yield	$Y_1 = 31.39 + 1.29\,X_1 + 7.76\,X_2 - 1.15\,X_3 + 3.55\,X_2^2 + 1.78\,X_1.X_2$	0.92
Sugars	$Y_2 = 26.97 + 1.35\,X_1 + 8.94\,X_2 - 0.89\,X_3 + 3.24\,X_2^2 + 1.86\,X_3^2 - 1.61\,X_2.X_3$	0.89
GM	$Y_3 = 13.63 - 1.12\,X_1 + 0.83\,X_2 - 1.80\,X_3 + 0.81\,X_1^2 - 1.62\,X_2^2 + 0.37\,X_3^2 - 0.72\,X_1.X_2 + 2.57\,X_2.X_3$	0.83
AG	$Y_4 = 11.23 + 2.52\,X_1 + 8.28\,X_2 + 0.94\,X_3 + 5.04\,X_2^2 + 1.57\,X_3^2 + 2.36\,X_1.X_2 + 1.57\,X_1.X_3$	0.92

In such case, the greatest variability was observed when grouping the data by their m/V ratio, once the higher the m/V ratio, the higher the amount of soluble solids extracted (Fig. S3a). Considering the mass of water in relation to the mass of solids obtained, it can be estimated that the coffee solution exhibited 1–4% (w/w) of total solids. This range of values was distinct from those obtained during the industrial process of instant coffee. The industrial coffee production occurs at high temperatures (100–180 °C) and pressures to maximize the extraction of coffee compounds, obtaining extracts with high concentration of coffee solids (25–30%) in battery column percolators working through the countercurrent principle (Clarke, 2001).

3.2. Sugars content

The carbohydrate content of the extracts ranged from 17.8 to 43.4% (w/w), a 2.4-fold variation. This range includes the value obtained for the commercial soluble coffee used as reference in this study (34.5 ± 1.1%, w/w, Table S1), in line with literature reports of instant coffee products (35–39%, w/w) obtained either through a simulation of industrial processes or pure soluble coffee samples (Blanc, Davis, Parchet, & Viani, 1989; Capek et al., 2014; Leloup, 2006). To reach instant coffee-like carbohydrates content using MAE at at least 180 °C should be used (> 34.9%). MAE allowed to obtain a range of 23.3–43.4% (w/w) performing the extraction at 150 and 180 °C. This range is close to the one obtained by Blanc et al. (1989) (32–39%), but the MAE process was much faster. Beyond the importance of the energetic balance of the process, shorter extraction times is also preferential to keep the carbohydrates structural integrity, avoiding a continuous destruction of total carbohydrates (Blanc et al., 1989). Pareto chart (Fig. 2b) points out that temperature is the main parameter for the different sugars content in the extracts, with higher temperatures associated to an increase in their content, being this effect the only one with a clear distinction among the levels tested. In this study, the carbohydrates present in the MAE (23.8 ± 3.4) at 80 °C, as well as in the infusion extract (23.7 ± 3.8) are compared to home-extraction methods (15–30%) (Bekedam et al., 2006; Illy & Viani, 2005; Lopes et al., 2019; Petracco, 2001; Villalón-López, Serrano-Contreras, Téllez-Medina, & Gerardo Zepeda, 2018), and considerable different from instant coffee (up to 40%). The response surface plots in Fig. 3d-f reinforces the preponderance of temperature for different carbohydrates relative content in the coffee extracts (Fig. 3d,f), as equal extraction temperatures result in more similar carbohydrates content (Fig. 3e). It was found a positive and strong linear relationship ($r = 0.95$, $p < 0.0001$) between the extraction yield and extracts carbohydrate content. This means that the variation in the extraction yield should be related to the more or less carbohydrates extracted, highlighted by

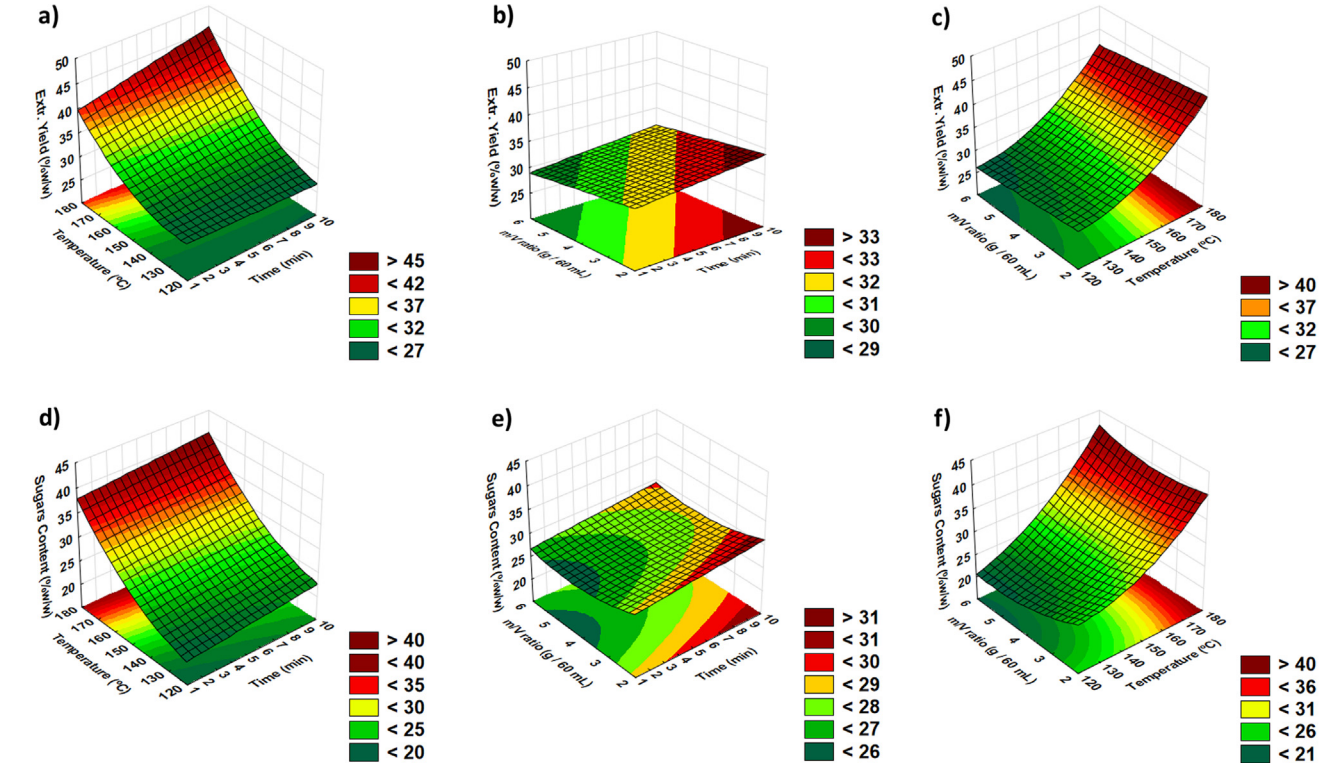

Fig. 3. Response surface plots (3D) of the models developed representing the variation of the overall MAE extraction yield (a-c, Y_1, %, w/w) and sugars content in the extract (d-f, Y_2, %, w/w) showing the effect of the different extraction parameters. In each plot, the remaining independent variable was maintained at their intermediate level: *time* (X_1) – 5.5 min; *temperature* (X_2) – 150 °C; *m/V ratio* (X_3) – 4 g/60 mL.

surface plots similarity (Fig. 3).

3.3. Sugars composition

The MAE coffee extracts exhibited mannose (25–57 mol%) and galactose (26–60 mol%) as the two main residues, with a dependent linear variation between them, once an increase in one residue followed the decrease of the other ($r = -0.96$, $p < 0.0001$). The arabinose molar content varied from 11 to 19%, while the rhamnose and glucose contents were kept at residual levels in all extracts (1–5 and 2–5 mol%, respectively). As the amount of uronic acids has been reported as vestigial (Nunes & Coimbra, 2001, 2002b), it was not performed the analysis of their content. The commercial instant coffee product (I.C.) showed galactose as the main sugar residue (52.1 mol%), followed by mannose (33.9 mol%) and arabinose (9.4 mol%), and residual amounts of glucose (3.1 mol%) and rhamnose (1.5 mol%). According to the sugars content, the I.C. sample was composed by 18.3% (w/w) of galactose and 11.9% (w/w) of mannose, in accordance with literature range for both residues: mannose (10.2–19.7%, w/w) and galactose (13.0–24.7%, w/w), with a preponderance of galactose usually verified in instant coffee products (Blanc et al., 1989; Leloup, 2006). At 180 °C, mannose and galactose accounted for 10.8–15.4% (w/w) and 15.3–26.1% (w/w), respectively, in accordance with literature for instant coffee. At the other temperatures tested, the extracts lacked the galactose content. Contrarily to instant coffee products, the MAE performed at 80 °C exhibited mannose as the main sugar residue (49.0 mol %, 12.1%, w/w), followed by galactose (26.6 mol%, 6.5%, w/w), and arabinose (13.3 mol%, 2.6%, w/w), a pattern relatable with the milder homebrewing coffee extraction methods, in this study tested by the infusion method (Table S1).

Mannose residues in a linear chain and branched with unique residues of galactose form the galactomannans (GM). Galactose is also component, together with arabinose, of the highly branched polysaccharide named type II arabinogalactans (AG) (Nunes & Coimbra, 2002a, 2002b). Based on coffee polysaccharides structural features, it may be estimated the content of GM and AG (Lopes et al., 2019; Passos et al., 2019) in the MAE extracts, the commercial I.C. sample, and in the experiments made at 80 °C through MAE and infusion method (Fig. 4). The I.C. sample showed a predominance of AG over GM, while the extractions at 80 °C showed GM as the main polysaccharide present (53–58%), in accordance with previous analyses of roasted coffee infusions (Lopes et al., 2019; Nunes & Coimbra, 2001; Oosterveld, Harmsen, Voragen, & Schols, 2003). Indeed, in hot roasted coffee brews, from infusion to espresso coffee, the GM are the predominant carbohydrate structures, while AG are present as major polysaccharides in cold coffee brews, once such structures are easily extracted and GM are more dependent on extraction conditions (Lopes et al., 2016, 2019; Nunes & Coimbra, 2001; Shin, 2017). Fig. 4 shows that even performing the extraction at, at least 120 °C, some of the MAE runs were more related to the coffee infusions, while others resembled the I.C. sample pattern. The GM ranged from 6.5 to 18.2% (w/w) (a 2.8-fold variation), while the AG content varied from 7.5 to 29.7% (a 4.0-fold variation). The pareto chart (Fig. 2c) showed that the amount of GM in the extracts was more dependent on m/V ratio, however time and temperature also exerted considerable influence. Increasing time and incrementing the m/V ratio led to the production of extracts with lower relative content of GM (Fig. 5a-c). Moreover, the interaction $X_2.X_3$ appeared as significant, meaning that the m/V ratio effect was more significant at lower temperatures, with lower m/V ratio associated to higher GM presence in the extracts, while at higher temperatures the content was more similar (Fig. 5c).

Pareto chart (Fig. 2d) highlighted that the temperature was the main effect responsible for the variation of AG content, which was also illustrated by the response surface models in Fig. 5d-f. The increase in the extraction time resulted in higher relative amount of AG (Fig. 5d,e). However, the significance of the interaction $X_1.X_2$ highlights that the effect of time was much more remarkable when the temperature of extraction was higher, leading to considerable differences (as AG content increased) between performing the extraction during 1 or 10 min in MW device (Fig. 5d). There was a linear and strong positive correlation between the increase in AG (Y_4) and the total sugars in the extract (Y_2, $r = 0.94$, $p < 0.0001$) and also extraction yield (Y_1, $r = 0.94$, $p < 0.0001$), meaning that the increase in the relative amount of carbohydrates in the extract or compounds extracted was accompanied by an increase in the preponderance of AG.

3.4. Colour of the extracts

$K_{mix,\ 405nm}$, a colour dilution factor, allows to measure the intensity of the brown colour of the coffee solutions and may also be seen as an indicative of the melanoidins content in the extract, the brown colour compounds with undefined structure formed during the roasting of the coffee beans (Bekedam et al., 2006; Lopes et al., 2016; Nunes et al., 2012). The higher the $K_{mix,\ 405nm}$, the browner the solutions and the extracts. The $K_{mix,\ 405nm}$ values ranged from 0.33 to 0.64 mL mg^{-1} cm^{-1}, a 2-fold variation along MAE conditions. The I.C. sample exhibited a higher value (0.68 mL mg^{-1} cm^{-1}), while the runs performed at 80 °C exhibited similar values: 0.59 and 0.60 for infusion and MAE experiment, respectively, in accordance with other infusion experiments (Lopes et al., 2019). Box plots of the data (Fig. S9) shows that longer extraction times, higher temperatures, and m/V ratios in the MAE experiments led to a decrease in $K_{mix,\ 405nm}$ values, indicative of a decrease in brown colour of the extracts (pictures of extracts in Fig. S9). As the extract became less brown with increasing temperatures of extraction, associated to higher extraction yields, the compounds additionally extracted (at higher temperatures) should be colourless when compared to the ones more easily extracted. Alternatively, these compounds may derive from the degradation of the browner compounds, with a consequent decreasing in the browning intensity. It was found a negative and strong correlation ($r = -0.81$, $p < 0.0001$) between the

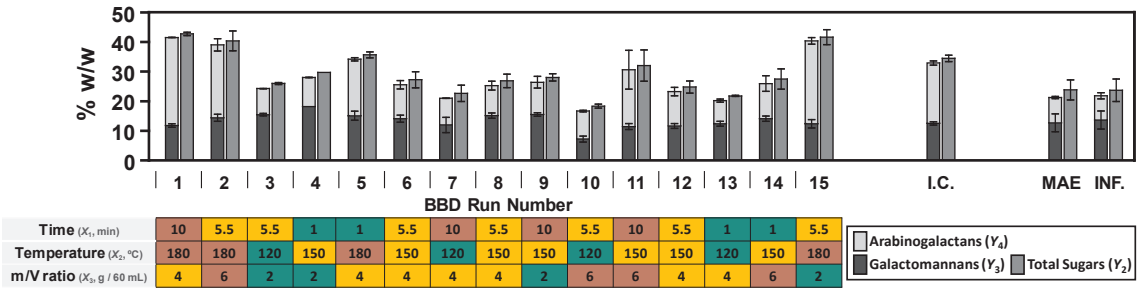

Fig. 4. Representation of estimation of the content of the galactomannans (Y_3, %, w/w, darker bars) and arabinogalactans (Y_4, %, w/w, lighter bars) as part of the total sugars determined (bars at the right) in the BBD runs, instant coffee sample (I.C.) and the experiments performed at 80 °C, through MAE and infusion method. For MAE runs, the results from the two reactors for the same condition were plotted together and the conditions used in each run are displayed in **green** for the lower level (-1), **orange** for the intermediate level (0) and **red** for the higher level (+1) in the three factors tested.

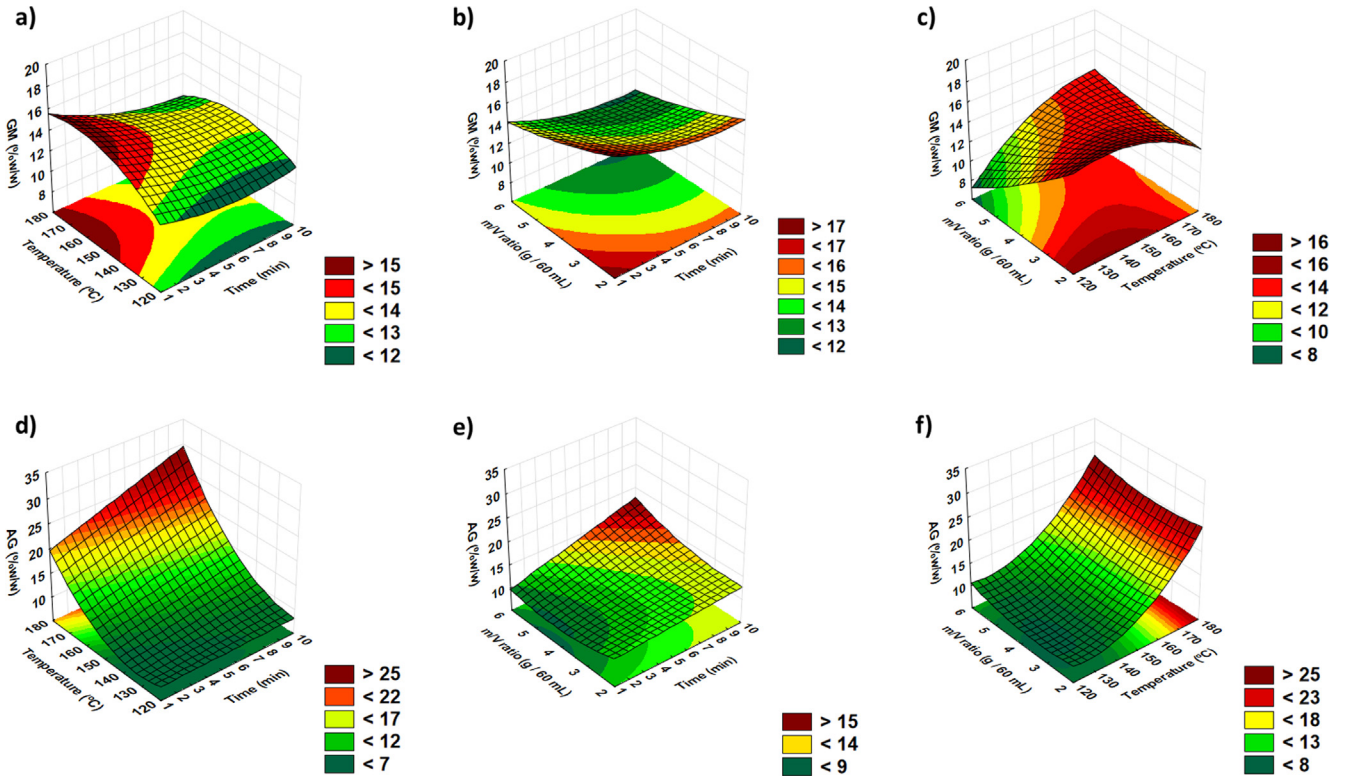

Fig. 5. Response surface plots (3D) of the models developed representing the variation of the galactomannans (a-c) and arabinogalactans (d-f) content in the extract showing the effect of the different MAE parameters. In each plot, the remaining independent variables was maintained at their intermediate level: *time* (X_1) – 5.5 min; *temperature* (X_2) – 150 °C; *m/V ratio* (X_3) – 4 g/60 mL.

content of AG in the extract and $K_{mix,\ 405nm}$ values, meaning that the extracted AG were less coloured than the compounds already present in the extract without the use of drastic conditions (180 °C). Thus, it may be obtained an extract rich in AG, comparable to instant coffee, but with a yellowish appearance, as observed in some commercial brands of instant coffee.

3.5. Caffeine and 5-CQA

The caffeine content in each extract after MAE experiment ranged from 3.7 to 7.3% (w/w), a 2.0-fold variation, while the analysis of I.C. sample revealed a value of 4.9% (w/w), in accordance with literature reports (2.4–5.2%, w/w) (Capek et al., 2014; Gant, Leyva, Gonzalez, & Maruenda, 2015; Leloup, 2006; Ludwig et al., 2014; Moreira, Monteiro, Ribeiro-Alves, Donangelo, & Trugo, 2005; Rodrigues & Bragagnolo, 2013). The extraction performed by infusion method and by MAE at 80 °C showed higher values (7.7–8.4%, w/w), in accordance with home brewing coffee methods (7.2–8.3%, w/w) (Petracco, 2001; Severini, Ricci, Marone, Derossi, & De Pilli, 2015). Literature shows that instant coffee exhibit lower content *per* serving compared to home brewing coffee methods (Ludwig et al., 2014; Moreira et al., 2005; Rodrigues & Bragagnolo, 2013; Villalón-López et al., 2018). MAE already proved to efficiently extract caffeine from green beans, achieving higher yields than conventional methods (Upadhyay, Ramalakshmi, & Jagan Mohan Rao, 2012). It was possible to establish a negative and strong correlation between the relative content of caffeine in the extracts and the extraction yield ($r = -0.93$, $p < 0.0001$) and carbohydrates content ($r = -0.92$, $p < 0.0001$). This suggests that the relative content of caffeine in the extract is more dependent on the overall extraction of carbohydrates than properly to caffeine itself, *i.e.* increasing the relative content of other compounds (as carbohydrates during instant coffee production) diminishes the preponderance of caffeine in the extract.

For 5-caffeoylquinic acid (5-CQA), the major chlorogenic acid present in coffee samples, a similar trend was observed. The amount of 5-CQA in the MAE extracts (1.1–2.1%, w/w) was in accordance with literature reports for the content present in instant coffee samples (0.4–3.5%, w/w) and with the I.C. sample content (1.0%, w/w) (Moreira et al., 2005; Trugo & Macrae, 1984). As caffeine, it was reported in literature the impoverishment in chlorogenic acids in instant coffee when compared to other beverages (Rodrigues & Bragagnolo, 2013), associated in the present study to the increment in extraction yield of carbohydrates ($r = -0.93$, $p < 0.0001$). In fact, the experiments at 80 °C (MAE and infusion) revealed a greater content (2.3–2.4%, w/w) than the remaining extracts, although arising from the same coffee, with extraction process as the unique source of differentiation, and values in accordance with other infusion procedures (1.9–2.9%, w/w) (Lopes et al., 2019). Efforts have been made in the enrichment of instant coffee products with chlorogenic acids to take advantage of the biological activities associated to these molecules (greatly destroyed by roasting process), namely using mixtures of green and roasted extracts (Corso, Vignoli, & Benassi, 2016; Gómez-Juaristi, Martínez-López, Sarria, Bravo, & Mateos, 2018; Hoelzl et al., 2010; Sarriá, Martínez-López, Mateos, & Bravo-Clemente, 2016).

5-CQA, as well as caffeine, can also be estimated through the measure of absorbance at the characteristic wavelengths of diluted solutions. It was found a strong positive correlation between 5-CQA content and $K_{mix,\ 325nm}$ ($r = 0.88$, $p < 0.0001$, Supplementary Material Table S13) and caffeine content and $K_{mix,\ 280nm}$ ($r = 0.89$, $p < 0.0001$), and a negative correlation between these parameters and sugar content ($r = -0.93$, $p < 0.0001$ for $K_{mix,\ 280nm}$ and $r = -0.94$, $p < 0.0001$ for $K_{mix,\ 325nm}$), highlighting that a decrease of preponderance of smaller molecules as caffeine and 5-CQA is accompanied by an increase in carbohydrates content.

3.6. Antioxidant activity

The antioxidant activity of the coffee extracts obtained via MAE was studied by DPPH method. This procedure relies on measuring spectrophotometrically (517 nm) the disappearance of the purple colour of the DPPH radical that was scavenged by antioxidants in solution, presenting the percentage of inhibition as the result. The results (Table S13) showed that inhibition ranged from 43 to 68% among the coffee MAE runs, with extracts prepared with 0.1 mg mL^{-1}. It was possible to split the values according to the temperatures analysed, with a decreasing inhibition percentage when extracts were obtained at higher temperatures. The reason for such pattern should be linked to the higher extraction of carbohydrates associated to higher temperatures, with a consequent decreasing in the preponderance of smaller molecules with higher antioxidant capacity than carbohydrates, as chlorogenic acids. This is illustrated by the negative correlation between carbohydrates content in the extracts (Y_2, %, w/w) and the inhibition percentage ($r = -0.76$, $p < 0.0001$) or the positive correlation between the latter and 5-CQA content (%, w/w) in the extract ($r = 0.76$, $p < 0.0001$). However, many other compounds present in coffee must also play important roles in the antioxidant activity of the coffee extracts, as highlighted the correlations with $K_{mix,\ 280nm}$ ($r = 0.79$, $p < 0.0001$) and $K_{mix,\ 325nm}$ ($r = 0.78$, $p < 0.0001$), that account with all compounds absorbing at 280 and 325 nm, respectively. Indeed, the analysis of 5-CQA solutions at different concentrations showed that the range of inhibition percentages obtained with MAE runs was obtained with 0.02–0.04 mg mL^{-1} of 5-CQA. As the amount estimated in each coffee sample was approximately 0.001 mg mL^{-1} (1% of the 0.1 mg mL^{-1} extract prepared), the results suggest that other molecules than 5-CQA should have higher impact for antioxidant capacity.

3.7. Application of MAE to obtain an instant coffee-like product

To test the feasibility of MAE to quickly obtain a composition similar to a commercial I.C. product a desirability approach was used. The objective was to obtain an extract with an amount of mannose of 11.9% (w/w), and 18.3% (w/w) of galactose, as well as 1.0% (w/w) of 5-CQA and 4.9% (w/w) of caffeine, attributing equal importance to these parameters, using the developed significant models ($p < 0.0001$), with high determination coefficients (Table S7–9, S12). Thus, setting the experimental conditions to 9.6 min of extraction time, 168 °C, and 4.0 g/60 mL as the m/V ratio, allowed to obtain high overall desirability ($D = 0.8655$), corresponding to an extract with 12.8, 18.3, 1.3, and 4.9% (w/w) of mannose, galactose, 5-CQA, and caffeine, respectively (Fig. 6). This extract would contain a slightly higher amount of mannose and 5-CQA than the proportion verified in the I.C. sample. In fact, the level of 5-CQA in MAE samples was always slightly higher than in the I.C. sample used as example. In addition, the use of these conditions was associated to a 40% extraction yield, which is close to the maximum of 47% achieved in this study. When 5-CQA was removed from the desirability approach, the overall desirability increased to $D = 0.9457$, with 7.8 min of extraction time, 170 °C, and 4.2 g/60 mL as m/V ratio, allowing to obtain great similarity with the I.C. sample (Fig. S10). On the other hand, as it was possible to modulate the arabinose content in the extract ($p < 0.0001$, $R^2 = 0.81$), the same strategy was used attempting to obtain similar content of this sugar residue. However, the region where MAE coffee extracts exhibited arabinose content related to the one found in I.C. sample (lower temperatures, Figs. S4 and S10) was incompatible to the ones that allowed to equalize the other parameters as, contrary to the high temperature used to produce instant coffee, promoting degraded AG, in MAE this degradation was not so pronounced.

According to the desirability approach, the conditions of MAE run 1 (10 min, 180 °C, 4 g/60 mL) were the ones that better approach the composition of commercial instant coffee sample (I.C.). FTIR allows to quickly compare the samples without their destruction or pretreatment,

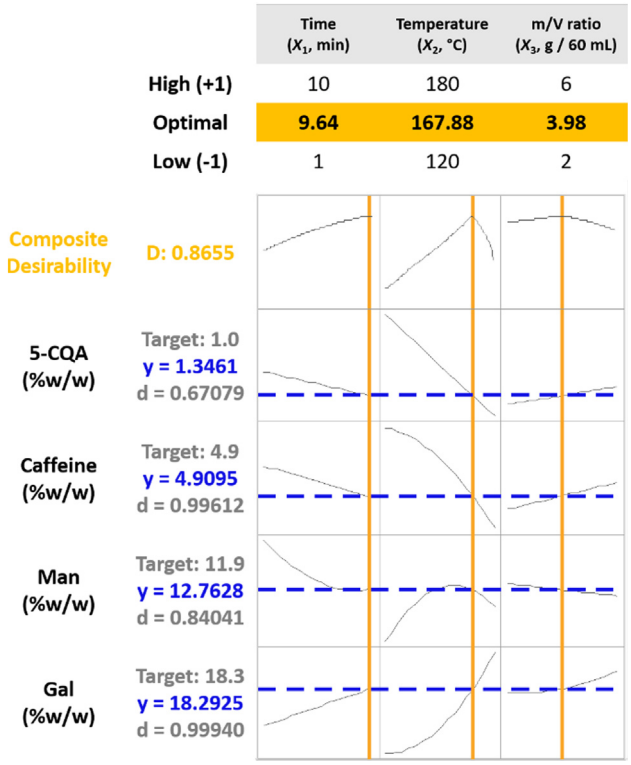

Fig. 6. Representation of desirability approach using instant coffee as a hypothetical goal for MAE conditions aiming to equal its composition through four parameters studied.

providing an overall chemical fingerprint of samples composition in a fast and inexpensive way. It was already used to detect adulterations in roasted and instant coffee or discriminate among coffee attributes as coffee species or sensorial quality (Barbin, Felicio, Sun, Nixdorf, & Hirooka, 2014) Fig. 7 evidences the overall great similarity between FTIR spectra of the samples, in accordance with the chemical analysis performed. The spectra have higher intensities in the carbohydrate region (800–1200 cm^{-1}) associated to their preponderance in the extracts (35–43% of the samples).

3.8. Holistic analysis of the MAE of coffee

To evaluate the extractability of the compounds, a holistic analysis

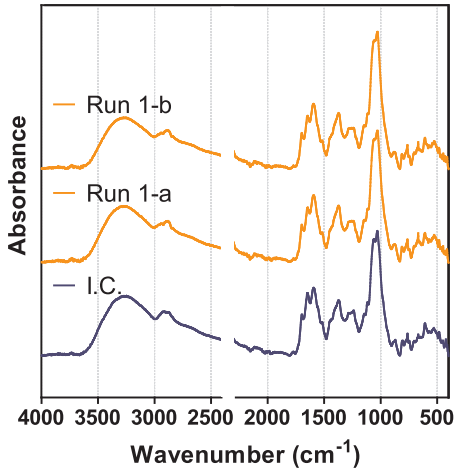

Fig. 7. FTIR spectra of Run 1-a, Run 1-b and I.C. samples in the 400–4000 cm^{-1} region.

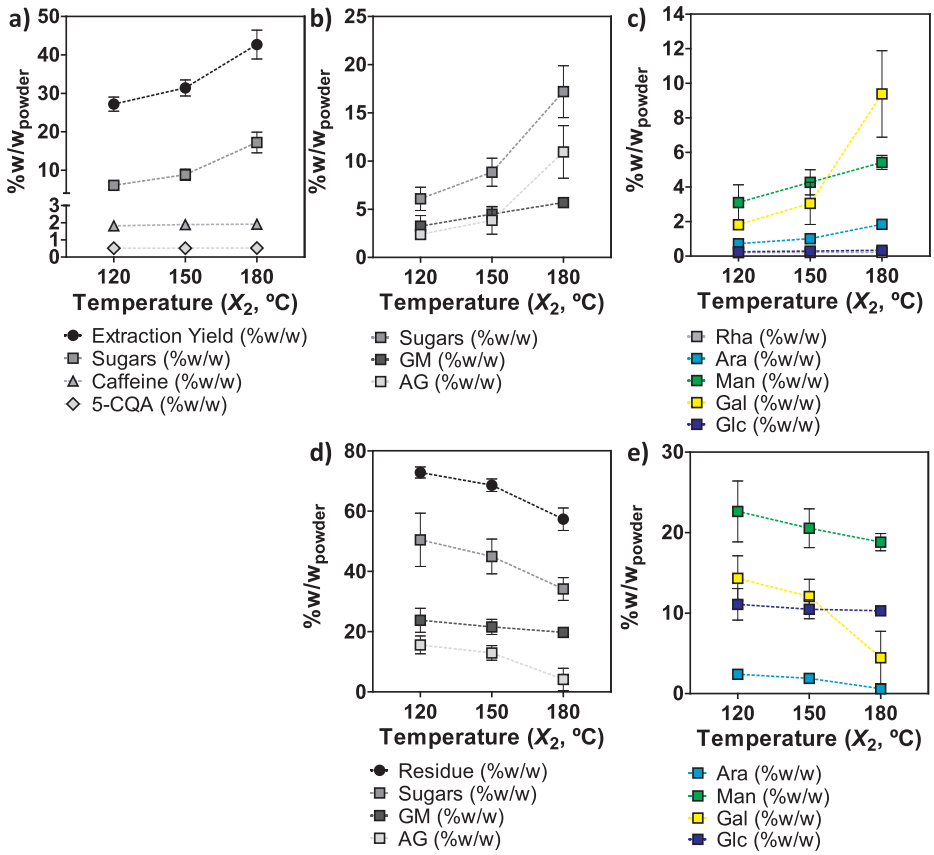

Fig. 8. Representation of the content of compounds extracted from coffee powder (a-c, %, w/w$_{powder}$) and content of compounds that remained in the residue (d,e, %, w/w$_{powder}$). The runs were grouped by extraction temperature. Results were expressed as mean ± standard deviation of 8 (120, 180 °C) and 14 (150 °C) runs.

of the extraction process was performed for the extracts obtained (Fig. 8a-c) and for the remaining residues (Fig. 8d,e). The results were grouped by the extraction temperature, the variable that led to higher responses variability. Fig. 8a highlights the concomitant increase of extraction yield and carbohydrates, while caffeine and 5-CQA exhibit similar values across the temperatures tested. As the initial roasted coffee sample presented 1.9% (w/w) of caffeine, in accordance with literature values (0.8–2.6%, w/w) (Gant et al., 2015; Hečimović, Belščak-Cvitanović, Horžić, & Komes, 2011; Ludwig et al., 2014), it was possible to infer that caffeine was effectively extracted throughout all MAE conditions tested. The same behaviour can be observed for 5-CQA. Regarding carbohydrates, Fig. 8a and 8d, reveals that although the considerable carbohydrates extraction, the residue left after MAE still contained a great fraction of carbohydrates to be extracted, namely GM, a high fraction of the residue, even at 180 °C (Fig. 8d). On the other hand, almost all AG content (> 90% in some runs) ended up in the extract in one step of MAE at 180 °C, which does not occur with milder conventional extractions. This justifies the extraction of AG from spent coffee grounds after a first MAE procedure, while predominantly GM are recovered only after successive extraction steps (Passos & Coimbra, 2013; Passos et al., 2014) Moreover, the GM cannot be extracted without the previous removal of AG. MAE may also be viewed as a rapid methodology to remove almost all galactose (ending with ≈5 mol %), providing a residue with a great predominance of GM and cellulose. The different content of GM and AG all over the design space, ranging the ratio of GM/AG from 0.4 to 1.9, highlighted that it is possible to modulate the preponderance of each of the structures, according to possible applications for providing different viscosity of coffee brews or even for health promoting effects due to their immunomodulating activities (Nosáľová et al., 2011; Simões et al., 2009). Fig. 8c,e highlights that the pattern followed by galactose was accompanied by arabinose, showing a strong positive correlation between the extractability of the two sugar residues along the experiments, both in extracts ($r = 0.97$, $p < 0.0001$) and residues ($r = 0.98$, $p < 0.0001$), in accordance with the occurrence of AG. The analysis of the residues confirmed that the greatest amount of mannose and mainly glucose remains in the residue after MAE.

4. Concluding remarks

This study shows that MAE can be used to obtain extracts with different carbohydrates, caffeine, chlorogenic acids and coloured compounds, approaching instant coffee composition with high extraction temperatures (180 °C), while in milder conditions at 120 °C and 150 °C the extracts are still comparable to home brewing methods. The higher extraction at 180 °C is associated to a substantial increase in AG extraction. Indeed, temperature exerted a crucial role in coffee extracts differentiation, although time and m/V ratio also lead to different values in the responses. Nevertheless, using less than 10 min of extraction, it was possible to obtain an extract with instant coffee-like composition. On the other hand, under a circular economy concept, MAE of roasted coffee also provides a galactomannan and cellulose rich residue able to be a source of valuable polysaccharides.

The contribution of each one of the 5 authors is as follows:

- Guido R. Lopes designed and performed all the experiments, analysed the data, and wrote the paper.
- Cláudia P. Passos was involved in the microwave experiments and co-wrote the paper.
- Carla Rodrigues, José A. Teixeira and Manuel A. Coimbra supervised all the experiments, analysed the data and co-wrote the paper.

All authors discussed the results and commented on the manuscript. No conflicts of interest were identified.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodres.2019.108864.

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