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Multi-frequency multimode modulated technology as a clean, fast, and sustainable process to recover antioxidants from a coffee by-product

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ABSTRACT

Coffee chaff is a major coffee roasting by-product that could be valued as a source of antioxidants. In the present work, we compared classic, but optimized, solid-liquid extraction conditions with a new concept, namely, the Multi-frequency Multimode Modulated (MMM) vibration technique. The extracts obtained by both methods were analysed and compared in relation to several parameters, namely, phenolics profile (by HPLC/DAD), 5-caffeoylquinic acid content, total phenolics content, and Ferric Reducing Antioxidant Power. Compared to an optimized solid-liquid extraction (using a hydroethanolic solvent (1:1) at 40 °C for 60 min), the acoustic probe allowed a higher recovery of antioxidants in only 10 min and using only water as extraction solvent. Moreover, the effects that arise from the acoustic cavitation in the medium allowed the suppression of the sample preparation step (grinding). These results show that this type of technology can be of high interest to recover antioxidants from natural matrices, in a green, fast and very efficient way.

1. Introduction

Food sustainability is a concept that has been attaining increasing attention in recent years. The reduction of industrial wastes can be seen as a challenge, but also as an opportunity to innovate, develop new products and technologies, with both economic and social benefits.

The industry of coffee (one of the largest commodities in the world) produces high amounts of different residues that represent a serious environmental problem (Mussatto et al., 2011). Therefore, it is mandatory to create effective strategies to deal with this problem. Several studies have been performed regarding the use and valorization of different coffee by-products (*e.g.* husks, defective beans and spent coffee grounds) for bioethanol and biodiesel production or as adsorbents (Caetano et al., 2014; Franca et al., 2008a, 2008b; Oliveira et al., 2008a, 2008b, 2008c). However, coffee by-products are extremely rich in a variety of bioactive compounds that can be recovered and used for innovative applications, not only in food industry, but also in cosmetic or pharmaceutical fields (Borrelli et al., 2004; Murthy and Naidu, 2012; Murthy et al., 2012; Panusa et al., 2013).

This study is focused in the by-product of coffee roast industry: coffee chaff (or silverskin). It is a thin pellicle that covers the green coffee bean and is detached during the thermal procedure due to the beans expansion. As it is not usually used to prepare coffee beverages, coffee chaff is separated from the beans by air flow and dispatched, afterwards, as firelighters or fertilizer. Nevertheless, it has been described as a relevant source of antioxidants and dietary fiber with a high potential for food applications (Borrelli et al., 2004; Costa et al., 2014; Napolitano et al., 2007; Pourfarzad et al., 2013) and its possible use in the cosmetic field is also under investigation (Rodrigues et al., 2016a, 2016b)

Organic solvents such as ethanol, methanol and acetone (pure or mixed with water) are usually employed to extract antioxidants from food and plant materials (Xu and Chang, 2007). In a previous

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research, our investigation group proposed an optimized method to extract antioxidants from coffee chaff, evaluating the effect of the major variables (solvent polarity, temperature and extraction time) in the recovery yields (Costa et al., 2014). As expected, the extracts composition varied significantly with the extraction conditions and a factorial experimental design showed that the use of a hydroethanolic solvent (1:1) at 40 °C for 60 min was a sustainable option to maximize the antioxidant compounds extraction and the antioxidant activity of the extracts. Even so, although very effective, the use of this classic solid-liquid extraction can still be time-, organic solvent-, and energy-consuming, especially concerning the high amounts of this by-product that are produced along the coffee roasting. Thus, the development of an economic, fast and efficient alternative extraction method is essential to achieve a real and profitable use of coffee chaff as a source of antioxidants. Inside the new developments of extraction techniques, such as supercritical fluid extraction (Turner et al., 2001) or microwave-assisted extraction (Wang et al., 2010), the ultrasonic-assisted procedure presents interesting advantages, such as (i) to accelerate the extraction process, and (ii) to promote a reduced damage of the molecular and structural properties of the matrix (Vilkhu et al., 2008) The useful effects of ultrasonic extraction are related to the efficient transformation of electric energy into mechanical vibration by means of an ultrasonic transducer (operating in resonance), which is in the last step radiated to a liquid medium. The physical, mechanical and chemical associated effects arising from acoustic cavitation are very complex (for instance, a small shift in amplitude and time could present a high impact on the final process efficiency) and, therefore, the extraction parameters should be optimized to achieve the highest extraction rates.

The main aim of this study was to investigate the effect of cavitation promoted by high acoustic pressure on the extraction of antioxidants from coffee chaff, focusing on the relationships among the ultrasonic amplitude and time of processing. A finite element model (FEM), which combines piezoelectric, structural, and acoustic modules was used to analyze and optimize the whole system. The results achieved using the proposed technique - Multifrequency Multimode Modulated (MMM) ultrasonic vibration - were compared to those obtained through the optimized solid-liquid extraction described by Costa et al. (2014) regarding different chemical parameters, namely, phenolics profile, total phenolics content, 5-caffeoylquinic acid levels, and ferric reducing antioxidant power (FRAP). The green technique proposed in this work was able to significantly increase the extraction performance, while simultaneously eliminated the use of the organic solvent, contributing to the economical and environmental sustainability of the process.

2. Experimental procedures

2.1. Samples and sample preparation

Coffee chaff obtained during the roasting of industrial coffee batches was provided by Bicafé- Torrefação e Comércio de Café Lda., a Portuguese coffee roaster. After reception, the sample was homogeneized, ground (GrindomixFig. GM 200, Retsch, Haan, Germany), and used to prepare both classic and MMM technology-based extractions. In this last case, non-ground aliquots were also used (Table 1).

2.2. Extracts preparation

2.2.1. Classic solid-liquid extraction

A classic solid-liquid extraction, previously optimized to extract antioxidant compounds from coffee chaff was used (Costa et al., 2014) Briefly, a rigorously weighted amount (~1.00 g) of ground sample and 50 mL of a hydroethanolic solvent (1:1) were mixed under constant magnetic stirring (600 rpm), for 60 min at 40 °C (E5CC, Omron Corporation, Kyoto, Japan). The final extracts were filtered and analysed. All extracts were prepared in triplicate.

2.2.2. Ultrasound extraction

2.2.2.1. Numerical simulation. In order to study the behavior of the acoustic energy distribution on the medium, numerical simulations have been carried out. The acoustic power, acoustic pressure and amplitudes of the whole system provided by the transducer were evaluated in numerical simulations function of driving frequency (frequencies comprised between 19.00 and 21.00 kHz). In compliance, optimal operation parameters of the transducer were optimized to produce the maximum acoustic intensity in the medium, and consequently improve the extraction performance, considering the influence of the boundary conditions in the dynamic response of the transducer.

Although the presence of cavitation bubbles modifies the acoustic properties of the medium, in most cases the bubbles are concentrated in small regions allowing to claim that linear acoustics may provide a qualitative perception of the acoustic field and the estimative location of resonance frequencies (Louisnard et al., 2009). In the present case, the propagation of ultrasonic waves in the medium (and ignoring the effect of cavitation flow) is governed by the Helmholtz equation (1) (Louisnard et al., 2009):

$$\nabla\left(\frac{1}{\rho}\nabla p\right)+\frac{\omega^2}{\rho c^2}p=0, \tag{1}$$

where ρ and c are the density and speed of sound of the medium (water in the present study), respectively; p is the acoustic pressure and ω is the angular frequency.

In contrary to what is presented in other studies (Louisnard et al., 2015), in which the activation of the liquid is made by a boundary condition described by a harmonic pressure with constant amplitude ignoring the coupling between solid and liquid, in this approach the liquid is acoustically activated by the radiator which is governed by linear elastic material model according to equation (2) (COMSOL, 2013):

$$-\rho\omega^2\boldsymbol{u}-\nabla\cdot\sigma=\boldsymbol{F}_v e^{i\varphi} \tag{2}$$

Furthermore, the coupling between the fluid domain (pressure waves) and the solid should be considered on the surface of radiation. Thus, the boundary load on the flat-end of radiator is given by (3) (COMSOL, 2013; Louisnard et al., 2009):

$$\boldsymbol{F}=-p\boldsymbol{n}_s, \tag{3}$$

where $\boldsymbol{n}_s$ represents the outward-pointing unit normal vector from the solid in direction to liquid domain. By the other side, the normal acceleration experienced by the fluid domain is set equal to the normal acceleration of the solid, which can be described by (4) (COMSOL, 2013; Louisnard et al., 2009):

$$-\boldsymbol{n}_a\cdot\left(-\frac{1}{\rho_0}\nabla p+\boldsymbol{q}\right)=\boldsymbol{a}_n \tag{4}$$

The set of equations were solved for the geometry presented in Fig. 1a which consider the interaction of a Ti radiator, physically activated by one piezoelectric transducer, with a water medium contained in a glass. The Acoustic-Piezoelectric Interaction, Frequency Domain Interface of the Acoustics Module available in the COMSOL software was used for the study. This interface has all the predefined Multiphysics couplings necessary to model the system

Table 1
Comparison of the extracts composition using different conditions of extraction.

Extract	Sample		MMM technology parameters			5-Caffeoylquinic acid		Total phenolics				Ferric Reducing Antioxidant Power	
	Ground	Entire	Frequency (kHz)	Input electric power (W)	Time (s)	μg/ mL of extract	mg/g of CC	μg GAE/ mL of extract	mg GAE/g of CC	μg CAE/ mL of extract	mg CAE/g of CC	μg FSE/ mL of extract	mg FSE/g of CC
1	×		19.8	250	60	13.0 ± 2.2^{b}	0.64 ± 0.11^{b}	110.3 ± 15.7^{g}	5.5 ± 0.7^{g}	239.7 ± 29.2^{e}	12.0 ± 1.5^{e}	1349 ± 116^{e}	65.7 ± 5.8^{e}
2	×		19.8	250	180	18.2 ± 0.6^{a}	0.91 ± 0.03^{a}	148.7 ± 6.9^{ef}	7.4 ± 0.3^{ef}	311.5 ± 12.9^{d}	15.6 ± 0.6^{d}	1771 ± 21^{cd}	88.5 ± 1.0^{cd}
3	×		19.8	250	300	17.4 ± 1.6^{a}	0.87 ± 0.08^{a}	171.4 ± 7.1^{cd}	8.6 ± 0.4^{cd}	353.7 ± 13.3^{bc}	17.7 ± 0.7^{bc}	1862 ± 111^{bc}	93.1 ± 5.6^{bc}
4	×		19.8	500	60	17.2 ± 1.0^{a}	0.86 ± 0.05^{a}	137.1 ± 4.0^{f}	6.9 ± 0.2^{f}	289.7 ± 7.5^{d}	14.5 ± 0.4^{d}	1639 ± 43^{d}	81.9 ± 2.2^{d}
5	×		19.8	500	180	17.7 ± 0.6^{a}	0.88 ± 0.03^{a}	158.6 ± 4.2^{de}	7.9 ± 0.2^{de}	329.8 ± 7.9^{cd}	16.5 ± 0.4^{cd}	1853 ± 59^{bc}	92.7 ± 3.0^{bc}
6	×		19.8	500	300	17.6 ± 1.0^{a}	0.88 ± 0.05^{a}	174.1 ± 8.2^{cd}	$8.7 \pm 0.4\ b^{cd}$	358.6 ± 15.2^{bc}	17.9 ± 0.8^{bc}	1909 ± 35^{bc}	95.5 ± 1.7^{bc}
7		×	19.8	500	300	17.2 ± 1.9^{a}	0.86 ± 0.09^{a}	179.6 ± 1.7^{bc}	$9.0 \pm 0.1\ b^{bc}$	369.0 ± 3.1^{abc}	18.4 ± 0.2^{abc}	2014 ± 45^{b}	100.7 ± 1.1^{b}
8		×	19.8	500	420	17.2 ± 1.4^{a}	0.86 ± 0.07^{a}	180.8 ± 4.8^{abc}	$9.0 \pm 0.2\ ab^{abc}$	371.3 ± 9.0^{ab}	18.5 ± 0.5^{ab}	1992 ± 46^{b}	99.6 ± 1.8^{b}
9		×	19.8	500	600	18.9 ± 0.7^{a}	0.94 ± 0.03^{a}	203.8 ± 2.0^{a}	$10.2 \pm 0.1\ a^{a}$	410.6 ± 3.0^{a}	20.5 ± 0.2^{a}	2446 ± 7^{a}	122.3 ± 0.4^{a}
10	×		Classic solid-liquid extraction*			19.1 ± 0.2^{a}	0.96 ± 0.01^{a}	198.3 ± 2.6^{ab}	$9.9 \pm 0.1\ ab^{ab}$	403.9 ± 4.8^{a}	20.2 ± 0.2^{a}	2266 ± 22^{a}	113.3 ± 1.1^{a}

Each condition was tested in triplicate and each extract was analysed in triplicate ($n = 9$). Different letters within each column represent significant differences at $p < 0.05$.
*Extraction conditions: hidroalcoholic solvent (1:1), constant magnetic stirring (600 rpm), 60 min at 40 °C. CC, coffee chaff; GAE, gallic acid equivalents; CAE, chlorogenic acid equivalents; FSE, ferrous sulfate equivalents.

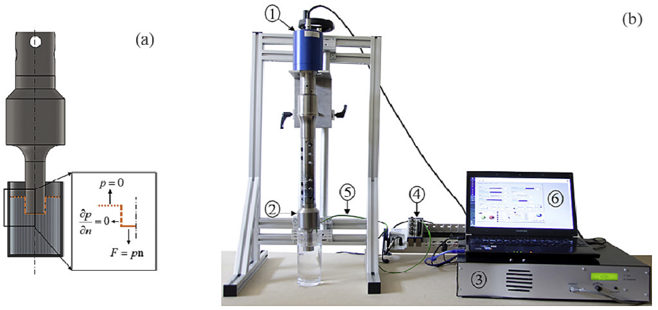

Fig. 1. Ultrasound-assisted device based in MMM (multi-frequency, multimode, modulated) technology. Legend: a) Schematic diagram of model geometry for simulation; b) Experimental set-up: 1) piezoelectric transducer, 2) acoustic radiator, 3) MMM technology-based generator, 4) CompactDAQ temperature acquisition, 5) thermocouple type S, 6) Windows compatible software (by MPInterconsulting).

regarding the acoustic-structure and electric-structure (piezo material). The boundary conditions considered were:

(i) $p = 0$ at the water-air interfaces corresponding to a total reflection conditions as soft walls; (ii) zero normal derivative of the pressure $\partial p/\partial t = 0$ at the side boundaries of the radiator (hard boundaries);

(iii) Acoustic impedance $Z = \rho c$ for soft glass boundaries of container, where ρ (2600 kg/m^3) and c (4545 m/s) are the density and sound velocity of the glass, respectively.

(iv) It is known that the intensity of a plane ultrasonic wave decreases exponentially with the propagation path according to equation 1=$I_0e^{(-\alpha x)}$. Thus, in the present study, a coefficient attenuation per meter of $\alpha = 5e^{-10}$Np/m was considered.

(v) In order to improve the accuracy of results, parameters corresponding to the coupling loss ($\eta_e = 0.02$), mechanical damping ($\eta_s = 0.02$) and dielectric loss ($\eta\varepsilon_S = 0.01$) were introduced in the model.

2.2.2.2. Equipment. The ultrasound device based in the MMM technology (Fig. 1b) was comprised by a piezoelectric transducer, an acoustic radiator, a MMM technology-based generator, a CompactDAQ for temperature acquisition, a type S thermocouple and a Windows compatible software developed by MP Interconsulting (Le Locle, Switzerland).

2.2.2.3. Extracts preparation. Each extract was prepared using a rigorous amount (~1.00 g) of sample (entire or ground, as described in Table 1) and 50 mL of distilled water. After being subjected to the MMM-based extractions, the mixture was filtered and analysed. Each condition was tested in triplicate.

2.3. Chemical analyses

2.3.1. Reagents and standards

Chlorogenic acid, caffeine, gallic acid, trolox, Folin–Ciocalteu's phenol reagent, DPPH• (2, 2-diphenyl-1-picrylhydrazyl), ferric chloride, TPTZ (2,4,6-tripyridyl-s-triazine) solution, ferrous sulfate heptahydrate, sodium acetate, glacial acetic acid, and HPLC grade methanol were all obtained from Sigma–Aldrich (St. Louis, USA). Sodium carbonate anhydrous and absolute ethanol were purchased from Merck (Darmstadt, Germany). All other reagents were of analytical grade. Ultrapure water used for analysis was treated in a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.3.2. Total phenolics content

Total phenolics were determined according to Alves et al. (2010). Briefly, 500 µl of a diluted extract (1:10) were mixed with 2.5 mL of Folin–Ciocalteús reagent (1:10) and 2 mL of a Na_2CO_3 solution (7.5% m/v). The mixture was incubated during 15 min at 45 °C, followed by 30 min at room temperature. Absorbance readings were performed at 765 nm. The total phenolics content was obtained from two calibrations curves prepared with gallic acid (10–100 mg/L; $r = 0.9996$) and cholorogenic acid (5–150 mg/L; $r = 0.9998$) and, thus, expressed as both µg of gallic acid equivalents (GAE)/mL of extract and µg of chlorogenic acid equivalents (CAE)/mL of extract. The total phenolics content per g of coffee chaff is also presented (Table 1).

2.3.3. Ferric reducing antioxidant power (FRAP) assay

The FRAP assay was performed according to Costa et al. (2014). In brief, 90 µl of extract (1:10 dilution) were mixed with 270 µl of deionized water and 2.7 mL of the FRAP reagent (containing 0.3 M acetate buffer, 10 mM TPTZ-solution, and 20 mM of ferric chloride). After vortexing, the mixture was kept at 37 °C, protected from light during 30 min. Absorbance was then measured at 595 nm. Ferrous sulfate was used as standard to prepare a calibration curve (50–450 mg/L, $r = 0.9998$) and the ferric reducing power was expressed as µg of ferrous sulfate equivalents (FSE)/mL of extract and mg of FSE/g of coffee chaff.

2.3.4. 5-Caffeoylquinic acid content

The chromatographic analysis was performed in a HPLC integrated system (Jasco, Japan) equipped with an AS-950 automated injector (20 µl loop), two Jasco PU-2080 Plus HPLC pumps, and an MD-2010 Plus multiwavelength diode array detector. The compounds were separated using a reversed-phase Tracer-Excel ODSA (5 µm; 250 × 4 mm) from Teknokroma (Barcelona, Spain). A solvent system of acetic acid:water (0.2:99.8) (A) and methanol (B) was used with the following gradient: 0 min, 7.5% B; 10 min, 20% B; 12 min, 30% B, 20 min, 35% B; 28 min, 40% B. Elution was performed at a flow rate of 1 mL/min. The phenolic compounds were monitored at 320 nm. The compounds were identified by comparing retention times, elution order and UV absorption spectra with those of literature and a standard (Alves et al., 2010). Chromatographic data were analysed using Borwin-PDA Controller Software (JMBS Developments, Le Fontanil, France). The main antioxidant compound of coffee chaff, 5-caffeoylquinic acid (5-CQA), was quantified and the results were expressed as µg of 5-CQA/mL of extract and mg of 5-CQA/g of coffee chaff.

2.4. Statistical analyses

Statistical analysis was performed using IBM SPSS v. 20 (IBM Corp., Armonk, 241 NY, USA). Data are expressed as mean ± standard deviation. The Shapiro-Wilk test was used to evaluate data normality. The one-way ANOVA was used to assess significant differences between samples, followed by Tukey's HSD or Dunett T3 post-hoc test (selected based on the equality of the variances) to make pairwise comparisons between means. The level of significance for all hypothesis tests (p) was 0.05.

3. Results and discussion

3.1. Numerical simulation

The MMM (multi-frequency, multimode, modulated) technology is characterized by synchronously exciting many vibration modes through the coupled harmonics and sub-harmonics in solids and liquid containers. This technology produces high intensity multimode vibrations that are uniform and repeatable, which avoid the creation of stationary and standing waves, so that the whole vibrating system is fully agitated, improving cavitation.

The ultrasound parameters, material properties and boundary conditions were computed based on the equations presented in the Section 2.2.2. In the present study, two depths (5 and 15 mm) of acoustic radiator in the liquid and two levels of input electric power of transducer (500 and 250 W) were evaluated. Contrarily to the traditional process of extraction where solvents, mechanical mixing and a fixed temperature are used, in the present approach these issues are not considered, since the applied acoustic intensity is enough for:

(i) Converting the displacement of piezoelectric into kinetic energy of the liquid (creating acoustic streams able to promote the homogenization of the mixture);
(ii) Increasing the temperature of the medium due to bubbles collapse, which can promote and accelerate the extraction.

According to the eigenfrequency results of the acoustic radiation, the first longitudinal compression mode was located at $f_0 = 20.18$ kHz, matching well with the operation frequency of the transducer, as can be confirmed by the results of electric impedance of transducer and acoustic radiator (red line) presented in Fig. 2. As previously mentioned, numerical simulations were performed to evaluate the distribution of displacement on the flat-end of radiator for two different depths of the radiator in water. Furthermore, the electric impedance (blue line, Fig. 2) was characterized to know the shift of resonance frequency (f_0) when the ultrasonic system was operated in water. It can be observed that the addition of water promoted a change of resonance frequency from $f_0 = 20.18$ kHz to $f_0 = 19.80$ kHz ($f_0 = (f_s + f_p)/2$, where f_s was 19.70 kHz and f_p equal to 19.90 kHz).

Fig. 3 presents the axial displacement behavior of the radiator along the frequency range, when it was immersed in water at different depths and using an electric power of 500 W. Although the results suggest that for the operation parameters and conditions used in this study a decrease in the immersion depth presents an increase of displacement amplitude, in terms of absolute value the displacement was not significant. Once this situation was verified, numerical simulations were performed to characterize the

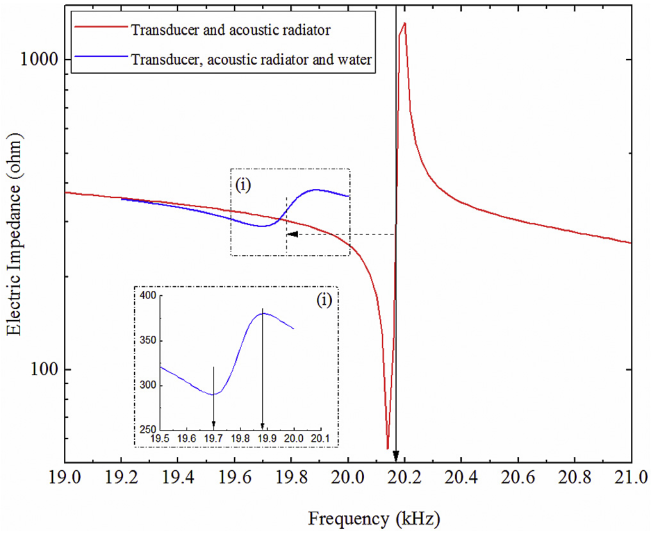

Fig. 2. Numeric results of electric impedance of the system (obtained when the input electric power was 500 W).

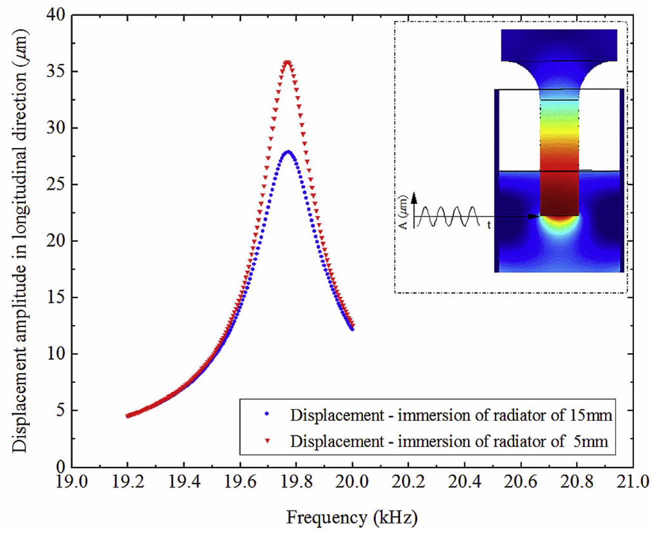

Fig. 3. Numeric results of the displacement amplitude measured at a point on the surface flat-end of radiator function of driving frequency (obtained when the input electric power was 500 W).

acoustic power on the medium when the radiator was 15 mm immersed in water.

Fig. 4 presents the evolution of acoustic power numerically acquired in the medium for two different levels of electric power of transducer for frequencies ranging between 19.20 kHz and 20.00 kHz. As can be observed, a reduction of the transducer input electric power imply a decreasing of 50% on the acoustic power for a resonate frequency ($f_0 = 19.85$ kHz), which in turn results in a lower acoustic pressure value in the medium. In order to validate the numerical results, a comparison of the numerical acoustic pressure distribution with the corresponding experimental cavitation field was performed, for two electric power of transducer (250 and 500 W). The results are illustrated in Figs. 5a and 6, respectively. According to the numerical results (Figs. 5a and 6a), there are two areas in the container medium where high values are reached: one around of the flat-end of radiator and other located far away from the radiator. Figs. 5b and 6b show images extracted from high-speed video frames, showing the behavior of acoustic cavitation in the medium at different location areas relatively to the flat-end of radiator. For a 50% increase of the input electric power of transducer, dense clouds of cavitation bubbles are generated and propagated across the medium, as can be clearly observed in Fig. 6b. This is in accordance to Moussatov et al. (2003) that reported that a 2-fold increase on the acoustic intensity (W/cm^2) results into acceleration of bubbles motion, producing a high quantity of streamers and consequently promoting an enlargement of active cavitation zone in the medium. The location of those areas are in agreement with the simulation observations (Figs. 5a and 6a). Since a high acoustic pressure is the prerequisite for cavitation, which is responsible for the extraction of antioxidants from coffee chaff, these results (Figs. 5a and 6) demonstrate that, for the same shape of acoustic radiator, an increase of 50% of electric power of transducer introduces more energy-emitting surfaces and therefore multiple reactive zones. Moreover, it can be seen that the resonant frequency characterized in experimental tests was $f_0 = 19.95 \pm 0.0025$ kHz, which is very narrow with numerical results ($\Delta = 0.10$ kHz). The value of ± 0.0025 kHz corresponds to the variable frequency-sweeping oscillations around its central operating frequency (f_0) of whole system according to the MMM Technology bases, maximizing the conversion of electric energy into acoustic energy transferred to the medium. The results obtained for different levels of electric power are in agreement with those of Sajjadi et al. (2015) that reported that a power increase imposes a great influence on hotspot conditions, generating a large cavitation zone. Furthermore, as demonstrated by Sajjadi et al. (2015) and Servant et al. (2001), the use of numerical simulation can predict the sites where mechanical active bubbles (cavitation) are produced. In order to better illustrate the impact of this extraction technology on the real sample, Figs. 5c and 6c show the effect of the implosion bubbles originated by cavitation on an aluminum foil placed at 10 mm from the flat-end of radiator. These results were obtained for the respective amplitudes of the acoustic radiator only after 5 s of sonication. According to these pictures, it is evident that the energy of the acoustic radiator unit was directly focused on a localized zone, thereby providing a different level of efficiency of cavitation into the medium which was increased for the highest electric power (500 W). Moreover, the results of the acoustic pressure transferred to the medium are in agreement with literature, where it is stated that the threshold of acoustic pressure to develop cavitation in water is around 0.06–0.1 MPa (Eskin and Eskin, 2014). The agreement between computational simulation and experimental results allowed to optimize the sonochemical reactor in order to improve the cavitation zones of the medium.

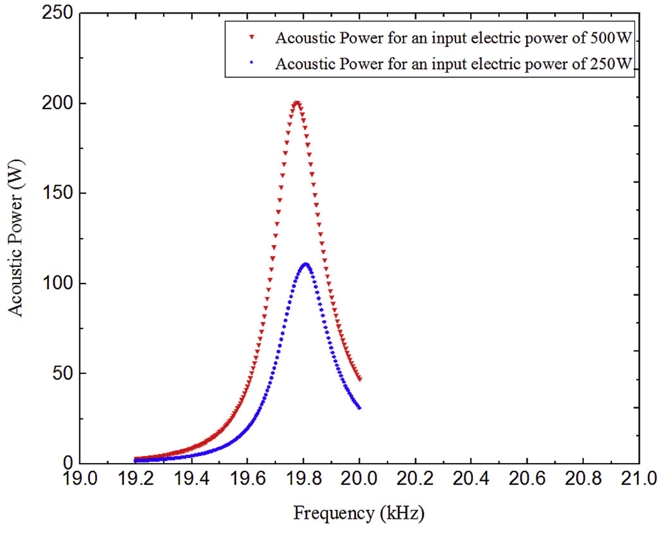

Fig. 4. Numerical results of acoustic power measured on the medium as function of driving frequency (radiator immersed 15 mm in water).

3.2. Experimental results

Table 1 details the antioxidant profile of the chaff extracts obtained with the different experimental conditions (frequency (kHz), input electric power (%) and time (s)) of the MMM-based extraction technology. As previously mentioned, the results were compared to those obtained using a classic solid-liquid method previously optimized to recover antioxidants from coffee chaff (Costa et al., 2014). This previous study has already been an attempt to develop a sustainable method to extract these compounds, by avoiding the use of high temperatures of extraction and the use of high percentages of an organic solvent (in this case ethanol, which was already selected due to its safety and efficacy to extract such compounds). Indeed, from a total of 100 different conditions (regarding time, temperature and solvent polarities) an extraction using a hydroethanolic solvent (1:1), at 40 °C for 60 min, was selected as the more adequate option to achieve antioxidant-rich extracts in a compromise between sustainability and extraction

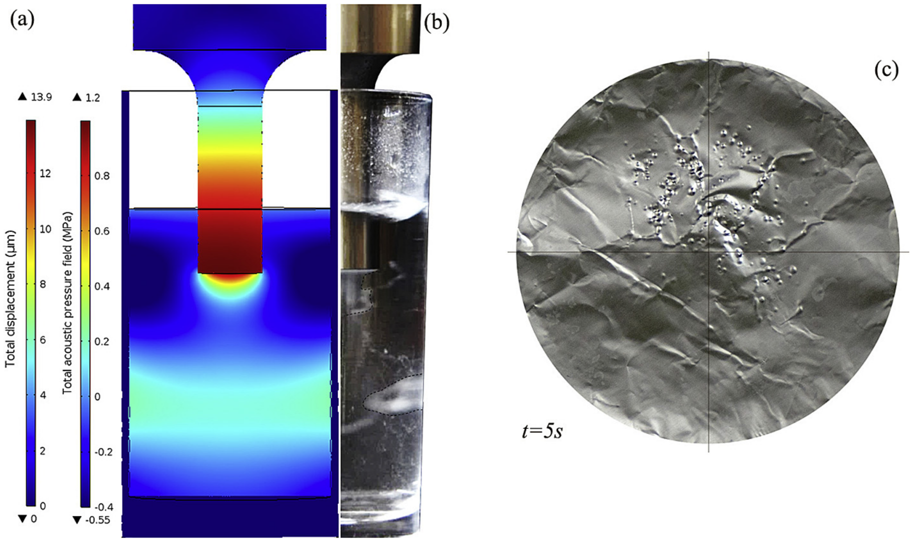

Fig. 5. Simulation of acoustic pressure in the sonicated medium (input electrical power of 250 W and $f_0 = 19.80$ kHz) **(a)**; Photograph of resonance cavitation field in the experimental container (input electric power of 250 W and $f_0 = 19.95 \pm 0.0025$ kHz) **(b)**; Effect of implosion bubbles on an aluminum foil after 5 s of sonication **(c)**.

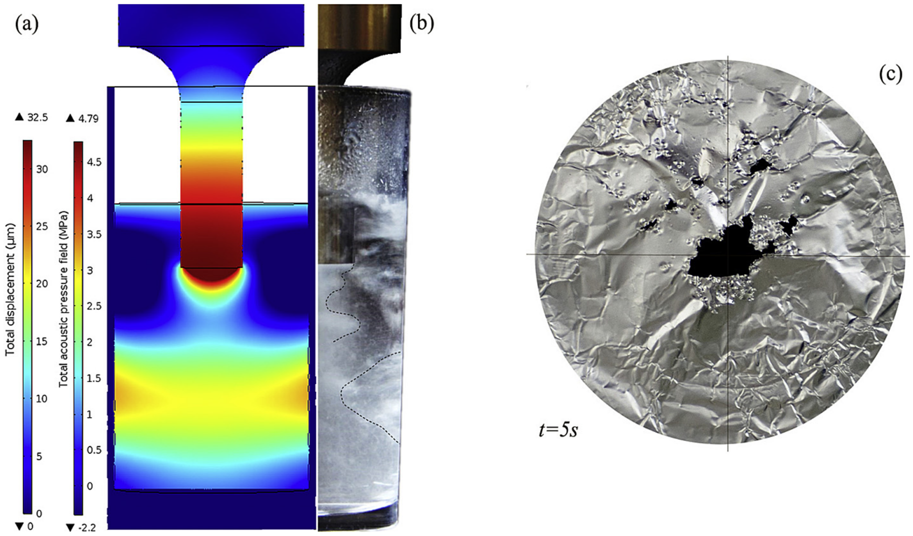

Fig. 6. Simulation of acoustic pressure in the sonicated medium (input electrical power of 500 W and $f_0 = 19.80$ kHz) **(a)**; Photograph of the resonance cavitation field in the experimental container (input electric power of 500 W and $f_0 = 19.95 \pm 0.0025$ kHz) **(b)**; Effect of implosion bubbles on an aluminum foil after 5 s of sonication **(c)**.

efficiency.

Chlorogenic acids are the major antioxidants in coffee. They are phenolic compounds formed by the esterification of cinnamic acids, such as caffeic, ferulic, and *p*-coumaric acids, with (-)-quinic acid (Farah et al., 2008). 5-CQA is the major compound of this group not only in beans (Alves et al., 2010) but also in coffee by-products (including chaff) (Narita and Inouye, 2012). Besides being highly bioavailable in humans, several biological effects, such as antihypertensive action, vasoreactivity improvement, inhibition of fat accumulation, and modulation of glucose metabolism, have been attributed to chlorogenic acids (Blum et al., 2007; Ochiai et al., 2004; Shimoda et al., 2006; Suzuki et al., 2002). Therefore, the recovery of such compounds from coffee chaff is very interesting not only for health purposes but also having in view the valorization of a industrial residue that is usually dispatched.

In the present work, using the referred classic optimized method (Costa et al., 2014) we were able to obtain extracts (Table 1, condition 10) containing ~19 µg of 5-CQA/mL of extract (corresponding to 0.96 mg/g of coffee chaff). This result is in complete accordance to the amount quantified by Narita and Inouye, 2012 that reported 1.1 mg/g of coffee chaff. In what concerns to the MMM technology, all the tested conditions described in Table 1 were able to extract similar amounts of 5-CQA (no significant differences, $p > 0.05$) compared to the classic method, except the first one (input electric power: 250 W, 60 s) that extracted significantly lower ($p < 0.05$) amounts of this individual compound. Indeed, in only 180 s, using only water as extraction solvent, and without heating, it was possible to obtain a similar concentration ($p > 0.05$) of 5-CQA than that achieved with the classic method (40 °C, 60 min), which represents a huge saving of energy and time.

Nevertheless, as mentioned before, coffee chaff is a very complex matrix, containing other minor phenolic compounds and other chlorogenic acids besides 5-CQA. Fig. 7 depicts a chromatogram obtained by HPLC/DAD analysis that shows the phenolic profile of coffee chaff. The compounds were tentatively identified based on their relative retention time, elution order, and UV spectral

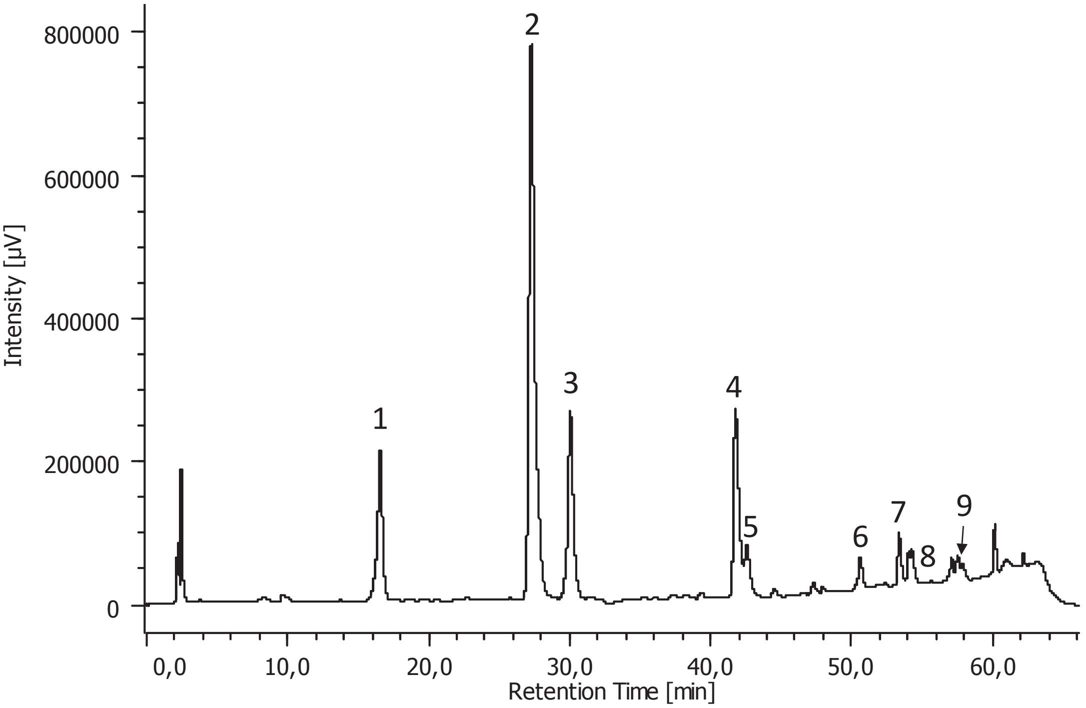

Fig. 7. Chromatogram (recorded at 320 nm) of a coffee chaff extract obtained using the MMM-based extraction technology. Legend: 1) 3-caffeoylquinic acid, 2) 5-caffeoylquinic acid, 3) 4-caffeoylquinic acid, 4) 5-feruloylquinic acid; and 5) 3-feruloylquinic acid; 6 and 7) dicaffeoylquinic acids; 8) caffeoyltryptophan; 9) caffeoylferuloylquinic acid.

characteristics, which were compared to previously published data (Alves et al., 2010; Bresciani et al., 2014; Regazzoni et al., 2016). Besides the major phenolic (5-CQA), 4-caffeoylquinic acid, 3-caffeoylquinic acid, 5-feruloylquinic acid and 3-feruloylquinic acid were also present. Two dicaffeoylquinic acids, caffeoyltryptophan and a caffeoylferuloylquinic acid were identified in comparatively lower amounts. In the absence of standards for the quantification of these individual phenolics, the total phenolics content was determined for each type of extract, in order to evaluate the extraction efficacy. The results were expressed as total chlorogenic acid equivalents, but also as gallic acid equivalents which simplifies the comparison with literature data. For instance, in our previous work, we reported ~300 µg of GAE/mL of extract (Costa et al., 2014). Using the same methodology of extraction, in this work we obtained ~200 µg of GAE/mL of extract which is related to the different composition of the industrial batch regarding coffee species and roast degree. In another study, Toschi et al. (2014) reported 0.39–0.73 g gallic acid equivalents per 100 g of coffee chaff. In this work, we quantified higher values: 1–2 g/100 g depending on the extraction procedure used. Indeed, significantly higher amounts of GAE (and CAE) were obtained using an input electric power of 500 W during 10 min (Table 1, condition 9), without any need of grinding the sample, results that were not statistically different ($p > 0.05$) to those obtained with the classic extraction method.

Besides phenolic compounds, coffee chaff also contain other antioxidant compounds, such as melanoidins, which are formed during the beans roast (Borrelli et al., 2004; Costa et al., 2014; Pourfarzad et al., 2013). Therefore, it can be reductive to analyze only phenolics, and in order to get a larger overview of the extracts antioxidant profile, their antioxidant activity was also evaluated using the FRAP assay. The principle of this method is the reduction of ferric 2,4,6-tripyridyl-s-triazine (TPTZ) by the antioxidants of the sample, originating a blue color. By this way, chemical compounds with redox potentials lower than 0.7 V (the redox potential of Fe^{3+}-TPTZ) are detected, which is a reasonable screen for the ability of these extracts to maintain the redox status in a biological system (Benzie and Strain, 1996). The results were comparable to those obtained for total phenolics: condition 9 was also the most effective and no significant differences were found ($p > 0.05$) compared to the classic optimized method. Therefore, we select this MMM-based procedure as a sustainable, fast and clean alternative to obtain the coffee chaff antioxidants, without the need of direct temperature application, organic solvents or sample preparation.

4. Conclusions

The MMM technology has the potential to produce high intensity multimode vibrations, creating a uniform and homogenous distribution of cavitation and acoustical activity on the system. At the same time, it avoids the creation of stationary and standing waves and the whole vibrating system is fully agitated, with sample fragmentation and heat production. This improves highly the yield of extraction compared to the fixed frequency ultrasonic systems.

This study aimed to contribute to coffee chaff valorization and recycling, taking advantage of its potential health properties since its extracts can be applied in products such as food or cosmetic ones. The aspects presented in this work established the potentiality of ultrasound as a green extraction technique to overcome drawbacks that arise from conventional procedures. The major advantages of ultrasound assisted extraction are the less energy and time requirements and no need of organic solvents. The effects that arise from the acoustic cavitation in the medium can also allow the elimination of the sample preparation step. The variables of the process (like electric power and sonication time) have a strong influence on the extraction performance. The numerical results achieved on the model that was prepared and simulated recurring to the Acoustic-Piezoelectric Interaction Module available in the COMSOL software were validated against experimental ones. Furthermore, the developed model can be extrapolated to calculate ultrasonic operation conditions in other different media, allowing the maximization of extraction. Overall, the results presented in this study show that this type of technology can be of high interest to recover antioxidants from coffee chaff or other natural matrices, in a clean and very efficient way. The potential of this technology to extract other type of chemical compounds should also be highlighted. This procedure can thus be of high interest to several industries (*e.g.* food industry, pharmaceutical or cosmetics) since it may replace other extraction methods that use, for instance, environmentally hazard solvents. The wide application potential of this technology can also contribute to attain sustainable issues and circular economy principles.

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