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Polyphenols from coffee (*Coffee arabica L.*) Shell and pulp extracted by ultrasound applying surface response methodology

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ABSTRACT

Coffee (*Coffee arabica L.*) has polyphenols in large quantities and these can be extracted with different technologies including ultrasound (UAE) that can be used in food and medicine. The objective of the research was to find the optimal amplitude (%), amount of ethanol (%) and sonication time to find a large amount of phenolic compounds. The extraction was optimized by a Box-Wilson design using as response variables the centered composite face (CCFC) and polyphenols (TPC). A quadratic equation with $R^2 = 0.989$ was obtained. The optimal parameters were 95 % radiation amplitude, 55 % ethanol concentration and 9 min extraction time. The upgraded espresso strip and mash separate revealed a TPC of 41.16 ± 0.020) mg GAE/g, a DPPH antioxidant performance of 57.02 ± 0.040 mmol Trolox same (TE) and a TEAC antidiabetic ability of 46.86 ± 0.020 mmol Trolox same (TE). The trial results were near the anticipated outcomes, which shows the viability of the models guaranteeing the certainty of the outcomes.

1.Introduction

Espresso is a tropical plant that develops somewhere in the range of 10 and 2000 m above ocean level. Moreover, espresso is a significant business item. In 2017 alone, an annual worldwide creation of 158.93 billion 60 kg packages, in addition, an amount of more than 5 billion dollars was recorded for green coffee beans (Jayeola et al., 2018; Global Espresso Association, 2021). Furthermore, espresso refreshment arranged from cooked ground beans is the most polished off drink subsequent to drinking water and tea (Wongsa, 2019).

The popularity of espresso items is connected with their sensory uniqueness and lovely taste (Pereira et al., 2021). Espresso utilization has expanded around the world. One reason for this persistent increment incorporates the rebranding of espresso as a useful food (Gemechu, et al., 2020). The bioactive parts of coffee consolidate polyphenols such as chlorogenic acids, cafestol, alkaloids such as caffeine, diterpenes such as cafestol and different secondary compounds (Wu, et al., 2021). Ordinary coffee usage has been connected with a healthy profile in buyers in both smartness, diminished danger of disease

improvement (type 2 diabetes, misery, pointless way of acting, threatening development, The results on the gastrointestinal and microorganisms present in the stomach are very good (liver injury and involvement of neural networks and parts of the heart) and the valuable results on the gastrointestinal issue and the microorganisms present in the stomach are very good (Samoggia, 2020).

Espresso creation begins during in-ranch handling, in this step, espresso seeds are gotten with a humidity of somewhere in the range of 10% and 12%, which permits the espresso to be shipped without loss of quality (Haile and Kang, 2019). Coffee by-products start in the processing chain in the field, where coffee seeds are formed by layers among them the skin, tail, etc. (Oliveira, et al., 2021). Coffee by-products account for about half 50% of the total coffee cherry and these residues have always been used for animal feed for the generation of compost among others (Bondam, et al., 2022), Currently these coffee residues as utilitarian trimmings have been a saving grace for the food industry since from these secondary metabolites are extracted to improve the diet of people (Iriondo-DeHond, et al., 2019).

Although it is true that polyphenols are free in different plants and foods, they need to be extracted by various methods, one of them being solid-liquid, which is the most commonly used (Ramón-Gonçalvez, et al., 2019). But this method causes damage to the environment because they make use of solvents such as water, methanol, ethyl acetate, etc., (Hobbi, et al., 2021). Therefore, new environmentally friendly and ecological alternatives are required for the extraction of polyphenols. Ultrasound is a state-of-the-art technology that allows large quantities of bioactives, including polyphenols, to be obtained by means of frequency and extraction time parameters (González-González, et al., 2022). A few creators have successfully applied this technology to recuperate polyphenols from various by-items, for example, grape (Gambacorta et al., 2017), mango peel (Safdar et al., 2017), pomegranate peel (Nag & Sit, 2018), passion fruit rind (Pereira et al., 2021), pitahaya peel (Bhagya Raj & Dash, 2020) and lemon (Papoutsis et al., 2018).

However, there is still no research proposing optimization models of bioactives for large-scale use, so the objective of the research was to propose an optimization model by extracting total polyphenolics (TPC) using ultrasound (UAE) in addition to DPPH radical scavenging activity and Trolox equivalent antioxidant capacity (TEAC) from coffee (*Coffee arabica L.*) husk and pulp by applying the reaction surface analysis.

2.Materials and methods

2.1.Plant material

Coffee husk and pulp were collected between April and May 2019 from the company "Café orgánica" located in Chanchamayo (11º03'00" S; 75º18'15" W), Junín region (Peru). These residues were washed with household water and then dried at 48h at 60°C, crushed, passed through a mesh with a diameter of 500 µm and deposited in plastic bags bags and sealed to prevent the passage of oxygen. To determine the moisture present in the residues, the gravimetric difference was used after drying in an oven at 110°C until there was no reduction in weight.

2.2.Chemicals

Standardssuch as gallicacidmonohydrate, sodium carbonate, Folin-Ciocalteu, 2,2-diphenyl-1-picrylhydrazyl (DPPH), CH3OH (methanol), 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic corrosive (Trolox), 2,2-azino-bis (3-ethylbenzothiazoline-6-sulfonic corrosive) ABTS and K2S2O8 (potassiumpersulfate) wereused. All reagents and solvents were bought from Sigma-Aldrich (Lima, Peru).

2.3.Extracts

The extracts rich in polyphenols were extracted by means of an ultrasound (EAU), Kisker 053275 (Kisker Ultrasonic, Steinfurt, Germany) having a capability of 1.4 L, frequency of 42 kHz and 230 V. For this purpose a solvent called ethanol with a concentration of

50% was used. To obtain each extract, 5 g of sample was taken and 50 mL of solvent was added to an Erlenmeyer flask. This mixture was put in an ultrasonic sonicator taking into account the runs provided by the software (Response Surface). Then, at that point, the sonication is initiated and afterward the arrangements are centrifuged at 400 rpm for 15 min and sifted with a Whatman N° 1 paper. The discovered arrangement is kept in dark jars at 5°C until usage. Preferably, all analyses were carried out. Around the same time of extraction to keep away from changes in the outcomes because of capacity.

2.4.Determination of total phenolic compounds (TPC)

Polyphenols were calculated by Folin-Ciocalteu described by (Singleton & Rossi, 1965). This process was carried out using a UV-Vis spectrophotometer (Hitachi U-2001, Japan). As a first method, 500 uL of Folin-Ciocalteu and 40 uL of concentrate were added to a cup and covered from light with aluminum foil. After the combination rested for 10min, 500 µL of 10% Na2CO3 was added and 10 mL of ultrapure water made up the remainder. Then, at that point, the absorbance values were estimated at 755nm frequency with a clear ready with 40 uL of ultrapure water. Previously, a standard bend with 6 places (0.1; 0.2; 0.4; 0.5; 0.6; and 0.9 mg/mL) was planned. The TPC was communicated in grams of gallic corrosive per 100 g of tests on a dry mass premise (g gallic corrosive reciprocals/100 g live weight).

2.5.Antioxidant activity

To determine the antioxidant capacity, the reference was taken as mentioned by (Brand-Williams et al., 1995) and worked with an absorbance of 515 nm. The 2, 2-diphenyl-1-picrylhydrazyl radical (DPPH) standard was made by adding ethanol (80%) and ultrapure water (20%). Before this, a 6-point standard bend (0.1, 0.2, 0.3, 0.5, 0.6, 0.7 and 0.8 mM) of TROLOX. Subsequent data are counted as reciprocal mmol TROLOX/100g dry matter. Three replicates were used.

2.6.Antioxidant capacity as a function of TROLOX (TEAC)

To compute the worth of the antioxidant capacity by decolorization of the extreme cation ABTS (2,2-azino-bis (3-ethylbenzo-thiazoline-6-sulfonic corrosive)), utilized by (Rice-Evans et al., 1996). The ABTS solution was made by diluting 0.38 g in 10 mL ultrapure water. Absorbance values were reported using a wavelength of 734 nm with the aid of a spectrophotometer. A calibration curve (range 0.1 - 0.8 mM) of 5 mM TROLOX was made beforehand. The data obtained were accounted for in mg TROLOX/100g of dry matter.

2.7.Experimental Design

The experimental runs were carried out in two stages. The first was a Box-Wilson factorial design (central composite design (CCD)). The factors considered were radiation sufficiency (X1), ethanol fixation (X2) and extraction time (X3), making a sum of 17 trials with 8 factorials, 6 beginning stages and 3 recreates at the main issue.

As a subsequent step, the most delegate factors were analyzed to know how to choose the ideal levels of the free factors by method for the RSM and their collaborations. The factor levels are shown in table 1.

Table 1. Variables chosen for the response surface approach and factorial design.

Independent Variables	Level of the coded variable			
	Symbol	low	Middle	High
		-1	0	+1
Radiationamplitude (%)	X_1	90	95	100
Ethanolconcentration (%)	X_2	50	55	60
Extraction time (min)	X_3	8	9	10

2.8.Validation of the model

To validate the model, the adjusted and predicted R^2 was used as a parameter. Likewise, the validity of the model was carried out with an ANVA analysis. It was possible to optimize the independent variables: radiation amplitude, concentration of ethanol and duration of extraction. The ideal circumstances were found by applying the prescient condition produced through the reaction surface methodology. Toward the end, the trial and anticipated values were contrasted with approve the model.

2.9.Statistical analysis

An ANOVA was utilized to notice the meaning of the free factors and their impact on the associations ($p < 0.05$). The model was made valid considering the values of the coefficients of determination (R^2), adjusted (R_{adj}^2), and predicted (R_{Pre}^2), the significance (p), and the lack of fit tests

2.10.Content of total phenolic compounds by HPLC-DAD

To know the exact amount of polyphenols in the optimized extract, the methodology proposed by (Fedosov et al., 2016) was followed. For this, 1.5 mL of extract was degassed using an ultrasound then centrifuged at 5500 rpm. In addition, chromatographic profiling was performed using an HPLC-DAD (Jarco) with a 5um Ultra C18 stainless steel column (250 mm x 4.6 mm) to separate the different acids. Two solvents were utilized for the portable stage, dissolvable A (0.1% formic corrosive in water) and dissolvable B (0.1% formic corrosive in a combination of acetonitrile and methanol). The stream rate was set at 1 mL/min with the accompanying inclination 0 min, 92% An and 8% B; 15 min, 70% An and 30%; 25 min, 0% An and 100 percent B; 33 min, 0% An and 100 percent B; 33.5 min, 92% An and 8% B. To detect polyphenols, 330 nm UV was applied for hydroxycinnamic acids and chlorogenic acids; the injection amount used was 5 μL.

3.Results and discussions

3.1.Determination of the extraction process parameters and adjustment of the model

Of the model Table 2 shows the conditions for generating an ultrasound-assisted extraction as radiation amplitude (X1, %), ethanol concentration (X2, %), and extraction time (X3, minutes) on polyphenol concentration (TPC), antioxidant capacity (DPPH) and TROLOX antioxidant activity (TEAC). The DPPH ranged from 31.22 and 57.02 mM Trolox, the TEAC assay ranged from 27.03 to 46.85 mM Trolox, and the polyphenols ranged from 27.09 to 41.16 mg GAE/g.

The TPCs of coffee by-products ranged from 27.09 to 41.16 mg GAE/g obtained with a 70% ethanol: water mixture. These outcomes are like those found by Affonso et al. (2016) who reported 35.39 ± 3.69 mg GAE/g sample using the same methodology. In contrast, Silva et al. (2020) found higher TPC values (90.95 ± 1.73 mg chlorogenic acid equivalent/g) using only coffee (*Coffea arabica L*) husk with the aid of an ultrasound and a 50:50 v/v ethanol: water mixture. However, the present results differ with that reported by Heeger et al. (2017) who reported a lower TPC (0.2 mg GAE) because they used only coffee husk and water as extraction solvent. Other results, reported by Xu et al. (2015) show slightly higher TPC values (88.34 mg GAE/g sample) because the feedstock used was subcritical water over spent coffee grounds using a solid-liquid ratio (14.1 to 26.3g/L). Likewise, Marcelo-Diaz et al. (2017) obtained much higher TPC values (1429.09 mg GAE/g residue) this because they used high-tech ultrasound with optimization plus (30 to 90) min sonication time with a liquid-to-solid ratio (10 to 40 mL/g) and ethanol concentration (20 to 93.8)%. In contrast, Caballero-Galván et al. (2018) found lower polyphenol values (0.01267 ± 0.031 mg GAE/g sample), this because they used a solvent/solid ratio of 20:1, temperature of 50°C, sonication time of 60 min at 20 kWh. Finally, Palupi & Praptiningsih, (2016) reported slightly low values of phenolic compounds (17.75 mg GAE/g sample) compared to our

results, this can be attributed to the fact that they used conventional solid-liquid extraction.

Table 2. Under various experimental circumstances, a composite face-centered composite design (CCFC) of the three factors, the three levels, and the response observations is used.

Experiments	Extractionconditions			Answers		
	X1	X2	X3	TPC	DPPH	TEAC
	(%)	%(y/v)	Min	mg GAE/g	mM TE	mM TE
1	90	50	8	27.09	33.84	27.03
2	95	55	9	40.64	56.73	45.57
3	95	55	9	40.23	55.94	46.49
4	95	60	9	37.02	49.88	44.15
5	95	55	8	38.28	52.19	42.73
6	100	50	10	31.79	34.92	35.21
7	95	55	10	38.36	53.13	43.91
8	90	50	10	32.26	42.54	36.27
9	100	60	8	39.62	45.55	33.38
10	90	55	9	37.97	50.71	43.08
11	95	50	9	32.43	42.88	34.77
12	100	55	9	40.39	48.23	37.12
13	100	60	10	37.57	42.33	31.33
14	90	60	8	32.15	43.21	35.80
15	90	60	10	32.78	44.60	36.68
16	95	55	9	41.16	57.02	46.85
17	100	50	8	28.88	31.22	30.59

X1 - radiation amplitude, X2 - ethanol concentration, X3 - extraction time, TPC - total phenolic compounds, DPPH - antioxidant activity, TEAC - TROLOX equivalent antioxidant capacity (TE).

From Table 3, it is observed that the most representative variable was radiation amplitude ($P \leq 0.001$) and ethanol concentration ($P \leq 0.001$) which had a significant effect of 99.9%. In contrast, extraction time showed a significant effect of 95%. Also, the interaction for phenolic content of X1X2 was statistically significant with positive effects. In contrast, X1X3 and X2X3 showed a significant effect, nonetheless, with a detrimental impact on TPC output at 99%.A linear effect of ultrasonic radiation frequency on the extraction process was observed achieving an increase in polyphenol content (Medina-Torres et al., 2017).

A higher frequency of radiation produces a greater rupture of the cell walls, which form a greater number of bubbles by cavitation (Dzah et al., 2020). In like manner, ethanol fixation creates changes in the physical properties of the arrangement, like density, solubility and dynamic viscosity, which influence the polyphenol content (Parra-Campos & Ordóñez-Santos, 2019). Finally, sonication time is directly related to ultrasound power, which improves the yield of polyphenols during extraction (Kumar et al., 2021). However, long ultrasound sonication times can destroy the phenolic content by equation 4 (Wang et al., 2020).

$$Fenoles = -993.08X1 + 20.39X1 + 4.10X_2 + 54.41X_3 + 0.05X_1X_2 - 0.24X_1X_3 - 0.12X_2X_3 - 0.21{X_1}^2 - 0.03{X_2}^2 - 1.61{X_3}^2 \quad (1)$$

Trolox comparable antioxidant capacity (TEAC) and DPPH radical scavenging activity

(TEAC) in coffee (*Coffea Arabica L.*) peel and pulp ranged from 31.22 to 57.02 mM trolox and from 27.03 to 46.85 mM trolox, respectively. These results are lower than what was found by Silva et al. (2020) who reported (84.20 ± 0.03 mM TE/g) for DPPH and (97.21 ± 0.01 mM TE/g) for ABTS using only coffee husk as raw material with the aid of a high-tech ultrasound and a 50:50 v/v ethanol: water mixture. Likewise, Silva et al. (2018), reported values of (28.76 ± 0.24 mM TE/g) for DPPH and (16.20 ± 0.07 mM TE/g) for ABTS, these qualities being lower than those announced in the current examination; these qualities found may be connected with the traditional strong fluid extraction strategy involving methanol as extraction dissolvable. In contrast, (Affonso et al., 2016), found higher values (96.21 ± 1.26 mM TE/g) by DPPH when using a residual coffee bean cake with an ethanol: water mixture (70:30 v/v) as extraction solvent. Other results, reported by Xu et al. (2015), showed similar values (38.28 mMol TE/g) for DPPH but higher values for ABTS (88.65 mMol TE/g), using residual ground coffee with a solid-liquid ratio of 14.1 to 26.3 g/L. Likewise, Campos-Vega et al. (2015), showed lower values (0.56 mMol TE/g) for DPPH and (0.13 mMol TE/g) for ABTS, using roasted coffee residues after being consumed as a beverage. Also, Heeger et al. (2017) reported lower values (0.92 mMol TE/g) for ABTS using only coffee husk and water (10 mL) as extraction solvent at 85°C for 15 min. In contrast, Sangta et al. (2021), showed higher values (99.44 ± 0.64 mMol TE/g) for DPPH and (93.13 ± 0.40 mMol TE/g) for ABTS, using Arabica coffee pulp and a mixture of ethanol: water (80:20 v/v) as extraction solvent. Other results, reported by (Kieu Tran et al., 2020), reported lower values (0.60 ± 0.03 mg TE/g) for DPPH and (10.90 ± 0.63 mg TE/g) for ABTS when using wet coffee (*coffeacanephora*) pulp, treated by hot air at 70 °C and a methanol: water (50:50 w/v) mixture as extraction solvent.

Measurable analysis shows that all factors had an impact on DPPH antioxidant capacity and trolox antioxidant activity (TEAC) and accounted for a large difference of 95%. The collaboration terms for phenolic content X1X2 were statistically huge and with constructive outcomes, while X1X3 and X2X3 were critical, yet with adverse consequence on TPC yield at close to 100%.

This is significant for the antioxidant capacity of polyphenols due to the hydrogen content for their stability (Vuolo et al., 2018). Comparable impacts of factors on TEAC and TPC were seen in revealed by (Dzah et al., 2020; Haile and Kang, 2020), which detailed an upward linkage (R=0.98, Sig<0.001) for both total phenols and oxygen uptake capacity (ORAC). Similarly, Kwak et al. (2017), detailed that not entirely set in stone by the 2, 2-diphenyl-1-picryl (DPPH) strategy in concentrates correlated positively with total polyphenol concentration (R=0.97, P 0.002). These data demonstrate that polyphenol concentration increases the antioxidant capacity of DPPH and Trolox to comparable levels (TEAC). Additionally, the amount of radiation given to the UAE had an impact on the extraction of polyphenols more successfully.

In like manner, Zardo et al. (2019), utilized a ultrasound-helped extraction and presumed that the extraction yield relies upon the idea of the plant material. The main effects of coffee cherry deliveries are due to the cell wall breaking down due to cavitation, the lowering of the size of molecules, mass exchange escalation that add to further developed arrival of polyphenol content during extraction (Agarwal et al., 2018).

The outcomes got showed that the ideal ethanol focus was equivalent to 55% for antioxidant capacity (Table 2). Similar result than those reported by (Prakash Maran et al., 2017) where they reported similar concentrations for polyphenol yield and antioxidant capacity of ultrasonically extracted coffee residues. The use of hydroalcoholic ethanol mixtures is suitable for extracting compounds with the principle of different polarities of total phenols and their approval for use in people (Medina-Torres et al., 2017). The performance of DPPH antioxidant exercise and antioxidant activity identical to TROLOX

(TEAC) were extended as a function of time was kept somewhere in the range of 5 and 10 min, however slowly diminished when the time was drawn out (Fig. 2B and 3B). The vast majority of the polyphenols in the burst cells were delivered in the underlying 10-min period since ultrasound improved the delivery. In addition, the quantity of microbubbles made by ultrasound expanded as the time (> 10 min) that harmed the substance in arrangement was drawn out. Thus, the polyphenol structure and antioxidant capacity were destroyed, resulting in its stability because of the ongoing deflation of microbubbles (Dzah et al., 2020).

3.1.Determination and validation of optimum conditions

The Derringer function methodology was applied using the optimal conditions of amplitude radiation (95%), ethanol concentration (55%) and extraction time (9 min) following the condition to think about the trial values and those anticipated through the created experimental equations (Equation 1, 2 and 3).

$$DPPH = -3220.03 + 36.29X_1 + 39.80X_2 + 82.58X_3 + 0.05X_1X_2 - 0.36X_1X_3 - 0.24X_2X_3 - 0.34{X_1}^2 - 0.21{X_2}^2 - 2.17{X_3}^2 \quad (2)$$

$$ABTS = -3221.63 + 33.47X_1 + 42.44X_2 + 72.3X_3 - 0.051X_1X_2 - 0.376X_1X_3 - 0.189\,X_2X_3 - 0.226{X_1}^2 - 0.2\,{X_2}^2 - 1.795X_3 \quad (3)$$

Table 3 shows the outcomes determined by eliminating the non-critical factors to get the fitted coefficients of the model. The Fisher's F test values for TPC, DPPH and TEAC were 71.21, 85.98 and 62.29 respectively, which are viewed as extremely high. The outcomes show a low P < 0.0001 demonstrating that the model is highly critical.

The coefficient of assurance R2 for TPC, DPPH and TEAC were 0.989, 0.991 and 0.939, respectively. These outcomes demonstrate a decent connection among's exploratory and anticipated values. The adjusted R2 for TPC and DPPH was 0.975 and 0.979, respectively, which shows the models give real results. Interestingly, the TEAC introduced a worth of 0.863, yet the absence of fit was not huge. The lower upsides of coefficient of variety found for TCP (1.95%), DPPH (2.45%) and TEAC (5.94%) show a serious level of accuracy in the examinations.

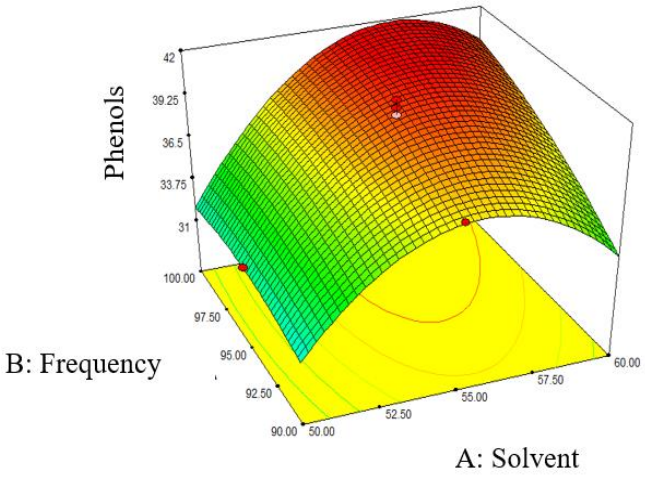
Table 3. ANVA of the grade two model with SR for TCP, DDPH and TEAC.

Totalphenoliccompounds	**Sum ofsquares**	***Df***	**Mean square**	**F Value**	***p*-value Prob> F**	**Prob>*F***
TPC						
1	**2**	**3**	**4**	**5**	**6**	**7**
Model	312.3	9	34.7	71.2	<0.0001	***
***X₁*-Amplitude**	71.8	1	71.2	146.1	<0.0001	***
***X₂*-Ethanol**	25.6	1	25.6	52.5	0.0002	***
***X₃*-Time**	4.6	1	4.6	9.3	0.0185	*
X₁X₂	14.9	1	14.9	30.7	0.0009	***
X₁X₃	11.3	1	11.3	23.3	0.0019	**
X₂X₃	3.0	1	3.0	6.2	0.0413	*
***X₁*^2**	72.6	1	72.6	149.1	< 0.0001	***
***X₂*^2**	1.5	1	1.5	3.0	0.1229	nsp
***X₃*^2**	6.9	1	6.9	14.2	0.0070	**
Residual	3.4	7	0.5			

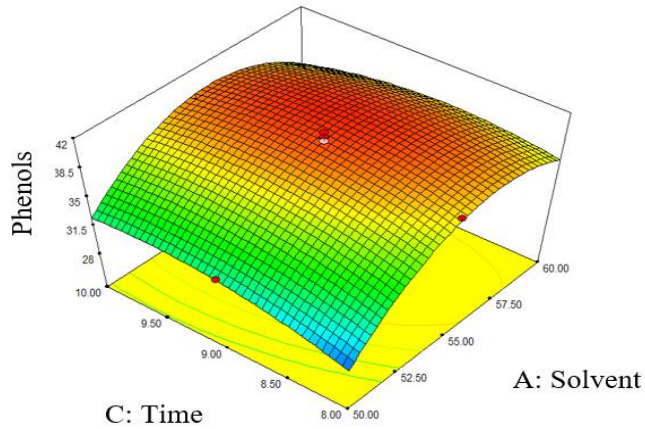
Lackoffit	2.9	5	0.6	2.7	0.29	nsp
Pure Error	0.4	2	0.2			
Cor Total	315.7	16				
Std. Dev.	0.7					
C.V. %	1.9					
R-Squared	0.989					
Adj R-Squared	0.975					
Pred R-Squared	0.937					
DPPH						
Model	991.2	9	110.1	85.9	< 0.0001	***
***X_1*-Amplitude**	162.4	1	161.4	126.0	< 0.0001	***
***X_2*-Ethanol**	15.9	1	15.9	12.5	0.0096	**
***X_3*-Time**	13.3	1	13.3	10.4	0.0147	*
X_1X_2	13.3	1	13.3	10.4	0.0146	*
X_1X_3	25.3	1	25.3	19.8	0.0030	**
X_2X_3	11.6	1	11.6	9.0	0.0198	*
***X_1*^2**	191.4	1	191.4	149.4	< 0.0001	***
***X_2*^2**	76.9	1	76.9	60.1	0.0001	***
***X_3*^2**	12.6	1	12.6	9.8	0.0165	*
Residual	8.9	7	1.3			
Lackoffit	8.3	5	1.7	5.3	0.1650	nsp
Pure Error	0.6	2	0.3			
Std. Dev.	1.1					
C.V. %	2.4					
R-Square	0.991					
Adj R-Square	0.979					
Pred R-Square	0.959					
TEAC						
Model	560.6	9	62.3	62.3	0.0017	**
***X_1*-Amplitude**	30.5	1	30.5	5.9	0.0455	*
***X_2*-Ethanol**	12.6	1	12.6	2.4	0.1630	nsp
***X_3*-Time**	19.2	1	19.2	3.7	0.0955	**
X_1X_2	13.2	1	13.2	2.5	0.1543	nsp
X_1X_3	28.2	1	28.2	5.5	0.0521	*
X_2X_3	7.1	1	7.1	1.4	0.2791	nsp
***X_1*^2**	85.6	1	85.6	16.5	0.0048	**
***X_2*^2**	67.5	1	67.5	13.0	0.0086	**
***X_3*^2**	8.6	1	8.6	1.7	0.2374	nsp
Residual	36.2	7	5.2			

*X1 - radiation amplitude, X2 - ethanol concentration, X3 - time to be able to extract, TPC - Polyphenols, DPPH - antioxidant capacity, TEAC - TROLOX antioxidant activity (TE). Significance: ***P ≤ 0.001, **P ≤ 0.01, *P ≤ 0.05, 0.05 ≤ fcsp ≤ 0.1 (sig. (Rezende et al., 2017)), nsp> 0.1 (no sig.)*

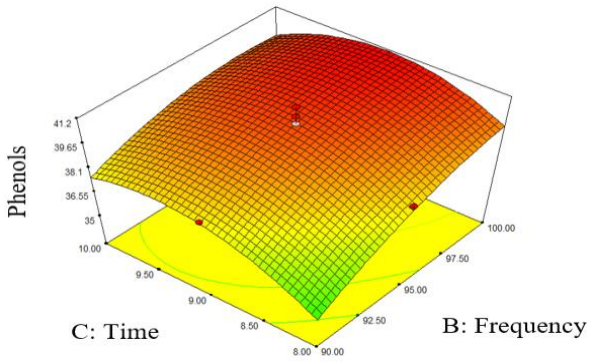
Equations 1, 2, and 3 of the second-request polynomial conditions were displayed as images by 3D response surface (Figure 1, 2 Y 3).



A

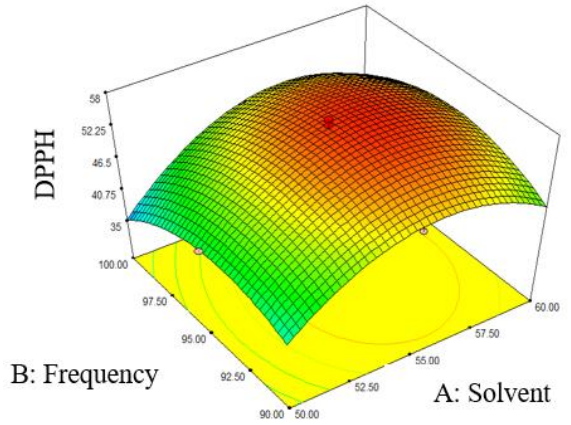


B



C

Figure 1. Response surface plots (3D) of total polyphenols (CPT) as a function of the factors: A - amplitude and ethanol concentration, B - ethanol concentration and extraction time, C - amplitude and extraction time.



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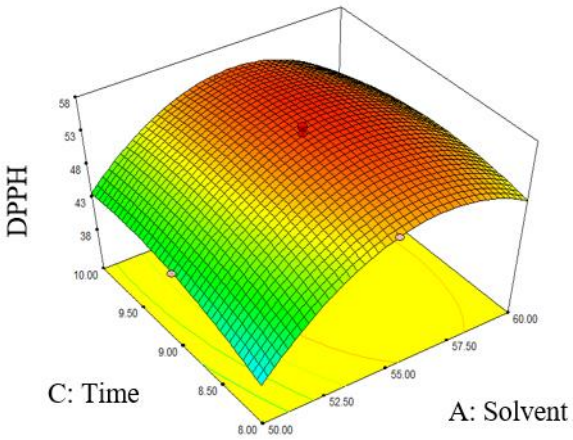

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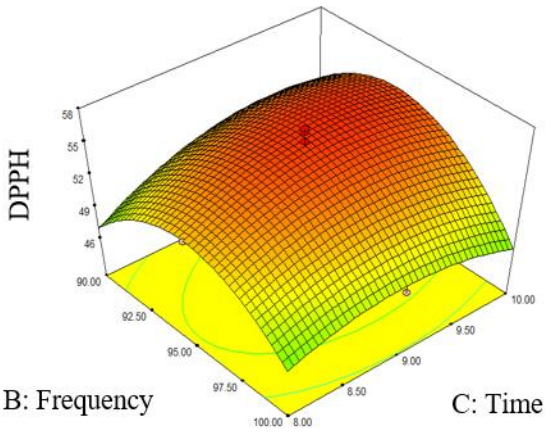
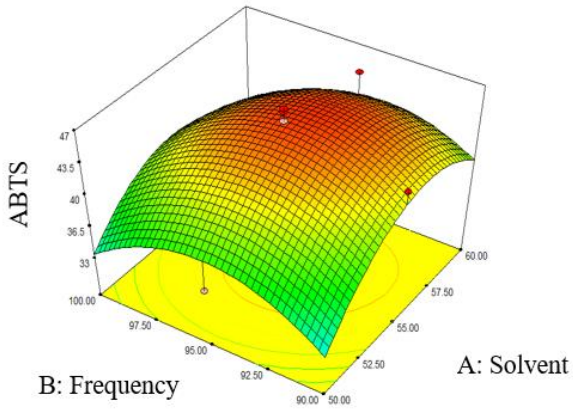
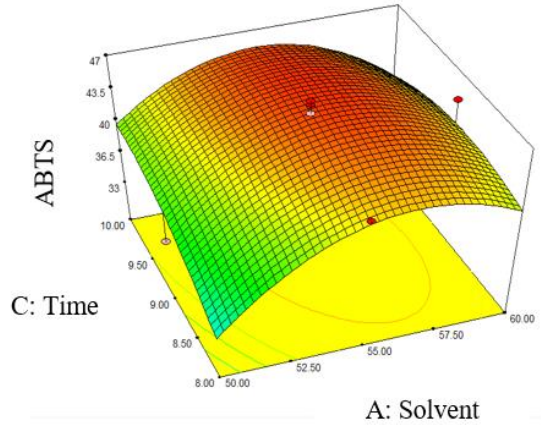


C

Figure 2. Response surface (3D) plots of DPPH radical scavenging activity as a function of factors: A - amplitude and ethanol concentration, B - ethanol concentration and extraction time, C - amplitude and extraction time.



A



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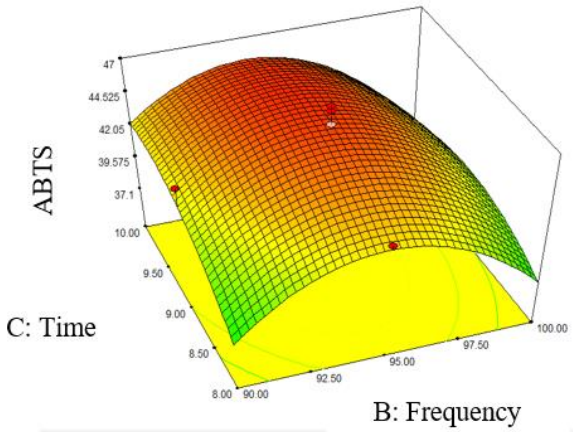

C

Figure 3. Response surface plots (3D) of Trolox equivalent antioxidant capacity (TEAC) as a function of factors: A - amplitude and ethanol concentration, B - ethanol concentration and extraction time, C - amplitude and extraction time.

Table 4 shows the experimental and predicted values under optimum conditions for TPC, DPPH and TEAC. The got upsides of TPC, DPPH and TEAC were contrasted and the anticipated qualities. As noticed, comparable qualities were tracked down between the exploratory and anticipated values, proving that the developed quadratic models are appropriate. The ideal results found were 41.16±0.02 mg gallic acid/g for polyphenols, 57.02 ±0.014 mM trolox equivalent DPPH, and 46.86 ±0.02 mM trolox equivalent for Trolox antioxidant activity (TEAC) (Table 4). The ideal circumstances found were 41.16±0.02 mg gallic acid/g for polyphenols 57.02 ±0.014 mM trolox equivalent DPPH, and 46.86 ±0.02 mM trolox equivalent antioxidant activity (TEAC) (Table 4).

Table 4. Values that were predicted and tested under ideal circumstances.

Optimunlevels	Predictedvalues			Experimental values		
	TPC (mg GAE/g of residue)	DPPH (mM TE)	TEAC (mM TE)	TPC (mg GAE/g of residue)	DPPH (mM TE)	TEAC (mM TE)
X1 = 95 %	41.006	56.84	46.06	41.16±0.02	57.02±0.04	46.86±0.02
X2 = 55 %						
X3 = 9 min						

TPC, DPPH and TEAC are expressed as mean (n = 3) ± standard deviation (S.D.).

3.2.Quantification of polyphenols in the optimum extract by HPLC

Figure 4 and Table 5 present the analytes quantified in the optimized polyphenol extract where basically two derived analytes predominate: hydroxybenzoic (1.49 ± 0.02 mg/mL) and chlorogenic acid (1.41 ± 0.02 mg/mL). These results are similar to those found by Husniati & Oktiani, (2019) who reported close values of chlorogenic acid (0.40 ± 0.02 mg/mL) using organic coffee cherry as raw material based on its degree of maturity with a mixture of (1:250 w/v). In like manner, (Silva et al., 2020) used a water: ethanol combination in a ratio of (50 and 50 v/v) as extraction solvent with the help of an ultrasound, obtained a lower amount of chlorogenic corrosive from coffee husk. On the contrary, Affonso et al. (2016) detailed higher upsides of chlorogenic corrosive when water was utilized as extraction dissolvable in green espresso (Coffea arabica L.). Likewise, Duangjai et al. (2016) presented higher values (14.74 ppm) of chlorogenic acid in fresh coffee pulp. Other results, reported by De Luca et al. (2018) found of lower values of chlorogenic acid (0.27 mg/mL) contained in green coffee beans extracted with a methanol: water ratio (70:30 v/v). In contrast, Macheiner et al. (2019) found higher values (80.3 ± 2.9 mg/g) in green tea infusion, which contains a major source of chlorogenic acids. Also, Ramón-Gonçalves et al. (2019) revealed values lower than 0.4 mg/mL using coffee grounds used with the extraction solvent methanol/water (20:80 v/v). Finally, Kieu Tran et al. (2020) reported lower values of chlorogenic acid determined by HPLC-DAD (0.97 ± 0.18 mg/g) using wet coffee (coffeacanephora) pulp treated with hot air at 70 °C as raw material.

Table 5. Retention time and quantification of hydroxycinnamic and chlorogenic acids evaluated in the optimum polyphenolic extract of coffee (*Coffea arabica L.*) residues.

Peak N°	Compound	Retention time (min)	Concentration (mg/mL)
1	Neochlorogenicacid	7.87	0.04 ± 0.00
2	Chlorogenicacid	10.59	1.41 ± 0.02

3	Hydroxybenzoicderivative[a]	10.77	1.49 ± 0.01
4	Hydroxynnamicderivative[b]	11.68	0.03 ± 0.00
5	Hydroxynnamicderivative[c]	14.13	Trazas
6	Flavonol derivative[d]	14.50	0.03 ± 0.00
7	Hydroxynnamicderivative[b]	16.47	0.02 ± 0.00
8	Hydroxynnamicderivative[b]	21.61	0.01 ± 0.00
9	Acid 4,5 dicafeoilquínico	21.85	0.02 ± 0.00
10	Hydroxynnamicderivative[b]	22.10	Traces
11	Hydroxynnamicderivative[b]	22.45	Traces
12	Hydroxynnamicderivative[b]	23.21	Traces
TOTAL			**3.05 ± 0.04**

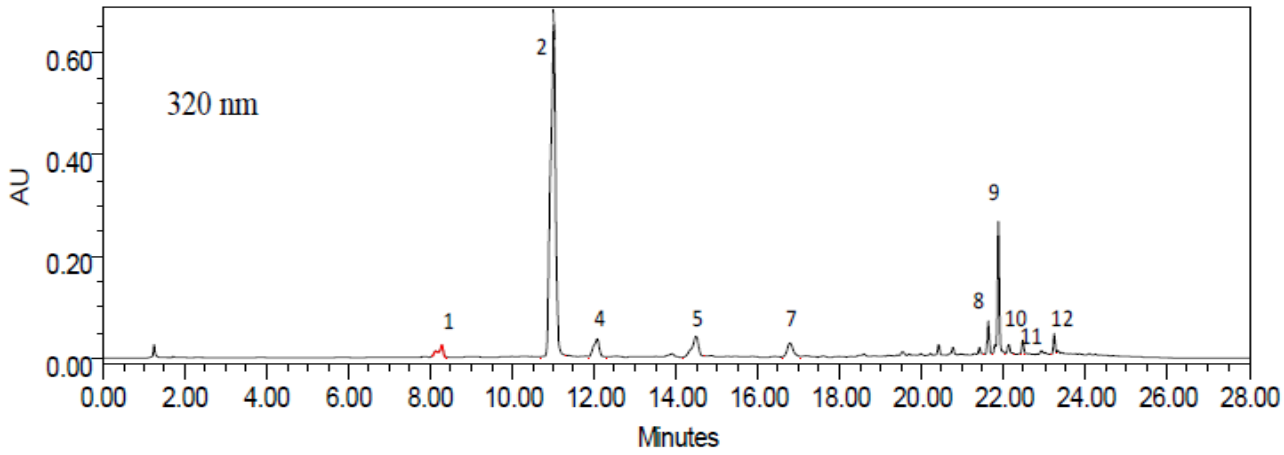

Figure 4. Chromatograms of chlorogenic and hydroxycinnamic acids in the optimum polyphenol extract of coffee (*Coffea arabica L.*) residues.

4.Conclusions

The CCFC design allowed optimization of the independent and interacting variables for the phenolic compound content of coffee (*Coffea arabica L.*) residues. Ethanol concentration, sonication frequency and extraction time were the most influential variables in the ultrasound-assisted extraction. Surface response analysis showed the optimum extraction condition for ethanol concentration (55%), radiation amplitude (95%) and extraction time (9 min) to obtain the maximum polyphenol content. The developed models showed an adjusted R of 0.982, 0.991 and 0.939 for TPC, DPPH and TEAC, respectively. The models were shown accurate since experimental and predicted values behaved similarly. These models guarantee the sufficiency and reliability of the findings. Thus, these results indicate that coffee (*Coffea Arabica L.*) residues are a promising potential wellspring of phenolic intensifies that can be easily recuperated, the most representative analyte being chlorogenic acid.

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Availability of Data

Requests for data can be made to the corresponding author.

Conflicts of Interest

There are no competing interests.

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