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Antioxidative polyphenolics obtained from spent coffee grounds by pressurized liquid extraction

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ABSTRACT

Spent coffee grounds are produced in huge amount by cafeterias, restaurants and industries, which could be a good natural antioxidants resource. In this study, extraction conditions for total phenolics and caffeine from spent coffee grounds were optimized by pressurized liquid extraction (PLE) method with water and ethanol using statistical experimental design. The process was optimized by Plackett–Burman design to screen the most important variables for the extraction of total phenolics and caffeine firstly, and then central composite design (CCD) was performed to obtain the optimum conditions of the preferential factors for extraction. Temperature and weight of sample loading influenced the extraction efficiency of total phenolics and caffeine at 95% level ($P < 0.05$) significantly. Optimized conditions were determined as 195 °C, sample loading 0.8 g. Ten different cultivar coffees were compared under the optimized conditions, and found that total phenolics in the range of 19–26 mg GAE/g DW, DPPH activity and ABTS activity located in 16–38 mg and 10–28 mg VE/g DW, respectively. Caffeine and 5-CQA range 3–9 and 51–201 mg/g DW, respectively. The results showed that these residues processed by PLE possessed potential health benefits and could be used as an ingredient or additive in food and cosmetic industries.

1. Introduction

Coffee is one of the most important crops for beverage, which is distributed in tropic and subtroptic zone. Millions of coffee cups are consumed every day producing spent coffee grounds (SCG) in tons around the world. For example, Starbucks, the biggest coffee chain shop, which has business receipts more than 100 million dollar every year (Tan et al., 2014). In recent years, natural biological components from plants become important research contents as they are functional and healthy as pharmaceutical and food for human. Immediately, coffee bean was found containing plenty biological components such as caffeoylquinic acids (CQA), melanoidins, caffeine and others (Bravo et al., 2012; Ncube et al., 2014), which exhibited many bioactivities, such as antioxidative activity, anti-carcinogenic and anti-mutagenic activity (Ramalakshmi et al., 2009). Phenolics CGA family is well known secondary metabolites in green coffee beans, which contribute to coffee's bitterness with various biological activities, such as: antioxidative activity, protective effect on cardiovascular and reduce brain injury (Lee et al., 2012).

Extraction is one kind of processing, which gets extracts from materials by the effects of pressure, temperature, solvent and other parameters. Extraction technique decides the quality of extracts from plant materials and industrial residues as which decides the content of biological components in extracts. Pressurized liquid extraction (PLE) has been considered as a green and efficiency method for extraction/processing due to its decreased solvent use, light- and oxygen-free environment, and short operating time (Shang et al., 2011). Spent coffee grounds contains many bioactive components although an effective extraction of bioactive compounds can be achieved when prepare production of soluble (or instant) coffee. The components might be extracted with solvents (ethanol, methanol, etc.) with normal extraction methods such as Soxhlet, conventional solid–liquid method and supercritical fluids extraction (Yen et al., 2005; Ramalakshmi et al., 2008, 2009; Mussatto et al., 2011; Andrade et al., 2012).

Statistical tools (i.e., factorial or semi-factorial experiments) are normally used for extraction experiments to optimize the conditions for acquiring the best conditions for targets. These tools have been used in several extraction processes such as immersion, ultrasound assisted

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extraction, and PLE from various plant materials (Devesa et al., 2007; Zhang et al., 2007; Santos et al., 2012; Wang et al., 2013).

This study was designed to obtain extracts containing bioactive components with high efficiency from SCGs by PLE technology. Ten different spent coffee grounds under the optimal extraction conditions were operated to get information on the differences of total phenolics, antioxidative activity and content of active components.

2. Materials and methods

2.1. Chemicals and sample preparations

Ethanol used for extraction was purchased from Daejung (Gyonggi, Korea). All HPLC grade solvents were purchased from Fisher Scientific (Pittsburgh, PA., U.S.A.). The chemicals, Folin–Ciocalteu's reagent, gallic acid, caffeine, 5-caffeoylquinic acid (5-CQA), 2,2-azinobis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), 1,1-diphenyl-2-picrylhydrazyl (DPPH·), potassium persulfate and ascorbic acid were purchased from Sigma-Aldrich Chemicals (St. Louis, Mo., U.S.A.).

Nine Arabica green coffee beans (Brazil Cerrado NY2, Colombia Supremo Medlin, Panama Esmeralda Geisha, Tanzania AA, Hawaiian Kona, Indonesia Mandheling G1, Kenya AA Tatu Specialty, Ethiopia Sidamo G4, Ethiopia Yirgacheffe G1), and one Robusta green coffee bean (Uganda Robusta) were obtained from Brownhaus Coffee Company (Seoul, Korea). Green coffee beans were harvested in 2013-2014. Green coffee beans were roasted at 190~210 using an indirect hot blast roaster (Type R-002BZB, Fuji Royal Coffee Machine Manufacturing Co., Tokyo, Japan). Green coffee beans were roasted, varying the roasting time to produce the medium level of roasted coffee beans. The spent coffee grounds were obtained by Magnifica Automatic Coffee Maker (Delonghi Australia Pty Limited, Prestons, Australia) and were dried in an oven at 60℃ to 15% moisture content and stored for extraction.

2.2. Plackett–Burman design

Important factors of PLE for TP and caffeine extraction were screened by Plackett–Burman design (PBD) as the first optimization step. In consideration on the parameters of PLE, six independent parameters were used as variables: X_1 = temperature (°C), X_2 = concentration of ethanol solvent in water (%), X_3 = static time (min), X_4 = pressure (psi), X_5 = sample loading weight (g) and X_6 = flush (%). In order to determine how the key variables significantly affect extraction efficiency, variables were set at two levels: −1 for low level and +1 for high level, as seen in Table 1. Twelve experimental designs based on PBD from six variables were built by Design-Expert statistical experiment design software 7.0.0 (Sta-Ease Inc., Minneapolis, MN, USA). Analysis of Variance (ANOVA) was performed to screen the effect of each variable on TP and caffeine extraction at a 95% significance level ($P < 0.05$). The design matrix was shown in Table 2.

Table 1
Independent variables and their levels in the statistical analysis of Plackett-Burman design.

Symbols	Parameters	Experimental values		F value	P value[a]
		Low level (−1)	High level (+1)		
X_1	Temperature (°C)	80	160	8.53	0.0315
X_2	Concentration of ethanol solvent (%)	25	75	8.77	0.5091
X_3	Static time (min)	5	20	4.42	0.896
X_4	Pressure (psi)	500	2500	0.74	0.4303
X_5	Weight of sample (g)	0.5	2.5	36.72	0.0018
X_6	Flush (%)	20	100	1.53E−03	0.9703

[a] $^*P_b < 0.05$, $^{**}P_b < 0.01$ by ANOVA analysis.

Table 2
TP and caffeine in the spent coffee grounds from PLE experimental sets designed by CCD.

Run	Independent variables[a]				EE (mg/g)[b]		
	X_1	Code X_1	X_2	Code X_2	TP[c] (mg/g)	Caffeine[d] (mg/g)	ABTS[e] (mg/g)
1	160	1	1	−1	22.64	9.27	17.19
2	160	1	2	1	12.35	4.50	9.43
3	120	0	1.5	0	13.85	5.82	11.07
4	40	−2	1.5	0	7.87	4.92	6.72
5	200	2	1.5	0	16.22	5.87	15.19
6	120	0	0.5	−2	15.38	6.36	13.02
7	120	0	1.5	0	15.07	5.76	12.58
8	120	0	1.5	0	14.77	5.71	11.69
9	80	−1	2	1	9.75	5.31	9.90
10	120	0	1.5	0	13.35	5.75	12.13
11	80	−1	1	−1	14.10	6.40	12.94
12	120	0	1.5	0	14.37	5.98	12.83
13	120	0	2.5	2	9.91	4.09	8.94

[a] X_1 = temperature; X_2 = concentration of ethanol solvent.
[b] Values are expressed as mean ± standard deviation of triplicate experiments.
[c] TP was expressed as milligrams of gallic acid equivalents (GAE) per g dry sample of SCG (mg/g).
[d] Caffeine results were expressed as milligrams of caffeine per g dry samples (mg/g).
[e] ABTS was expressed as milligrams of Vc equivalents (GE) per g dry sample of SCG (mg/g).

2.3. Pressurized liquid extraction

A fully automated ASE 200 system (Dionex, Sunnyvale, CA, USA) was used to perform the PLE process. Brazil SCG was loaded into the stainless steel cell (11 mL); and sea sand (particle size 30–50 mesh, Fisher Chemicals) was loaded before and after loading of the sample to avoid any void spaces. The extraction cell was laid up the carrousel and delivered to the experimental conditions given in Table 2. The extraction process was the same with the previous research (Shang et al., 2011). The extraction solution from PLE was filled to 30 mL with extraction solvent and filtered through a 0.45 μm membrane filter (Agilent Technologies, USA) prior to injection into HPLC system for quantification of active components, TP and antioxidative activity assays.

2.4. Central composite design

Two significant factors, temperature (X_1) and sample loading weight (X_2) from PBD results were selected and set at five levels in a full second-order central composite design (CCD) to optimize the significant variables of the PLE. Considering the energy and efficiency for extraction, other parameters of PLE process were set at: 70% ethanol, 10 min static time, 1500 psi of pressure, and 40% flush volume of the extraction cell. CCD of 13 experiments with five replicates at the center point were employed to optimize the TP and caffeine extraction. The actual levels for X_1 and X_2 were coded at five levels as seen in Table 2. Three-dimensional plots of two factors versus TP and caffeine were carried out by Design-Expert statistical experiment design software.

2.5. Determination of total phenolic content

The total content of phenolic compounds in SCG extracts was determined by using the Folin-Ciocalteu reagent according to the colorimetric method described by Shang et al., 2014. Simply, SCG extract supernatants were diluted (1:1) with distilled water, and then used as sample solutions. Each solution (2 μL) was diluted with 78 μL water, and then mixed with 20 μL Folin-Ciocalteu's reagent for 5 min. Subsequently, 100 μL sodium carbonate solution (20%, w/v) was added. After incubation for 30 min in the dark at room temperature, the absorbance was measured at 730 nm by the Synergy HT-Multi-microplate reader (Bio-Tek Instruments, Winooski, VT, USA). The final result was