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RAPID COMMUNICATION

Phenolic compound extraction from spent coffee grounds for antioxidant recovery

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Abstract−As the popularity of coffee beverage increases, an upsurge in the amount of solid residue, known as spent coffee ground (SCG), is inevitable. Currently, SCG is disposed of in the form of solid waste. However, there is a considerable amount of some valuable compounds including phenolic compounds in SCG. In this work, SCG was adopted as a natural antioxidant source for recovering phenolic compounds by an extraction method. An aqueous ethanol solvent (30% v/v) was used at different conditions of temperature, extraction time, and liquid/solid ratio. The amounts of phenolic compounds were analyzed by the well-known Folin-Ciocalteu method, and values were expressed as the weight of gallic acid equivalent (GAE). The highest extraction yield (87.3%) was reported at the highs of process variables; temperature=60 °C, extraction time=150 min, and liquid/solid ratio=50 mL/g, based on a full factorial experimental design. The statistical Student's t-test applied to the three operating factors revealed that temperature and liquid/solid ratio are more significant than the extraction time. A correlation equation was proposed to quantitatively analyze the effect of the factors on the reduction yield which could be further used to design and optimize the extraction process.

Keywords: Spent Coffee Ground, Phenolic Recover, Extraction, Aqueous Ethanol, Waste Reduction

INTRODUCTION

Coffee is one of the most common global drinks with widespread popularity throughout the world. Cultivated in over 70 countries, primarily in the equatorial regions, coffee is the second largest traded commodity after petroleum. According to the International Coffee Organization (ICO) [1], around 160 million 60-kg bags of green coffee beans were produced worldwide in 2017. Of the several species, the two most commonly and commercially grown species of genus Coffea are Arabica and Robusta. In general, coffee beverages from Arabica are more highly regarded than those from Robusta, since Robusta tends to produce bitter drinks with less flavor than Arabica [2]. For these reasons, about 75% of coffee plants cultivated worldwide is Arabica. Most of Robusta is used in the instant coffee industry for soluble coffee extract [3].

Republic of Korea or South Korea is the sixth largest coffee importing country, and the amount of the imported coffee was around 2.3 million bags in 2017 increased by about 7% from the previous year [1]. In the past, the domestic coffee market of South Korea was focused on instant coffee, but in the 2000s, the coffee market grew rapidly as the number of international and national coffee specialty stores increased.

During the coffee brewing process to produce espresso beverages or manufacture instant coffee, roasted coffee powder is in contact with hot water or steam, and solid residue with high humidity which is known as spent coffee ground (SCG) is generated [4]. Most of the mass of the coffee powder remains in SCG since only a small amount of material is extracted by the brewing process. Although there is a considerable amount of some valuable compounds such as carbohydrates, proteins, and phenolic compounds in SCG, the commercial and industrial value of SCG is not recognized. SCG is usually disposed of in the form of solid waste or simply incinerated. However, SCG is highly pollutant due to its high organic material content [5] and toxic nature compounds such as caffeine, tannins, and polyphenols [6]. Furthermore, methane which is a kind of greenhouse gases, would be produced from landfills. Therefore, disposal of SCG requires controlled management on disposal sites. Similarly, burning of SCG can have negative effect on the atmosphere by emitting greenhouse gases. In recent years, this increasing awareness has called for the development of more suitable methods to reduce waste and protect the environment.

Most research efforts have focused on the direct use of SCG rather than the recovery of value-added compounds by chemical processes. The heat value of SCG (~5,000 kcal/kg) is comparable to coal, and it has been commonly used as fuel of industrial boilers in soluble coffee process [5]. The possibility of using SCG as adsorbent for treating contaminated waters was investigated to remove basic dyes from aqueous solution [7] or heavy metal ions from drinking water [8,9]. In agricultural applications, solid state cultivation was carried out by using SCG as substrates to produce edible mushroom [10], and the use of SCG for lettuce cultivation was studied to find the effect of SCG on carotenoid and chlorophyll content in lettuce [11]. As a raw material for biofuel, SCG was used to produce ethanol by fermentation [12] and biodiesel from extracted oil [13,14].

Traditionally, the beneficial effects of coffee are solely attributed to the most interesting ingredient, caffeine, but it is now acknowledged that there are other healthful compounds. SCG contains large

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amounts of fatty acids, amino acids, polyphenols, minerals, and polysaccharides [15], and the use of SCG as a valuable source of natural antioxidants is a promising, but little explored, option [16].

Polyphenols are important antioxidants used to prevent diseases such as cancer, cardiovascular, inflammation, neuro diseases, and high blood pressure [17]. Polyphenols represent a group of more than 10,000 different compounds containing aromatic rings with hydroxyl groups [18]. Recently, interest in natural phenolic compounds from plants has grown since synthetic antioxidants have several drawbacks. Phenolic compounds in coffee have attracted much attention by virtue of their strong antioxidant and metal-chelating properties. It was revealed that chlorogenic acid (CGA) was the major phenolic component in green coffee beans by analysis using high-performance liquid chromatography [19]. The polyphenols in coffee are partially extracted in beverages; the SCG contains substantial amounts of polyphenols and is considered as a source of natural bioactive compounds. The content of total caffeoylquinic acids in SCG ranges from 2 to 13 mg/g, depending on the species and brewing methods [15].

Extraction is a widely accepted separation process for research as well as industrial purposes, and various approaches have been developed to investigate new materials and applications [20,21]. In practice, extraction techniques contacting solid and liquid are applied to isolate valuable natural compounds from plant materials because of their ease of use, efficiency, and applicability. The separating process of extraction has been widely accepted for obtaining polyphenols from natural sources as well [22]. Various extraction techniques, including simple solid-liquid extraction using organic solvents, microwave–assisted extraction, and supercritical fluid extraction, have been explored to recover polyphenols from SCG with high antioxidant activity [23-25], However, much research on the solid-liquid extraction process is still required because process variables such as time of contact, temperature, pH, and solvent-to-feed ratio are the important parameters affecting the yield of a target substance.

The objective of this work was to investigate extraction conditions for recovering antioxidant phenolic compounds from SCG as a part of the coffee waste management, since the amount of piled up SCG and the expected amount of SCG to be generated demands a prompt solution for the environment. A traditional extraction method contacting solid-liquid was applied with aqueous ethanol solvent. The effect of extraction parameters on polyphenol extraction yield was analyzed based on the obtained experimental results.

MATERIALS AND METHODS

1. Chemicals

An aqueous ethanol solvent was applied to extract phenolic compounds from SCG. Ethanol (purity 99.5%, Sigma-Aldrich) was diluted by distilled deionized water. Gallic acid (or 3,4,5-trihydroxybenzoic acid) (purity 98%, ACRO Organics) was adopted as a phenolic standard required for the quantitative analysis of phenol compounds. The content of phenolic compounds was analyzed by using Folin-Ciocalteu's phenol reagent (Sigma-Aldrich) with sodium carbonate (purity 99.9%, Fisher Chemical) and hydrochloric acid (1 M, Daehwa). All the chemicals were analytical grade and used as purchased without further treatment.

2. SCG Preparation

SCG was recovered from spent coffee capsules which contained coffee ground for automatic espresso machines. The obtained SCG was dried in a heating oven at 60 °C for more than 12 hours to prevent microbial spoilage. Dried SCG to be used for extraction was loaded in plastic bags and stored in the dark at room temperature before use.

3. Analytical Measurements of Total Phenolics

The total phenolic compounds in the extract was determined by a colorimetric method reported in a literature [26], which uses a Folin-Ciocalteu reagent. A more detailed analytical technique description can be found elsewhere [27]. In brief, 1 ml of extraction solution was transferred to 100 ml volumetric flask with HPLC grade water. The solution was mixed with 5 ml of Folin-Ciocalteu's phenol reagent and 15 ml of sodium carbonate solution (20 g in 100 ml) was added to make the volume to exactly 100 ml with HPLC grade water. The absorbance was measured by means of a benchtop UV-Vis spectrophotometer (QDI-1000, CRAIC) and maximum value was read at about 760 nm. A calibration curve was set by using gallic acid standard solutions. Therefore, the content of extract phenolic compounds was expressed as the weight of gallic acid equivalent (GAE). The total phenolic content in SCG was evaluated by a multi-stage extraction, which was carried out until almost all the phenolic compounds were recovered into extract solution.

4. Extraction Procedure

The experiments were carried out using 30% (v/v) aqueous ethanol solvent. According to common experimental design with two levels of three factors, the extraction conditions used in each experiment were set to the 2^3 full factorial design shown in Table 1 with different temperature, extraction time, and solvent/solid ratio. Four replicated experiments at level 0 (see Table 1) were also conducted and, thus, a total of 12 ($=2^3+4$) runs were carried out to evaluate the effect of process variables. The experiments were run in random order. The extractions were performed in batch mode. One gram of prepared SCG and an appropriate amount of solvent were poured into 100-ml screw-top Pyrex flasks, which were maintained during the experiment time in a water bath. The temperature of the water bath was kept within ±0.5 °C from the desired values. Magnetic agitation was continued in the flask during the experiments. After experiments, SCG extract was filtered through 0.22 μm filters and three samples of the liquid were taken for phenolic content analyses.

RESULTS AND DISCUSSION

The total amount of phenolic compound in SCG was determined as 16.52±0.38 mg GAE/g. The result is comparable with the data

Table 1. Extraction conditions and levels of the experimental design

Factors	Code	Level		
		−1	0	1
Temperature (°C)	X_1	20	40	60
Extraction time (min)	X_2	30	90	150
Liquid/Solid ratio (mL/g)	X_3	10	30	50

of a published investigation [28], which also found that almost a third of polyphenolic compounds from roasted and ground coffee remained in SCG.

The greatest extraction yield was achieved at the upper end on the parameters (Run 8 in Table 1), and the least one was obtained at the opposite end (Run 1 in Table 1). They were calculated as 87.3 and 53.3% of the total amount of phenolic compounds in SCG, respectively. As could be generally expected, the extended extraction time, the higher temperature, and the increased liquid/solid ratio enhanced the recovery efficiency. However, there are differences in the extent to which these factors affect the extraction efficiency and, thus, statistical analysis is required for more accurate comparisons.

The effects of the factors on the extraction can be analyzed by viewing the results in a cubical space (Fig. 1). The effects (E) of the main factors can be calculated by the following equation, which is the difference between the average of the highs and that of lows [29]:

$$E_i = \frac{\Sigma Y_{i+}}{n_{i+}} - \frac{\Sigma Y_{i-}}{n_{i-}} \quad (1)$$

where i refers to the main factors (1, 2, and 3 for temperature, extraction time, and liquid/solid ratio, respectively). The Y means the extracted amount and n refers to the number of data points. The results are −4.6, 0.38, and 2.15 for E_1, E_2, and E_3, respectively. The effect of temperature is larger than those of extraction time and liquid/solid ratio.

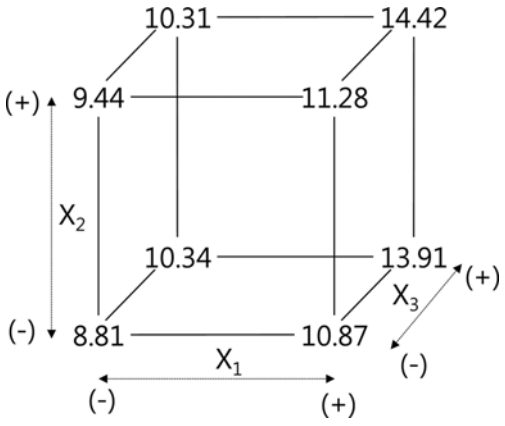

Fig. 1. Cube plot of extracted amount with factors; X_1 (T, temperature), X_2 (t, extraction time), and X_3 (R, liquid/solid ratio).

Table 2. Experimental results on phenolic extraction

Run id.	X_1	X_2	X_3	Y (mg GAE/g)
1	−1	−1	−1	8.81±0.30
2	+1	−1	−1	10.87±0.27
3	−1	+1	−1	9.44±0.16
4	+1	+1	−1	11.28±0.15
5	−1	−1	+1	10.34±0.10
6	+1	−1	+1	13.91±0.12
7	−1	+1	+1	10.31±0.29
8	+1	+1	+1	14.42±0.20
9	0	0	0	12.63±0.13
10	0	0	0	12.98±0.14
11	0	0	0	12.18±0.26
12	0	0	0	12.46±0.38

In addition, the effects caused by interactions of factors should be considered to completely analyze the extraction process. The full-factorial design is suitable for estimating all three two-factor interactions as well as the three-factor interaction. The following polynomial equation was adopted to quantitatively evaluate the effects of three factors and their interactions on the extraction efficiency [30].

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{123} X_1 X_2 X_3 \quad (2)$$

where βs are the coefficients associated with the coded factors, including the two- and three-factor interactions. The factors are made dimensionless and normalized within −1 and +1. Therefore, the coefficients of Eq. (2) can be directly compared with one another. The signs of the coefficients indicate the tendency of the change of the dependent variable (extraction yield) on the respective independent variables. A positive (or negative) value of a coefficient means that the factor associated with the coefficient is in direct (or inverse) proportion to the dependent variable. The coefficients in Eq. (2) were determined by fitting the experimental data and the values are reported in Table 3.

Table 3. Coefficients of Eq. (2) and their t-statistics

Coefficient	Factor	Value	t-Value
β_0	-	11.172	94.47
β_1	Temperature	1.447	12.24
β_2	Time	0.190	1.61
β_3	L/S ratio	1.073	9.07
β_{12}	Temperature - time	0.040	0.34
β_{13}	Temperature - L/S ratio	0.472	4.00
β_{23}	Time - L/S ratio	−0.070	−0.59
β_{123}	Temperature - time - L/S ratio	0.095	0.80

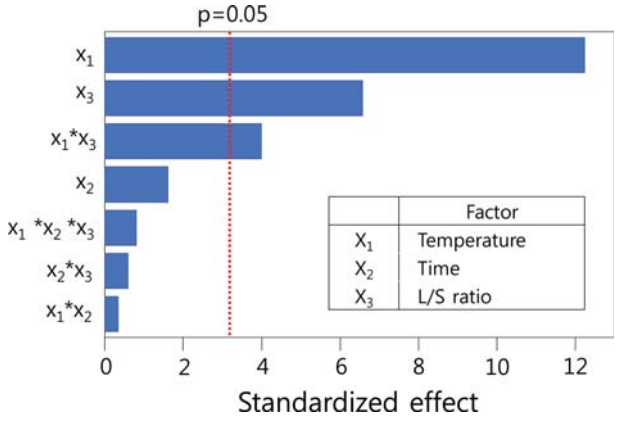

Fig. 2. Pareto chart for the effects of factors and their interactions; X_1=temperature, X_2=extraction time, and X_3=liquid/solid ratio.

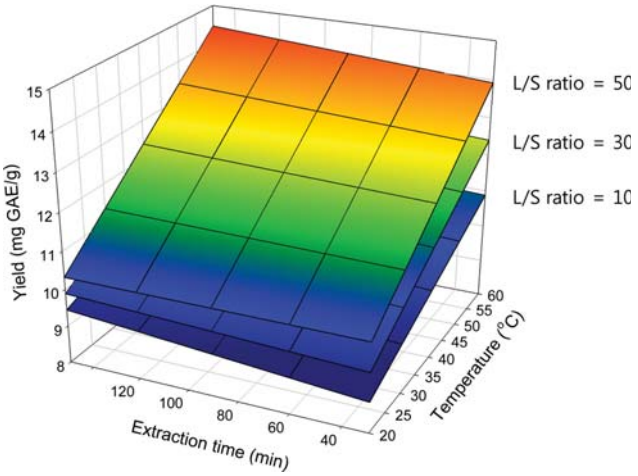

Fig. 3. Extraction yield calculated by a model with uncoded factors.

A Pareto chart is presented as Fig. 2 to analyze the effect of each operating factor on the extraction. In Fig. 2, the standardized effects of each coefficients of Eq. (2) are illustrated as horizontal bars, and the effects of statistical significance can be identified by the vertical line at 95% confidence level ($p<0.05$). As can be noted, two main factors, temperature and L/S ration denoted as X_1 and X_3, respectively, and a two-factor interaction of them, have a considerable influence.

The extraction yield behavior can be visualized in three-dimensional surface plots using the proposed model as presented in Fig. 3. The surfaces describe the variations of the yield as a function of process factors in the investigated range of values. As can be observed, the high temperature was beneficial for the recovery of phenolic compounds, but the limit should be set by considering the vapor pressure of aqueous ethanol solvent. The extraction time is relatively insignificant for the extraction. The result is understood by the general extraction behavior that the extraction rate is decreased with time and the most of extractable materials dissolve into solvent at the early stage of the extraction.

CONCLUSIONS

Solid-liquid extraction technique was applied to obtain phenolic compounds from SCG. An aqueous ethanol solvent (30% v/v) was used with varying process conditions such as temperature, extraction time, and liquid/solid ratio. The amounts of phenolic compounds were analyzed by the well-known Folin-Ciocalteu method, and values were expressed as the weight of gallic acid equivalent (GAE).

The total amount of phenolic compounds in SCG was 16.52± 0.38 mg GAE/g, and the highest extraction yield (87.3%) was reported at the highs of process variables; temperature=60 °C, extraction time=150 min, and liquid/solid ratio=50 mL/g. The Student's t-test applied to the three operating factors revealed that temperature and liquid/solid ratio are more significant than the extraction time. A correlation equation was proposed to quantitatively analyze the effect of the factors on the reduction yield. The coefficients of the equation were determined by regressing the full factorial experimental results. The equation with the coefficients reliably reproduced the experimental results and could be further used to design and optimize the extraction process.

The results of the present study suggest the possibility on the use of SCG as natural phenolic source, and the aqueous ethanol could be applied to recover the phenolic compounds as an environmentally friendly and cost-effective solvent, and the proposed technique of using aqueous ethanol as an effective solvent for phenolic compound extraction from SCG would be commercially realized in the industrial field.

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