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Comparative Analysis of Supercritical Carbon Dioxide and Subcritical Water Extraction for Sabah Coffea Canephora

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Abstract

This work provides a thorough comparative analysis of the green extraction process, viz. supercritical carbon dioxide and subcritical water extraction methods for Sabah *Coffea canephora*. Rigorous experiments were conducted using supercritical carbon dioxide (temperature ranging from 40 to 80 °C and pressure from 10 to 30 MPa) and subcritical water (temperature ranging from 120 to 180 °C with extraction times from 5 to 15 min). The optimum conditions for supercritical carbon dioxide extraction were obtained at 79 °C and 30 MPa at the maximum extract yield (8.549%), total phenolic content (4.563 mg/g gallic acid equivalent), total flavonoid content (0.763 mg/g quercetin equivalent) and antioxidant activity (63.34%). Meanwhile, subcritical water extraction is the best extraction method for *Coffea canephora*, which was obtained optimum conditions at 180 °C and 15 min of extraction time with a maximum extract yield of 44.477%, total phenolic content of 6.481 mg/g gallic acid equivalent, total flavonoid content of 13.816 mg/g quercetin equivalent and 77.586% of antioxidant activity. In conclusion, this understanding contributes to developing optimized conditions for green extraction methods, expanding the potential applications of Sabah *Coffea canephora* in industries, including pharmaceuticals and functional foods.

Keywords: Antioxidant activity; Coffea canephora; Supercritical carbon dioxide extraction; Subcritical water extraction; Total flavonoid content; Total phenolic content

1. Introduction

The coffee industry is primarily influenced by two main types, namely Arabica and Robusta, which have gained global recognition [1]. According to the International Coffee Organization, robusta coffee supplies up to 40% of the world's coffee and is a critical export for many tropical developing countries. The dominant coffee species grown in Malaysia is Robusta coffee (*Coffea canephora*), which thrives in the region's favorable conditions with ideal temperatures ranging from 22 to 28 °C. With rainfall and temperatures projected to change in Southeast Asia, especially Malaysia, climate variability and change is a fundamental threat to the future sustainability of coffee production [2]. In 2022, Malaysia's Ministry of Agriculture reported that the country made a

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significant contribution to the worldwide production of Robusta coffee, with a total yield of 4,150.5 metric tons of coffee crops. Tambunan, Sabah, with an altitude of 750 m, is one of Malaysia's most produced Robusta coffee, with about 936.1 metric tonnes in 2022, based on the Ministry of Agriculture. The coffee variety known as Robusta is distinguished by its elevated levels of caffeine and chlorogenic acids compared to Arabica coffee. These concentrations typically fall within the range of 0.9% to 1.2% for caffeine and 5.5% to 8.0% for chlorogenic acids, as supported by multiple works [3]. To date, there is no work on exploring the chemical composition of Sabah Robusta coffee, which could be a little on the climatic drivers of Robusta coffee bean characteristics.

The exploitation of green coffee beans within the nutraceutical and pharmaceutical industries has garnered increasing interest despite the ongoing dispute about the effects of caffeine and other chemicals in roasted coffee. According to Anissi et al. [4] highlighted the presence of antioxidants and radical scavenging properties in coffee beans. The antioxidant effects of coffee are mainly attributed to chlorogenic acids [5]. However, the high caffeine content in coffee extracts limits their use in supplements due to its impact on the nervous system [6], leading to the frequent need for decaffeination processes. Therefore, proper extraction methods are required to separate these active compounds from the coffee beans.

The introduction of technology has revolutionized the extraction of substances for the food industry. Innovative extraction methods like supercritical fluid extraction (SFE) and subcritical water extraction (SWE) have emerged to meet public demand for chemical-free compounds guided by principles of green chemistry. These advanced techniques aim to address limitations associated with methods [7], [8].

Supercritical carbon dioxide (SC-CO_2), commonly known as carbon dioxide (CO_2), is the solvent used in SFE [9]. CO_2 is preferred due to its favorable characteristics, such as a low critical point (at 7.38 MPa and 31.1°C), chemical inertness, cost-effectiveness, widespread availability, ease of separation from the extracted product, non-toxicity, and well-established status as a solvent [10]. Using SC-CO_2 extraction allows for controlling how well CO_2 dissolves compounds by adjusting parameters. This control enables the production of extracts with purity and selectivity [11]. The distinctive properties of SC-CO_2 are high density, low viscosity, high diffusivity, negligible surface tension, and zero solvent residue, rendering it a novel choice for extraction processes.

SWE is another nonconventional extraction process, an emerging extraction used for extracting bioactive compounds from natural plants. SWE uses water at temperatures above its boiling point but below its critical point (100 to 374 °C) since its excellent solvent properties could achieve efficient extraction. Because water is a solvent, it has economic advantages, reducing production costs [12]. It exhibits immense selectivity in terms of polarity while extracting different molecules. These are vital because SWE's pH can be adjusted by temperature changes, providing exact control over the extraction process and enhancing stability, especially during polyphenol recovery [13]. Thus, SWE can behave similarly to organic solvents like methanol and ethanol. In addition, SWE has a shorter extraction time of 30 minutes because a longer extraction time reduces bioactive compounds' stability, either oxidized or degraded. In line with the increasing demand for eco-conscious practices across various sectors, this sustainable technique offers an alternative to traditional extraction methods [14].

Various extraction methods have been employed to extract compounds from coffee beans. Oliveira et al. [15] used conventional solid-liquid extraction (SLE) with different solvents, including acetone, ethanol, ethyl acetate, hexane, isopropanol, and petroleum ether, on green coffee beans. This yielded a total phenolic content (TPC) ranging from 246.92 to 4048.34 mg GAE/100 g and antioxidant activity (AOA) ranging from 39.18 to 481.98 g/g. Dong et al. [16] applied several extraction techniques, such as ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), ultrasonic/microwave-assisted extraction (UMAE), and pressurized liquid extraction (PLE), to green coffee beans, finding a TPC of 14.40 to 26.33 mg GAE/100 g oil and an AOA of 1.41 to 1.83 µmol Trolox/g oil. Other extraction methods, including hydrothermal [17], enzymatic-assisted extraction [18], and natural deep eutectic solvent extraction (NADES) [19], have also been worked. Most reported work has focused on Arabica coffee, with relatively few works on Robusta coffee.

This work aims to extract green Robusta coffee beans by means of SC-CO_2 and SWE with the maximum value of extract yield, total phenolic content (TPC), total flavonoid content (TFC), and antioxidant activity (AOA). Moreover, this work seeks to identify the most efficient green extraction technique and explore the general chemical composition of Sabah Robusta coffee.

2. Materials and Methods

2.1. Green Robusta Coffee Beans Preparation

The sun-dried fruit of robusta coffee was obtained from a plantation in Tambunan, Sabah, Malaysia. The beans were separated from the fruits. Grinding and sieving were also done to produce an average 300 µm particle size. After that, the ground beans were packed in a vacuum-sealed container and then placed inside a freezer maintained at -20 °C for preservation purposes to help maintain their fresh nature.

2.2. Chemicals

Kras Instrument and Services (Johor, Malaysia) provided carbon dioxide and CO_2 with a purity of 99.99%. The analysis utilized analytical-grade chemicals obtained from VNK Supply and Services company, such as sodium carbonate, Na_2CO_3, gallic acid, $C_7H_6O_5$, quercetin, $C_{15}H_{10}O_7$, aluminum chloride, $AlCl_3$, 2,2'-diphenyl-1-picrylhydrazyl (DPPH), and methanol, CH_3OH.

2.3. Supercritical Carbon Dioxide (SC-CO_2) Extraction

The approach for extraction of SC-CO_2 was conducted using the methodology described in the earlier work conducted by Abdul Aziz et al. [20], with some modifications. The experimental apparatus consisted of a 15 mL extraction vessel with dimensions of 1.4 cm in internal diameter and 33 cm in length. Additionally, a CO_2 pump (Supercritical 24, Japan), a back-pressure regulator (Jasco BP 2080, Japan) with a restrictor valve, and an oven (Memmert, Germany) were involved in the extraction process. Afterward, around 3 ± 0.05 g of ground coffee beans were measured and transferred into the extraction vessel, which was subsequently placed in the oven. The back-pressure regulator's heater (Jasco BP 2080, Japan) was adjusted to a temperature of 50 °C. The liquid carbon dioxide (CO_2) with a purity of 99.99% was initially cooled to a temperature of 6 °C and then kept at a consistent flow rate of 5 mL/min. The extraction process was carried out within a temperature range of 40 to 80 °C and a pressure range of 10 to 30 MPa, followed by 3 hours. Samples were collected and recorded at 15-minute intervals after extraction, and the total extract yield was measured by a weight balance (Kern & Sohn, Germany). The extracts were stored in a freezer (Libherr EFL 3505, USA) at a temperature of -20°C for subsequent analysis.

2.4. Subcritical Water Extraction (SWE)

The SWE procedure was followed according to the method presented in previous work by Rizkiyah et al. [21], with some modifications. The setting of the apparatus consisted of a 25 mL extraction vessel (internal dimensions of 1.4 cm diameter and 13 cm length). This comprised a SWE system, which included a water pump (Eldex Opto Metering Pump, USA), a back pressure regulator (Swagelok, USA), and an oven (Memmert, Germany). The extraction involved several parameters, including temperatures from 120 to 180 °C and 5 to 15 minutes extraction times. First, a weight measurement of 3 ± 0.05 g of ground coffee beans was taken and then transferred into the extraction vessel. Before starting the extraction process, the extraction vessel and water were heated to attain a uniform temperature throughout the process. Distilled water was pumped through at a rate of 5 mL/min while maintaining constant pressure at 10 MPa was achieved through control valve adjustment. The oven temperature varied accordingly, and test conditions were changed. Then, the obtained extract was subsequently dried using a vacuum evaporator at a temperature of 60 °C. The extract was stored in a refrigerator (Liebherr EFL 3505, USA) at a temperature of -20 °C to avoid any potential deterioration.

2.5. Total Phenolic Content (TPC) Analysis

TPC of the Robusta coffee bean extracts was determined using the Folin-Ciocalteu (FC) method, as described by Elhassaneen et al. [22]. The initial step involved diluting the extracts in methanol, resulting in a solution prepared with 0.14 mg/mL concentration. Then, 4 mL of distilled water and 1 mL of FC reagent were added to this solution. The solution was allowed to stand at room temperature for 5 minutes without disturbing it. After that, 2.5 mL of 7% sodium carbonate solution was introduced and allowed to sit for 30 minutes. The solution's absorbance was measured at 765 nm, and the calibration curve was obtained at $Y = 0.0231X + 0.066$, with an R^2 value of 0.8077 using gallic acid as the standard. The TPC was quantified by measuring in milligrams of gallic acid equivalents (GAE) per gram of the sample (mg/g).

2.6. Total Flavonoid Content (TFC) Analysis

The TFC was determined using the aluminum chloride (III) ($AlCl_3$) method by Loizzo et al. [23]. 2 mL of the extract solution was combined with 2 mL of $AlCl_3$ solution at 2% concentration. After allowing the mixture to settle for about 15 minutes, the absorbance was quantified at a wavelength of 510 nm. The calibration curve was prepared with quercetin as standard and had an equation $Y = 0.0231X + 0.066$, with an R^2 value of 0.8077. The TFC is expressed in milligrams per gram of sample (mg/g), equivalent to quercetin (QE).

2.7. Antioxidant Activity (AOA) Analysis

The AOA of Robusta green coffee beans was analyzed using the 2,2'-diphenyl-1-picrylhydrazyl (DPPH) assay method, as described by Tepsongkroh et al. [24]. To start with, a solution was formulated by dissolving 4 mg of DPPH powder in methanol to obtain a concentration of 0.1 mM. The final mixture was then carefully mixed and covered with aluminum foil to reduce the effect of light on it. In the centrifuge, 2 mL of the sample was mixed with DPPH solution (0.1 mM) that had been generated. The mixture was then placed in a dark at room temperature for 30 minutes. The UV-Vis spectrophotometer measured the absorption (Abs) at a wavelength of 517 nm. The Abs value obtained was later converted into AOA percentage (AOA%) via the equation (1) below:

$$AOA\% = \left[\frac{Abs_{control} - Abs_{sample}}{Abs_{control}}\right] \times 100\% \quad (1)$$

Where $Abs_{control}$ is an absorbance for a blank sample and

Abs_{sample} is the absorbance value of the sample.

2.8. Multiple Optimization via Design Expert Software

This work employed an experimental design to optimize two fundamental variables for SC-CO_2 and SWE extraction. SC-CO_2 conditions were exerted by a pressure range of 10 to 30 MPa and temperature range of 40 to 80 °C, while SWE was performed at a temperature range of 120 to 180 °C and extraction time ranging from 5 to 15 minutes for SWE. The main objective of the work was to attain the optimum response of extract yield, TPC, TFC, and AOA. The experimental design of the green Robusta coffee beans for both SC-CO_2 extraction and SWE was conducted using a Central Composite Design (CCD) with a face-centered model (α=1). The parameters were established at three coded levels, namely -1 (minimum), 0 (midpoint), and +1 (maximum). The acquired outcomes were examined utilizing Design Expert Software version 13. Table 1 and Table 2 illustrate the experimental methodology employed for extracting SC-CO_2 and SWE of the Robusta coffee beans, respectively.

Table 1. Design of experiment for SC-CO_2 extraction

T	P	Y (%)	TPC (mg/g GAE)	TFC (mg/g QE)	AOA (%)
0	0	9.093	6.092	0.776	62.320
0	0	10.543	2.987	0.760	59.490
0	+1	9.693	3.082	0.797	59.730
+1	-1	2.270	2.411	0.762	61.650
0	-1	5.940	5.934	0.765	61.370
-1	+1	10.120	4.017	0.744	49.310
-1	0	4.913	5.685	0.753	60.790
+1	0	5.117	7.968	0.735	59.410
0	0	6.287	5.879	0.722	61.060
0	0	2.713	2.913	0.744	61.680
0	0	4.443	3.957	0.812	58.440
-1	-1	4.460	6.198	0.801	59.610
+1	+1	8.613	2.195	0.753	63.340

T is temperature, and P is pressure.

Table 2. Design of experiment for SWE

T	t	Yield (%)	TPC (mg/g GAE)	TFC (mg/g QE)	AOA (%)
-1	-1	10.543	4.459	13.241	84.578
0	0	14.033	2.165	13.138	80.971
0	0	19.877	2.525	13.093	70.224
+1	-1	37.440	1.414	13.404	82.470
0	0	21.883	1.558	13.108	86.890
-1	0	12.513	1.385	13.241	81.555
+1	0	32.447	3.896	13.449	90.549
-1	+1	27.560	7.273	13.404	64.558
0	-1	15.797	3.117	13.182	56.860
+1	+1	44.290	7.172	13.404	62.932
0	0	21.793	4.848	15.923	78.887
0	0	28.113	1.212	15.390	88.110
0	+1	34.383	1.732	15.627	80.030

T is temperature, and t is extraction time.

The operating parameters for both methods of extraction of green Robusta coffee beans were optimized using response surface methodology (RSM). The RSM model, also known as the regression equation, integrates linear and quadratic variables, along with interaction terms, to derive the first and second-order polynomial equations using the experimental data, as described in the following equation (2) :

$$Y = B_0 + \sum_{i=1}^{k} B_i X_i + \sum_{i=1}^{k} B_{ii} X_i^2 + \sum_i \sum_j B_{ij} X_i X_j \quad (2)$$

Y is the predicted response, B_0 is a constant, B_i, B_{ii}, B_{ij} are the coefficients for linearity, X_i and X_j are independent variables. The F-test was employed to evaluate the statistical testing of the model, aiming to determine the mathematical correlation between the input and output parameters. The calculated F-value must exceed the tabulated F-value in order to indicate a meaningful association [25]. The model's significance was assessed using analysis of variance (ANOVA) on the correlation factor, R^2.

3. Results and Discussion

3.1. Optimization of SC-CO_2 Extraction

Table 1 shows the results of extract yield, TPC, TFC, and AOA of Robusta coffee beans extracted using SC-CO_2 extraction. The maximum values for each response were observed to be around 10.543% for extract yield, 7.968 mg/g GAE of TPC, 0.812 mg/g QE of TFC, and 63.34% of AOA. Conversely, the minimum values for each response were approximately 2.27% for extract yield, 2.195 mg/g GAE of TPC, 0.722 mg/g QE of TFC, and 49.31% of AOA. The graphs in Fig. 1 illustrate the relationship between temperature and pressure on the extract yield, TPC, TFC, and AOA of Robusta coffee bean extract.

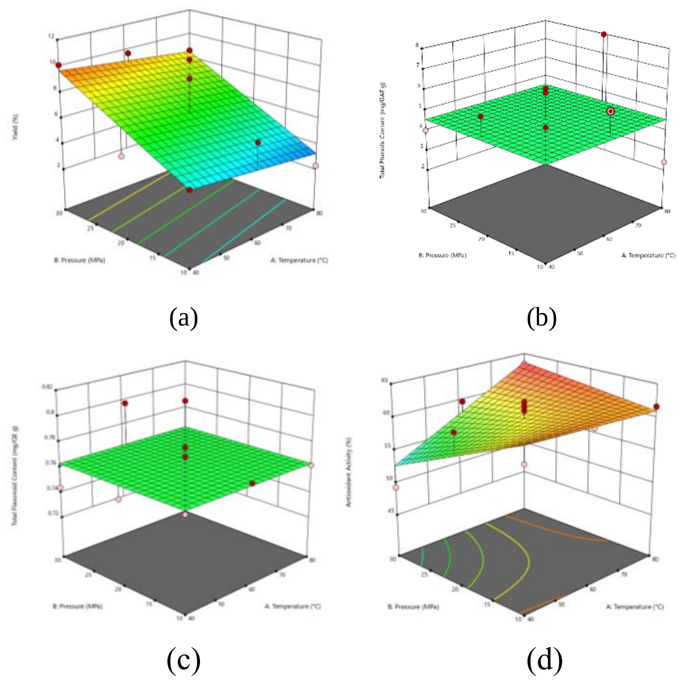

Figure 1. 3D response surface graph on the effect of temperature and pressure in SC-CO_2 extraction of Robusta coffee beans on (a) extract yield, (b) TPC, (c) TFC, and (d) AOA

The 3D response surface graph demonstrates that temperature and pressure significantly influenced the extract yield and AOA of Robusta coffee beans. However, alterations in temperature and pressure have no impact on the values of TPC and TFC. An increase in pressure from 10 to 30 MPa results in an increase in the extract yield. This is due to the rise in solvent density, which in turn enhances the solvation power of CO_2. Conversely, the AOA diminishes as pressure increases because the viscosity of CO_2 increases and the diffusivity reduces, resulting in a decrease in the interaction between the solvent and the sample. The temperature effect decreased the extract yield and AOA as the temperature increased from 40 to 80 °C. This temperature rise could potentially destroy the chemical compounds present in Robusta coffee beans.

An analysis of variance (ANOVA) was conducted to examine the significant response regarding the extract yield and AOA, as shown in Table 3. An analysis using the F-test was performed for both reactions. The computed F-value for the extract yield was 4.11, and the tabulated F-value at a 95% confidence level was 4.1028 ($F_c > F_t$). Therefore, a notable correlation exists between the extraction parameters of SC-CO_2 and the yield of the extract. In addition, the AOA exhibited a noteworthy correlation with the SC-CO_2 extraction parameters, with F_c (5.01) surpassing F_t (3.8625).

Pattaraprachyakul et al. [26] demonstrated a comparable pattern of the inconsequential influence of process parameters on SC-CO2 extraction. The authors examined the impact of pressure, temperature, and ethanol concentration on the extraction of coffee oil. The work findings indicate that the temperature has a negligible effect on the output of coffee oil. In contrast, the extraction of wasted coffee grounds using SC-CO2 demonstrated a lack of substantial impact from temperature (ranging from 40 to 70 °C) and pressure (ranging from 14 to 19 MPa) on the concentration of diterpenes [27].

The extracted yield and AOA exhibited a computed correlation coefficient (R^2) of 45.1% and 46.8%, respectively. The aforementioned values suggest that the model did not effectively capture the experimental data and that the regression models could not accurately account for the observed changes. The regression models for extract yield and AOA in the SC-CO_2 extraction of Robusta coffee bean extract are represented by (3) and (4), respectively. The optimal operational parameters for the extraction of SC-CO_2 from Robusta coffee bean extract were determined to be 79 °C and 30 MPa. These conditions resulted in the highest recorded values for extract yield (10.5%), TPC (4.563 mg/GAE g), TFC (0.763 mg/QE g), and AOA (63.34%).

Table 3. ANOVA table for the SC-CO_2 extraction of Robusta coffee beans

	SS	df	MS	F-value	R^2
Extract Yield					
Regression	43.41	2	21.70	4.11	0.4510
Residual	52.84	10	5.28		
Total	96.24	12			
AOA					
Regression	89.42	3	29.81	5.01	0.468
Residual	53.58	9	5.95		
Total	143.0	12			

SS is the sum of squares, df is degree of freedom, MS is mean squares as equations (3 and 4).

$$Yield = 2.972 - 0.029T + 0.263P \quad (3)$$

$$AOA = 73.918 - 0.177T - 1.070P + 0.015TP \quad (4)$$

3.2. Optimization of SWE

The extract yield, TPC, TFC, and AOA of Robusta coffee bean extract were optimized under SWE conditions, similar to SC-CO_2 extraction, as shown in Table 2. Approximately 44.29%, 7.273 mg/g GAE, 15.923 mg/g QE, and 90.549% of extract yield, TPC, TFC, and AOA were achieved as the highest responses, respectively. The extract yields for TPC, TFC, and AOA were found to be approximately 10.543%, 1.212 mg/g GAE, 13.093 mg/g QE, and 56.86%, respectively, indicating the lowest response. Fig. 2 depicts the three-dimensional response surface graph illustrating the relationship between temperature and extraction time of SWE on the extract derived from Robusta coffee beans.

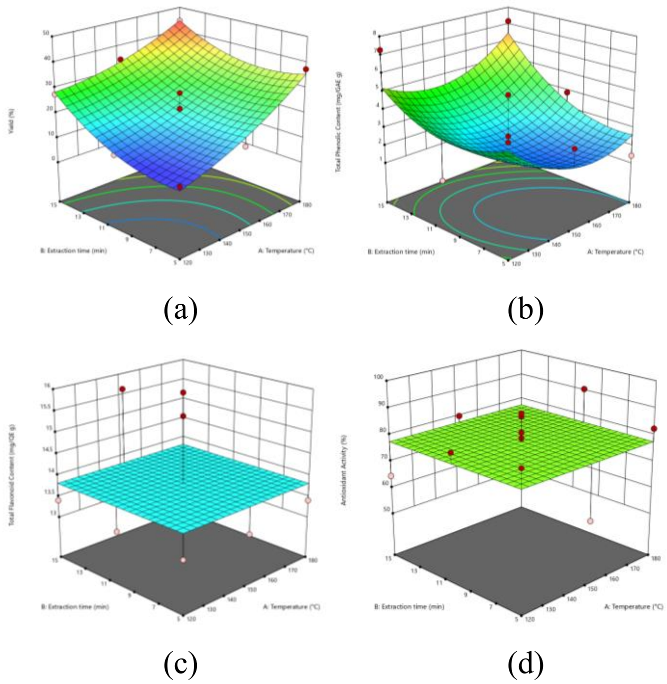

Figure 2. 3D surface graph on the effect of temperature and extraction time of SWE on the Robusta coffee beans extract of (a) extract yield, (b) TPC, (c) TFC, and (d) AOA.

The 3D response surface graph demonstrates that the temperature and extraction time of SWE substantially influences both the extract yield and TPC of Robusta coffee bean extract. Nevertheless, temperature and extraction time alterations have no impact on the TFC and AOA values. Raising the temperature can modify the dielectric constant of water, thereby enhancing its solubility comparable to that of organic solvents, resulting in an enhanced yield of extraction. Elevating the water temperature will result in a reduction in viscosity and surface tension, hence facilitating the infiltration of water into the coffee beans sample. As depicted in Fig. 2, extending the extraction time from 5 to 15 minutes increases the extract yield and TPC. Within a span of 15 minutes, the solubility of phenolic compounds escalated as a result of heightened hydrogen bond degradation at elevated temperatures. Nevertheless, a lengthier extraction period can diminish the concentration of phenolic chemicals since they undergo chemical instability through oxidation or degradation [28].

An ANOVA was conducted to examine the significant response, as indicated in Table 4, for the extract yield and TPC. The F-value obtained for the response of extract yield was 13.03, but the F-value computed at a 95% confidence level was 3.9715 ($F_c > F_t$). Therefore, a notable correlation exists between the extraction parameters of temperature and extraction time in SWE concerning the yield of the extract. The extracted yield was found to have a coefficient of correlation (R^2) of 90.3%. These values show that the extract yield model accurately represented the experimental data and that the regression models could account for the variations. However, the F-test conducted to assess the response of TPC to the extraction condition of SWE did not yield statistically significant results, as the magnitude of F_c (1.23) was smaller than that of F_t (3.9715). The regression model for extract yield in SWE of Robusta coffee bean extract is represented by (5). The optimal operating conditions for SWE on the extract of Robusta coffee beans were 180 °C and 15 minutes. These conditions resulted in the highest performance, with an extract yield of 44.477%, a TPC concentration of 6.481 mg/GAE g, a TFC concentration of 13.816 mg/QE g, and an AOA concentration of 77.586%.

Xu et al. [29] have similarly documented insignificant characteristics of SWE in the extraction of spent coffee ground extracts. It was determined by the authors that temperature has a considerable impact on the TPC but does not have a significant effect on the AOA. Meanwhile, the extraction time has no significant impact on TPC. However, it does have a considerable impact on AOA. The competing impact of the conditions on each response is obviously shown in the work.

$$Yield = 26.816 - 0.492T - 0.566t - 0.017Tt + 0.003T^2 + 0.226t^2 \quad (5)$$

Table 4. ANOVA table for the SWE of Robusta coffee beans extract

	SS	df	MS	F-value	R^2
Extract Yield					
Regression	1175.09	5	235.02	13.03	0.903
Residual	126.22	7	18.03		
Total	1301.31	12			
TPC					
Regression	25.20	5	5.04	1.23	0.468
Residual	28.67	7	4.10		
Total	53.87	12			

SS is sum of squares, df is degree of freedom, MS is mean squares.

4. Conclusions

In conclusion, SWE extraction technique gave a highest extract yield (44.477%), TPC (6.481 mg/GAE g), TFC (13.816 mg/QE g), and AOA (77.586%) compared with SC-CO_2 extraction with the extract yield (10.5%), TPC (4.563 mg/GAE g), TFC (0.763 mg/QE g), and AOA (63.34%). SWE showed a significant comparison between SC-CO_2 even though the operating temperature is very high, about 180 °C, but shorter extraction time. Unique properties of water in SWE, such as dielectric constant and pH, help improve the extraction of Robusta coffee beans. However, both SWE and SC-CO_2 do not leave behind any organic solvent residues, which implies that it is possible to use the extracted coffee directly for food, pharmaceutical, and nutraceutical applications, providing opportunities for its application in various commercial domains as eco-friendly products of such kind of coffee extract.

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Abbreviations

AOA	Antioxidant activity
ANOVA	Analysis of variance
R^2	Correlation of coefficient
df	Degree of freedom
FC	Folin-Ciocalteu
GAE	Gallic acid equivalent
MS	Mean squares
P	Pressure
QE	Quercetin equivalent
SWE	Subcritical water extraction
SS	Sum of squares
SC-CO_2	Supercritical carbon dioxide
T	Temperature
t	Time
TFC	Total flavonoid content
TPC	Total phenolic content

Conflict of interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

Author Contribution Statement

Khurun Hizar S.A. and Yangun C.E.: Proposed the problem statement.
Mahat N.S. and Ahmad Zaini M.A.: Developed the methodology.
Roslan J., Kobun R., and Ronie M.E.: Performed and verified the analytical methods.
Putra N.R., Abdul Razak A.H., and Ruslan M.S.H. performed and validated the optimization process.
Mohammad Ridwan N. and Mamat H.: Performed a review and editing of the manuscript.
Abdul Aziz A.H.: Supervised the work on the concept and funding of the work.

References

[1] O. Gligor *et al.*, “The Effect of Extraction Methods on Phytochemicals and Biological Activities of Green Coffee Beans Extracts,” *Plants*, vol. 12, no. 4, pp. 712, Jan. 2023, doi: https://doi.org/10.3390/plants12040712.

[2] J. Kath *et al.*, “Not so robust: Robusta coffee production is highly sensitive to temperature,” *Glob. Change Biol.*, vol. 26, no. 6, pp. 3677-3688, Jun. 2020, doi: https://doi.org/10.1111/gcb.15097.

[3] E. Olechno, A. Puścion-Jakubik, M. E. Zujko, and K. Socha, “Influence of Various Factors on Caffeine Content in Coffee Brews,” *Foods*, vol. 10, no. 6, p. 1208, May 2021, doi: https://doi.org/10.3390/foods10061208.

[4] J. Anissi, M. El Hassouni, A. Ouardaoui, and K. Sendide, "A comparative study of the antioxidant scavenging activity of green tea, black tea and coffee extracts: A kinetic approach," *Food Chem.*, vol. 150, pp. 438–447, May 2014, doi: https://doi.org/10.1016/j.foodchem.2013.11.009.

[5] S. A. Abrahão, R. G. F. A. Pereira, S. M. da S. Duarte, A. R. Lima, D. J. Alvarenga, and E. B. Ferreira, "Compostos bioativos e atividade antioxidante do café (Coffea arabica L.)," *Ciênc. Agrotec.*, vol. 34, no. 2, pp. 414–420, Apr. 2010, doi: https://doi.org/10.1590/s1413-70542010000200020.

[6] O. Babova, A. Occhipinti, and M. E. Maffei, "Chemical partitioning and antioxidant capacity of green coffee (Coffea arabica and Coffea canephora) of different geographical origin," *Phytochem.*, vol. 123, pp. 33–39, Mar. 2016, doi: https://doi.org/10.1016/j.phytochem.2016.01.016.

[7] C. Picot-Allain, M. F. Mahomoodally, G. Ak, and G. Zengin, "Conventional versus green extraction techniques — a comparative perspective," *Curr. Opin. Food Sci.*, vol. 40, pp. 144–156, Aug. 2021, doi: https://doi.org/10.1016/j.cofs.2021.02.009.

[8] M. Garcia-Vaquero, G. Rajauria, and B. Tiwari, "Conventional extraction techniques: Solvent extraction," in *Sustainable Seaweed Technologies*, Elsevier, 2020, ch. 7, pp. 171–189, doi: https://doi.org/10.1016/b978-0-12-817943-7.00006-8.

[9] A. H. Abdul Aziz *et al.*, "Solubility of Rosmarinic Acid in Supercritical Carbon Dioxide Extraction from Orthosiphon stamineus Leaves," *ChemEngineering*, vol. 6, no. 4, pp. 59, Aug. 2022, doi: https://doi.org/10.3390/chemengineering6040059.

[10] N. R. Putra *et al.*, "Procyanidin and proanthocyanidin extraction from Arachis hypogaea skins by using supercritical carbon dioxide: Optimization and modeling," *J. Food Process. Preserv.*, vol. 45, no. 9, pp. e15689, Sep. 2021, doi: https://doi.org/10.1111/jfpp.15689.

[11] N. H. Arsad *et al.*, "Solubilization of eugenol from Piper betle leaves to supercritical carbon dioxide: Experimental and modelling," *Results Eng.*, vol. 17, pp. 100914, Mar. 2023, doi: https://doi.org/10.1016/j.rineng.2023.100914.

[12] A. S. Zaini *et al.*, "Comparison of Alliin Recovery from Allium sativum L. Using Soxhlet Extraction and Subcritical Water Extraction," *ChemEngineering*, vol. 6, no. 5, pp. 73, Sep. 2022, doi: https://doi.org/10.3390/chemengineering6050073.

[13] D. Lachos-Perez *et al.*, "Subcritical water extraction of flavanones from defatted orange peel," *J. Supercrit. Fluids*, vol. 138, pp. 7–16, Aug. 2018, doi: https://doi.org/10.1016/j.supflu.2018.03.015.

[14] C. Cannavacciuolo, S. Pagliari, R. Celano, L. Campone, L. Rastrelli, "Critical analysis of green extraction techniques used for botanicals: Trends, priorities, and optimization strategies-A review," *TrAC, Trends Anal. Chem.*, vol. 173, pp. 117627, Apr. 2024, doi: https://doi.org/10.1016/j.trac.2024.117627.

[15] É. R. Oliveira, R. F. Silva, P. R. Santos, F. Queiroz, "Potential of alternative solvents to extract biologically active compounds from green coffee beans and its residue from the oil industry," *Food Bioprod. Process.*, vol. 115, pp. 47-58, May 2019, doi: https://doi.org/10.1016/j.fbp.2019.02.005.

[16] W. Dong *et al.*, "Comparison of the effect of extraction methods on the quality of green coffee oil from Arabica coffee beans: Lipid yield, fatty acid composition, bioactive components, and antioxidant activity," *Ultrason. Sonochem.*, vol. 74, pp. 105578, Jun. 2021, doi: https://doi.org/10.1016/j.ultsonch.2021.105578.

[17] T. Sato *et al.*, "Hydrothermal extraction of antioxidant compounds from green coffee beans and decomposition kinetics of 3-o-caffeoylquinic acid," *Ind. Eng. Chem. Res.*, vol. 57, no. 22, pp. 7624-7632, May 2018, doi: https://doi.org/10.1021/acs.iecr.8b00821.

[18] B. Prandi *et al.*, "Extraction and chemical characterization of functional phenols and proteins from coffee (Coffea arabica) by-products," *Biomolecules*, vol. 11, no. 11, pp. 1571, Oct. 2021, doi https://doi.org/10.3390/biom11111571.

[19] E. Yuniarti, F. C. Saputri, A. Mun'Im, "Natural Deep Eutectic Solvent Extraction and Evaluation of Caffeine and Chlorogenic Acid from Green Coffee Beans of Coffea canephora," *Indian J. Pharm. Sci.*, vol. 81, no. 6, pp. 1062-1069, Nov. 2019, doi: https://doi.org/10.36468/pharmaceutical-sciences.604.

[20] A. H. Abdul Aziz, N. R. Putra, L. Nian Yian, N. A. Mohd Rasidek, and M. A. Che Yunus, "Parametric and kinetic study of supercritical carbon dioxide extraction on sinensetin from Orthosiphon stamineus Benth. leaves," *Sep. Sci. Technol.*, vol. 57, no. 3, pp. 444–453, May 2021, doi: https://doi.org/10.1080/01496395.2021.1917613.

[21] D. N. Rizkiyah *et al.*, "Optimization of Red Pigment Anthocyanin Recovery from Hibiscus sabdariffa by Subcritical Water Extraction," *Processes*, vol. 10, no. 12, p. 2635, Dec. 2022, doi: https://doi.org/10.3390/pr10122635.

[22] Y. Elhassaneen, S. El-Waseef, N. Fathy, and S. Sayed Ahmed, "Bioactive Compounds and Antioxidant Potential of Food Industry By-products in Egypt," *Am. J. Food Nutr.*, vol. 4, no. 1, pp. 1–7, Feb. 2016, doi: https://doi.org/10.12691/ajfn-4-1-1.

[23] M. R. Loizzo *et al.*, "The Influence of Ultrafiltration of Citrus limon L. Burm. Cv Femminello Comune Juice on Its Chemical Composition and Antioxidant and Hypoglycemic Properties," *Antioxidants*, vol. 8, no. 1, pp. 23, Jan. 2019, doi: https://doi.org/10.3390/antiox8010023.

[24] B. Tepsongkroh, K. Jangchud, and G. Trakoontivakorn, "Antioxidant properties and selected phenolic acids of five different tray-dried and freeze-dried mushrooms using methanol and hot water extraction," *J. Food Meas. Charact.*, vol. 13, pp. 3097–3105, Aug. 2019, doi: https://doi.org/10.1007/s11694-019-00232-2.

[25] N. R. Putra *et al.*, "Optimization and solubilization of interest compounds from roselle in subcritical ethanol extraction (SEE)," *Alex. Eng. J.*, vol. 65, pp. 59-74, Feb. 2023, doi: https://doi.org/10.1016/j.aej.2022.09.037.

[26] W. Pattaraprachyakul, R. Sawangkeaw, S. Ngamprasertsith, and I. Suppavorasatit, "Optimization of Coffee Oil Extraction from Defective Beans Using a Supercritical Carbon Dioxide Technique: Its Effect on Volatile Aroma Components," *Foods*, vol. 12, no. 13, pp. 2515, Jan. 2023, doi: https://doi.org/10.3390/foods12132515.

[27] H. M. A. Barbosa, M. M. R. de Melo, M. A. Coimbra, C. P. Passos, and C. M. Silva, "Optimization of the supercritical fluid coextraction of oil and diterpenes from spent coffee grounds using experimental design and response surface methodology," *J. Supercrit. Fluids*, vol. 85, pp. 165–172, Jan. 2014, doi: https://doi.org/10.1016/j.supflu.2013.11.011.

[28] W. Mikucka, M. Zielinska, K. Bulkowska, I. Witonska, "Subcritical water extraction of bioactive phenolic compounds from distillery stillage," *J. Environ. Manage.*, Vol. 318, pp. 115548, Sep 2022, doi: https://doi.org/10.1016/j.jenvman.2022.115548.

[29] H. Xu, W. Wang, X. Liu, F. Yuan, and Y. Gao, "Antioxidative phenolics obtained from spent coffee grounds (Coffea arabica L.) by subcritical water extraction," *Ind. Crops Prod.*, vol. 76, pp. 946–954, Dec. 2015, doi: https://doi.org/10.1016/j.indcrop.2015.07.054.