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Hydrodistillation of Coffee By-Products to Recover of Bioactive Compounds: the Spent Coffee Ground and Coffee Silvers Skin Case-Study

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Coffee industry produces large amounts of residues, mainly associated with roasting and consumption. Among these residues, coffee silver skin (CSS) and spent coffee grounds (SCG) are the most generated. In recent years, CSS and SCG have been object of increasing attention by researchers to study their possible reuses. The growing interest in the use of natural compounds has made it possible to study these residues as a source of bioactive compounds such as caffeine (CAF) and chlorogenic acids (CGAs). Nowadays, a great variety of techniques can be used for recovering of bioactive compounds from biomasses as raw materials. However, we need to evaluate more sustainable methodologies that, for instance, do not require the use of organic solvents. Accordingly, water is often accounted as the greenest solvent because of the its non-harmful character for both environment and human health. In our study, hydrodistillation (HD) process has been tested as a green method to recover and differentiate valuable compounds from SCG and CSS. HD is a variant of steam distillation in which the matrix is in direct contact with the solvent. In the present experiment, water has been chosen as a green solvent. Basically, the HD process allows merging the autohydrolysis extraction in mild temperature conditions (about 100°C), inside the boiler, with the continuous recovery of a condensate fraction with potentially different composition than the water-extract inside the boiler. In our experiment three matrices have been used, SCG, CSS and coffee powder as benchmark. Two fractions have been obtained, the condensate fraction, recovered in condenser column, and the water-extract, i.e. a phytocomplex recovered inside boiler. The two fractions of each processed matrix were characterized and then differentiated by chemical and physical analyses (total dissolved solids, electrical conductivity, oxidation-reduction potential and pH). Furthermore, compositional profiles were analyzed with HPLC technique, confirming the presence of compounds of interest such as caffeine and chlorogenic acids. In conclusion, the HD process allowed us to obtain two different fractions with different chemical and physical features, depending on the coffee residues (SCG and CSS). This could allow for a wider spectrum of possible uses of coffee residues available to the interested industry.

1. Introduction

Each year, coffee production results in millions of tons of residue. Spent coffee grounds (SCG) and silverskin (CSS) are produced in the largest quantities. SCG are the solid residue obtained during the processing of roasted coffee powder with hot water or steam to prepare instant coffee and other beverages (Ballesteros et al., 2017). CSS is a by-product of the coffee roasting process and consists of the innermost skin of the coffee bean. During roasting, a variety of chemical and structural changes occur which lead to the separation of this tegument from the beans (Zuorro te al., 2013).
Currently, these residues have no specific use, and are mostly considered as waste that is released into the environment. The toxic character of this organic matter, in particular SCG, makes it a significant source of pollution, and incorrect management can have negative effects (Mussatto et al., 2011a). In recent years,

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growing concern about the need to carefully manage these residues has encouraged researchers to study possible reuses. In particular, increasing demand from the pharmaceutical and food industries has led to the study of agro-food residues as a source of natural compounds. Recent studies have shown that both SCG (Ballesteros et al., 2014a) and CSS (Costa et al., 2014) are a natural source of bioactive compounds, and could be considered as new functional ingredients (Borrelli et al., 2004). Caffeine (CAF) and chlorogenic acids (CGAs) have attracted particular interest due to their significant benefits. There are currently several techniques for recovering bioactive compounds from biomass. Of these, organic solvents are widely used for their high extraction capacity, however, they are highly polluting for the environment (Conde and Mussatto, 2016). In recent years, several studies have investigated the use of water as an extraction solvent. For example, Bravo et al. (2013) recovered bioactive compounds from SCG with good results in terms of efficiency and convenience. In another study, Ballasteros et al. (2017) reported the use of an autohydrolysis technique to recover bioactive compounds from SCG with water as the extraction solvent. Similarly, an earlier study demonstrated that autohydrolysis, under mild reaction conditions, is a technology with great potential to recover phenolic compounds from SCG (Conde and Mussatto, 2016). A recent study has evaluated various operative variables, and identified the optimal conditions for phytochemical recovery at mild temperatures (100–110°C), obtaining extracts with concentrations of phytochemicals comparable to those of other studies (Angeloni et al., 2019). Costa et al. (2014) reported that the use of a hydroalcoholic mixture (50% water: 50% ethanol) was the best compromise between the recovery of bioactive compounds and a sustainable CSS extraction process. In the present study, we test hydrodistillation (HD) extraction as an environmentally friendly alternative method to recover valuable compounds from SCG and CSS. HD is a variant of steam distillation, in which the matrix is in direct contact with the solvent. This conventional technology is generally used for the extraction of secondary metabolites from plants. The process uses steam as an extraction agent to vaporize volatile compounds in the matrix. Subsequently, the mixture of steam and volatile compounds is collected and condensed again in the boiler in a recirculation circuit. When water is used as a solvent, the matrix being processed probably undergoes autohydrolysis under mild temperature conditions (about 100° C). Thus, it can simultaneously obtain two, potentially different fractions: the condensate fraction, recovered in the condenser column, and the water-extract, i.e. a phytocomplex that is recovered inside the boiler. The aim of this study was to use HD extraction to recover bioactive compounds from SCG and CSS in order to obtain two fractions that could be characterized and differentiated. The applied technique can be considered as green, because it exploits resources and operations with a reduced environmental impact, First, it uses water as an alternative solvent; second, it produces co-products instead of waste (Chemat et al., 2012) creating residues that can be used by other industries.

2. Materials and method

2.1 Materials

Three varieties (Kaapi Royal AA, India; Santos, Brasile; Yirgacheffe gr.2, Ethiopia) of CSS and coffee powder were provided by a local company in Florence (Torrefazione Piansa, Firenze), while SCG were produced using a conventional bar machine (gs3, LaMarzocco, Italy). Coffee powder was studied as a benchmark. Before extraction, moisture was measured for each matrix with a conventional drying oven (Heraeus Function Line, Thermo Scientific Heraeus, USA) for 24h at 104°C (2.2 % Coffee Powder; 64.3 % SCG; 7.9 % CSS). Then, dry matrices were extracted using a stainless-steel essential oil distiller (Spring 12 l, Albrigi Luigi Store, Italy), equipped with its own induction plate (Konig HA-INDUC-11). The internal solvent was commercial, deionized water, while tap water was used for the cooling circuit.

2.2 Methods

The three matrices (CSS, SCG and Coffee Powder) were extracted by HD. Three replicates were conducted for each matrix for each variety, making a total of 27 extractions. Extractions were conducted at 1200 W for 30 min. The solid/ liquid ratio differed for the three matrices (1/3 for Coffee Powder; 1/15 for SCG and 1/50 for CSS) due to their different overall mass. After each extraction, two fractions were obtained: the condensate fraction, recovered from the condenser column, and the water-extract, recovered from inside the boiler. We term the sample obtained from the condensate fraction the hydrolate (HY), while the water extract is termed the phytocomplex (PT). Then, all samples were filtered to separate solids and liquids. Finally, physical and chemical analyses were performed.

2.3 Physical and chemical analyses

Each sample obtained was analyzed. TDS (total dissolved solids) were measured with a VST Lab Coffee III digital refractometer (VST, USA). The laser refractometer records the intensity of the light reflected by the solution under examination, directly returning a TDS% value (Angeloni et al., 2019b). Electrical conductivity

was measured with a platinum cell conductivity probe sensor (Vernier, USA), and data were collected with LabQuest 2 software (Vernier, USA). Oxidation-reduction potential (ORP) was measured using an ORP sensor (Vernier, USA), here again, data were collected with LabQuest 2 software (Vernier, USA). Finally, a digital pH meter (GLP 21, Crison Instruments, Spain) was used to determine pH (Angeloni et al., 2019b).

2.3.1 Measurement of caffeine with UV–vis spectrophotometry

Caffeine characterization was determined following the procedure given in Angeloni et al. (2019a). Absorbance was measured by UV–vis spectrophotometry at room temperature at a wavelength of 273 nm. Once the calibration curve had been determined (five points) and the regression coefficient had been calculated (y = 16.82x + 3.35 and R^2 = 0.97). For this, 0.1 mL of Coffee Powder extract was dissolved in 100 mL deionized water; while 0.1 ml of CSS and SCG extract were dissolved in 5 mL deionized water in order to obtain two dilutions: 1:1000 for Coffee Powder extract and 1:50 for CSS and SCG extract.

2.3.2 Total phenolic compounds by Folin–Ciocalteu (FC) assay

For all samples, Folin–Ciocalteu reducing capacity was evaluated following the method given in Bravo et al. (2013). In this study, only Coffee Powder PT samples were diluted before analysis (at 1:10 in demineralized water), while all other samples were analyzed without further processing. A volume of 500 µL Folin–Ciocalteu reagent was added to a mixture containing 100 µL extracted sample (as-is or diluted) and 7.9 mL demineralized water. After 2 min, 1.5 mL of a 7.5% sodium carbonate solution was added. Next, the sample was incubated in darkness at room temperature for 90 min. Absorbance was measured at 765 nm in a Lambda 25 UV–vis spectrophotometer (Perkin–Elmer Instruments). Gallic acid (GA) was used as the reference, and results were expressed as milligrams of GA equivalent per gram of SCG, CSS and Coffee Powder dry matter (mg GAE/g SCG dm)

2.3.3 High-performance liquid chromatography with diode-array detector analysis

Samples were centrifuged at 12000 rpm for 5 min and diluted 1:10 with water before high-performance liquid chromatography with diode-array detector (HPLC-DAD) analysis. HPLC was carried out using an Agilent HP 1100 system equipped with an auto sampler, column heater module and quaternary pump, coupled to a DAD all from Agilent Technologies (Palo Alto, CA, USA). An Infinity Lab 150 mm × 3 mm i.d., 2.7 m Poroshell 120, EC-C18 column (Agilent Technologies) was used, equipped with a pre-column of the same phase, and maintained at room temperature. Injection volume was 5 L. The elution method was performed at a flow rate of 0.4 mL/min using water at pH 3.2 by formic acid (solvent A) and acetonitrile (solvent B). All solvents were Chromasolv™ for HPLC grade (Sigma Aldrich S.R.L.). The multistep linear solvent gradient technique is described in detail in other work (Angeloni et al., 2019a). Starting at 95% A, and going up to 10% A, over 24 min (the total analysis time) UV–vis spectra were recorded in the range 220–600 nm. Chromatograms were registered at 330 nm for CGA, and 278 nm for caffeine. Caffeine and CGA were identified by comparing their retention times and UV–vis spectra to those of the respective standard, when possible, or with published data otherwise (Angeloni et al., 2019a). CGA was evaluated by HPLC-DAD using a five-point calibration curve (5-caffeoyl-quinic acid, purity 99%) (Extrasynthèse, Genay, France) at 330 nm (0–1.315 _g; R^2= 0.9988), and caffeine content was determined by HPLC-DAD using a five-point calibration curve from Extrasynthèse (purity 95%) at 278 nm (0–0.34 _g; R^2 = 0.9999).

2.3.4 Measurement of VOCs

As reported Angeloni, et al. (2020), a photoionization sensor (PID) was used to detect volatile organic compounds (VOCs) of each sample. 10 gr of SCG and CSS and 1 gr of coffee powder were introduced in a container of 100 ml (Sarsted, Germany). Then, each sample was placed on a digital magnetic stirrer with heating plate (M2-D PRO ARGOlab, Italy) at 300 rpm and 35 ° C. Thus, VOCs were measured with PID sensor (Alphasense, United Kingdom) for a time of 1800 s. Then, all data were collected with a graphical interface LabQuest2 (Vernier, USA) and analyzed.

2.4 Statistical analyses

Conventional analysis of variance (ANOVA) was used to compare means determined for each fraction obtained. The tested factors were considered significantly different at $p < 0.05$. All statistical analyses were performed using R software (version 3.6.0 for Windows). In cases where the F-test was significant at the $p \leq 0.05$ level, multiple pairwise comparisons of group means were checked for significance using the *post hoc* Tukey Honest Significance Difference test ($p < 0.05$).

3. Results and discussion

3.1 Physical and chemical analyses

Physical and chemical characteristics of all samples were analyzed in order to characterize the two fractions (PT and HY) of the three extracted matrices (Coffee Powder, SCG, and CSS). Significant differences are reported. TDS, electrical conductivity, ORP, and pH results are reported in Table1. Regarding TDS, as expected, values were highest for both Coffee Powder fractions (PT and HY), with values of 6.95 and 3.14 %, respectively, and a significant difference was found between them. No significant differences were found between the other samples. Regarding electrical conductivity, highest values were obtained for the Coffee Powder PT fraction (2590.38 µS/cm), followed by the respective HY fraction (1230.00 µS/cm). Lower values were obtained for SCG PT and HY fractions (488.97 and 204.84 µS/cm) and CSS (557.26 and 204.84 µS/cm). With respect to the ORP analysis, no significant differences were found for Coffee Powder PT and HY fractions. However, significant differences were observed for the two fractions of SCG and CSS. Specifically, higher values were found for SCG and CSS PT (343.87 and 366.09 mV), and lower values for the respective HY (278.78 and 306.78 mV). Finally, turning to pH, significant differences were found for Coffee Powder PT and HY fractions, while no significant differences were found for the two fractions of SCG and CSS.

Table 1: Physical and chemical characteristics of the two fractions: phytocomplex (PT) and hydrolate (HY) and the three matrices: Coffee Powder, spent coffee grounds (SCG) and coffee silverskin (CSS). Means and standard deviation are reported. Letters (a-e) indicate statistically significant differences at the TukeyHSD post-hoc test ($p < 0.05$).

Fraction	Matrix	TDS (%)	Electrical conductivity (µS/cm)	ORP (mV)	pH
PT	Coffee powder	6.95 ± 5.12 [a]	2590.38 ± 1826.82 [a]	254.12 ± 40.05 [b]	4.31 ±0.85 [c]
PT	SCG	0.39 ± 0.28 [c]	488.97 ± 378.70 [c]	343.87 ± 120.05 [a]	4.78 ± 0.16 [b]
PT	CSS	0.25 ± 0.17 [c]	557.26 ± 497.34 [c]	366.09 ± 91.42 [a]	5.42 ± 0.84 [a]
HY	Coffee powder	3.14 ± 4.60 [b]	1230.00 ± 1645.48 [b]	246.08 ± 47.49 [b]	3.66 ± 0.86 [d]
HY	SCG	0.17 ± 0.24 [c]	204.84 ± 277.58 [e]	278.78 ± 105.00 [b]	4.79 ± 0.49 [b]
HY	CSS	0.15 ± 0.22 [c]	285.74 ± 426.99 [d]	306.78 ± 82.87 [b]	5.93 ± 0.96 [a]

3.2 Caffeine and total phenolic compounds

Concentrations of caffeine and total phenolic compounds are reported in Table 2. All samples were analyzed and interactions between the two fractions (PT and HY), and the three matrices (Coffee Powder, SCG and CSS) are reported. In general, caffeine content in the PT fraction was higher than the HY fraction. In particular, caffeine content in the Coffee Powder PT fraction (3.42 mg/g) was significantly higher than the respective HY (3.19 mg/g), and the same trend was found for the other matrices studied. Highest content was obtained for SCG (3.21 mg/g) and CSS PT fractions (2.90 mg/g), while lowest yields were obtained for CSS (2.49 mg/g) and SCG fractions (2.30 mg/g) HY, respectively. Regarding the PT fraction, our results agree with the current literature (Bravo et al., 2012; Cruz et al., 2012; Angeloni et al., 2019a) who reported 3.59 mg/g, 4.52 mg/g and 3.10 ±1.98 mg/g for SCG, respectively. Panusa et al. (2017) reported a maximum of 3.75 mg/g for CSS. Unsurprisingly, caffeine concentration in CSS was lower than in SCG. The high concentration of bioactive compounds in SCG is presumably due to the Espresso coffee technique that was used. Concerning phenolic compounds, significant differences were found between the two fractions (PT and HY) and the three matrices (Coffee Powder, SCG and CSS). In general, highest concentrations were obtained for PT with respect to HY. The highest value was obtained for SCG PT (21.47 mg/GAE g), while the lowest value was obtained for CSS PT (5.43 mg/GAE g). Yields were lowest for HY and, in this case, no significant differences were measured for SCG (1.96 mg/ GAE g) and CSS (2.11 mg/ GAE g). Concerning the PT fraction, Panusa et al. (2013) reported a maximum yield of 17.43 mg/g of phenolic compounds for SCG using water as an extraction agent. Lower concentrations were reported by Ballesteros et al. (2014b) using organic solvents for CSS, in a range between 5.26 and 13.53 mg GAE/g. However, Conde and Mussatto (2016) used a hydrothermal pretreatment, and measured 32.92 mg/g and 19.17 mg/g for SCG and CSS, respectively. The latter result was probably due to a short extraction process, but the method is less sustainable due to the greater number of operations.

Table 2: Recovered caffeine and phenolic compounds for the two fractions: phytocomplex (PT) and hydrolate (HY) and the three matrices: Coffee Powder, spent coffee grounds (SCG) and coffee silverskin (CSS). Means and standard deviation are reported. Letters (a-e) indicate statistically significant differences at the TukeyHSD post-hoc test (p < 0.05).

Fraction	Matrix	Caffeine (mg/g)		Phenolic compounds (mg/GAE g)	
PT	Coffee powder	3.42 ± 0.10	a	17.67 ± 2.34	b
PT	SCG	3.21 ± 0.21	b	21.47 ± 4.22	a
PT	CSS	2.90 ± 0.18	c	5.43 ± 0.60	c
HY	Coffee powder	3.19 ± 0.23	c	0.20 ± 0.07	e
HY	SCG	2.30 ± 0.03	e	1.96 ± 0.42	d
HY	CSS	2.49 ± 0.70	d	2.11 ± 0.25	d

3.3 HPLC-DAD analysis

Figure 1 shows HPLC-DAD chromatograms at 330 nm. Different chemical profiles were obtained for the two fractions of the three matrices. Here, we only report the chromatogram of six samples (two fractions of each matrix) for further characterization and differentiation. This analysis confirmed other differences found between the two fractions and the three matrices, and this aspect will be explored in more detail in subsequent studies.

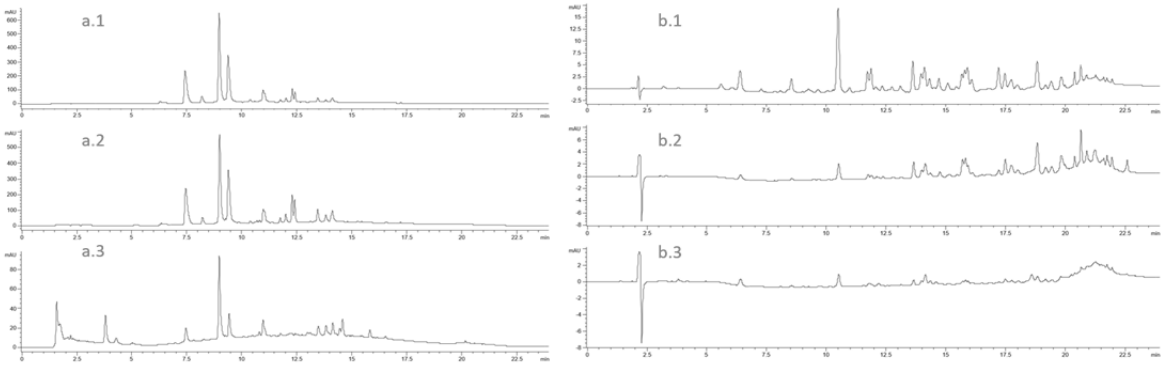

Figure 1: HPLC-DAD chromatograms at 330 nm for the two fractions (a: PT and b: HY) of the three matrices (1: Coffee Powder, 2: SCG and 3: CSS).

3.4 Measurement of VOCs

Table 3 shows VOCs measured for each sample. As we expected, HY fraction has reported higher values than the PT fraction. In particular, Coffee Powder HY (1610.83 mV/g) was significantly higher than the respective PT fraction (30.31 mV/g). On the other hand, no significant different were found between the other matrices of the two fractions.

Table 3: VOCs measured for the two fractions: phytocomplex (PT) and hydrolate (HY) and the three matrices: Coffee Powder, spent coffee ground (SCG) and coffee silverskin (CSS). Means and standard deviation are reported. Letters (a-b) indicate statistically significant differences at the TukeyHSD post-hoc test (p < 0.05).

Fraction	Matrix	VOC (mV/g)	
PT	Coffee powder	30.31 ± 13.42	b
PT	SCG	2.79 ± 0.40	b
PT	CSS	5.97 ± 2.05	b
HY	Coffee powder	1610.83 ± 528.37	a
HY	SCG	166.19 ± 25.25	b
HY	CSS	81.91 ± 10.48	b

3. Conclusions

The two fractions showed interesting characteristics. Caffeine was detected for each fraction of Coffee Powder, SCG and CSS. High amounts of phenolic compounds were detected in the PT fraction of each of the matrices, while levels were lower in the HY fraction. TDS, electrical conductivity, ORP and pH results made it possible to characterize each of the fractions of each of the matrices. HPLC-DAD analysis revealed different

chemical profiles, and this aspect will be investigated in more detail in future studies. Finally, measurements of VOCs shown different characteristics, in particular for Coffee Powder. Our green method was able to extract a considerable amount of bioactive compounds from industrial coffee waste, compared to conventional systems. The efficiency of our method will be improved in future studies. In particular, we will examine the use of low-impact pre-treatments to increase the amount of bioactive compounds that are extracted, reduce the amount of water needed, and shorten the extraction time.

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