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Coffee by-Products: Nowadays and Perspectives

Laura Sofía Torres-Valenzuela, Johanna Andrea Serna-Jiménez and Katherine Martínez

Abstract

Coffee is one of the most consumed products around the world; 2.25 billions of coffee cup are consumed everyday in the world. For coffee crop production, different by-products are produced, such as coffee peel, coffee husk, parchment, and spent coffee grounds. These by-products have several problems associated at the final disposition. In this book chapter, we study the main coffee varieties produced in the world, the by-products produced, and its composition and finally assess the potential of supramolecular solvents (SUPRAS) and water as green solvents for high-added-value compound extractions. Bioactive compounds were extracted from fresh and dried coffee peel in an acceptable rate for industrial applications. SUPRAS offer advantages in terms of rapidity (5 min) and simplicity (stirring and centrifugation at room temperature), thus avoiding costly processes based on high pressure and temperature. Extractions carried out using water as solvent is another technique of extraction mixing temperature (above 60°C) and time (4.5 min) obtained a beverage or solution with presence a bioactive compounds how caffeine, chlorogenic acid and polyphenols.

Keywords: agri-food waste, by-products, coffee husks, coffee peel, spent coffee grounds

1. Introduction

Coffee is a tropical perennial plant from the *Coffea* genus of the Rubiaceae family. Although there are more than 103 species recognized nowadays, only 2 are responsible for world trade (arabica and canephora) [1]. The arabica variety constitutes more than 60% of the coffee that is commercialized in the international market and is cataloged by the consumers as the best coffee for its exceptional organoleptic characteristics [2]. This is due to the great variety of chemical compounds, which are responsible for granting the sensory quality and stimuli to the nervous system [3].

Coffee beverage is the result of the preparation of a drink by infusion from roasted and ground beans, with characteristic aroma and flavor, which have made it the second most consumed product in the world [3]. In the case of Colombia, coffee has been cataloged as one of the country's main export products. For the above statement, coffee continues to be an activity of great importance. In this agricultural value chain, the by-products correspond to 80% of the total volume; the coffee industry generates about 2 billion tons of agro-waste, which represent a great pollution hazard [4]. Coffee pulp, husks, silverskin, peel, and spent coffee grounds are common coffee by-products [5].

Generally, coffee is internationally traded as green coffee [6], and it is obtained either by the wet, semi-wet, or dry methods. Typically, wet-processed coffee beans have a higher consumer acceptance than the dry-processed ones [7]. Wet coffee process consists of several steps, namely, de-pulping, fermentation, washing, de-hulling, and drying [8]. Depending on the processing method, either wet or dry, coffee pulp and husk are the first by-products and account for 29 and 12% of the overall coffee cherry [5]. Pulp and husk are rich in carbohydrates (35–85%), soluble fibers (30.8%), mineral (3–11%), proteins (5–11%), and bioactive compounds such as tannins, cyanidins, chlorogenic acid, caffeine and polyphenols [5, 6].

The disposal of agro-waste is a growing issue that can cause phytosanitary problems and cross-contamination in food industries [9]. As a consequence, new strategies to manage or benefit from agro-waste are urgently needed. One of the most promising options is to valorize the bioactive components present in the by-products [10]. In this sense, a growing field of studies highlights the presence of various bioactive compounds in agro-waste with potential applications in functional foods and nutraceutical developments [4, 9, 10]. The recovery of bioactive compounds improves the economic feasibility of the main processes, by producing secondary streams of value-added compounds.

This chapter assesses the usability of SUPRAS and water extraction for the recovery of high-added-value compounds from coffee peel. The method is simple and rapid and could be a sustainable strategy for coffee waste valorization.

2. Origin of coffee

Today, there are countless legends that talk about the origin and discovery of coffee. One of the most accurate ones mentions that coffee originated in the high plateau of Abyssinia and occurred in a wild form known as arabica. It was accidentally discovered by an Ethiopian shepherd named Kaldi. He noticed a strange behavior in his goats when eating fruits and leaves from a certain shrub, so he collected a sample and took it to a monastery [3], where possibly the cherries were mixed in the infusions or thrown into the fire allowing to feel a greater aroma and a better flavor [3].

The Arabs were the first to regularly consume coffee and give a primary role to its cultivation; hence, they are considered the pioneers in the establishment of coffee crops. Subsequently, coffee spreads to Mecca, Medina, and Syria and next to Aden and Cairo, covering the entire Muslim world around 1510 and Turkey in the year 1554 (www.cafedecolombia.com). The introduction of coffee in America was approximately in 1718 starting with the Dutch colony of Suriname, followed by plantations in French Guiana. In 1730, it was the British who introduced coffee into Jamaica and later spread to the rest of the continent [11].

Historically, it has been recognized that coffee was introduced to Colombia via the Venezuelan border by a traveler who came from French Guiana and carried a coffee plant. Thus, the first crops were in the North Santander and, later, in the departments of Antioquia, Tolima, Caldas, Valle del Cauca, Risaralda, Quindío, Cundinamarca, and Nariño, among others. The variety that was initially cultivated in Colombia was the Typica variety. At the end of the 1920s, a second variety was introduced, known as Bourbon, due to its higher yields; however, since the 1980s, the “Colombia” variety has been cultivated, coming from the Caturra variety and the Timor Hybrid, which is resistant to rust [12].

In Colombia, mainly arabica coffee is cultivated, due to this species produce a soft drink and of greater acceptance in the national and international market. The varieties of arabica are low or tall, and have red or yellow fruits. Some varieties of

Variety	Description
Typica	Arabica, pajarito or national Coffee trees are fairly tall Its new leaves or bud are bronzed or reddish. The leaves are elongated Susceptible to rust Greater percentage of large beans than the varieties Caturra and Bourbon Planting density, 2500 trees per hectare
Bourbon	More branches than the Typica variety Lighter green buds than the other leaves Leaves are rounded Produces 30% more than Typica Susceptible to rust Planting density, 2500 trees per hectare
Tabi	Derived from crossing the Timor Hybrid with the Typical and Bourbon varieties Large bean, more than 80% supreme coffee Excellent quality ideal for obtaining specialty coffees Planting density, 3000 trees per hectare Susceptible to rust
Caturra	Lighter green buds than the other leaves Leaves are rounder than Bourbon's Low-to-medium body Produces less than Bourbon and more than Typica Behaves well in the coffee zone Susceptible to rust Planting density, up to 10,000 trees per hectare
Colombia variety	The bud of the plants is bronzed Durable resistance to coffee rust attack Production equal to or greater than Caturra Type of bean and quality of beverage are similar to other varieties of arabica coffee

Table 1.
Colombian coffee varieties.

Arabica species are the Maragogype, Bourbon, Tabi, Typica, Castillo, Caturra, and Colombia, being these last three varieties the ones that are cultivated in greater proportion (see **Table 1**).

Internationally, 80% of the world's production corresponds to the arabica species, which is cultivated mainly in Colombia, Brazil, and in some Asian countries such as India or in Africa such as Kenya and Ethiopia [12]. The remaining 20% corresponds to the species canephora and is generally cultivated in Africa, Brazil, and Indonesia, with differentiating factors such as resistance to rust and a higher caffeine content [13].

The first commercial production of coffee was made in 1835. In this opportunity, 2.560 sack bags were exported from Cucuta. In 1927, the National Federation of Coffee Growers was founded to promote the development of Colombian coffee culture. This organization makes the process of purchasing, storing, and exporting coffee, as well as accompanying and advising coffee growers from different regions of the country. In this way, coffee cultivation was consolidated as one of the country's main agricultural activities [3]. Today, the sector continues to be an important articulating axis in the country's rural development and providing economic stability despite the coffee crises represented by high production costs and low harvest levels. To date, the National Federation of Coffee Growers has reported a participation of 560,000 farms dedicated to coffee cultivation, which translates to 948,000 hectares of which 27% are harvested with the variety Colombia. The rest corresponds mainly to the varieties Typica, Caturra, and Bourbon [12], with 66% of the cultivated area

in the country, being cataloged as the product with greater participation among the other registered crops [14], providing approximately 785 thousand rural jobs directly and 1.5 million indirectly (www.federaciondecafeteros.org).

3. Characteristics of coffee

Coffees are berries obtained from a perennial and topical plant (cafeto) [3]. The coffee beans are morphologically very variable and have different shapes, colors, and sizes. Internally, seeds are found (usually two per fruit), which are processed and used to prepare infusions [3].

Plants have a cleft in the central part of the seed. Depending on the species, it is possible to find small shrubs or trees larger than 10 m. The leaves are simple, opposite, and with stipules and present variability both in size and texture. The plant has white and tubular flowers, which are complete, i.e., all organs are in the same flower [2]. The root is a vital organ for the coffee plant, because through it, the plant takes the water and nutrients for its growth and also is an anchor to the soil [3]. The coffee plant has a main root that can reach a depth of up to 50 cm, from which other thick roots are available to support the thinner ones in charge of absorbing nutrients. The stem forms the skeleton of the coffee tree along with the branches with leaves, flowers, and finally, the fruits (www.cafedecolombia.com).

Because of the union of the grain of pollen with the ovule, the fruit and seeds are formed. The coffee fruit is a cherry that is divided into three layers: epicarp or skin, which is the outermost layer; mesocarp or pulp, which forms a sweet and aromatic pulp of mucilaginous nature, protected by a yellow cellulose layer called parchment or endocarp; and finally a silvery layer, which covers the two oval-shaped grains called endosperm [11].

3.1 Chemical composition of coffee

Coffee has a number of chemical components, mainly water and dry matter, such as minerals, organic substances (carbohydrates, lipids, proteins), alkaloids (caffeine and trigonelline), carboxylic and phenolic acids, and volatile compounds responsible for the aroma. All together result in a great diversity and complexity of structures; however, these may have modifications in any of their stages, either from the crop or the mill [15].

The chemical composition varies depending on the species [16]. In the case of *Coffea arabica*, it has a higher lipid and sucrose content than *Coffea canephora*. The robusta differs by its higher content of polysaccharides, caffeine, chlorogenic acids, and ashes. **Table 2** shows the most representative chemical components in arabica and robusta species.

Additionally, within the varieties cultivated in Colombia are differences (see **Table 3**), due to the intrinsic factors, soil fertilization, atmospheric conditions, sowing density, and planting age, among others [15].

Water: The water content of the bean is one of the most relevant factors in all coffee processes, from germination to roasting. In the fresh fruit, the water content is between 70 and 80% [25]. After the dry process, the water content is reduced up to 10–12% to improve the stability and avoid microbial proliferation, prolonging its shelf life [16].

Carbohydrates: Among the main polysaccharides in coffee are mannan or galactomannan (polymer of mannose and galactose), constituting 50% of the polysaccharides, 30% of arabinogalactan (polymer of galactose and arabinose), 15% of cellulose (polymer of glucose), and 5% of peptic substances [16]. The beans in an optimum

Chemical component*	Puerta [16]		Echeverry et al. [17]		Komes [18]	
	Arabica	Robusta	Arabica	Robusta	Arabica	Robusta
Polysaccharides	50.8	56.40	38	41.5	N.D	N.D
Sucrose	8.00	4.00	N.D	N.D	N.D	N.D
Reducing sugars	0.10	0.40	N.D	N.D	N.D	N.D
Protein	9.80	9.50	10	10	N.D	N.D
Amino acids	0.50	0.80	N.D	N.D	N.D	N.D
Caffeine	1.20	2.20	1.3	1.4	0.76–1.82	1.51–3.33
Trigonelline	1.00	0.70	1	0.7	0.88–2.76	0.75–3.42
Lipids	16.20	10.00	17	11	N.D	N.D
Aliphatic acids	1.10	1.20	2.4	2.5	N.D	N.D
Chlorogenic acids	6.90	10.40	2.7	3.1	4–8.4	7–14.4
Minerals	4.20	4.40	4.5	4.7	N.D	N.D
Aromatic compounds	Traces	Traces	0.1	0.1	Traces	Traces
Melanoidins	N.D	N.D	23	23	25	25

*Expressed in percentage, on a dry basis.
 N.D. Non-determined.

Table 2.
 Chemical composition of the coffee beans of the arabica and robusta species.

Coffee variety	Fiber (%)	Lipids (%)	Proteins (%)	Caffeine (%)	Chlorogenic acids (%)	Ash (%)
Bourbon	21.75	15.27	13.90	1.15	7.37	3.78
Caturra	18.85	13.98	14.79	1.13	6.97	3.39
Colombia yellow fruit	18.45	13.07	14.45	1.16	7.55	3.49
Colombia red fruit	16.69	14.27	13.92	1.19	7.42	3.52
Typica	18.71	13.99	14.59	1.20	6.66	3.43
Robusta	15.53	11.42	15.66	2.10	8.08	3.96

Source: Puerta [16].

Table 3.
 Chemical composition of coffee bean in the different varieties sown in Colombia.

ripening stage have a higher sucrose content than defective and immature beans. In the arabica species, the sucrose content ranged between 6 and 9%, while robusta contains 3–7% of sucrose [16]. Monosaccharides and some disaccharides such as lactose and maltose may oxidize to form alcohols and acids in the fermentation process or may react with the amino acids in roasting to form melanoidins, which are responsible for the coloration (enzymatic browning) of the roasted coffee [16].

Lipids: Triglycerides, linoleic, and palmitic acid are mainly presents (~ 75% of coffee lipids). The unsaponifiable matter constitutes 20 to 25% of the lipids of coffee. Sterols are 2.2% of coffee lipids and contain β -sitosterol, stigmasterol, campesterol, and $\Delta 5$ avenasterol. Cholesterol constitutes 0.11% of the dry weight of coffee beans (0.044% in robusta coffee) [16].

Nitrogen compounds: Nitrogen constitutes between 1.30 and 3.23% of the dry weight of the green coffee beans, after the roasted decreased up to 1.51 and 2.14% [16].

Alkaloids: Alkaloids are the substances responsible for giving the bitter taste of coffee, the most representative are caffeine, trigonelline, paraxanthine, theobromine, and theophylline [16]. Caffeine is a methylxanthine, which have attributed health benefits, such as improve the central nervous, cardiovascular, respiratory, renal, and muscular system [19]. For the above statement, caffeine is important in the pharmaceutical industry. Also it has important bioactive properties, so it may be cataloged as a functional ingredient, which can be used in different food matrices [20].

Chlorogenic acids: They are a series of phenolic esters derived from the union of an ester between caffeic acid and quinic acid [3]. The chlorogenic acid content in green coffee is 7% and reaches 4% after roasting [3]. A volume of 200 mL of roasted and ground coffee could provide between 70 and 350 mg of chlorogenic acid [16]. Coffee beans contain more than 40 chlorogenic acids, especially esters of quinic acid such as CQA, di-CQA, and FQA [16]. This compound has a significant antioxidant capacity and also a stimulant, expectorant, diuretic, choleric, and antihepatotoxic effects [21].

3.2 By-products of coffee processing

The coffee bean is picked after reach the commercial ripening stage; it next must be quickly transformed into dry parchment coffee, to avoid accelerated fermentation because the entire bean includes high water and sugar content [22]. For these purposes the external layer is removed from the coffee bean and only 5% of the biomass is used to produce a coffee crop, the rest remains in a residual form as leaves, branches, green fruits, pulp, mucilage, parchment, and silverskin, among others [22]. There are two primary methods for processing coffee, to obtain green coffee (traded coffee beans): wet and dry. In the dry process, no layers are removed, and coffee cherries are laid out in the sun to dry. In the wet process, the fruit covering the layer is removed before they are dried. Approximately 40% of all coffee around the world is wet processed [23], because it is considered to produce superior tasting offers [8, 24]. In the wet process, it has been estimated that 40–45 L of wastewater are produced per kilogram of coffee [25].

In Colombia, the wet process has been implemented for decades, which generates a contamination of 115 g of COD per kilogram of cherry coffee [22]. To overcome this problem, new methods were developed; one of these is the Belcosub technology, in which the fruit is de-pulped. The external layer is transported without water, and the organic residues are reused; however, these do not generate a significant value. This system avoids up to 74% of the contamination of water resources, since less than 5 l/kg of dry parchment are used [22]. The most recent technology suggested by the National Federation of Coffee Growers is the ecological mill without dumping (Ecomil) that reduces the amount of water to 0.5 l of water per kilogram of dry parchment, implementing tanks generally in stainless steel that do not need water for coffee emptying. In addition, the water resulting from this process goes directly to purifying tanks with microorganisms and a series of filters that allow the water that falls to water sources to be clean and do not generate any pollution [22].

As mentioned above, a large amount of coffee bean components are removed. It is important to highlight that approximately 43.58% of the weight of the dried fruit are these by-products [22]. The valorization of these by-products through the recovery of bioactives has increasingly become of interest for food, pharmaceutical, and cosmetic industries [26–30].

A promising option to recover these bioactive compounds is the coffee pulp, which involves the epicarp and part of the mesocarp of the fruit. This by-product

By-product	Process	Final use	References
Fresh pulp	Dried	Biocomponents	[40]
Fresh pulp	Chopped	Animal feed	[41, 42]
	Silage		[43]
Fresh and dried pulp	Washing, drying, blending, and freezing extracts with hot water	Biocomponents extraction, antioxidant activity, and bacterial inhibitory activity	[44]
Husk	Supercritical carbon dioxide	Extraction of caffeine	[45]
Fresh and dried pulp	Mixtures of solvents with ethanol and milli-Q water in different mixtures and sonication—maceration	Antioxidant activity, cytotoxicity on human epithelial gastric cells, and biocomponents profile	[46]
Silverskin	Subcritical water (25–270°C)	Antioxidant activity	[47]
	Batch culture fermentation bifidobacteria	Prebiotic potential dietary fiber	[48]
Parchment	Water extraction, concentration, and dried	Inhibitory effect of a on hyaluronidase	[49]
	Ethanol extraction mixed with temperature	Biocomponents extraction, antioxidant activity	[50]
Fresh pulp	Fermentation	Ethanol	[51, 52]
Fresh pulp and mucilage			[53]
Parchment	Hydrolysis and fermentation		[54]
Fresh pulp	Pretreatment with <i>Mycotypha</i> sp. and biomethanization	Biogas	[55]
	Pretreatment with <i>Streptomyces</i> sp. and biomethanization		[56]
Parchment	Hydrolysis and biomethanization		[57]
Pulp and rejected grain			[58]
Fresh and dried pulp	Co-digestion biomethanization		[59–63]
Parchment	Microwave and traditional heating	Pyrolysis	[64]
Husks	Combustion furnace as well as in a fluidized bed combustion chamber at pilot scale		[65]
	Vermicomposting with <i>Eudrilus eugeniae</i> and <i>Trichoderma viride</i>	Compost	[66]
Parchment	Composted parchment with a mixture of organic amendments, pulp with bovine manure, and the legume <i>Milletia ferruginea</i>		[67]
Pulp	Compost with <i>Trichoderma</i> sp., <i>Streptomyces</i> sp., <i>Azotobacter</i> sp., and <i>Bacillus</i> sp.		[68]
Husk	Solid-state fermentation with <i>Rhizopus</i> , <i>Phanerochaete</i> , and <i>Aspergillus</i> sp.	Evaluate the reduction of caffeine and tannins	[69]

By-product	Process	Final use	References
Dried coffee leaves, coffee cherry husk, coffee parchment skin, silverskin, and spent coffee ground	Solid-state fermentation	Produced the fungus <i>Pleurotus florida</i>	[70]
Pulp		Production of an extract rich in chlorogenic acid	[71]
Coffee husk and pulp dried	Hydrolysis and sterilization; fermentation using <i>Rhodotorula mucilaginosa</i>	Carotenoids production	[72]

Table 4.
Alternatives for added value of coffee pulp.

contains significant amounts of caffeine and another component [31]. The reported chemical composition (expressed in dry mass) includes polyphenols (1.5–2.9%), total sugars (4.1%), protein (4–13.3%), lignin (17.5–19.3%), lipids (1.7–2.5%), cellulose (18–63%), total fiber (18–60.5%), ash (6–10%), tannins (1.8–9%), carbohydrates (44–89%), reducing sugars (12.4%), nonreducing sugars (2%), caffeine (1.2–1.5%), and chlorogenic acid (1.6%) [5, 31–33].

3.3 Nowadays uses of coffee by-products

Coffee consumption has increased significantly, which generates an increase in waste amount [32]. These wastes have pollution problems. Discharges of wastewater from industrial activities have become a global issue of concern [34]. Different alternatives to both mitigate the negative effects in the discharges of coffee by-products and generate added-value alternatives have been evaluated. For this purpose, different studies have been carried out to evaluate alternative uses and reduce the toxic effect on the environment [35].

According to CONAMA Resolution No. 430 from 05/13/2011, the concentration of phenols should be lower than 0.5 mg L^{-1} [36], due to when phenolic compounds are discharged into the environment will lead to the degradation process of organic materials difficult to degrade [37]. Coffee by-products are the polyphenols and also carbohydrates, proteins, and pectins, making them potential sources of agro-industrialization for various industries, as well as renewable economic resources that can be given a high added value [32]. **Table 4** presented alternatives for coffee by-product reuse.

Among the alternatives previously proposed for the food and nonfood industry, emphasis will be placed on the production of extraction of caffeine both from the beans and from the different by-products obtained.

Considering that caffeine is an alkaloid that possesses antioxidant capacity and increases energy availability, cognitive performance, and neuromuscular coordination, among others [38], one of the alternative uses of coffee and its by-products has focused on the extraction of this compound of functional interest, both for the food and non-food sectors. However, in recent years, new extraction techniques have been sought in order to reduce the generation of waste, with a lower consumption of chemical reagents and therefore improve the efficiency of the process, reducing process times [39].

4. SUPRAS extraction

Two amphiphiles (decanoic acid and hexanol) and two dispersion solvents (THF:water and ethanol:water) were selected for the study to generate a variety of

SUPRAS based on previous promising results [73–75]. Hexanol has the advantage over decanoic acid for the possibility of removal by evaporation if further steps are required after the extraction of bioactives, while decanoic acid is a more biocompatible and renewable option. Thus, this offers different strategies for amphiphile recovery and reutilization in industrial purposes, being usually easier the operation with liquid phases. Ethanol was tested together with THF, the first considered biocompatible and authorized for use in food and the second easily removable by evaporation due to its high vapor pressure (143 mm Hg at 20°C) and relatively low boiling point (66°C). The coacervating agent (external stimuli driving the self-assembly synthesis of SUPRAS) is water in both cases, as a poor solvent for the amphiphiles promoting the aggregation as described before [76]. The type of amphiphile and of the dispersion solvent and the composition of the ternary mixture in the bulk solution (amphiphile, organic solvent, water) give rise to SUPRAS with different final composition and microstructure and volumes which can influence the extraction efficiency [73]. Thus, SUPRAS binding interactions and restricted access properties (conferred by the size of the aggregates) can be tuned depending on the amphiphile functional groups (OH, COOH) providing hydrogen bonds for extraction and dipole–dipole interactions, the alkyl chain length (C6, C10) giving dispersion interactions and the dispersion medium composition (providing hydrogen bonds, dipole–dipole interactions, and dispersion forces under different ratios of ethanol:water or THF:water mixtures).

Figures 1 and **2** show the caffeine and chlorogenic acid extraction with SUPRAS. As expected, recoveries were influenced by the amphiphile nature and bulk solution composition of the ternary mixture (amphiphile, water, organic solvent). Under all the tested SUPRAS, the caffeine extraction efficiency was in the range 31–68% ± 2.8%, while the chlorogenic acid extraction efficiency was between 0 and 26 ± 2.5%.

The highest caffeine extraction was obtained with hexanol as amphiphile and ethanol:water as dispersion solvent for the design of the SUPRAS (maximum at

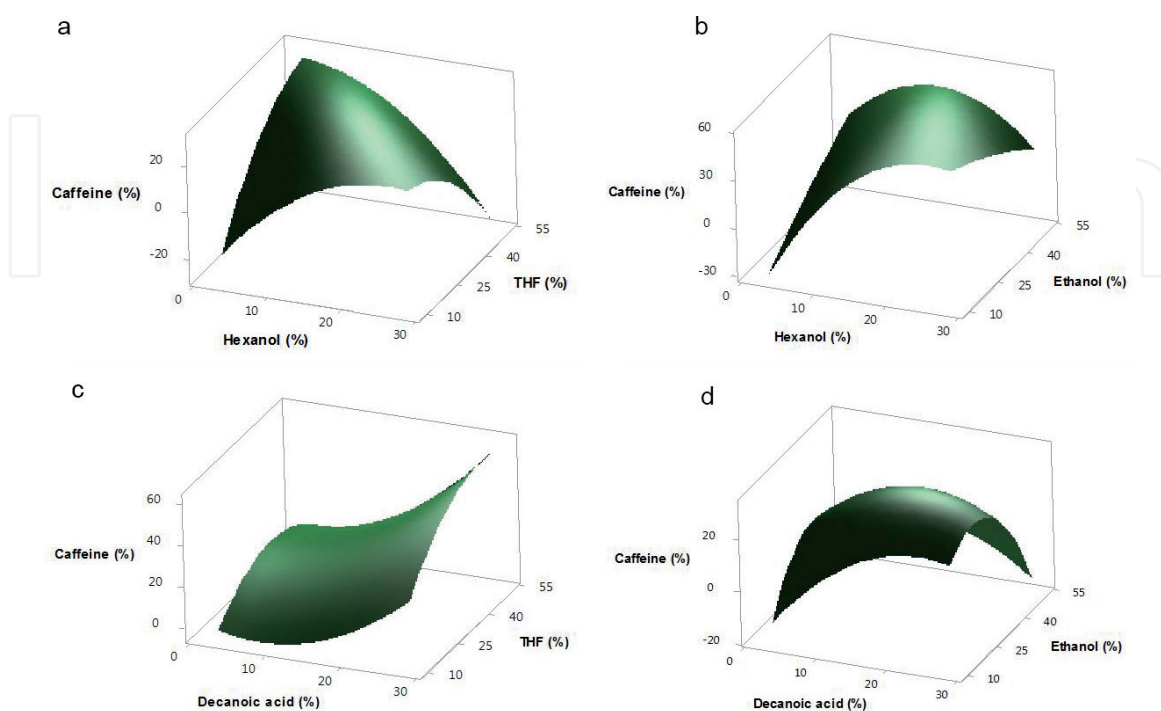


Figure 1. Surface response plots for caffeine extraction from coffee peel with (a) hexanol, THF; (b) hexanol, ethanol; (c) decanoic acid, THF; and (d) decanoic acid, ethanol.

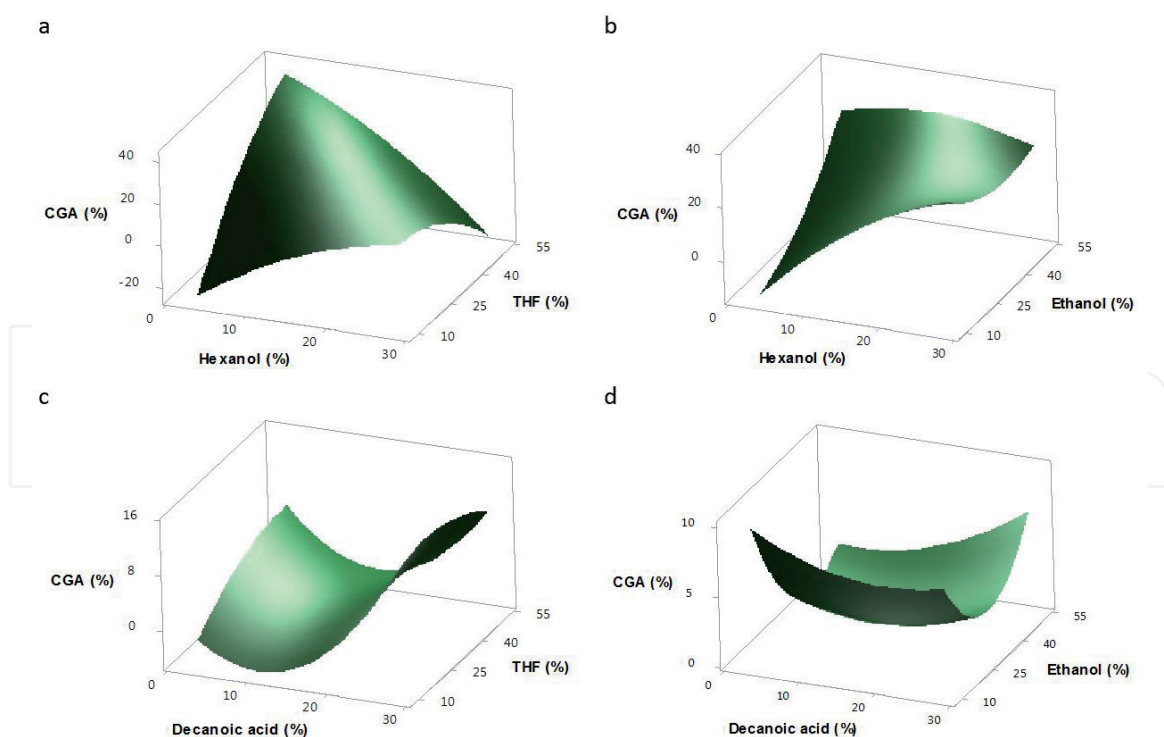


Figure 2.

Surface response for chlorogenic acid extraction from coffee peel with (a) hexanol, THF; (b) hexanol, ethanol; (c) decanoic acid, THF; and (d) decanoic acid, ethanol.

$69 \pm 0.9\%$ with 7% of hexanol and 15% of ethanol). The range obtained for the other SUPRAS was $45\text{--}56 \pm 1.1\%$, $31\text{--}56 \pm 2\%$, and $39\text{--}65 \pm 7.5\%$ with hexanol-THF, decanoic acid-THF, and decanoic acid-ethanol, respectively.

SUPRAS based on ethanol:water were indeed more suitable than those based on THF:water to extract caffeine with both amphiphiles. A possible explanation is that ethanol as protic solvent can extract caffeine more efficiently than THF (aprotic solvent), acting as hydrogen bond donor for caffeine, which contains hydrogen bond acceptors' groups only. Additionally, the dielectric constant of ethanol is higher than that of THF (24 and 7.5, respectively). This parameter is a relative measure of the chemical polarity and could enhance the extraction of the polar bioactives by dipole-dipole interactions. With respect to the amphiphile, hexanol was the best choice, and the highest efficiency rates ($69 \pm 0.9\%$) were obtained in SUPRASs formed with this organic alcohol. The higher polarity of hexanol over decanoic acid could be the reason for the higher extraction efficiency of the polar bioactive compounds. Furthermore, the smaller size of hexanol aggregates, due to its shorter alkyl chain length, could generate SUPRAS with greater surface area, and, consequently, it will provide more available binding interactions for the bioactive components.

Chlorogenic acid extraction rates were lower than caffeine rates, and no clear correlation was found with the SUPRAS synthetic conditions. Its higher polarity could lead to losses in the equilibrium competing phase (i.e., calculated $\log P$ -0.4 and -0.1 for chlorogenic acid and caffeine, respectively). Furthermore, chlorogenic acid is a bigger molecule than caffeine; its molar mass is 354.31 g/mol, and its topological polar surface area is 165 Å^2 , while for caffeine, values of 194.19 g/mol and 58.4 Å^2 are calculated. The higher contact polar area of caffeine could enhance the recoveries too. Caffeine is the most routinely ingested bioactive substance. Its consumption possesses health benefits, including lower risks of Parkinson's and Alzheimer's disease, a favorable effect on liver function, energy expenditure, and a decreased risk of developing certain cancers (endometrial, prostatic, colorectal, liver) [77]; it can stimulate fat oxidation, thermogenesis, and energy expenditure

subsequently, which reduces body weight [78]. Caffeine is consumed daily, in the United States 89% of the population 19 years of age or older consumes some form of caffeine daily, but the primary source of caffeine is coffee (64%) [79].

Chlorogenic acid is the major polyphenol in edible plants with many health-promoting properties [80]. It has a strong antioxidant activity, anti-lipid peroxidation, anticancer effects [81], anti-inflammatory activity, inhibition of α -amylase, and α -glucosidase linked to type 2 diabetes and anti-obesity properties [82]; it also has antimicrobial properties [83]. Due to the beneficial effects of this bioactive component, it has been used for the preparation of functional materials in food and pharmaceutical areas [80].

5. Water extraction

The processing of every 60,000 tons of dried coffee beans produces approximately 218,400 tons of fresh pulp and mucilage or mesocarp [84]. Generally, the pulp is removed with mechanical movements generated by pulping and constitutes about 29–43% (w/w) of the fruit [6, 85]; the pulp a potential use has been identified by the compounds present such as anthocyanins, caffeine, and phenolic compounds with which an important added value can be generated [46, 86, 87]. In this study dried pulp was employed for the biocomponents extractions, using hot water as solvent, the dried pulp of arabica variety was selected with 10–12% of humidity, the response surface methodology was used to determine the effect of solvent temperature (water) (60–90°C) and extraction time (1–8 min) on the functional characteristics of the infusions obtained.

For the preparation of the infusions, dried pulp was taken and placed in infusers. Each sample was deposited in a beaker with 250 mL of the solvent (water) at a different time and temperature conditions. The samples were quantified polyphenol content by the Folin–Ciocalteu method reported by [44, 46]; the quantification of caffeine and chlorogenic acid was done by high-performance liquid chromatography (HPLC).

The chromatographic separation was performed in a Shimadzu Prominence with a UV detector and quaternary pump system (Shimadzu, Japan); the samples were filtrated in a cellulose filter of 25 μ m, and the filtrated sample (20 μ L) was conducted using a C8 Restek column (Restek Corporation, USA). The mobile phase consisted of 0.1% acetic acid and 30% methanol in water v/v; the injection volume was 20 μ L. The mobile phase flow rate was 0.5 mL/min (35°C). The reference standards were used for identification, and calibration curves were obtained for quantification chlorogenic acid and caffeine.

The peak of caffeine was observed at the elution time of 11.59 min. The caffeine extracted from 3.3 g of coffee pulp ranged between 21–51 mg/L and did not depend on the extraction temperature from 65 to 90°C, the time has an effect in time upper 4.5 min [47], and the values of caffeine were higher (**Figure 3a**). The chlorogenic acid had a similar behavior of caffeine (**Figure 3b**) with range values 5–9 mg/L; this indicates that those substances are stable during extraction and heat treatment and storage of the beverage [84].

In the extraction process, this type of biocomponents is the solvent, since the type of compound to be extracted depends on the type of solvent used for the capacity they possess which is directly related to their polarity. Extractions using water improved the extraction of phenolic compounds, caffeine and chlorogenic acid due to it polarity [84, 88].

Therefore, coffee pulp can be a raw material with a high content of compounds, and its consumption (e.g., in infusions or extracts) can help prevent degenerative diseases, taking into account that a relationship has been established between

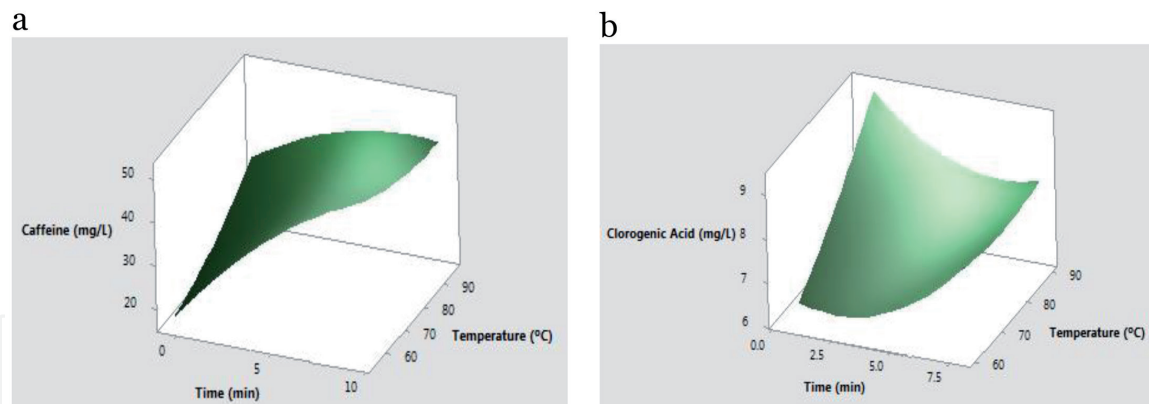


Figure 3. Surface response for (a) caffeine and (b) chlorogenic acid using water as solvent.

consumption of biocomponents such as polyphenols, caffeine, and chlorogenic acid and the reduction of risks of chronic diseases, including obesity and diabetes [5, 6, 32, 89]. The coffee pulp has potential for use in the food, pharmaceutical, and cosmetic industry, becoming an alternative for products to generate added value and reduce negative effects on the environment and improve the profitability of producers within of circular economy and biorefineries.

6. Conclusion

This study shows the ability of SUPRAS, nanostructured solvents made up of assembled amphiphile aggregates and water, for valorization of coffee waste. The results proved that these solvents offer excellent extraction capacity of high-added-value compounds with interest for the food, pharmaceutical, and cosmetic industry.

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