

Effect of falling-film freeze concentration on bioactive compounds in aqueous coffee extract

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Abstract

Falling-film freeze concentration (FFFC) is a technology used to concentrate liquids by freezing. This study demonstrated the effect of FFFC on bioactive compounds in coffee extract and their antioxidant activity. Coffee extract containing 5% solids was freeze-concentrated in 2 successive steps. The main bioactive compounds, chlorogenic acids and caffeine were detected by RP-HPLC. The antioxidant activity and phenolic content were assessed by ABTS, DPPH, and Folin-Ciocalteu assays. The solution was concentrated 2.09 times after 2 FFFC steps. A concentration index of 2.1 was obtained for bioactive compounds for the concentrated fraction. The antioxidant activity was preserved and a correlation between antioxidant activity and the content of bioactive compounds was confirmed. Coffee bioactive compounds were distributed in proportion to the total solids content of the ice and liquid. Overall, the results showed that FFFC is an effective technique to concentrate liquids that preserves the functional properties of the coffee extract.

Practical applications

The falling film freeze concentration is a new freeze concentration technique which is in development to be used in future industrial applications of food fluids concentration. This study demonstrates the preservation of bioactive compounds and bioactivity of this technique applied to the concentration of coffee extract. The research has applications in the coffee industry in the production of concentrated coffee extract and freeze-dried soluble coffee.

1 | INTRODUCTION

The chemical complexity of food systems has prompted much research on the development of processing technologies that preserve sensitive biological compounds from thermal degradation, such as proteins, lipids, organic acids, vitamins, phenols, and aromatic compounds (Huang, Xiao, Burton-Freeman, & Edirisinghe, 2016). In the food industry, the nutritional and sensory properties of the product may be affected by the processing of raw materials at high temperatures, as is the case for concentration by evaporation. Thus, freeze concentration (FC) has been implemented as an alternative in the food industry (Moreno, Quintanilla-Carvajal, et al., 2015; Moreno, Raventós, et al., 2015; Sánchez, Ruiz, Auleda, Hernandez, & Raventos, 2009).

FC is a concentration technology that consists of cooling solutions until ice is formed, which is then separated from the liquid, to increase the solids content (Moreno, Hernández, Raventós, Robles, & Ruiz, 2014; Petzold, Niranjana, & Aguilera, 2013; Sánchez, Hernández, Auleda, & Raventós, 2011). Its main advantage is the preservation of the nutritional, sensory, and functional quality of processed products

due to low operating temperatures (Aider, de Halleux, & Melnikova, 2009; Boaventura et al., 2013; Zhang et al., 2016). When an aqueous solution is subjected to temperatures below freezing, a solid ice phase is formed that traps some solute-containing clusters, which are removed to increase the concentration of the initial solution (Raventós, Hernández, Auleda, & Ibarz, 2007).

Suspension FC, which very efficiently separates the water obtained, is the technique most widely used in the industry but is considered costly (Petzold & Aguilera, 2013; Robles et al., 2016). Thus, other techniques are currently being developed, such as the falling-film technique, which may yield concentrated high-purity products using simple and inexpensive equipment. (Raventós et al., 2007). Falling-film freeze concentration (FFFC) consists of circulating the liquid to concentrate it on a cooling vertical plate such that a single ice sheet is formed on the cold surface (Belén et al., 2012; Flesland, 1995; Sánchez et al., 2011). Specifically, the liquid film falls over ice increasing its concentration.

Coffee is one of the most highly consumed foods worldwide due to its organoleptic and sensory characteristics. Currently, its functional

properties, mostly the antioxidant activity due to hydroxycinnamic acids (chlorogenic, ferulic, caffeic, and coumaric acids), caffeine, and other compounds have further promoted the consumption of coffee (Jeszka-Skowron, Zgoła-Grzeskowiak, & Grzeskowiak, 2014; Vignoli, Bassoli, & Benassi, 2011). Specifically, the antioxidant capacity of coffee beverages is attributed to phenolics and other compounds induced by roasting, such as caffeine, and chlorogenic acids (CGAs) (Bedoya-Ramirez, Cilla, Contreras-Calderón, & Alegría-Torán, 2017). CGAs that are abundant in coffee include caffeoylquinic acids (CQAs) and their final concentrations in the beverage are important for quality assessment (Kwan, SunYoo, & Takayuri, 2009). Coffee is the main source of CGAs for humans (Hecimovic, Belscak-Cvitanovic, Horzic, & Komes, 2011). The most abundant CGA in the coffee beverage is 3-caffeoylquinic acid (3-CQA) and its constitutional isomers, such as 4-CQA cryptochlorogenic acid (c-CGA) and 5-CQA neochlorogenic acid (n-CGA). Although coffee extract contains more than 17 different acids (Nisiteo, Komes, Belzac-Cvitanovic, Horzic, & Budec, 2012). Coffee consumption reportedly aids in the control and prevention of some chronic and degenerative diseases (Nkondjock, 2009; Muriel & Arauz, 2010; Liang & Kitts, 2014).

Concentration processes are necessary when the concentrations of metabolites are low (Nuhu, 2014) and in the manufacturing of certain products, such as freeze-dried soluble coffee and concentrated liquid coffee extract. In these processes, final quality must be assured. FFFC is an alternative to the concentration of coffee extract that preserves the functional quality of coffee. Specifically, the preservation of functional compounds after block FC of coffee extract (Moreno, Raventós, Hernández, & Ruiz, 2014b) and yerba mate extract (Boaventura et al., 2013) has been reported. Moreover, Belén et al. (2013) studied the preservation of tofu isoflavones by FFFC. However, to the best of our knowledge, the effect of FFFC on the levels of bioactive compounds or the activity of coffee extract has not yet been reported. Thus, the objective of this research was to evaluate the effect of FFFC on the levels of bioactive compounds in coffee extract and their antioxidant activity.

2 | MATERIALS AND METHODS

2.1 | Materials

Coffee solutions were prepared from freeze-dried coffee extract provided by a local company (National Federation of Coffee Growers of Colombia, Chinchina, Colombia) at an initial total solids content of 5% m/m. The coffee was dissolved in distilled water at 30°C and stirred to completely dissolve the solids according to the method reported by Moreno et al. (2014b).

2.2 | FC tests

FC was performed using the FF technique reported by Moreno, Raventós, Hernández, and Ruiz (2014a). For the experiment, an apparatus with plates was used, as shown in Figure 1. The equipment consisted of a stainless steel cooling plate (1), which contained a 53% by

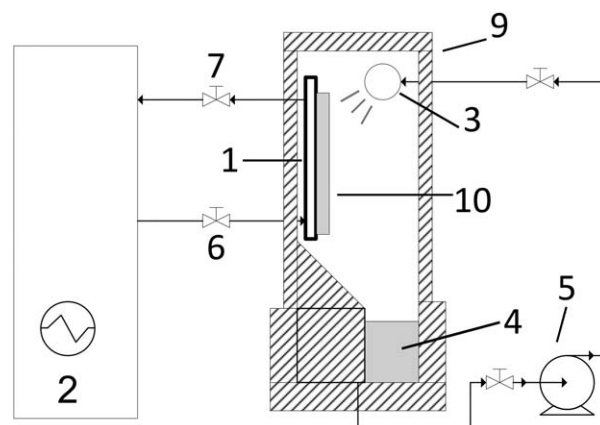


FIGURE 1 Experimental setup

mass ethylene glycol-water mixture that served as a cooling fluid and circulated continuously. This fluid entered through (6) and returned through (7). The fluid temperature was controlled by a thermostatic bath (2) (Polstat, Vernon Hills, Illinois, USA) and ranged from -30 to 150 ± 0.01 °C.

The coffee solution was dispersed from duct (3) that featured circular holes, which allowed the liquid to form a thin layer on the cooling plate and fall into the storage container (4). The coffee solution was continuously recirculated within the equipment by a peristaltic pump (5) (Master Flex, Model 77601-10, Vernon Hills, Illinois, USA) at a flow rate range of 50 mL s^{-1} . The liquid was pumped through a pipeline (8). During this process, the sample water content contacted the plate and was frozen (10). The equipment was covered by a chamber (9), which maintained a thermally isolated system.

The coffee solutions were concentrated in two steps according to the diagram shown in Figure 2. The total soluble solids content of the solution was monitored every 30 min using an Atago refractometer (PAL-BX/RI, Atago, Japan). °Brix measured in the samples were converted to a percentage of total solids using the equation: $\% \text{Solids} = 0.87\% \times \text{°Brix}$, as reported by (Moreno, Quintanilla-Carvajal,

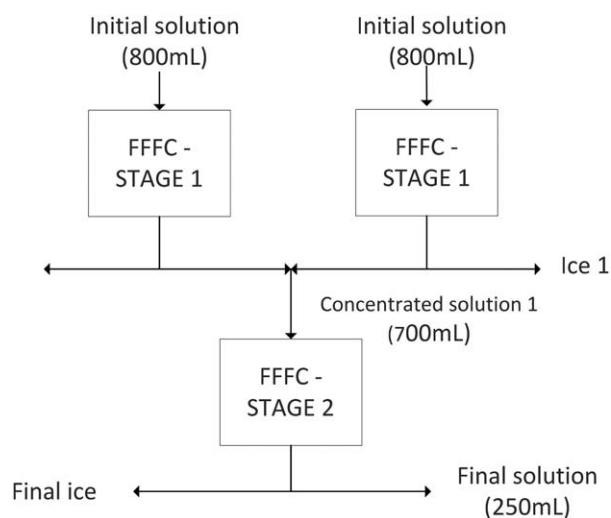


FIGURE 2 Flowchart of FC tests

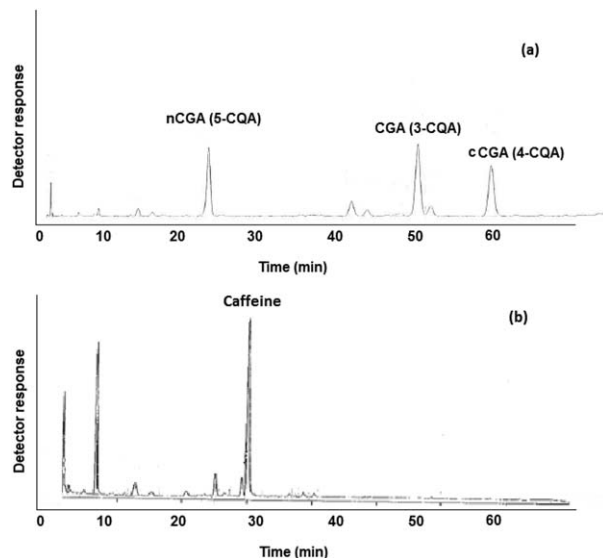


FIGURE 3 Typical chromatogram of coffee extract. (a) chlorogenic acids (b) caffeine

et al., 2015; Moreno, Raventós, et al., 2015). Each step was completed when the concentration index (CI) reached a range of 1.4–1.5.

2.3 | Quantification of bioactive compounds

CGAs (CGA, c-CGA) and caffeine were identified in aqueous coffee samples and quantified by reverse-phase high precision liquid chromatography (RP-HPLC) based on the methodology used by Fujioka and Shibamoto (2008) for the analysis of coffee beverages. A chromatographic analysis was performed on a LaChrom chromatograph (Merck-Hitachi, Germany-Japan) equipped with a quaternary pump, online degassing system, and a diode array detector (UV/VIS). Separation was carried out on a reversed phase C18 Gemini column (250 mm × 4.6 mm, and 5 μm) (Phenomenex) at 25°C and a flow rate of 1.0 mL/min. Detection was carried out at 325 nm for CGAs and 276 nm for caffeine. The mobile phase consisted of a gradient of mobile phase A (2% acetic acid) and mobile phase B (methanol).

2.4 | Antioxidant activity assays

To determine the content of phenolic compounds and antioxidant activity by 1,1-diphenyl-2-picryl-hydrazyl (DPPH) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), each of the samples obtained from the FC in steps 1 and 2 (initial solution, concentrated solution, and ice fraction) were diluted 1:100 and 1:1,000 with distilled water, respectively. The analyses were performed on a UV/VIS spectrophotometer (iMARK microplate reader, BIO-RAD, Waltham, Massachusetts). The solutions were prepared immediately before use, and the samples were analyzed in triplicate using methanol as a blank.

2.4.1 | ABTS assay

The method reported by Vignoli et al. (2011) was used with modifications. Briefly, 3.5 mM ABTS radical (Sigma-Aldrich), which was first activated by adding 12.5 mM potassium persulfate prepared in 10%

phosphate buffer at pH 7.4, was diluted in distilled water. The solution was then stored at 4°C in complete darkness for 12 hr. The resulting solution was stable for 48 hr. Prior to the analysis, the absorbance of the solution was adjusted to 0.8 ± 0.2 nm. To determine the antioxidant activity, 200 μL of activated ABTS (ABTS +) was added to 50 μL of sample, and the mixture was incubated at room temperature for 30 min in complete darkness. Subsequently, the absorbance was measured at 735 nm. The antioxidant capacity is expressed as g of Trolox equivalent antioxidant capacity (TEAC) per 100 g of coffee dry matter (dm) on a dry basis and as mg of TEAC per mL on a solution basis (Bravo, Monte, Juaníz, De Peña, & Concepción, 2013).

2.4.2 | DPPH assay

This technique was used following the method described by Moreno et al. (2014b) and Vignoli et al. (2011). Briefly, the DPPH solution was prepared at a concentration of 0.6 mM in methanol, and the absorbance was adjusted to 1.1 nm prior to testing. For the analysis, 50 μL of DPPH was added to 75 μL of each sample, and the absorbance was measured at 515 nm after a 30-min incubation at room temperature in complete darkness. The antioxidant capacity is expressed as TEAC g/100 g of coffee dry matter and TEAC mg/mL of solution.

2.4.3 | Total phenolic compounds

The phenolic compounds were assessed using the Folin-Ciocalteu method described by Ramalakshmi, Rao, Takano-Ishikawa, and Goto (2009) with modifications. In this assay, 10 μL of each sample (initial solution, concentrated solutions, and ice fraction) was diluted 1:100 with distilled water. Subsequently, 180 μL of distilled water, 30 μL of the sample, 15 μL of Folin-Ciocalteu reagent (Sigma), and 45 μL of 2% w/v sodium carbonate were added to each microplate well, followed by the addition of 30 μL of distilled water. The samples were incubated for 2 hr at room temperature before measuring the absorbance at 750 nm.

The phenolic compounds were quantified by interpolating readings from the samples based on calibration curves. The results are expressed as mg of gallic acid equivalents (GAE) per 100 g of coffee (dry matter) and mg of GAE per mL of solution.

2.5 | Data analysis

For the concentrated solutions and the ice fraction obtained from each step and globally, the following parameters were determined for the FC.

2.5.1 | Average partition coefficient (k)

This coefficient is a measure of the amount of solute occluded in the ice phase (Chen, Chen, & Free, 2000; Moreno et al., 2014a) and is defined by Equation 1.

$$K = \frac{C(s,ice)}{C(s,liq)} \quad (1)$$

where

Cs liq = solids content of the final liquid solution and

Cs ice = solids content of ice.

2.5.2 | Efficiency of FC (eff)

This parameter is a measure of the recovery of solids in the FC solution compared to the amount of solid that has been occluded in the ice phase. It is defined by Equation 2 (Farah, Zaki, Noritza, & Mazura, 2015; Raventós et al., 2007; Toci & Farah, 2008).

$$\text{eff} = (\text{Cs}_{\text{liq}} - \text{Cs}_{\text{ice}}) / (\text{Cs}_{\text{liq}}) \times 100 \quad (2)$$

where

Cs_{liq} = solids content of the final liquid solution and

Cs_{ice} = solids content of ice.

2.5.3 | Concentration index

The concentration index (CI) represents the number of times the concentration of the solution has been increased and is defined by Equation 3 (Miyawaki, Liu, Shirai, Shakashita, & Kagitani, 2005).

$$\text{CI} = (\text{C}_{\text{s liq}}) / (\text{C}_{\text{s 0}}) \quad (3)$$

where

Cs_{liq} = solids content of the final liquid solution and

Cs₀ = solids content of the initial solution.

2.5.4 | Solute yield at each stage (Y_{stage})

Solute yield represents the amount of solute or coffee solids recovered from the original solution at each stage of FC. Y was defined as the relationship between the mass of solute present in the freeze-concentrated liquid and the mass of the solute present in the initial solution, as calculated by Equation 4 (Moreno et al., 2014a; Nakagawa, Maebashi, & Maeda, 2010):

$$Y_{\text{stage}} = m_{\text{s liq}} / m_{\text{s 0}} \quad (4)$$

where Y is the solute yield, m_{s liq} is the solute mass in the liquid fraction, and m_{s 0} is the initial solute mass.

2.5.5 | Ice-loss percentage (IL)

The percentage of loss of bioactive compounds was calculated using Equation 5 (Ramos, Delgado, Bautista, Morales, & Duque, 2005).

$$\text{IL} = \frac{\text{C}_{\text{s ice}}}{\text{C}_{\text{s ice}} + \text{C}_{\text{s liq}}} \times 100 \quad (5)$$

where

Cs_{ice} = solids content of ice and

Cs_{liq} = solids content of the final liquid solution.

2.5.6 | Total phenolic content retention

The total phenolic content retention (TPC retention) indicates the amount of phenolic compounds preserved in the freeze-concentrated fraction respect to the initial extract (Orellana-Palma, Petzold, Pierre, & Pensaben, 2017)

$$\text{TPC retention (\%)} = \frac{\text{C}_{\text{s 0}} / \text{C}_{\text{s liq}} \times (\text{final phenolic content})}{(\text{Initial phenolic content})} \times 100 \quad (6)$$

2.6 | Statistical analysis

All analyses were performed in triplicate, and the results are presented as the mean and standard deviation. Correlations between variables were established using the Pearson correlation test. The analyses were performed using the SPSS software.

3 | RESULTS AND ANALYSIS

3.1 | Effect of FFFC on bioactive compounds in coffee extract

The bioactive compounds in coffee extract, CGAs and caffeine, were identified by chromatography. Typical chromatograms are shown in Figure 3. The major compounds were 5-CQA, 3-CQA, and 4-CQA, which yielded signals at 22, 50, and 60 min, respectively, and caffeine, which produced a signal at 29 min. These results are consistent with those reported by Fujioka and Shibamoto (2008) and Moreno et al. (2014b) for coffee beverages.

The contents of CGAs and caffeine after FC were analyzed by comparing the values obtained in the final solution at the end of the second stage of the process and in the ice fraction to those of the initial solution. The values found by RP-HPLC for each compound are reported as contents on a wet and dry basis in Table 1. The concentration of CGA was higher than that of c-CGA, a result consistent with studies by Fujioka and Shibamoto (2008), Bravo et al., (2013) and Trugo and Macrae (1984). The values obtained in this research for bioactive compounds fall within the content ranges reported in other studies of coffee beverages. For example, Ludwig et al. (2012) analyzed the impact of time and the beverage-making process on compounds with antioxidant activity. The reported 5-CQA concentrations between 34 and 70 mg/100 mL in filter-brewed coffee and between 29 and 201 mg/100 mL in espresso coffee made from 6% w/v Guatemala coffee solutions. Moreover, Fujioka and Shibamoto (2008) measured the CGA and caffeine levels in several commercial coffee beverages; the major component was caffeine, with values between 10.9 and

TABLE 1 Changes in bioactive compounds, polyphenols content, and the antioxidant activity of coffee during falling film FC

	Initial	Final	Ice	Ice loss %	CI
Wet basis (mg/mL)					
CGA	0.29 ± 0.01	0.60 ± 0.01	0.38 ± 0.01	138.52	2.1
c-CGA	0.20 ± 0.00	0.42 ± 0.02	0.26 ± 0.01	138.62	2.1
Caffeine	1.21 ± 0.01	2.58 ± 0.13	1.62 ± 0.07	38.56	2.1
DPPH	10.2 ± 0.13	19.0 ± 1.1	11.2 ± 2.2	47.15	1.9
ABTS	33.6 ± 0.138	43.3 ± 0.1	38.6 ± 0.2	37.1	1.3
Polyphenols	4.3 ± 6.35	16.7 ± 2.56	9.8 ± 4.48	37.03	3.9
Dry basis (mg/100 g)					
CGA	0.0055 ± 0.0	0.0055 ± 0.000	0.0055 ± 0.000	50.51	1.0
c-CGA	0.0037 ± 0.00	0.0038 ± 0.000	0.0038 ± 0.000	49.94	1.0
Caffeine	0.0229 ± 0.00	0.0235 ± 0.000	0.0238 ± 0.000	50.30	1.0
DPPH	0.194 ± 0.02	0.173 ± 0.00	0.165 ± 0.02	48.75	0.9
ABTS	0.639 ± 0.03	0.395 ± 0.00	0.568 ± 0.00	58.99	0.6
Polyphenols	0.082 ± 0.01	0.152 ± 0.01	0.145 ± 0.04	48.68	1.9

16.5 mg/g, followed by 5-CQA, with concentrations of 2.13–7.06 mg/g, and 4-CQA, with concentrations of 1.44–4.27 mg/g.

Table 1 shows the CI determined for the concentrated solution and final ice phase for the three metabolites in a wet and a dry basis after two stages of FFFC. The wet basis (wb) considers the total volume of the solution and indicates the level of concentration increasing. The dry basis (db) is a comparison with the total solids of the extract (dm) and it is useful to determine the level of preservation of the bioactive compounds. The final solution obtained a CI of 2.1 (wb) and 1.0 (db). This result shows the FFFC effective to increase the concentration of bioactive compounds. If the solids content is higher in the extract after FC, the concentration of bioactive compounds should increase. However, analyzing the content on dry basis allows the preservation of these compounds to be assessed. Accordingly, the values in Table 1 indicate that bioactive compounds were preserved showed by the value of 1 for the CI. Moreover, when the concentrated coffee extract is redissolved, the resultant beverage is expected contain the same concentrations of CGAs and caffeine.

Conversely, The CI of the ice phase was 1.3 (wb), showing that a portion of solutes remained in the ice to be recovered. The occlusion phenomenon generated during FC caused some soluble solids to be present in the final ice fraction. This value may be expressed for coffee based on the volume of the extract or based on the dm content. The ice loss percentage of the compounds tested on a dry basis was approximately 50% for all 3 cases, which indicates that CGAs and caffeine are distributed equally in the solids present in the final 2 fractions of the process and bioactive compounds are not selectively retained in the ice. Similar results were reported for other functional compounds during FC (Aider & de Halleux, 2008; Boaventura et al., 2013; Chen, Chen, & Free, 1998; Moreno et al., 2014b). Therefore, FC prevents the loss of bioactive compounds during the processing of coffee solutions.

Moreover, the total content of phenolic compounds was determined. The results are reported as GAE and are shown in Table 1. Specifically, their concentration increased during FC. The final solution reached a concentration 4 times (CI 3.9) higher than that of the original solution. These data confirm that FC effectively removes water without decreasing the content of polyphenols naturally present in coffee solutions.

The CIs for polyphenols were higher than those obtained for the bioactive chlorogenic acids and caffeine content of each solution, which may be attributed to the chemical nature of these compounds. Specifically, they are highly water-soluble and are consequently distributed in both solid and water phases. Similarly, this increase in phenolic compounds is likely a result of the associations found between high-molecular-weight melanoidins and polyphenols. These compounds are more resistant to oxidation and consequently react with the Folin-Ciocalteu reagent to significantly contribute to the final result of the test. The content of phenolic compounds in the ice fractions increased in the 2nd step, with a CI of 2.3. This increase is due to occlusion. The polyphenols preservation expressed as the total phenolic content retention defined by Equation 5 was calculated for the final liquid fraction after two stages of FFFC. A value of 88.9% of TPC retention

was obtained. This value is comparable to those reported by Orellana-Palma et al. (2017) with centrifugal block FC of blueberry juice, which reported values from 80% to 95%. This result shows the effectivity of FFFC on polyphenol preservation.

In the ice fractions, the total polyphenol content directly correlated with the number of FC steps. The possibility of hydrogen-bond formation with water molecules is high because of the number of hydroxyl groups in these compounds, which reduces the amount of interstitial water available to freeze alone and consequently increases the concentration of these compounds in the ice obtained (Aider & de Halleux, 2008). This parameter is directly related to the retention of solids in the ice being formed and therefore, also with the efficiency of the process, which decreased over time as concentration progressed and reached a loss percentage in ice of 48.68%.

3.2 | Effect of FFFC on antioxidant activity

The antioxidant activities of the initial solution, the solution obtained after 2 steps, and its respective ice fraction were determined using the ABTS and DPPH assays and Trolox as a reference standard. The results are shown in Table 1. Specifically, the antioxidant activity per volume of coffee solution increased after the FC. The DPPH assay showed an increase of the antioxidant activity, which was equivalent to the action of Trolox to degrade this free radical, of 1.9 times in the final solution of coffee. The ABTS assay showed higher Trolox equivalent values than the DPPH assay. Specifically, the antioxidant activity of the solution obtained value of 43.27 mg/mL. The ice fraction had a CI of 1.1.

The results expressed on a dry basis (g of Trolox equivalent per 100 g of solid matter) showed CI values close to 1. The antioxidant activity of the final solutions against the 2 radicals slightly decreased during each step and resulted in final CI values of 0.9 for DPPH and 0.6 for ABTS. The increase in the antioxidant activity measured by DPPH and those in the total solids and bioactive compounds were similar. The activity measured by ABTS also increased after FC, albeit to a lesser degree, which may explain why these 2 radicals react easily with hydrogen donors, such as phenolic compounds, given that DPPH is more selective (Ludwing et al., 2012). Moreover, the antioxidant activity against the 2 radicals, reported as TEAC mg/mL, directly correlated with the content of phenolic compounds. The Folin-Ciocalteu method is based on electron transfer, but the reducing power against this compound is not restricted to phenolic compounds. Caffeine and low- and high-molecular-weight compounds, such as melanoidins, which are induced by Maillard reactions, have also been demonstrated to be able to transfer electrons and hydrogen (Yazheng & Kitts, 2011), which significantly contributes to the antioxidant potential of coffee beverages.

Compared with the results reported by Boaventura et al. (2013) for the FC of mate, the final solution obtained exhibits high antioxidant activity against the DPPH radical. According to these authors, a concentration of 3.88 TEAC μ g/mL was sufficient to inhibit 50% of this radical. Similar values are reported by Santini et al. (2011). In this study, the Trolox-equivalent concentration of the final solution was 84.13 mmol/L, which proves the effectiveness of the technique in preserving the bioactivity of the compounds present in coffee.

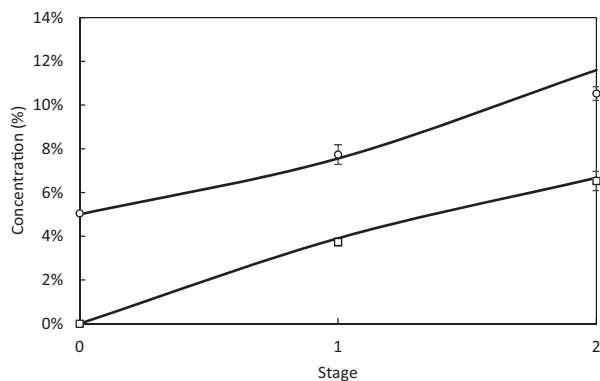


FIGURE 4 Experimental solid concentration in liquid (○) and ice (□) at each stage of falling film FC. (line), predicted data

The results show the preservation of the bioactivity of the coffee extract after two stages of FFFC. A validation in a multistep process is recommended. Moreno et al. (2014) proposed a multistep process to reach values of 30% of total solid content showing the technical feasibility of the process. However, the energy consumption is a challenge for the process optimization. Pazmiño et al. (2016) calculated 10.3 Kwh/1,000 kg of ice removed of energy requirement for a multistep process. Commercial data reported specific energy consumption of 14.7 kWh to evaporate 1,000 kg of water for evaporation concentration, showing a comparable value.

3.3 | Correlation between bioactive compounds and total solid content

The solids content of the liquid and ice fractions in the 2 FFFC steps are shown in Figure 4. Specifically, the concentration of total soluble solids of coffee increased to 11% in the 2 steps, whereas the concentration in ice was 7% at this point. The solid line represents the data predicted by the model proposed by Moreno et al. (2014a), which was used to predict the solids content in relation to the concentration step for coffee extract. The experimental data fit the model well. This model can predict an increase in concentration of up to 33% in 6 successive steps, which meets the industrial processing requirements for freeze-concentrated coffee extract.

The performance indicators of FC shown in Table 2 can be calculated from the concentration data. Specifically, the CI increased during the process. At the end of step 2, the concentration of the solution was doubled, which corresponded to a CI of 2.09, over an average

TABLE 2 Initial coffee solid concentration (C_{s0}), concentration index (CI), Average partition coefficient, concentration efficiency (Eff), and solute yield at each stage (Y_{stage}) of falling film FC tests

Stage	C_{s0} (%)	CI	K	Eff (%)	Y_{stage}
1	5.05 ± 0.0	1.55 ± 0.07	2.09 ± 0.17	51.92 ± 4.2	0.38 ± 0.02
2	7.8 ± 0.35	2.09 ± 0.05	1.61 ± 0.06	38.06 ± 2.38	0.26 ± 0.03

Average and standard deviation.

time of 4 hr. In a study by Hernández, Raventós, Auleda, and Ibarz (2009) on the FC of apple and pear juice, CI values of 2.08 and 2.35 were obtained in 14 hr starting from solutions with initial concentrations of 14.5 and 13.1°Brix. The difference in operation time was due to the differences in the scale of the operation and the concentrations of the initial solutions. The obtained CI values were similar to the CI values of bioactive compounds in the two fractions, which proves that bioactive compounds are distributed in proportion to the total solids contents of the ice and concentrated liquid. A comparable result was obtained for the block FC of coffee extract (Moreno et al., 2014b).

The efficiency of FC is inversely correlated with the concentration of the initial solution. As the solution content increases, solutes tend to move by diffusion to the region of lower concentration. Simultaneously, the solids present in the liquid-solid interface do not easily move and are trapped in the ice sheet being formed (Hernández et al., 2009). Therefore, the content of solutes in the solid phase increases as the solution is concentrated at each step, which decreases the efficiency. The decrease in efficiency is also demonstrated by the increased occlusion of solids, as indicated by the increased partition coefficient values in steps 1 and 2. Specifically, the amount of solids retained in the ice fraction (k) was greater in step 2 than in step 1. These results agree with those reported by Hernández et al. in 2009, who used 4 concentration steps for FC of apple juice and reported that the process efficiency decreased as the solids content increased in the solution. Moreover, the same trend was reported for solutions of simple sugars (Raventós et al., 2007). The differences between the 1st and 2nd step may also be due to the rate of ice production when concentrations are low, which is influenced by the large temperature difference between the liquid and refrigerant (Sánchez et al., 2009). This temperature difference inversely correlates with the solids content and consequently directly affects the efficiency of concentration.

The solute yield reached values of 0.38 and 0.26. Those values represent the percentage of solute recovered from the initial solution. Y_{stage} decreased with the step of concentration due to the solid occlusion. The occlusion of solids in the ice phase increased during each step because a higher solids content generates more interactions with the web of ice crystals being formed (Chen, Chen, & Free, 1999; Gu, Watanabe, Suzuki, & Miyawaki, 2008). Additionally, melanoidins, which are high-molecular-weight compounds that are soluble in water and constitute 25% of the coffee dry weight, may decrease the flow rate of the solutes due to their size, which contributes to their occlusion within the ice fractions being formed.

The correlation between bioactive compounds and antioxidant activity in coffee extract was analyzed based on the Pearson coefficient, and the results are shown in Table 3. This analysis demonstrated that antioxidant activity is due to the presence of the bioactive components, with correlation coefficients between 0.982 and 0.986 for DPPH and between 0.965 and 0.970 for ABTS as a significance level of 0.10. A direct correlation was also established between bioactive compounds, with significance levels of 0.05 and 0.01. This type of correlation was also established by Vignoli et al. (2011), who reported correlation coefficients of 0.88 and 0.82 between total polyphenols and

TABLE 3 Correlations between antioxidant activity and bioactive compounds concentration

	DPPH	ABTS	5-CQA	4-CQA	Caffeine	Polyphenols
DPPH	1	0.906	0.986	0.982	0.982	0.938
ABTS	0.906	1	0.965	0.969	0.970	0.997
5-CQA	0.986	0.965	1	1.000	1.000	0.983
4-CQA	0.982	0.969	1.000	1	1.000	0.986
CAFEINA	0.982	0.970	1.000	1.000	1	0.987
PF	0.938	0.997	0.983	0.986	0.987	1

DPPH and ABTS, respectively. Moreover, López-Galilea, di Leonardo, de Peña, and Cid (2006) reported a correlation coefficient of 0.83 for caffeine and DPPH and Boaventura et al. (2013) for mate, reported a correlation coefficient of 0.99 between polyphenols and DPPH and 0.86 between CGA and DPPH. The antioxidant activity and the contents of polyphenols and bioactive compounds were similar to those published for a block FC study of aqueous coffee solutions (Moreno et al., 2014). According to these results, FFFC and block FC effectively preserve the functional quality of coffee extract.

4 | CONCLUSIONS

FFFC effectively removes water from aqueous coffee extract. Specifically, this technique increased the solids content of coffee 2.1 times in 2 process steps. The content of bioactive compounds, CGAs, caffeine, and total polyphenols increased in proportion to the increase of total solids in coffee extract. The concentration of bioactive compounds on a dry basis was preserved during two stages of FC. The antioxidant activity of coffee extract also increased during FC and was preserved when calculated with respect to coffee (dm). These data show that the FC beverage exhibits the same functionality as the original extract. Moreover, antioxidant activity correlates with the contents of CGAs and caffeine. These 3 bioactive compounds represent the major antioxidant fraction of coffee and are relevant to the functionality of the beverage. The results of this study demonstrate that FFFC is an effective technique to concentrate coffee solids and preserve the bioactive compounds and functionality of the coffee beverage.

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