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RESEARCH

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Plant-based pecan nut cake beverage enrichment of phytochemicals and antioxidant properties using multi-stage block freeze concentration

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Abstract

Pecan nut (*Carya illinoinensis*) processing to obtain oil generates circa 37% of press cake, which is currently underutilized and primarily employed as animal feed. Due to its nutritional- and bioactive-rich composition, pecan nut cake (PNC) can be used as raw material for plant-based beverages, whose properties may be enhanced using a non-thermal technology based on block freeze concentration (BFC). The effect of five-stage BFC on total solids content (TSC), pH, color parameters, retention of phytochemicals, and the antioxidant activity (AA) of a pecan nut cake beverage (PNB) was assessed in this work. BFC afforded 98% (w/w) solids retention after three stages and 85% efficiency after four stages. The process also provided a 254% concentration factor in stage 5. In the last step, approximately a 64% increase in TSC and a slight decrease (7.3%) in pH compared to the control PNB was observed. In addition, total phenolic compounds, condensed tannins, total flavonols, and AA were significantly ($P < 0.05$) improved after the BFC, resulting in a 2.6-10.2- and 1.9-5.8-fold increase in phytochemicals and antioxidants, respectively. On the other hand, BFC caused the darkening of concentrates due to TSC and bioactive compounds retention. The processing strategy evaluated herein indicated a great potential of PNC as a raw material for obtaining high-quality ingredients for the food industry, which may reduce agro-industrial waste production and add value to a coproduct rich in nutrients and biocompounds with potential biological activity.

Keywords: *Carya illinoinensis*, Press cake, Waste valorization, Plant-based beverage, Bioactive compounds, Cryoconcentration

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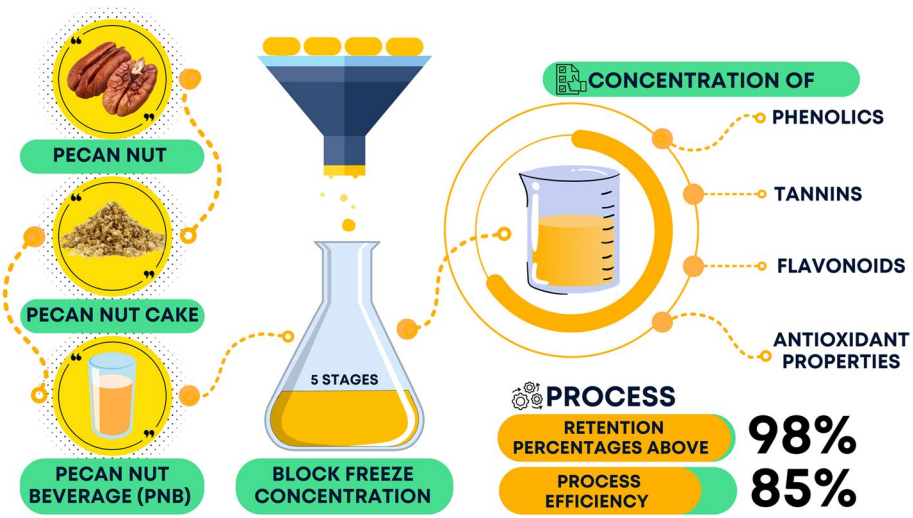
Graphical Abstract



Background

Pecan nut (*Carya illinoinensis* (Wangenh.) K. Koch) is globally appreciated for its sensory and nutritional properties, which include mostly lipids (65.9–78.0%) and proteins (6.0-11.3%) (Venkatachalam et al. 2007). Worldwide, pecan nut production has grown progressively from 91,215 metric tons in 2011/2012 to 129,510 metric tons in 2021/2022, representing a 30% rise in the last decade. Mexico and the United States account for 45% and 39% of the global production of pecan nuts, respectively. Emerging producers include South Africa (8%), Brazil (2%), and China (2%) (International Nut and Dried Fruit Council 2022; Martins et al. 2019). Brazil reached its highest production record of 5.4 metric tons in 2021 and harvested 4.2 metric tons in 2022 after years of increasing production (IBPecan 2022).

The industrial cold pressing of pecan nuts currently provides a high-quality extra virgin pecan oil but yields a high volume of press cake, representing about 370 g per kg of nuts (Maciel et al. 2020). Pecan nut cake (PNC) has pleasant sensory characteristics and is rich in proteins, fibers, and minerals such as Mn, K, Mg, and Zn. It also has a high content of bioactive compounds, main phenolics such as catechin, epigallocatechin, and epicatechin (Atanasov et al. 2018; Maciel et al. 2020; Salvador et al. 2016; Wakeling et al. 2001). Due to the rich composition, press cakes can be raw material to obtain non-dairy plant-based beverages for human consumption as an alternative to valorize such coproducts (Demoliner et al. 2020; Łopusiewicz, Kwiatkowski, et al. 2022; Łopusiewicz, Śmietana, et al. 2022).

Plant-based food market represented USD 40.21 billion in 2021 (Vantage Market Research 2022) and is expected to increase at a Compound Annual Growth Rate (CAGR) of 11.90%, reaching up to USD 161.9 billion in 2030 (Statista 2021). Likewise, the plant-based beverage market, valued at USD 25.94 billion in 2021, is expected to grow to USD 66.53 billion by 2028 (Grand View Research 2021). The United States Department of Agriculture - USDA (2020) highlights that Brazil is the sixth-largest consumer of foods and beverages associated with health and well-being, estimated at USD 26 billion in 2019. Such products also represent an alternative for consumers with food restrictions, such as those with lactose intolerance (hypolactasia), allergy to milk protein, cholesterol problems, and those adept at a vegetarian or vegan diet (Aydar et al. 2020; Paul et al. 2020; Qamar et al. 2020). Furthermore, the nutritional profile free of lactose and casein and the absence of direct correlation to increased cholesterol and low allergenic rates have been indicated as important criteria for choosing plant-based beverages as alternatives to milk-based ones (Sethi et al. 2016; Silva et al. 2020).

The quality of plant-based beverages can be improved using concentration technology. However, due to the loss of nutritional and bioactive compounds caused by thermal-based methods like evaporation, non-thermal technologies such as block freeze concentration (BFC) have been reported as an alternative to preserve thermolabile components, vitamins, polyphenols, and volatile compounds and enhance nutritional and sensory

characteristics in those beverages (Demoliner et al. 2020; Moreno, Raventós, Hernández, & Ruiz 2014; Orellana-Palma, Zúñiga, Takhar, Gianelli, & Petzold, 2017). Also known as freeze-thaw concentration, BFC can be applied to food liquid solutions over freeze-thaw cycles. During the process, the concentrated portion is continuously separated from the ice fraction by gravitational thawing for many cycles (Petzold et al. 2015).

BFC has been successfully employed to enrich the properties of various food products such as whey (Barros, Silva, Canella, et al. 2022; Barros, Silva, Verruck, et al. 2022), persimmon (Silva et al. 2021), apple juice (Miyawaki et al. 2016; Zielinski et al. 2019), yerba mate aqueous extract (Nunes et al. 2014), coffee (Moreno et al. 2014), tofu (Benedetti et al. 2015), orange juice (Haas et al. 2022; Patricio Orellana-Palma et al. 2019), goat milk (Canella et al. 2020), wine (Petzold et al. 2016), and sapucaia nut cake beverage (Demoliner et al. 2020). Nevertheless, no report has been found on this topic regarding pecan nut beverages. Therefore, this study aimed to evaluate the effect of BFC on the retention of soluble solids, color parameters, three classes of phytochemicals, and the in vitro antioxidant capacity of a pecan nut cake beverage.

Materials and methods

Chemicals

Gallic acid, Folin-Ciocalteu reagent, 2,2-diphenyl-1-picrylhydrazyl (DPPH), tripyridyl-2,4,6-s-triazine (TPTZ), thiobarbituric acid (TBA), methanol, (+)-catechin, quercetin, and ascorbic acid were purchased from Sigma-Aldrich (São Paulo, Brazil). All other chemical reagents and solvents used in the experiments were of analytical grade. Aqueous solutions were prepared using ultrapure water by the Milli-Q system (Millipore, São Paulo, Brazil).

Pecan samples and pecan nut cake beverage (PNB)

Pecan samples of the Barton variety were supplied by Divinut Indústria de Nozes Ltda (Cachoeira do Sul, Brazil). The pecan nut cake (PNC) was obtained according to Maciel et al. (2020). First, the particle size has been standardized using a #60 Tyler mesh. Then, PNC was vacuum-packed in a low-density polyethylene bag and kept under refrigeration until further use. The proximate composition of the PNC was: 40.5 ± 0.33 g 100 g $^{-1}$ of carbohydrates; 21.87 ± 0.06 g 100 g $^{-1}$ of protein;16.64 ± 0.06 g 100 g $^{-1}$ of lipids; 13.01 ± 0.19 g 100 g $^{-1}$ of fiber; 5.03 ± 0.11 g 100 g $^{-1}$ of moisture; 2.97 ± 0.07 g 100 g $^{-1}$ of ashes; and 398.81 kcal of energy).

The pecan nut cake beverage (PNB) was prepared as described by Gul et al. (2017), with modifications. Firstly, 0.6 kg of PNC was mixed with 9 L of water (1:15 w/v). Then, the mixture was homogenized at 10,000 rpm for 10 min at 25 °C in an Ultra-Turrax (model T 25 Digital S32, IKA®, São Paulo, Brazil) protected from light. Finally, the PNB was filtered using a cheesecloth and stored in low-density polyethylene containers at 4.0 ± 2 °C until further analysis.

Block freeze concentration process

The experimental procedure of the multi-stage gravitational block freeze concentration (BFC) process is illustrated in Fig. 1. Firstly, 8.0 L of PNB were placed in polypropylene cups with 200 g capacity, 8.5 and 4.0 cm inner diameter and height, respectively. Then, these cups containing PNB were frozen at − 20 ± 1 °C in a static freezer (model FE 18, Electrolux, São Carlos, Brazil). Once the PNB was frozen, 50% of the initial volume was thawed at controlled room temperature (20 ± 2 °C). The thawed liquid was the concentrate of the first BFC stage (C1). This procedure was repeated in the second

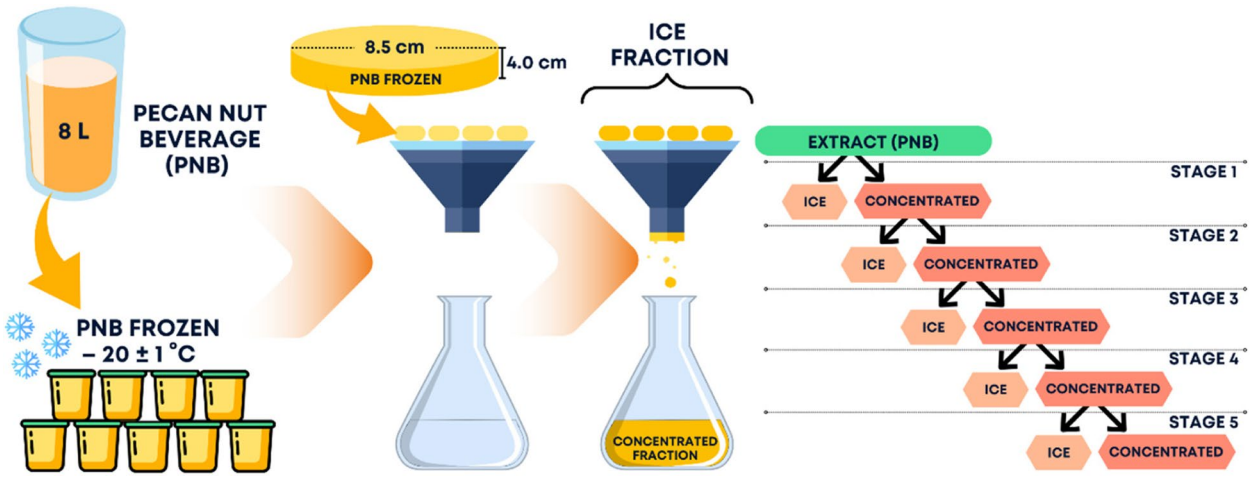


Fig. 1 Schematic diagram of the multi-stage gravitational block freeze concentration process of pecan nut cake beverage

(C2), third (C3), fourth (C4), and fifth (C5) freeze concentration stages. The ice and concentrate fractions remaining from each freeze concentration stage were submitted to physicochemical and chemical analysis.

Physicochemical and color analysis

The physicochemical properties of PNB, concentrate (C1-C5), and ice (I1-I5) fractions were carried out according to the Association of Official Analytical Chemicals (AOAC 2005). The total solids content (TSC) (925.09) was determined by drying the samples to constant weight at 105 ± 2 °C for 24 h, and the result was expressed in grams per 100 g. The pH (981.12) was recorded at room temperature (25 ± 2° C) using a PHS-3 BW pHmeter (BEL, Piracicaba, Brazil). The color was evaluated as described by Pathare et al. (2013) in quintuplicates using a Chroma Meter CR 400 colorimeter (Konica Minolta, Osaka, Japan). The results were expressed according to the Commission Internationale de l'Eclairage color system (CIELab) and presented as L^*, a^*, and b^* parameters. Chroma (C^*) and hue angle (h) were calculated by Eqs. 1 and 2.

$$C^* = \left[\left(a^{*2}+b^{*2}\right)^{\frac{1}{2}}\right] \tag{1}$$

$$h = tan^{-1}\left(\frac{b*}{a*}\right) \tag{2}$$

Browning index (BI) and the total color difference (ΔE^*) were calculated by Eqs. 3 and 4 (Mohapatra et al., 2010):

$$BI = 100 \times \left(\frac{X - 0.31}{0.17}\right) \tag{3}$$

where $X = \frac{(a^*+1.75L^*)}{(5.645L^*+a^*-3.012b^*}$

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2\left(\Delta b^*\right)^2} \tag{4}$$

Total phenolics

Total phenolic compounds (TPC) were estimated using the Prussian Blue (PB) method (Price & Butler 1977) with modifications (Margraf et al. 2015). Condensed tannins (CT) content was evaluated by the vanillin test (Horszwald & Andlauer 2011). Total flavonols (TF) were estimated as described by Granato et al. (2016). TPC, CT, and TF were expressed in mg of gallic acid equivalent (GAE), catechin equivalent (CE), and quercetin equivalent (QE) per 100 g, respectively.

In vitro antioxidant assays

Antioxidant analyses were carried out in microplates. The ferric reducing antioxidant power (FRAP) assay was performed according to Benzie & Strain (1996). The cupric reducing antioxidant capacity (CUPRAC) method was performed according to Apak et al. (2008). The results for FRAP and CUPRAC were expressed in mg of ascorbic acid equivalent (AAE) per 100 g (mg AAE 100 g^{-1}). The total reducing capacity (TRC) of hydrophilic and lipophilic compounds was performed according to Berker et al. (2013) and expressed in mg QE 100 g^{-1}. The scavenging activity of the 2,2-diphenyl-1-picryl-hydrazyl (DPPH) radical was performed according to Brand-Williams et al. (1995), and the results expressed in percentage of inhibition, according to Eq. 5, where A_{517} is the absorbance at 517 nm:

$$\%\text{Inhibition} = \left[1 - \left(\frac{A_{517}\text{sample}}{A_{517}\text{blank}}\right)\right] \times 100 \tag{5}$$

The inhibition of lipid peroxidation (ILP) was determined using the method described by Margraf et al. (2016). The ILP was expressed as a percentage of inhibition, using Eq. 6, where A_{532} is the absorbance at 532 nm:

$$\%\text{Inhibition} = \left[1 - \left(\frac{A_{532}\text{sample}}{A_{532}\text{blank}}\right)\right] \times 100 \tag{6}$$

Response variables from the BFC process

The behavior of the BFC process was evaluated by different variables based on TSC or TPC, as following described:

The concentration index (CI) was calculated by Eq. 7, based on TSC (Meneses et al. 2021):

$$CI = \frac{Cs_{LIQ}}{Cs_0} \tag{7}$$

Where CI is the concentration index, Cs_{LIQ} is TSC (%w/w) in the individual fraction, and Cs_0 is the TSC of the initial solution.

The average distribution coefficient (k), which is the ratio between the solids in the ice fraction (CS_{ICE}) and the solids in the liquid fraction (CS_{LIQ}), was assessed from Eq. 8 (Meneses et al. 2021):

$$k = \frac{CS_{ICE}}{CS_{LIQ}} \tag{8}$$

Concentrate yield (Y) was based on TPC and calculated by Eq. 9, according to Moreno et al. (2014):

$$Y(\%) = \frac{C_f \times m_f}{E_i \times m_i} \times 100 \quad (9)$$

where C_f is TPC (mg GAE 100 g^{-1}) of the concentrate fractions, E_i is TPC (mg GAE 100 g^{-1}) of PNB, m_f is the concentrate fraction mass (g), and m_i is the PNB mass (g).

The efficiency (*eff*) of the freeze concentration process related to the TPC was adapted from Sánchez et al. (2011) and calculated by Eq. 10:

$$eff(\%) = \frac{C_f \times I_f}{C_f} \times 100 \quad (10)$$

where C_f is TPC (mg GAE 100 g^{-1}) of the concentrate fractions and I_f is TPC (mg GAE 100 g^{-1}) of ice fractions.

The concentration factor (CF) of each freeze concentration stage was obtained as a function of TPC using Eq. 11 adapted from Moreno et al. (2014):

$$CF(\%) = \frac{C_f}{E_i} \times 100 \quad (11)$$

where C_f is TPC (mg GAE 100 g^{-1}) from each BFC stage and E_i is TPC (mg GAE 100 g^{-1}) of PNB.

Validation of BFC results

A mass balance was calculated to validate the experimental results according to Sánchez et al. (2011). The comparison between the mass balance and theoretical data, calculating the predicted ice mass ratio (W_{pred}) (kg of ice per kg of beverage), was done by Eq. 12:

$$W_{pred} = \frac{E_i - C_f}{I_f - C_f} \quad (12)$$

where E_i is TPC (mg GAE 100 g^{-1}) of PNB, C_f is TPC (mg GAE 100 g^{-1}) of the concentrate fraction, and I_f is TPC (mg GAE 100 g^{-1}) of each ice fraction.

The deviation between experimental and theoretical data was expressed as root.

mean square (RMS), as described in Eq. 13.

$$RMS(\%) = 100\sqrt{\frac{\sum\left(\frac{w_{exp}-w_{pred}}{w_{exp}}\right)2}{N}} \quad (13)$$

where W_{exp} and W_{pred} correspond to the experimental and the predicted ice mass ratio,

respectively, while N is the number of repetitions performed.

Statistical analysis

Results were expressed as a mean ± standard deviation (SD) of the triplicate analysis. The homogeneity of variances was verified using the Brown-Forsythe test. The differences ($P<0.05$) between the results were determined using a one-way analysis of variance (ANOVA), and the Fisher's Least Significant Difference (LSD) test was applied when statistically significant differences were detected. Finally, statistical correlations based on Pearson's coefficient (r) were calculated to verify the existence and intensity of the association between the response variables. All statistical analyses were performed using Action v. 2.6 (Statcamp, São Paulo, Brazil), Statistica 13.3 (TIBCO Software Inc., Palo Alto, USA), and OriginPro 2021 (OriginLab Corporation, Northampton, USA) software.

Results and discussion

Physicochemical properties of PNB and freeze concentrates

Total solids content (TSC), pH, and color parameters of the PNB and the corresponding concentrate (C1-C5) and ice (I1-I5) fractions obtained in the BFC stages are displayed in Table 1. Significant differences ($P<0.05$) in the TSC values were detected all over the freeze concentration process. A reduction of 75% in solutes from PNB was verified in the first stage of BFC (C1). On the other hand, TSC presented a significant linear increase in the subsequent steps compared to C1. The final concentrate fraction (C5) showed 64% more solutes than the previous fraction (C4) and about sevenfold more TSC compared to the initial fraction (C1). Therefore, employing a five-stage process was essential to improve the product's quality regarding solutes retention. This linear effect on the BFC was also reported by Jaster et al. (2018), Orellana-Palma et al. (2019), and Orellana-Palma et al. (2020) for strawberry pulp, orange juice, and pineapple juice, respectively.

Similar to the concentrate fractions, the initial ice (I1) showed a 63% retention of TSC in comparison to PNB. However, no significant ($P<0.05$) variations in TSC values were verified for I2 to I4. In addition, < 2% solids remained at the end of the process in I5. The crystalline phase on the first concentration cycle is responsible for a high entrapment of soluble solids in BFC. Furthermore, water recrystallization during isothermal thawing may cause gelation effects, which also influence the content of solutes in BFC stages (Sequera et al. 2019). This behavior confirms that BFC allows targeting the highest solids content in concentrate fractions rather than ice fractions,

Table 1 Total solids content (TSC), pH, and color parameters of the pecan nut beverage (PNB) and its concentrate (C1-C5) and ice (I1-I5) fractions over a five-stage block freeze concentration

Sample	TSC (g 100 g^{-1})	pH	*L**	*a**	*b**	*C**	*h*
PNB	$8.62 \pm 0.01^{b,A}$	$6.32 \pm 0.01^{a,C}$	$36.81 \pm 1.43^{a,A}$	$2.84 \pm 0.25^{a,B}$	$7.22 \pm 0.34^{b,c,B}$	$7.76 \pm 0.41^{a,B}$	$68.58 \pm 0.86^{e,D}$
C1	2.09 ± 0.05^{e}	6.31 ± 0.04^{a}	31.56 ± 0.20^{b}	0.88 ± 0.03^{d}	7.38 ± 0.09^{a}	$7.44 \pm 0.09^{b,c}$	83.17 ± 0.20^{a}
C2	2.66 ± 0.13^{d}	6.20 ± 0.04^{b}	29.72 ± 0.12^{c}	1.25 ± 0.02^{c}	$7.31 \pm 0.06^{b,c}$	$7.41 \pm 0.06^{b,c}$	80.32 ± 0.13^{b}
C3	4.80 ± 0.12^{c}	6.11 ± 0.01^{c}	27.71 ± 0.04^{d}	1.88 ± 0.06^{b}	7.04 ± 0.04^{c}	7.29 ± 0.03^{c}	75.07 ± 0.48^{c}
C4	8.66 ± 0.10^{b}	5.99 ± 0.01^{d}	23.56 ± 0.02^{e}	1.94 ± 0.02^{b}	5.03 ± 0.02^{d}	5.39 ± 0.02^{d}	68.94 ± 0.23^{e}
C5	14.20 ± 0.10^{a}	5.86 ± 0.05^{e}	21.87 ± 0.10^{f}	1.33 ± 0.11^{c}	3.67 ± 0.20^{e}	3.91 ± 0.15^{e}	70.02 ± 2.55^{d}
I1	5.42 ± 0.16^{B}	6.41 ± 0.03^{B}	38.88 ± 0.57^{B}	4.64 ± 0.16^{A}	9.54 ± 0.34^{A}	10.61 ± 0.37^{A}	64.08 ± 0.17^{E}
I2	0.61 ± 0.10^{D}	6.56 ± 0.03^{A}	32.98 ± 0.45^{C}	0.28 ± 0.08^{D}	5.86 ± 0.13^{D}	5.87 ± 0.14^{D}	87.26 ± 0.69^{A}
I3	0.68 ± 0.10^{D}	6.53 ± 0.01^{A}	33.06 ± 0.04^{D}	0.31 ± 0.03^{D}	6.36 ± 0.01^{C}	6.37 ± 0.01^{C}	87.24 ± 0.27^{A}
I4	0.69 ± 0.16^{D}	6.56 ± 0.02^{A}	34.27 ± 0.14^{D}	$0.47 \pm 0.02^{C,D}$	6.65 ± 0.05^{C}	6.67 ± 0.05^{C}	85.92 ± 0.19^{B}
I5	1.64 ± 0.10^{C}	6.31 ± 0.01^{C}	30.20 ± 0.03^{D}	0.71 ± 0.02^{C}	7.42 ± 0.01^{B}	7.45 ± 0.01^{B}	84.55 ± 0.14^{C}

*L**, *a** and *b**, CIELab parameters; C*, chroma; *h*, hue angle

Significant differences ($P < 0.05$) between concentrate (C1-C5) and ice (I1-I5) fractions compared to PNB in each column are indicated lowercase and capital letters, respectively

resulting in a low range of TSC entrapped in ice crystals. Furthermore, the lower the solutes in ice fractions, the higher the efficiency of the BFC (Moreno et al. 2014; Sánchez et al. 2011). Therefore, the obtained data suggest a highly efficient process regarding solids retention.

The pH was significantly affected ($P < 0.05$) by the BFC stages, with a slight and gradual decrease in values for concentrate fractions when compared to the control beverage. Furthermore, minor variations were observed in ice fractions throughout the BFC process. These results may be attributed to the low TSC at the end of the process, suggesting a decrease in the content of the organic acids. Demoliner et al. (2020) found similar results for the pH of concentrate and ice fractions of sapucaia nut cake beverage. Since plant-based beverages comprise an emulsion system, the pH is used as a quality parameter indicating the product's stability (Liu et al. 2016). Though, some factors, such as the mineral content and the protein profile, might significantly affect the stability of nut beverages due to the electrostatic screening effect, influencing the pH. Those effects may be prevented by pasteurizing and demineralizing the beverage to a certain extent (Habibi et al. 2019).

The multi-stage BFC significantly ($P < 0.05$) influenced the color parameters of concentrate and ice fractions. The luminosity (L^*) presented a gradual decrease for both fractions compared to the PNB. However, the highest L^* values were observed for ice fractions. Figure 2a illustrates the viewpoint of each fraction over BFC on the three-dimension CIELab color space. The image demonstrates that PNB was positioned on the quadrant with reddish colors and low luminosity. Conversely, concentrate fractions were distributed on quadrants tending to yellowish colors with similar patterns exhibited by C1, C2, and C3. Ice fractions were positioned on a high luminosity quadrant, confirming its low solutes or coloring pigments.

The positive values of a^* and b^* coordinates in concentrate fractions indicate a trend to red and yellow, respectively. A significant decrease (69%) on a^* parameter in step C1 *versus* PNB was attributed to the high solids content in the feedstock beverage. Although significant ($P < 0.05$) variations on a^* coordinate were observed from C1 to C5, those fluctuations were considered negligible. In contrast, a substantial increase (63%) was observed in I1 compared to PNB. Nevertheless, the values sharply decreased from I1 to I5, suggesting low pigments in ice fractions. The b^* coordinate related to the yellowish color presented slight variations from C1 to C3, followed by a significant decrease ($P < 0.05$) at the end of the BFC (C5). Significant variations were also observed in ice fractions; nonetheless, their values revealed discrepancies undetectable to the human eye. The BFC stages significantly ($P < 0.05$) affected the saturation (C^*) and hue angle (h) parameters. After the BFC, the C^* values decreased by half, causing an intensity reduction in concentrate fractions compared to PNB. On the other hand, the h scores (towards 90°) confirmed a yellow-orange hue trend for all fractions.

The browning index (BI) and total color difference (ΔE^*) evolution over the BFC stages are shown in Fig. 2b and c, respectively. BI value for PNB was 27.12. Compared to the control feedstock solution, there was an increasing trend in BI for the concentrated fractions up to stage 3, ranging from 28.16 ± 0.22 to 33.78 ± 0.16. Nevertheless, a moderate decrease (17%) in BI for C4 and

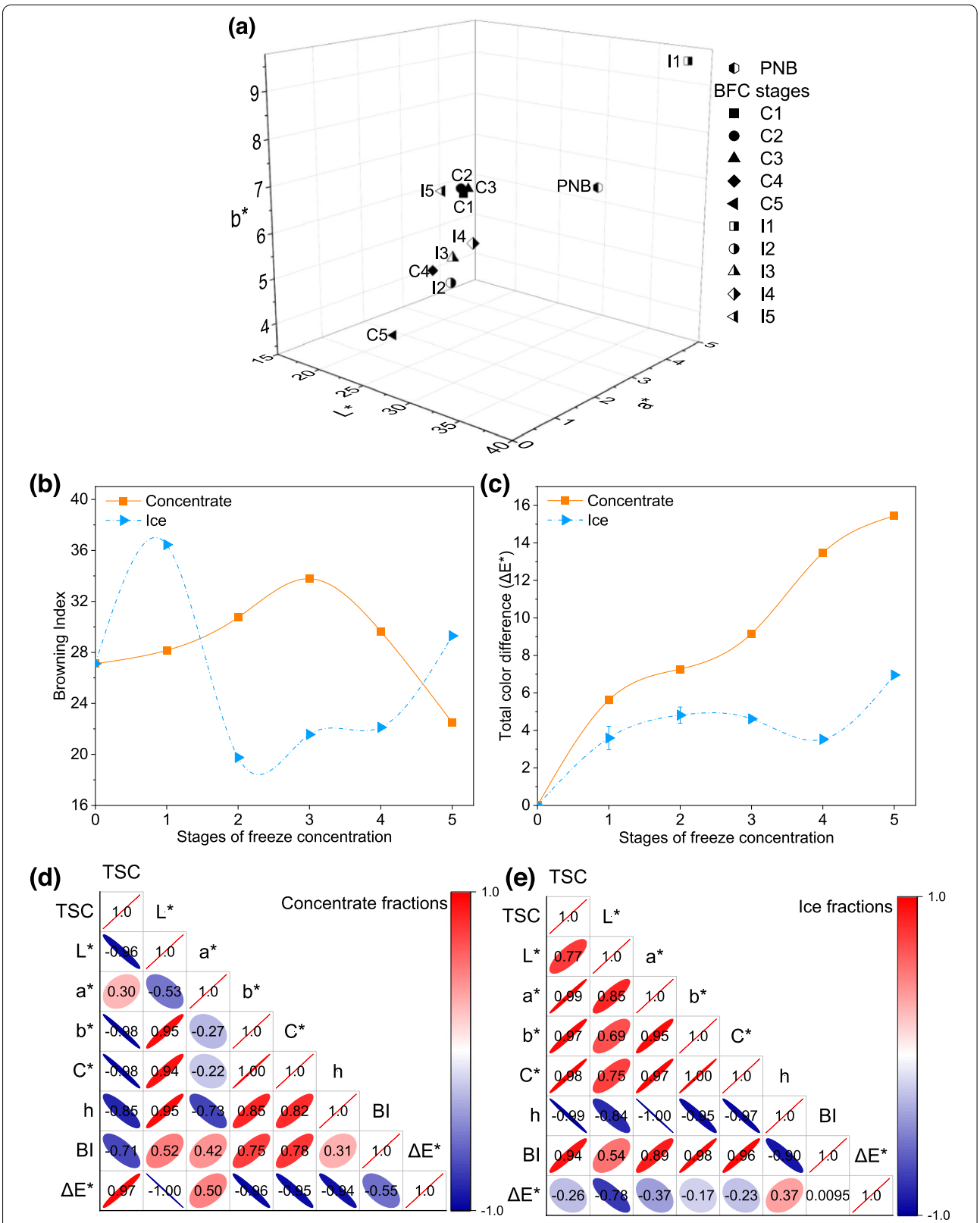


Fig. 2 Evolution of CIELab color parameters (**a**), Browning Index (**b**), total color difference (**c**) and the correlogram for total solids content (TSC) and the color parameters of concentrate (**d**) and ice (**e**) fractions of pecan nut cake beverage (PNB) over five block freeze concentration stages

C5 *versus* PNB was observed, indicating reduced turbidity of concentrate fractions after concluding the BFC process. The last concentrate fraction (C5) showed a BI value of 22.50 ± 0.83. On the contrary, BI values from ice fractions (36.44 ± 0.83 to 29.30 ± 0.04) decreased after the first cycle, followed by an increase in the third stage, thus showing the opposite behavior of concentrate fractions. The ΔE^* varied statistically ($P < 0.001$) from 5.62 ± 0.19 to 15.44 ± 0.06 for concentrate fractions and 3.59 ± 0.63 to 6.95 ± 0.03 for the ice fractions, respectively. Figure 2c shows that ΔE^* values have increasingly grown from C1 to C5, presenting about 175% difference between the first and fifth stages. Conversely, a 93% variation in ΔE^* values was observed between I1 and I5. As the ΔE^* values for both concentrate and ice fractions were > 3, the differences in color perception in the BFC process surpassed the human visual discrimination threshold in all cases, as reported elsewhere (Orellana-Palma et al. 2017; Pathare et al. 2013).

Correlations among TSC, color parameters, BI, and ΔE^* are displayed in Fig. 2d (concentrate fractions) and 2e (ice fractions). Strong negative correlations were observed between TSC against L^*, b^*, C^*, h, and BI for the concentrate fractions, related to the increasing concentration of compounds and solids over the process. On the other hand, high positive correlations between TSC contrasted with L^*, a^*, b^*, C^*, and BI were found on ice fractions due to the lower content of colored compounds and solids. Orellana-Palma et al. (2017; 2020) and Zielinski et al. (2019) point out that the darkening of the beverages could be attributed to the increase in TSC over the BFC process. The yellowish-orange color of pecan nut is ascribed to bioactive compounds such as flavan-3-ols (Eitenmiller & Pegg 2008; USDA 2018), which may have contributed to the color parameters of PNB. As further commented, TSC can also be correlated with TPC. Therefore, the color sensory perceptions of a pecan nut-based beverage may be influenced by its phenolic profile. Other sensory characteristics of plant-based beverages can also be key factors for the consumers choices; thus, the sensory analysis of PNB may be considered in further studies.

Additionally, practical applications of BFC have been reported and indicated that beverages and juices usually maintain their nutritional properties after concentration processes, whose content is noticeably enhanced. For example, Haas et al. (2022) found that a three-stage BFC enhances orange juice's nutritional and bioactive properties. Silva et al. (2021) reported improved nutritional characteristics (soluble solids, glucose, and fructose) and bioactive compounds (total phenolics and flavonoids) in Fuyu persimmon juice after freeze concentration. The same pattern has been found in the content of sugars, organic acids, and phenolic compounds in grape juice (Dutra et al. 2021). Likewise, the content of proteins, glucose, galactose, and lactose in lactose-free milk has also been preserved or increased after BFC (Dantas et al. 2021).

Although industrial equipment for freeze concentration at pilot scales is available commercially, research using pilot plants is still scarce. However, some works have indicated the suitability of freeze concentration technologies to improve the properties of orange juice (Sánchez et al. 2010) and white must from Macabeo grape (Hernández et al. 2010). Therefore, notwithstanding the results of our research, future studies using the BFC of PNB could focus on the semi-industrial or pilot-plant scales.

Phytochemicals and antioxidant activity

The total phenolic (TPC), condensed tannins (CT), and total flavonols (TF) contents of PNB and its concentrated (C1-C5) and ice (I1-I5) fractions are shown in Table 2. PNB showed an average TPC of 395.29 ± 4.94 mg GAE 100 g^{-1}, while the CT and TF contents were 57.24 ± 2.08 mg QE 100 g^{-1} and 26.00 ± 4.40 mg CE 100 g^{-1}, respectively. These values were lower when compared to the aqueous extract of PNC (501.09 mg AGE 100 g^{-1} and 553.88 mg CE 100 g^{-1} for TPC and CT, respectively) reported by Maciel et al. (2020). Although the raw materials were similar, such discrepancies could be associated with the extraction and evaluation methods. The previous work measured bioactive compounds

Table 2 Bioactive compounds in pecan nut cake beverage (PNB) and its concentrate (C1-C5) and ice (I1-I5) fractions over a five-stage block freeze concentration

Sample	TPC (mg GAE 100 g^{-1})	CT (mg CE 100 g^{-1})	TF (mg QE 100 g^{-1})
PNB	$395.29 \pm 4.94^{d,A}$	$57.24 \pm 2.08^{e,A}$	$26.00 \pm 4.40^{d,A}$
C1	332.79 ± 11.72^{e}	57.19 ± 6.28^{e}	24.62 ± 5.08^{d}
C2	388.14 ± 7.62^{d}	79.89 ± 8.65^{d}	37.00 ± 3.14^{d}
C3	761.01 ± 24.55^{c}	160.02 ± 12.50^{c}	123.64 ± 9.17^{c}
C4	903.85 ± 18.76^{b}	251.11 ± 15.41^{b}	210.52 ± 8.64^{b}
C5	1008.03 ± 23.97^{a}	400.24 ± 25.25^{a}	264.42 ± 10.70^{a}
I1	407.66 ± 6.80^{A}	54.00 ± 3.43^{B}	19.98 ± 2.98^{B}
I2	169.97 ± 10.92^{C}	34.03 ± 1.24^{E}	9.50 ± 0.64^{C}
I3	138.67 ± 1.01^{D}	39.16 ± 3.65^{D}	10.92 ± 1.44^{C}
I4	131.90 ± 5.11^{D}	40.80 ± 1.47^{D}	13.16 ± 1.97^{C}
I5	245.79 ± 23.81^{B}	48.57 ± 2.21^{C}	$24.70 \pm 3.76^{A,B}$

TPC total phenolic content, *CT* condensed tannins, *TF* total flavonols, *GAE*, *CE*, and *QE* are gallic acid, catechin, and quercetin equivalents, respectively

Significant differences ($P < 0.05$) between concentrate (C1-C5) and ice (I1-I5) fractions compared to PNB in each column are indicated lowercase and capital letters, respectively

in PNC obtained with different solvents using the Folin-Ciocalteu assay, while this study employed the PB method. Several advantages, such as low reagent, time consumption, and higher selectivity, can be ascribed to PB over the Folin-Ciocalteu method. Furthermore, the PB assay avoids interferences from reducing substances, such as reducing polyphenols, sulfur dioxide, organic acids such as ascorbic acid, sugars (fructose and sucrose), and some amino acids (Margraf et al. 2015).

The first stage of BFC caused a slight decrease in TPC (15.8%), but no difference ($P < 0.05$) was observed in CT and TF contents for C1 compared to the PNB. Nevertheless, the phytochemical contents in the C1-C5 stages *versus* PNB increased linearly, and the differences were significant ($P < 0.05$). Thus, the TPC, CT, and TF contents at the end of the process were 155%, 599%, and 917% higher compared to PNB. Such increasing linear effect on biocompounds was also observed in the BFC of apple juice (Zielinski et al. 2019), yerba mate aqueous extract (Nunes et al. 2015), coffee extract (Moreno et al. 2014), orange juice (Orellana-Palma, González, et al. 2019), and blueberry and pineapple juice (Orellana-Palma et al. 2017b; Petzold et al. 2015). Similarly, a 194% increase in TPC has been reported for sapucaia nut cake beverage concentrated by five-stage BFC (Demoliner et al. 2020). Likewise, a three-stage BFC provided a 257 and 284% increase in the TPC of Red Delicious and Granny Smith apple juices, respectively (Zielinski et al. 2019).

BFC also provides feasible efficiency in retaining bioactive compounds compared to other concentration methods. For instance, Alaei et al. (2022) studied the concentration of tomato juice using an ultrasound-thermal concentrator under vacuum and verified increased vitamin C and lycopene content. Ekici and Ozaltin (2018) reported a higher TPC in tamarind sorbet using vacuum concentration compared to conventional heating. Similarly, vacuum concentration increased the TPC and anthocyanin content in poppy (*Papaver rhoeas* L.) sorbet (Ekici 2014). Furthermore, Mahmoud et al. (2017) found that the concentration of pomegranate juice based on rotary evaporation and microwave heating processes causes less damage to the antioxidant capacity, total phenolics and anthocyanins as compared to direct heat treatment. On the other hand, Dutra et al. (2021) reported significant losses in the content of bioactive compounds such as *trans*-caftaric acid, chlorogenic acid and furaneol after vacuum concentration of grape juice.

Results from the antioxidant activity of PNB, concentrate and ice fractions evaluated by FRAP, CUPRAC, TRC, DPPH, and IPL assays are presented in Table 3. Significant ($P < 0.05$) differences were found between the antioxidant capacity all over the BFC stages. In addition, a linear pattern ($P < 0.05$) regarding increased antioxidant activity for the concentrates (C1 to C5) in all assays has been observed. The final concentrate fraction (C5) showed the highest values for antioxidant activity, with an increase ranging from 64% (IPL) to 476% (CUPRAC) compared to the PNB. Although the first ice fraction (I1) presented a higher ($P < 0.05$) antioxidant capacity when compared to PNB, a decrease for most assays from I2 to I5 was verified. Such behavior is expected since most bioactive compounds from the beverage are gravitationally carried to the concentrate fractions.

Table 3 Antioxidant activity of pecan nut cake beverage (PNB) and its concentrated (C1-C5) and ice (I1-I5) fractions over a five-stage block freeze concentration

Sample	FRAP (mg AAE 100 g^{-1})	CUPRAC (mg AAE 100 g^{-1})	TRC (mg QE 100 g^{-1})	DPPH (% inhibition)	ILP (% inhibition)
PNB	$132.31 \pm 4.10^{e,B}$	$227.68 \pm 11.42^{e,B}$	$258.69 \pm 9.50^{d,A}$	$40.93 \pm 1.67^{d,B}$	$44.94 \pm 0.79^{f,B}$
C1	133.32 ± 12.30^{e}	240.93 ± 17.23^{e}	159.66 ± 9.70^{f}	32.70 ± 0.70^{e}	46.63 ± 2.21^{e}
C2	160.73 ± 14.81^{d}	312.44 ± 22.16^{d}	219.08 ± 12.02^{e}	43.82 ± 0.63^{c}	52.43 ± 1.15^{d}
C3	341.08 ± 15.47^{c}	575.16 ± 14.92^{c}	483.85 ± 5.20^{c}	41.31 ± 0.76^{d}	53.98 ± 2.11^{c}
C4	504.41 ± 17.47^{b}	1020.95 ± 24.44^{b}	889.28 ± 31.02^{b}	65.99 ± 0.69b	68.06 ± 0.74^{b}
C5	747.43 ± 23.36^{a}	1312.19 ± 66.00^{a}	1393.73 ± 14.21^{a}	76.45 ± 0.89^{a}	73.89 ± 1.21^{a}
I1	155.33 ± 5.72^{A}	280.92 ± 6.83^{A}	202.74 ± 4.12^{B}	42.64 ± 0.40^{A}	46.62 ± 0.90^{A}
I2	99.75 ± 8.83^{D}	147.97 ± 15.89^{C}	15.97 ± 1.84^{F}	$13.82 \pm 0.82^{D,E}$	21.69 ± 0.72^{E}
I3	96.66 ± 3.81^{D}	145.72 ± 8.57^{C}	41.30 ± 18.05^{E}	12.71 ± 0.83^{E}	31.22 ± 2.31^{C}
I4	89.85 ± 6.49^{D}	134.98 ± 3.31^{C}	83.79 ± 14.71^{D}	15.60 ± 0.99^{D}	30.03 ± 0.53^{D}
I5	107.31 ± 2.13^{C}	132.14 ± 25.86^{C}	95.73 ± 6.17^{C}	26.48 ± 0.80^{C}	33.78 ± 1.17^{C}

FRAP, ferric reducing antioxidant power; CUPRAC, cupric reducing antioxidant capacity; TRC, total reducing capacity; DPPH, 2,2-Diphenyl-1-picrylhydrazyl, ILP, inhibition of lipid peroxidation; AAE and QE are ascorbic acid and quercetin equivalents, respectively

Significant differences ($P < 0.05$) between concentrate (C1-C5) and ice (I1-I5) fractions compared to PNB in each column are indicated lowercase and capital letters, respectively

The antioxidant results for the concentrate fractions are in agreement with previous reports indicating increased antioxidant content of yogurt enriched with strawberry pulp (Jaster et al. 2018), apple juice (Zielinski et al. 2019), sapucaia nut cake beverage (Demoliner et al. 2020), orange juice (Orellana-Palma, González, et al., 2019), blueberry and pineapple juice (Orellana-Palma et al. 2017; Petzold et al. 2015) and coffee extract (Moreno et al. 2014) concentrated by BFC. The increase in antioxidant activity can be attributed to the retention of solids and the phenolic composition of the PNB, which was also enhanced after each BFC cycle. Figure 3 depicts the correlations among TSC, TPC, CT, and TF *versus* antioxidant activity measured by different methods in the concentrate (Fig. 3a) and ice (Fig. 3b) fractions. Strong and positive correlations were observed between the antioxidant activity (FRAP, CUPRAC, TRC, DPPH, ILP) *versus* TSC, TPC, CT, and TF of PNB and its concentrate and ice fractions. Compounds such as anthocyanidins, catechin, epigallocatechin, epicatechin, epigallocatechin, proanthocyanidins (USDA, 2019), gallic and ellagic acids (de la Rosa et al. 2014) are the most significant in pecan nut, which may contribute to the antioxidant capacity in its beverage.

Apak et al. (2016) emphasize that assays based on ILP weakly correlate with assays based on HAT or ET due to their action mechanisms. However, the present study found strong positive correlations between the biological-based ILP method, and the chemical assays based on FRAP, CUPRAC, TRC, and DPPH (Fig. 3a and b). Such a pattern indicates that besides presenting high in vitro antioxidant capacity, PNB may also have a great potential to prevent or delay in vivo lipid peroxidation.

It is noteworthy that each antioxidant assay has unique thermodynamic and kinetic characteristics, and the oxidizing power of each reagent against a specific antioxidant at a fixed time is naturally different from another. Therefore, more reliable results are achieved using techniques based on hydrogen atoms transfer (HAT) or electrons transfer (ET), especially metal complexes using Fe (III) or Cu (II), reduction of hydrophilic, lipophilic, and thiol compounds in addition to the ILP (metal chelation), which simulates the physiological conditions of lipid oxidation in vivo. Thus, an evaluation involving different multi-mechanisms provides a comprehensive antioxidant profile for PNB and its concentrates.

Parameters of the BFC process

The concentration index (CI), average distribution coefficient (k), concentrate yield (Y), process efficiency (eff), and concentration factor (CF) are shown in Fig. 4. As shown in Fig. 4a and b, CI increased progressively ($P<0.05$) in the concentrated fractions, while decreasing values were observed in the ice fractions. Similarly, the k values also reduced significantly from stages 1 to 5 (Fig. 4c). Such results suggested the high effectiveness of the process. As illustrated in Fig. 4d, growing trends in Y, *eff*, and CF values were observed. The Y values increased significantly ($P<0.05$) over each stage in BFC. A linear evolution was observed up to stage 3, which presented the maximum yield value (97.21%), followed by a decrease and subsequent stabilization near 60%. The observed concentrate yield was directly associated with increased TPC in concentrate fractions. The maximum Y values observed in this study were higher than those reported for apple juice (75–85%) (Miyawaki et al. 2016; Orellana-Palma, Lazo-Mercado, et al. 2020; Zielinski et al. 2019), goat milk (85–92%) (Canella et al. 2020), orange juice (60%) (Orellana-Palma et al. 2017) and blueberry juice (72%) (Orellana-Palma et al. 2017).

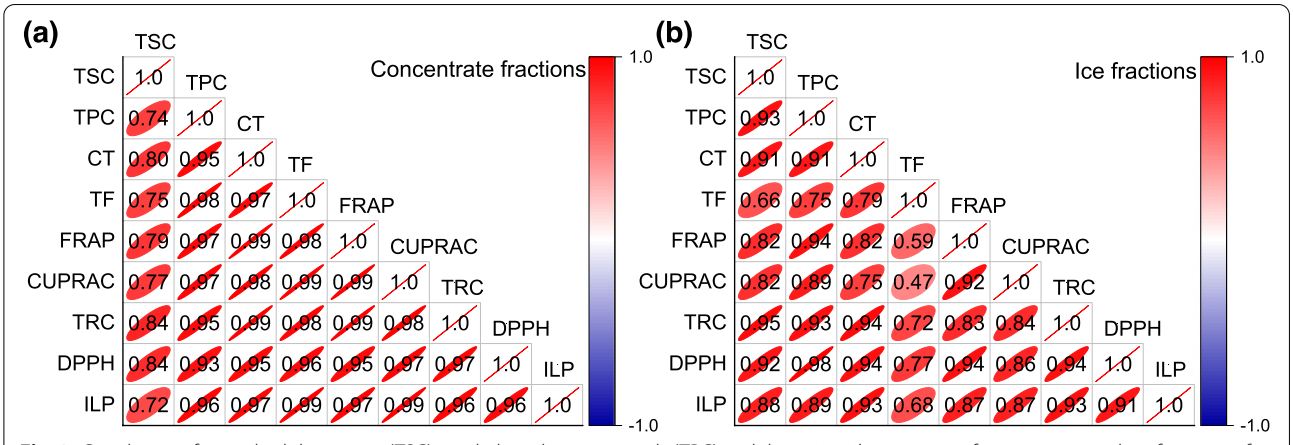


Fig. 3 Correlogram for total solids content (TSC), total phenolic compounds (TPC) and the antioxidant activity of concentrate and ice fractions of pecan nut cake beverage over multi-stage block freeze concentration

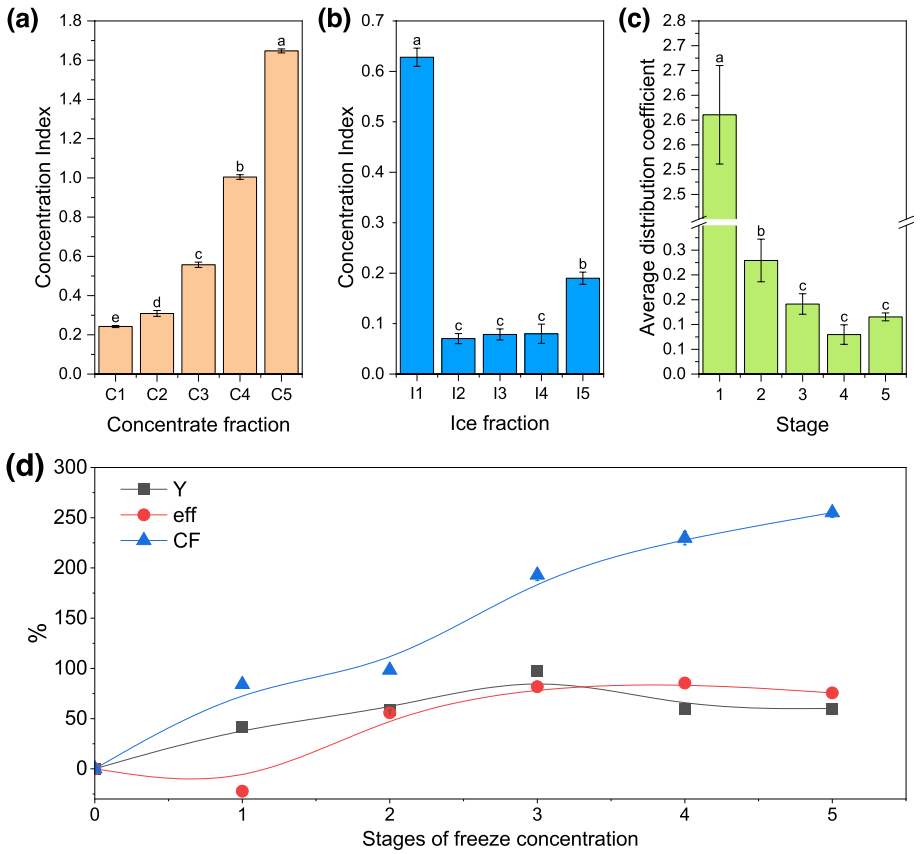


Fig. 4 Concentration index in concentrate (**a**) and ice (**b**) fractions, the average distribution coefficient (**c**), and the evolution of concentrate yield (*Y*), process efficiency (*eff*), and concentration factor (CF) based on total phenolics in block freeze concentration stages of pecan nut beverage (**d**)

As displayed in Fig. 4d, a linear behavior for the CF was revealed. Moreover, such a factor followed a growing trend up to the last stage, with increasing values of 84.1, 98.3, 192.9, 229.6, and 254.9% for C1, C2, C3, C4, and C5, respectively. Likewise, concentrate yield and CF values were directly correlated to the increase of TPC in the concentrate fractions.

Significant ($P < 0.05$) increasing values were recorded to *eff* over BFC stages. Efficiency progressively increased from stage C1 to C4, reaching a maximum of 85.4%, followed by a decrease to 75.6% in C5. Sánchez et al. (2011) highlight that decreased process efficiency comes from increased solute retention in ice fractions. Due to the increase in solution viscosity with increasing concentration, solutes accumulate at the ice-liquid interface, and the diffusion of these solids out of the interface becomes slow. These results are in line with those reported for apple juice (Miyawaki et al. 2016; Patricio Orellana-Palma, Lazo-Mercado, et al. 2020; Zielinski et al. 2019), goat milk added with NaCl (Canella et al. 2020), and blueberry and pineapple juice (Petzold et al. 2015).

The efficiency of freeze concentration can be linked to the content of a target compound trapped in the ice fractions and with TSC. The higher the TSC in concentrate fractions, the greater the efficiency of the BFC process. This behavior can be corroborated based on strong positive correlations detected between the TSC *versus* phytochemicals and antioxidants (Fig. 3a and b).

The BFC process was validated between experimental (W_{exp}) and predicted (W_{pred}) ice mass relationships. A good agreement was observed between W_{exp} and W_{pred} all over the BFC cycles. The maximum RSM value (17.6%) on the freeze concentration process was observed in stage C3. This performance can be attributed to the increase in the percentage of concentrate over the BFC stages. Lewicki (2000) indicated that RSM values lower than 25% represent a good fit. Thus, the freeze concentration process provided a liquid fraction with high values of TSC, phytochemicals, and attractive color, preserving important thermolabile bioactive compounds in the final concentrate of the pecan nut cake beverage.

Conclusion

An easy-to-prepare and low-cost pecan nut cake beverage was enriched using a non-thermal technology based on block freeze concentration. The process provided concentrated fractions with a higher bioactive compound content than fresh pecan nut cake beverage. Likewise, freeze concentration afforded high retention (98%) of total phenolics in the third stage of the process, while 85% efficiency and 254% concentration factor were verified in stages 4 and 5, respectively. Thus, PNB fractions showed a rich phytochemical and antioxidant composition with high bioactive potential constituting a promising alternative for the food industry. Furthermore, the present dataset should encourage industrial applications of pecan nut cake and other similar raw materials, which are often commercially neglected to be used as an ingredient for various industry sectors, adding value to them.

Abbreviations

*a**: Red/green coordinate; AA: Antioxidant activity; *b**: Yellow/blue coordinate; BFC: Block freeze concentration; BI: Browning index; *C**: Chroma; C1-C5: Concentrate fractions; CE: Catechin equivalent; CF: Concentration factor; CI: Concentration index; CT: Condensed tannins; CUPRAC: Cupric reducing antioxidant capacity; DPPH: 2,2-Diphenyl-1-picrylhydrazyl; *Eff*: Efficiency; FRAP: Ferric reducing antioxidant power; GAE: Gallic acid equivalent; *H*: Hue angle; I1-I5: Ice fractions; ILP: inhibition of lipid peroxidation; *K*: Average distribution coefficient; *L**: Luminosity; PB: Prussian blue; PNB: Pecan nut cake beverage; PNC: Pecan nut cake; QE: Quercetin equivalent; RMS: Root mean square; TBA: Thiobarbituric acid; TF: Total flavonoids; TPC: Total phenolic compounds; TPTZ: Tripyridyl-2,4,6-s-triazine; TRC: Total reducing capacity; TSC: Total solids content; *Y*: Concentrate yield; *ΔE**: Total color difference.

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Authors' contributions

Laércio Galvão Maciel: Conceptualization, Methodology, Investigation, Writing- Original Draft, Formal Analysis, Validation. Gerson Lopes Teixeira: Writing - Review & Editing, Formal Analysis, Validation, Visualization. The author(s) read and approved the final manuscript.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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