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Comparative study of block cryoconcentration in pomegranate juice: Centrifugation versus vacuum

Flor M. Vásquez-Castillo[1] | Eduard Hernández[1] | Milber O. Ureña-Peralta[2] | Isabel Achaerandio[1]

[1]Departament d'Enginyeria Agroalimentària i Biotecnologia, Universitat Politècnica de Catalunya (UPC) Barcelonatech, Barcelona, Spain

[2]Departamento de Ingeniería de Alimentos, Facultad de Industrias Alimentarias, Universidad Nacional Agraria La Molina, Lima, Peru

Correspondence
Eduard Hernández, Departament d'Enginyeria Agroalimentària i Biotecnologia, Universitat Politècnica de Catalunya (UPC) Barcelonatech, C/Esteve, Terradas, 8, 08860, Castelldefels, Barcelona, Spain.
Email: eduard.hernandez@upc.edu

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Abstract

Block cryoconcentration is a technique that can be applied to obtain fruit juice concentrates while preserving their nutritional, bioactive and organoleptic properties. Until now, the investigations present both the centrifugation and vacuum cryoconcentration method independently for different matrices, but with different purposes such as observing the effect of the initial freezing temperature, the freezing direction, whether radial or unidirectional, the effect of several cycles of cryoconcentration, comparing cryoconcentration with other concentration methods, etc. However, there is no study that compares both methods in the same matrix considering some common parameters such as cryoconcentration time. The objective of this research work was to compare two block centrifugation methods, centrifugation-assisted (CABC) and vacuum-assisted (VABC). A factorial experimental design was used. The operation conditions evaluated were 110 RCF and 2360 RCF, and 10 and 70 kPa at the same time conditions (4 and 12 min). Pomegranate juice was frozen at -20°C unidirectionally for 48 h before treatments. For the response studied—concentration index (CI), solute yield (SY, %) and efficiency (Eff, %)—CABC at 110 RCF for 12 min showed the best overall results (SY $=$ 59.2% and Eff $=$ 84.3%) and the desirability was .91. For VABC at 10 kPa for 12 min, the desirability was .98 but SY was lower. In both methods, the CI in one cycle was up to 3.0. The advantage of both systems is that in one cycle the CI, SY and Eff were higher than those obtained by other investigations on pomegranate juice.

Practical applications

Cryoconcentration is an emerging technology for concentrating a food solute in a solution based on the separation of ice crystals from a freeze-concentrated solution. The nutritional and sensory quality of cryoconcentrated fruit juices is higher than those concentrated conventionally by means of evaporation due to the low processing temperatures. Consumer demand for food rich in bioactive components for a healthy lifestyle is growing. With the use of the block freeze concentration technique, it is possible to produce a pomegranate juice concentrate with excellent nutritional properties. Two techniques for assisted block cryoconcentration of pomegranate juice—vacuum and centrifugal—were compared in a single cycle. Both methods showed better performance in once cycle than other cryoconcentration methods at lab scale. The generated knowledge in this study can be easily adapted for the juice industry in order to improve the process parameters of block freeze concentration in the elaboration of concentrated pomegranate juice.

KEYWORDS
block freeze concentration, desirability, efficiency, freezing rate, *Punica granatum*, solute yield

1 | INTRODUCTION

Pomegranate fruits have high antioxidant capacity due to their anthocyanin and phenolic compound content. Punicalagin, the main ellagitannin in pomegranate juice, promotes some beneficial properties for health because it reduces the effects of oxidative stress in cells. The evidence of the benefits of pomegranate phytochemicals has been recently reviewed (Laurindo et al., 2022). There are different varieties of pomegranate; the 'Wonderful' cultivar is the most consumed for its organoleptic characteristics as well as for its higher antioxidant activity, polyphenol content and very high acidity compared to the 'Mollar de Elche' accessions, as demonstrated by Mena et al. (2011).

Cryoconcentration is a method for concentrating a food solute in a solution based on the separation of pure ice crystals from a freeze-concentrated solution. As compared to evaporation and membrane technology, freeze concentration has some significant potential advantages for producing a high-quality concentrate because the process occurs at low temperatures where no vapor/liquid interface exists, resulting in no loss of volatiles (Petzold et al., 2013).

As the temperature below the freezing point decreases, the water becomes ice and the solids content of the juice becomes more concentrated. After the juice is frozen, this concentrate can be extracted by gravitational methods, by centrifugation and by vacuum. The cryoconcentrated solution has better nutritional, organoleptic and bioactive characteristics than the original fresh juice (Guerra-Valle et al., 2021).

There are different types of cryoconcentration: suspension, progressive and block cryoconcentration; of all of them, the simplest technique and that giving better results is block cryoconcentration. To improve the technique, it has been complemented by gravitational-assisted thawing and microwave-assisted thawing (Aider et al., 2008; Aider & de Halleux, 2008), by shaking (Iritani et al., 2013) and by ultrasound (Kawasaki et al., 2006). Suspension cryoconcentration is currently being used in the industry; the disadvantage is that it requires costly equipment and the operation is carried out in several steps: nucleation, growth and crystal separation (Petzold et al., 2013). The advantage of block cryoconcentration is that the design of the equipment is simpler (Miyawaki, 2018) and the process is a single step (Petzold & Aguilera, 2013). For this reason, other techniques with fewer costs and better yields are being studied at laboratory and pilot scale, including centrifugation-assisted block cryoconcentration (CABC) and vacuum-assisted block cryoconcentration (VABC). Some research groups have worked with both techniques independently for several food products, with promising results, such as sucrose solutions both by VABC (Petzold et al., 2013) and CABC (Petzold & Aguilera, 2013), blueberry juice by VABC (Orellana-Palma, Petzold, Andana, et al., 2017) and by CABC (Casas-Forero et al., 2021; Orellana-Palma, Petzold, Guerra-Valle, & Astudillo-Lagos, 2017; Petzold et al., 2015; Santana et al., 2020), and orange juice by VABC (Petzold et al., 2017, 2019) and by CABC (Orellana-Palma, González, & Petzold, 2019; Orellana-Palma, Petzold, Andana, et al., 2017). However, to the authors' knowledge, the two methods have not been compared to evaluate which of them gives better results. On the other hand, investigations of the cryoconcentration of pomegranate juice have used gravity-assisted cryoconcentration and microwave (Khajehei et al., 2015), CABC (Orellana-Palma et al., 2021) and a BL-20 crystallizer (Burdo et al., 2021). To fill this gap, the main aim of this research work was to compare the CABC and VABC methods in pomegranate juice to evaluate which of them the better obtains the concentration index, solute yield and efficiency of concentration.

2 | MATERIALS AND METHODS

2.1 | Materials

Fresh fruits of 'Wonderful' pomegranate (*Punica granatum*) from southern Israel were obtained at Mercabarna (Barcelona). The average weight of fruits was 450 ± 50 g.

2.2 | Experimental procedure

Two methods of block cryoconcentration (BC) were compared: CABC and VABC, and two factors were studied for each technique (centrifugation speed–time and vacuum pressure–time, respectively). The experimental design is indicated in Table 1, which was chosen considering previous investigations. Preliminary tests showed that if the

TABLE 1 Experimental design.

Experiment	Cryoconcentration				Time (min)
1	CABC	1000	rpm	110 RCF	4
2	CABC	1000	rpm		12
3	CABC	4600	rpm	2360 RCF	4
4	CABC	4600	rpm		12
5	VABC	10	kPa	Absolute pressures	4
6	VABC	10	kPa		12
7	VABC	70	kPa		4
8	VABC	70	kPa		12

Abbreviations: CABC, centrifugation assisted block cryoconcentration; VABC, vacuum assisted block cryoconcentration.

vacuum pressure of 10 kPa is applied for more than 12 min, vacuum pressure loss occurs due to the formation of pores in the top of the ice block. In total, 24 tests were carried out considering three replications.

The following response variables were calculated: concentration index (CI), solute yield (SY) and efficiency (Eff).

2.2.1 | Freezing procedure

The juice was extracted using a Moulinex Juice extractor, then it was vacuum-filtered with filter paper of approximately 10 μm of porosity using a Büchner funnel and Kitasato flask.

Juice solutions (45 g) contained in plastic centrifugal tubes (internal diameter $D = 27$ mm) were covered with a thermal insulation made of elastomeric foam (8 mm thickness, thermal conductivity $k = .035$ W·m^{-1}·K^{-1}) so the heat transfer during freezing occurred axially from top to bottom as recommended (Orellana-Palma, Petzold, Andana, et al., 2017). These samples were frozen in a static freezer at −20°C (Arcon Freezer model THC 520 ANI) for 48 h (Figure 1).

During freezing, the temperature in the samples was measured using K thermocouples (NiCr-Ni) connected to a Testo Data logger (176T4) at the geometric center of samples. The freezing rate (mm·min^{-1}) was calculated as the thickness divided by the freezing time (assuming that freezing occurs from one side) (Ramaswamy & Marcotte, 2005).

2.2.2 | CABC

The frozen samples were removed from the freezer and immediately placed in a refrigerated centrifuge (HETTICH ROTANTA 460 R, Tuttlingen, Germany) operated at 20 ± 1°C, using two centrifugation speeds: 1000 and 4600 rpm (110 and 2360 RCF, respectively) for 4 and 12 min, to force the separation of the solutes from the frozen samples. Then the tip of the centrifuge tube is cut, the concentrate is extracted weighed it and measure its concentration of total soluble solids, the frozen fraction remaining in the tube is weighed, thawed, and total soluble solids are measured.

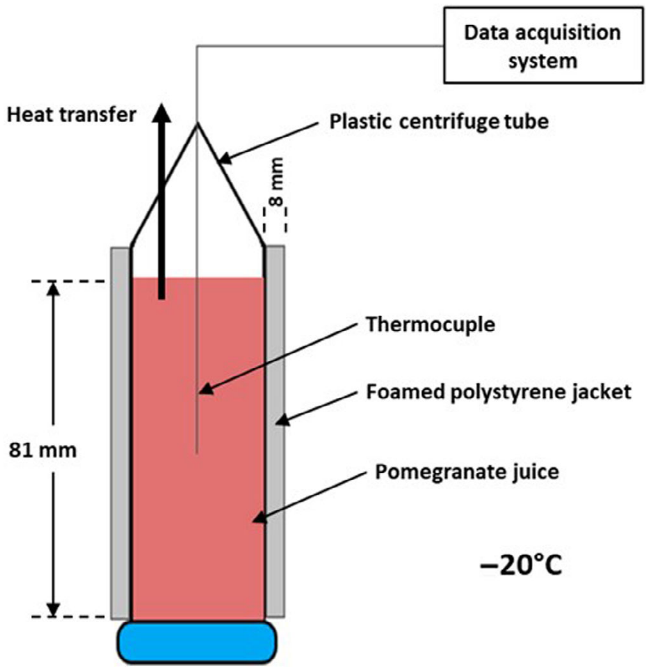

FIGURE 1 Freezing condition of pomegranate juice samples. The samples were frozen in a static freezer at −20°C for 48 h.

2.2.3 | VABC

This procedure was carried out following Petzold and Aguilera (2013). The samples were removed from the freezer, cut at the bottom of the tube and immediately taken to a suction stage generated by a vacuum pump (Comecta model, Spain; pump rate: 3.6 m^3·h^{-1}; vacuum limit: .1 mbar). The absolute pressures used were 10 and 70 kPa (91.3 and 31.3 kPa vacuum pressure), for 4- and 12-min. Vacuum pressure was monitored visually with the vacuum manometer of the pump and an external manometer during the experiment.

In both cryoconcentration methods, the weight and concentration of the initial juice, concentrate and ice fraction were measured at 20 ± 2°C with a refractometer (ATAGO DBX-55A, Tokyo, Japan) with a precision of ±.1°Brix.

2.3 | Process parameter calculations

2.3.1 | Concentration index

CI is a variable used to evaluate the increase in concentration at the end of the BC process. It is the relation between the final concentration of the solute in the concentrated liquid and the initial concentration of the sample, as shown in Equation (1):

$$\mathrm{CI} = \frac{C_s}{C_0} \tag{1}$$

where C_S and C_0 are the percentage of soluble solids (°Brix) in the concentrated and initial solutions, respectively (Orellana-Palma, Takhar, & Petzold, 2019).

2.3.2 | Solute yield

SY was defined as the relationship between the mass of total soluble solids present in the separated concentrated fraction and the mass of total soluble solids present in the initial sample, as seen in Equation (2) (Miyawaki et al., 2012; Moreno et al., 2014):

$$\mathrm{SY} = \frac{m_s}{m_0} \times 100 \tag{2}$$

2.3.3 | Efficiency of concentration

The efficiency was defined as the increase in the concentration of the solution relative to the quantity of total soluble solids remaining in the frozen fraction, Equation (3) (Hernández et al., 2010).

$$\mathrm{Eff}(\%) = \frac{C_s - C_f}{C_s} \times 100 \tag{3}$$

2.3.4 | Validation of results

The experimental results were validated with a mass balance after the BC process (W_e) (Equation (4)). Those were compared with the predicted value (W_p) according to Equation (5) (Petzold et al., 2015).

$$W_e = \frac{M_f}{M_f + M_c} \tag{4}$$

$$W_P = \frac{C_s - C_0}{C_s - C_f} \tag{5}$$

where W_e is the experimental value of the ice mass ratio (kg ice/kg initial sample), W_p is the predicted value of the ice mass ratio (kg ice/kg initial sample), M_f is the ice mass (kg) and M_c is the mass (kg) of the concentrated sample.

Finally, the root mean square (RMS) was calculated by Equation (6) to determine the fit between the experimental and predicted values) for N experimental points subjected to cryoconcentration.

$$\mathrm{RMS}(\%) = 100\sqrt{\frac{\sum[(W_e - W_p)/W_e]^2}{N}} \tag{6}$$

2.3.5 | Statistical design and analysis

A 2^2 factorial analysis for two response variables was performed to observe the significant factors and the adjusted model equations in both cryoconcentration methods. Then, a categorical multifactor design was performed using ANOVA to assess if there were significant differences between the treatments. A multiple range test with the Bonferroni method with a 95% confidence interval was used to compare set of means. Desirability was used as an indicator to evaluate which response variables have to be taken into consideration and thus find the model equation adjusted to those factor conditions.

To find the final freezing time, the optimization method of no significant variation in kinetics (NSVK) was used (Daza-La Plata et al., 2020). The STATGRAPHICS Centurion 19® program was used. The data were expressed as a mean ± standard deviation.

3 | RESULTS AND DISCUSSION

3.1 | Freezing curve

Figure 2 shows the freezing curve of the pomegranate juice samples. The average freezing point was −2.1 ± .1°C, which is within the range of most fruit juices of −1 to −2°C and the freezing point decreases as

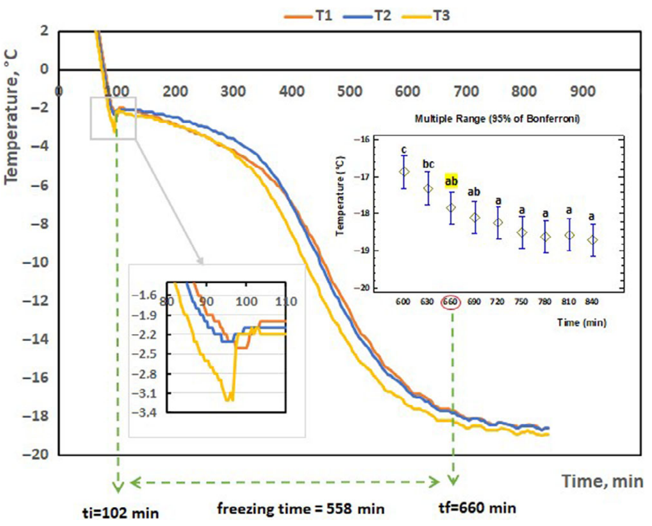

FIGURE 2 Freezing curve of the pomegranate juice sample (three independent experiments).

the juice is more concentrated (Ramaswamy & Marcotte, 2005) so the average subcooling point of −2.6 ± .5°C can be observed. That value is very common in solutions such as fruit juices since the more viscous and colloidal the solution, the lower the average subcooling point (Barreiro & Sandoval, 2006). There are several methods to measure the freezing time, as mentioned by Ramaswamy and Marcotte (2005). One of them is the procedure applied by Rayman Ergün et al. (2021) who considers the freezing time as the time taken to reach a temperature of −15°C from 0°C at the cold point. Taking into account this definition, in our experiment the freezing rate was .176 mm·min^{-1} (2.93 μm·s^{-1}). On the other hand, Barreiro and Sandoval (2006) and Orrego (2003) define the freezing time of a food as the time that elapses from when it starts freezing until it reaches the temperature of the freezer. In our case, the time to start freezing was 102 min and the final freezing time was 660 min determined according to the NSVK method (Figure 2).

The freezing rate was .145 mm·min^{-1} (2.42 μm·s^{-1}). These values show, based on freezing front propagation, a moderate freezing rate (Ramaswamy & Marcotte, 2005). In addition, these values of freezing rate were lower than the critical value (approximately 8 μm·s^{-1}) reported by Moreno et al. (2014) who stated that velocities higher than 8 μm·s^{-1} promote a faster freezing process. In cryoconcentration, that leads to the formation of occluded solutes in the ice that avoid the separation of the concentrated solution from the ice matrix.

3.2 | Evaluation of CABC

Figure 3 shows the Pareto diagram that resulted from the factorial analysis considering the three response variables CI, SY and Eff. In the CABC system, only time had a significant effect on CI, with $R^2 = 85.8\%$ (Figure 3a). As shown in Figure 3b,c, time and the interaction time–centrifugation speed had a significant effect on SY and Eff, with $R^2 = 97\%$ ($p < 0.05$).

For this analysis, the desirability function was .604, which was not close to 1; due to this and because CI only expresses how many times the product has been concentrated but without considering the solids that remain in the ice, a factorial design was used considering only two response variables, SY and Eff in the CABC. In this case, time and the interaction centrifugation speed–time had a significant effect on SY and Eff, with $R^2 = 97.4\%$ and 96.7%, respectively. With this analysis, the desirability function was .91, very close to 1. The best results were obtained at 1000 rpm (110 RCF) and 12 min (Figure 4).

There were significant differences between the treatments for the studied response variables: CI, SY and Eff. The initial juice had 15.8°Brix, reaching a maximum concentration of 50.9°Brix in a single step, with a CI of 3.2 to 3.0 in CABC; the treatments at 1000 rpm (110 RCF) for 4 min and 4600 rpm (2360 RCF) for 4 min had the highest CI values. The longer the centrifugation time, the higher the dilution in the concentration fraction, decreasing its total soluble solids content. Those phenomena might be due to the increase in the temperature inside the tube. Similar results were obtained by Orellana-Palma, González, and Petzold (2019) with orange juice at 1600 RCF for 14 min, they got 3.1.

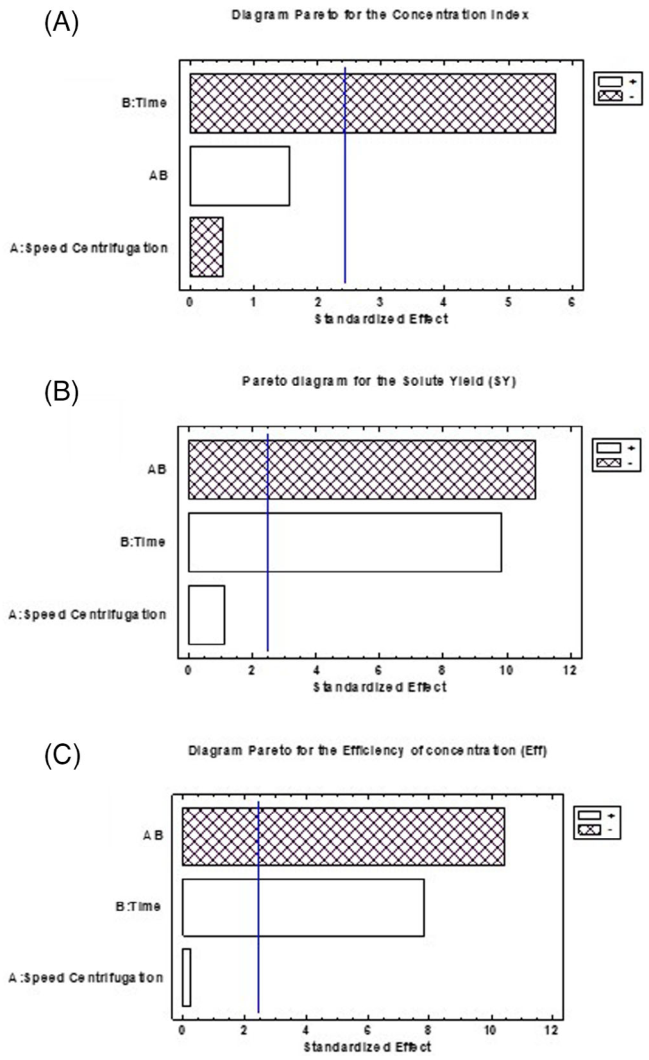

FIGURE 3 Pareto diagram for (a) CI, (b) SY, and (c) Eff by CABC.

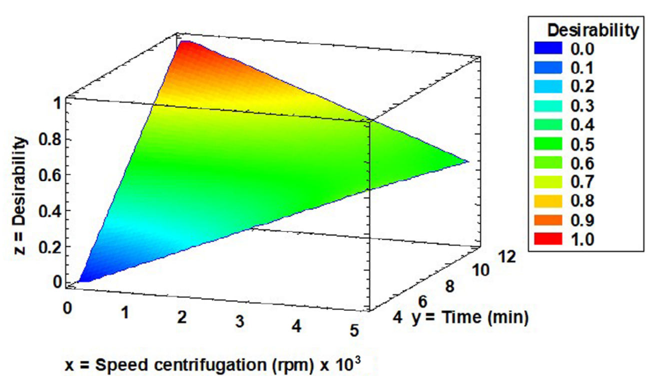

FIGURE 4 Estimated response surface for CABC.

Most investigations have obtained CI values in the range of 1.4–2.8 in a single cycle in various fruit juices such as blueberry juice 1.8 (Casas-Forero et al., 2021), 1.54 (Petzold et al., 2015), orange juice 1.8 (Orellana-Palma, Petzold, Andana, et al., 2017), calafate juice 1.86

(Orellana-Palma et al., 2020), pomegranate juice 2.0 (Orellana-Palma et al., 2021), apple juice 2.3 (Orellana-Palma et al., 2020), murta juice 1.8 and arrayan juice 2.0 (Guerra-Valle et al., 2021), pomelo juice 1.71 (Das et al., 2020), prickly pear juice 2.4 (Márquez-Montes et al., 2023) and maqui aqueous extract 2.16 (Bastías-Montes et al., 2019, 2022). Vidal-San Martín et al. (2021) used a centrifugation-filtration assisted cryoconcentration method (C-FABC) with an aqueous extract of maqui and calafate (10.5 and 6.8°Brix, respectively). CI of 5.1 and 5.8 were obtained, respectively, at 4000 rpm for 10 min in a frozen sample of 350 mL. Eff was higher than 96%. The high values of CI and Eff, in this work, they may be due to the addition of the filter that helps in the separation and recovery process.

Regarding SY, in our experiment 59.2 ± 3.9% was obtained for the treatment at 1000 rpm (110 RCF) for 12 min; the other treatments yielded less than 40%. This result was higher than that found for blueberry juice, 45% by Casas-Forero et al. (2021) and for orange juice, 42% (Orellana-Palma et al., 2018), but it was lower than for the juices of murta, 72% and arrayan, 82% (Guerra-Valle et al., 2021), pomelo, 61% (Das et al., 2020), and blueberry, 67% and pineapple, 66% (Petzold et al., 2015). Under these same centrifugation conditions, the Eff obtained was 84.3 ± 1.5%, very similar to that obtained for arrayan juice, 82% at 1878.24 RCF for 20 min (Guerra-Valle et al., 2021). However, in our experiments, the Eff obtained was higher than the majority of the published results, whose range fluctuates between 46% and 78%, for juices such as blueberry, 78% (Casas-Forero et al., 2021), 48% (Petzold et al., 2015), pineapple, 58.7% (Petzold et al., 2015), orange, 83.5% (Orellana-Palma, Petzold, Andana, et al., 2017), calafate, 69 and 76% (Orellana-Palma et al., 2020), murta, 76% (Guerra-Valle et al., 2021), prickly pear, 65% (Márquez-Montes et al., 2023) and pomelo, 73.7% (Das et al., 2020).

The investigations that applied C-FABC in three cycles obtained a higher Eff in the range of 95–99% in the third step (Bastías-Montes et al., 2019, 2022), that is 15% higher than the efficiency obtained in one cycle by CABC (Figure 5c) although, in the previous research works, the CI achieved was close to 2. In our experiments, the final fraction was concentrated three times (Figure 5a). Given the three variables of the process, the best treatment was at 1000 rpm (110 RCF) for 12 min, that is, at a lower speed and for a longer time (Figure 5). The higher the centrifugation speed, the higher breakage of the ice crystals may occur. The crystals may become smaller, therefore, there will be greater tortuosity, that may prevent the exit of all the concentrate. Consequently, the SY and Eff are lower. It should be noted that in our experiment the centrifugation force increases by 21 when the centrifugation speed increases 4.6 times. Simultaneously at a higher centrifugation speed, regardless of time, diffusion mechanism may take place that lead the concentrate to return to the frozen fraction and therefore low solute recovery and efficiency is obtained. At the lower speed and shorter time (1000 rpm and 4 min) there is very little time for the soluble solids content to be separated from the sample, and at the higher speed (4600 rpm either at 4 or 12 min) the centrifugation force might cause the ice to break and melt; that is why SY and Eff are lower.

The equations of the fitted model are:

$$SY = -23.3343 + .0140509x + 7.37199y - .00166782xy,$$
R^2 adjusted from 95.2%

$$Eff = 63.3343 + .00369907x + 1.89884y - .000457176xy,$$
R^2 adjusted from 94%

where x = centrifugation speed (rpm) and y = time (min).

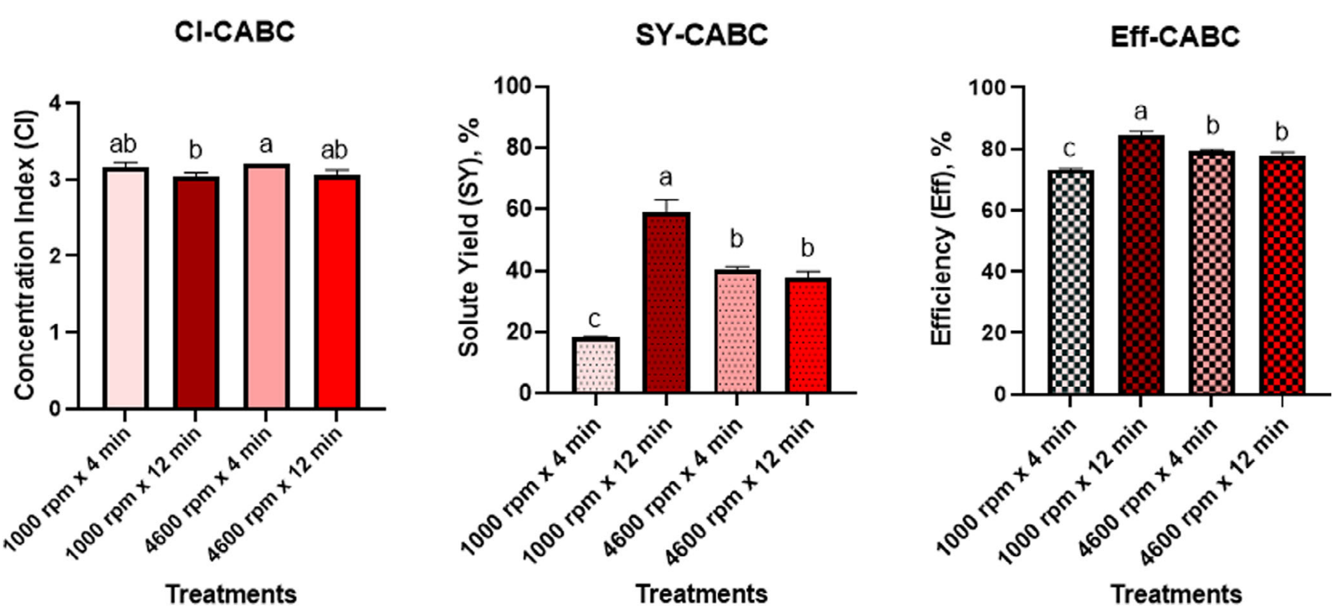

FIGURE 5 (a) CI, (b) SY, and (c) Eff by CABC.

3.3 | Evaluation of VABC

Figure 6 shows the Pareto diagram that resulted from the factorial analysis considering the three response variables CI, SY, and Eff, in which both factors and their interaction had significant effects for SY and Eff.

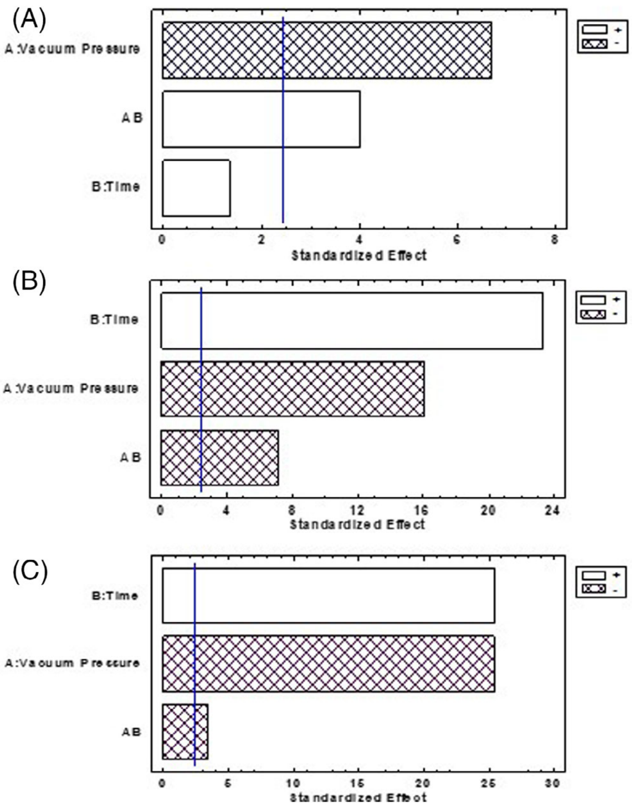

FIGURE 6 Pareto diagram for (a) CI, (b) SY, and (c) Eff by VABC.

In the VABC, it was possible to concentrate samples from 15.8 to 54.7°Brix, with the treatments at 10 kPa for 4 min and 10 kPa for 12 min obtaining the highest CI. These values were higher than the reported results in 15% (w/w) sucrose solution, 2.8 (Petzold et al., 2013), wine, 2.63 (Petzold et al., 2016) and orange juice, 2.3 at 60 min (Petzold et al., 2019). The absolute vacuum pressure used in our work and short time may help increase the CI. However, Orellana-Palma, Petzold, Pierre, and Pensaben (2017) reached a CI of 4.2 in blueberry juice at 80 kPa for 10 min. Regarding SY, it was 47.3 ± 1.2% for the treatment of 10 kPa for 12 min. The solids yield was higher than the value obtained by Orellana-Palma, Petzold, Pierre, and Pensaben (2017) at 80 kPa for 20 min, 40% for blueberry juice and lower than for sucrose solution at 15% (Petzold et al., 2013). An Eff of 81.9% was obtained, higher than that obtained by Petzold et al. (2013) for a 15% (w/w) sucrose solution, 78%; but it was lower than for wine, 90% obtained by Petzold et al. (2016) and for blueberry juice, 84% (Orellana-Palma, Petzold, Pierre, & Pensaben, 2017).

Figure 7 shows the comparison of the four VABC treatments for the three response variables. A maximum average CI of 3.4 and 3.3 was obtained with the treatments of 10 kPa for 4 min and 10 kPa for 12 min, showing no significant differences ($p > 0.05$); the mean maximum values of SY and Eff were 47.3% and 81.9%, respectively (10 kPa for 10 min).

In the VABC, the desirability function considering the three response variables was .86, and considering only SY and Eff it reached a value of .98 with a vacuum pressure of 10 kPa and a time of 12 min (Figure 8).

The fitted model equations are:

$$SY = -4.25833 - .0375x + 4.65903y - .0334028xy,$$
R^2 adjusted from 98.7%

$$Eff = 70.7417 - .0858333x + 1.04375y - .00395833xy,$$
R^2 adjusted from 99.2%

where x = vacuum pressure (kPa) and y = time (min).

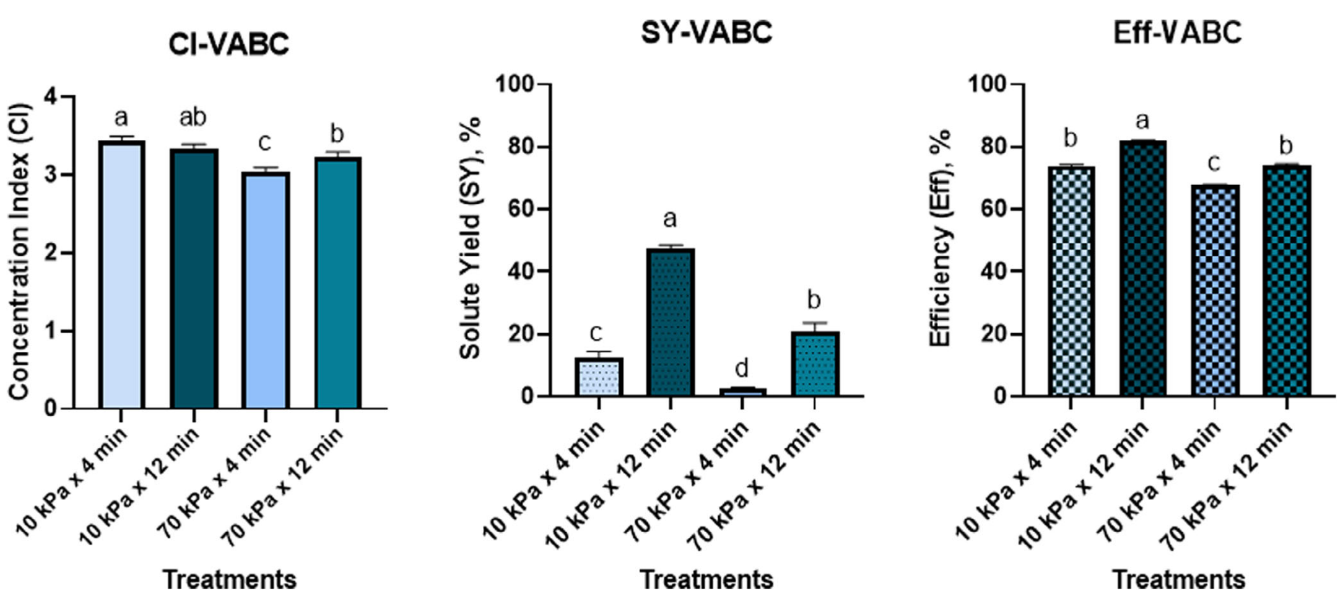

FIGURE 7 (a) CI, (b) SY, and (c) Eff by VABC.

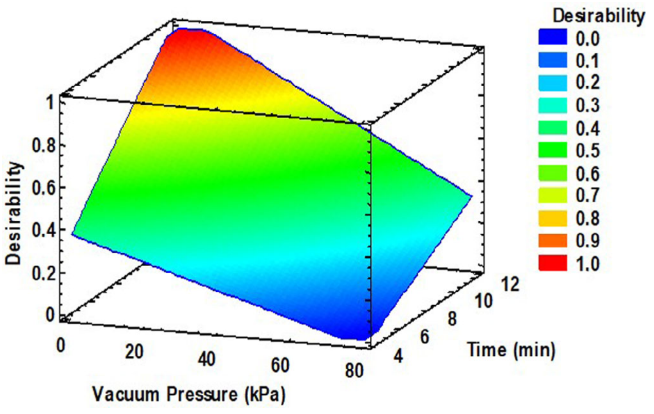

FIGURE 8 Estimated response surface for desirability VABC.

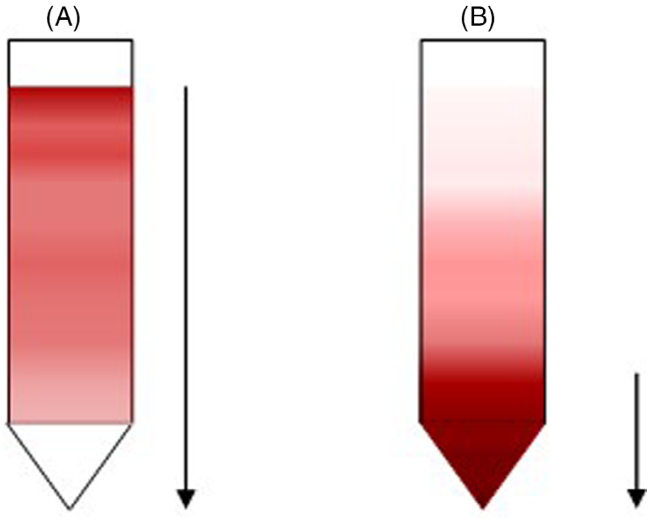

FIGURE 9 Scheme of the position of soluble solids in the tube: (a) VABC and (b) CABC.

TABLE 2 CI, SY, and Eff for the eight treatments.

Treatments	CI	SY	Eff
CABC			
1000 rpm (110 RCF)			
4 min	3.1 ± .0^{def}	18.4 ± .2de	73.3 ± .5^{d}
12 min	3.0 ± .0^{d}	59.2 ± 3.9^{a}	84.3 ± 1.5^{a}
4600 rpm (2360 RCF)			
4 min	3.2 ± .0^{bc}	40.1 ± 1.3^{b}	79.5 ± .3^{bc}
12 min	3.1 ± .1^{cd}	37.7 ± 2.1^{b}	77.9 ± 1.0^{c}
VABC			
10 kPa			
4 min	3.4 ± .1^{a}	12.7 ± 1.8^{cd}	73.9 ± .5^{d}
12 min	3.3 ± .0^{ab}	47.3 ± 1.2^{b}	81.9 ± .3^{ab}
70 kPa			
4 min	3.0 ± .1^{d}	2.4 ± .5^{d}	67.8 ± .3^{e}
12 min	3.2 ± .0^{b}	20.9 ± 2.7^{c}	73.9 ± .6^{d}

Note: Different superscript letters indicate significant differences ($p \leq 0.05$) among treatments.
Abbreviations: CABC, centrifugation assisted block cryoconcentration; VABC, vacuum assisted block cryoconcentration.

3.4 | Comparison between CABC and VABC

The eight treatments were compared applying a categorical multifactor design and multiple range test by the Bonferroni method ($p < 0.05$). A maximum CI of 3.4 was obtained with VABC at 10 kPa for 4 min. CI values were between 3.0 and 3.4 ($p < 0.05$); however, the maximum difference was 12% (Table 2). This method is recommended to obtain a high concentration of soluble solids, although SY and Eff were lower than for CABC (1000 rpm for 12 min).

In our one-step experiments, CI values, 3.1 are similar to those obtained by Orellana-Palma et al. (2021); however, they obtained the same value after three cycles of centrifugation. In addition, Khajehei et al. (2015), obtained a CI of 2 in four cycles of cryoconcentration assisted by gravity and by microwave. Moreover, Burdo et al. (2021) obtained a CI of 2.2. If we take into account some functional aspects of each method, in CABC the sample is closed and placed in a dark environment, which helps the phytochemicals not to oxidize or suffer degradation, which does not happen with VABC because it operates in open-system to facilitate the extraction.

As shown in Figure 9, in the CABC system, soluble solids such as sucrose, glucose, fructose and others are concentrated in the lower part of the tube so that it is easier to extract them; consequently, SY and Eff are better. On the other hand, in the VABC system those soluble solids are dispersed and it is more difficult to extract them, so that CI, SY and Eff turn out to be lower. It is probable that the results obtained in our investigation have been better than others, due to the composition of the fruit with which the juice is obtained, since the higher the soluble fiber content (mostly pectin) the juice has a higher viscosity, which generates structure of smaller ice crystals that occlude soluble solids, which will be more difficult to separate (either by centrifugation or vacuum) due to greater tortuosity. For example, the pomegranate is one of the fruits that contains less soluble dietary fiber, .5%, while the apple has .9% (Ramulu & Rao, 2003), orange 2% and blueberries 2.8% (Marlett & Vollendorf, 1994); murta contains .32%–1.14% pectin (López et al., 2018). It should also be noted that the way the sample is prepared can influence the results, for example, the pomegranate juice was filtered on filter paper with a porosity approximate than 10 μm, in which insoluble solids are retained while in other investigations the sample was filtered with a fine-mesh nylon cloth (.8 mm mesh), so while the juice contains more insoluble solids, the extraction of soluble solids becomes more difficult, the freezing time of the sample may also have influenced, since at longer freezing time the ice becomes more stable, which favors the extraction of soluble solids, in our case it was 48 h while in other investigations it was 12 h.

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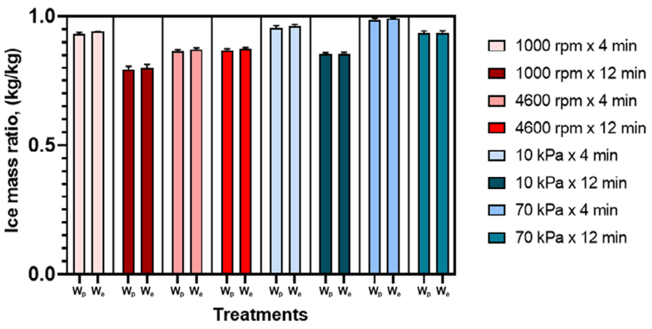

FIGURE 10 Experimental (W_e) and predicted (W_p) ice mass ratios as a function of cryoconcentration treatments.

3.5 | Validation of experimental results

To validate the experimental results, a mass balance of each cryoconcentration treatment was done, which was compared with the theoretical values (Equation (6) and Appendix 1).

The ice mass ratio (W) is lower in treatment 2: CABC 1000 rpm for 12 min. Good fitting was observed between experimental (W_e) and predicted (W_p) ice mass proportions in the eight treatments (Figure 10). The RMS values for CABC and VABC were .78% and .63%, which were less than 25%, which is what Lewicki (2000) considered as an acceptable fit, much less than the 7.3%, 5%, 2% and 4.9% reported by Hernández et al. (2010), Sánchez et al. (2010) and Petzold and Aguilera (2013), respectively.

4 | CONCLUSIONS

Both cryoconcentration methods (CABC and VABC) are suitable to concentrate pomegranate juice in one cycle. SY and Eff were chosen as the parameters to obtain a desirability close to 1, while CI represents the level of concentration that can be reached. CABC at 1000 rpm (110 RCF) for 12 min obtained a concentration of 47.9°Brix with an SY of 59.2% and average Eff of 84.3% in a single cycle. For VABC at 10 kPa and 12 min, values of CI and Eff were similar but SY was remarkably lower. The advantage of both systems is that in one cycle the performance is more satisfactory than other cryoconcentration methods with two or more operational cycles.

Efforts have to be made in the design of the cryoconcentration equipment and scale-up, together with recovery of the solutes retained in the ice block to translate the technology to an industrial scale. Both systems may lead to reduce equipment design and improve energy efficiency compared with current industrial cryoconcentration devices.

NOMENCLATURE

C_0	solute concentration in the initial sample (°Brix)
CABC	centrifugation-assisted block cryoconcentration
C_f	solute concentration in the ice fraction (°Brix)
C-FABC	centrifugation-filtration assisted cryoconcentration
CI	concentration Index
C_s	solute concentration in the concentrated (°Brix)
Eff	efficiency (%)
k	thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
M_c	concentrate mass (kg)
M_f	ice mass (kg)
m_0	mass of solute in the initial sample (kg)
m_s	mass of solute in the concentrate (kg)
NSVK	no significant variation in kinetics
RCF	relative centrifuge force (g)
RMS	root mean square (%)
rpm	revolutions per minute
SY	solute yield (%)
VABC	vacuum-assisted block cryoconcentration
W	ice mass ratio (kg/kg)
W_e	experimental ice mass ratio (kg/kg)
W_p	predicted ice mass ratio (kg/kg)

AUTHOR CONTRIBUTIONS

Flor M. Vásquez-Castillo: Conceptualization; data curation; formal analysis; investigation; methodology; software; writing and editing. **Isabel Achaerandio:** Conceptualization; data curation; investigation; methodology; supervision; writing – review and editing. **Milber O. Ureta-Peralta:** Validation, Formal analysis, Visualization. **Eduard Hernandez:** Conceptualization; data curation; investigation; methodology; supervision; writing – review and editing.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

ORCID

Eduard Hernández https://orcid.org/0000-0002-5337-6947
Milber O. Ureña-Peralta https://orcid.org/0000-0002-0716-0176

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APPENDIX 1: Primary experimental values

	Conditions			Initial sample		Concentrated fraction		Ice fraction		Validation of results (mass balance)		
				Initial weight	Initial soluble solids	Concentrate weight (g)	Soluble solids from concentrate	Ice weight (g)	Soluble solids from ice	Predicted value	Experimental value	Root mean square (RMS)
No.	Speed centrifugation (rpm)/ vacuum pressure (kPa)	Time (min)	Treatment	W_0	C_0	W_c	C_s	W_i	C_f	$V_p = (C_s - C_0)/(C_s - C_f)$	$V_e = W_i/W_0$	$((V_e - V_p)/W_e)^2$
1	1000 rpm	4	A	45.01	15.80	2.70	49.00	42.35	13.20	.927	.941	.00
2	1000 rpm	4	A	45.00	15.80	2.60	49.80	42.31	13.50	.937	.940	.00
3	1000 rpm	4	A	45.01	15.80	2.60	50.40	42.29	13.20	.930	.940	.00
4	1000 rpm	12	B	45.00	15.80	9.42	48.10	35.40	6.80	.782	.787	.00
5	1000 rpm	12	B	45.00	15.80	8.41	48.30	36.30	7.60	.799	.807	.00
6	1000 rpm	12	B	45.00	15.80	8.54	47.20	36.34	8.10	.803	.808	.00
7	4600 rpm	4	C	45.00	15.80	5.89	50.10	38.83	10.10	.858	.863	.00
8	4600 rpm	4	C	45.00	15.80	5.59	50.50	39.14	10.30	.863	.870	.00
9	4600 rpm	4	C	45.00	15.80	5.46	50.90	39.47	10.60	.871	.877	.00
10	4600 rpm	12	D	45.01	15.80	5.40	49.60	39.42	10.80	.871	.876	.00
11	4600 rpm	12	D	45.01	15.80	5.75	49.20	39.08	10.50	.863	.868	.00
12	4600 rpm	12	D	45.01	15.80	5.29	47.90	39.49	11.10	.872	.877	.00
13	10 kPa	4	E	45.01	15.80	1.40	54.70	43.60	14.30	.963	.969	.00
14	10 kPa	4	E	45.01	15.80	1.89	53.50	43.10	13.70	.947	.958	.00
15	10 kPa	4	E	45.01	15.80	1.75	53.00	43.21	14.10	.956	.960	.00
16	10 kPa	12	F	45.00	15.80	6.47	52.53	38.38	9.50	.854	.853	.00
17	10 kPa	12	F	45.00	15.80	6.17	52.93	38.71	9.70	.859	.860	.00
18	10 kPa	12	F	45.00	15.80	6.54	52.27	38.35	9.30	.849	.852	.00
19	70 kPa	4	G	45.00	15.80	.27	47.10	44.73	15.10	.978	.994	.00
20	70 kPa	4	G	45.00	15.80	.39	48.50	44.65	15.50	.991	.992	.00
21	70 kPa	4	G	45.01	15.80	.40	47.40	44.66	15.40	.988	.992	.00
22	70 kPa	12	H	45.00	15.80	3.36	50.70	41.70	12.90	.923	.927	.00
23	70 kPa	12	H	45.00	15.80	2.81	50.60	42.23	13.50	.938	.938	.00
24	70 kPa	12	H	45.00	15.80	2.60	51.65	42.39	13.50	.940	.942	.00
Sum $(\sum)/N$												.000
Root												.007
RMS %												.713