Concentration of acerola (*Malpighia emarginata* DC.) juice by integrated membrane separation process

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ABSTRACT

Acerola is a tropical fruit with a high antioxidant activity which may be attributed to its high vitamin C and anthocyanins content. The aim of this work was to produce a high quality concentrated acerola juice by an integrated membrane process, alternative to thermal evaporation. Acerola juice was clarified by the microfiltration process. The clarified juice was pre-concentrated by reverse osmosis process up to a total soluble solid content (TSS) of 28° Brix and after that the osmotic evaporation process (OE) was used to reach a TSS up to 55° Brix, corresponding to a concentration factor of 1.93. The vitamin C, anthocyanins content and antioxidant activity increased, respectively, 2.21, 1.41 and 2.28 folds in relation to the pre-concentrated juice when the OE was performed. The results showed that there was no change on the vitamin C content and antioxidant activity of the juice after its processing. However, it was verified a reduction on the anthocyanins content, probably due to the great instability on this pigment. The obtained results showed that the integrated membrane process may be used as an alternative to obtain high quality concentrated juice, as the final product still showed a very high antioxidant activity and a very high amount of vitamin C.

Keywords: Osmotic evaporation; Tropical fruit; Vitamin C; Anthocyanins; Reverse osmosis; Antioxidant activity

1. Introduction

Acerola is a red small tropical fruit characterized by its high vitamin C content, ranging from 800 mg/100 g to 4000 mg/100 g. The consume of three fruit units per day satisfies the vitamin C recommended dietary allowance for an adult [1].

The red color of mature acerola is related to the presence of anthocyanins which represent the most attractive phenolic compounds due to their biological properties since they are strong antioxidant compounds and their exuberant and attractive colors that varied from blue to red [2].

The production of food with a high content of these compounds leads to a decrease of additive usage resulting in healthier foods. Since it is a very perishable and acid fruit, acerola is usually consumed in a processed form [3].

Since it is a very perishable and acid fruit, acerola is usually consumed after being processed, in the form of pulps frozen and juices. The removal of water, through the concentration, besides guaranteeing the microbiological quality, presents advantages in reducing costs with packaging, storage and transport [4].

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Furthermore, the lower water activity of concentrated juices in relation to natural juices provides protection against the growth of microorganisms, increasing the shelf life of the product. The process of concentrating juices also allows changes in the quality, quantity and price of fruits. Concentrated juices can be used as ingredients in various products such as ice cream, jams and fruit-based drinks [5].

When conducted in multiple stages, vacuum evaporation, which is traditionally use by the industry today, has some disadvantages, including high energy consumption, the formation of "off-flavor", color changes and the degradation of thermosensitive compounds. These factors reduce the nutritional value and the sensory characteristics of the juice. These effects are largely attributable to the heat transferred to the juice during evaporation [6,7].

Crioconcentration and membrane separation processes such as reverse osmosis (RO) and osmotic evaporation (OE) techniques are alternatives to vacuum evaporation. These techniques can be used to obtain concentrated products that are more stable and are able to maintain most of the characteristics of fresh fruit, such as the fruit color, structure, aroma and nutritional value [8].

The crioconcentration process preserves the quality of the juice, but the concentration achieved (approximately 50° Brix) is lower than that obtained by evaporation (60–65° Brix), and the process consumes a significant amount of energy. The membrane separation processes employed not only affect the concentration but also the clarification, fractionation and sterilization of fruit juices, and thus can be used to obtain better quality products with reduced energy consumption due to the possibility of operating at moderate temperatures and pressures [9,10].

The membrane separation processes are present in various productive sectors. These processes do not involve phase changes and do not require chemical agents, thus representing a technological response to the demand for high quality products that are free of additives. The integration or replacement of some traditional operations by membrane separation technology allows energy consumption to be directly and indirectly rationalized, and at the same time improves the nutritional and sensory properties of the final product [11].

RO is a membrane separation process in which a hydraulic pressure that is greater than the osmotic pressure of the solution is applied to allow water to permeate from a high solute concentration to a lower concentration solution. This process can be applied to concentrate fruit juices, reducing the damage caused by heat treatment [12].

The main advantages of concentration by RO are as follows: high quality products are obtained due to a low operation temperature, resulting in the maintenance of thermosensitive compounds; it requires less power consumption. The main disadvantage of this technique is that a lower concentration level is obtained when compared to that achieved by thermal evaporation because the high osmotic pressure of fruit juice limits the efficiency of the process. Because of this limitation, the process of RO is generally used as a technique for pre-concentration reaching a maximum concentration up 25° Brix to 35° Brix [13].

The use of RO pre-concentration for many fruit juices has been studied by many authors, and the results are very promising. Fruit juices that are pre-concentrated are of good quality, showing that a high rate of retention has been obtained for those compounds with a high nutritional importance [14,15].

In the concentrated juice industry, which tries to achieve levels of concentration in the range 42–65° Brix, RO can be used as an initial step in the process of concentration, and is often followed by other processes such as OE [12].

OE is a promising membrane process that is usually applied to concentrate solutions under a concentration driven condition. The theoretical and practical aspects of this process have been studied since 1986. Other processes which also use as driving force the concentration gradient across the membrane are the osmotic distillation, osmotic concentration or gas membrane extraction [16,17].

This technology was developed to concentrate aqueous solutions containing thermosensitive compounds such as fruit juices and pharmaceuticals. The solution to be concentrated is separated by means of extraction, usually using a hypertonic solution (brine) and a microporous hydrophobic membrane. The hydrophobic nature of the membrane prevents liquid water from penetrating into the membrane pores. During the process, the driving force for mass transfer is the difference in the vapor pressure of water between the two sides of the membrane. The removal of water can be described by the following mechanism: water first evaporates at the interface of the diluted solution and the membrane. Water vapor then diffuses through the pores of the membrane and finally condenses at the interface of the membrane and the solution. The phenomenon of temperature polarization can be observed during this process, which is defined as a transfer of latent heat through the membrane. This transfer of latent heat causes a decrease in the temperature at the interface and an increase in evaporation at the condensation interface. This thermal effect reduces the driving force for water transport [18,19].

The water permeate flux can be increased by integrating OE and membrane distillation. In this case, the temperature difference between the solutions will also

serve as a driving force. Although the aqueous solution is heated slightly during the process, the method still works under mild conditions because the temperature difference applied does not exceed 10–15°C [5].

Generally, before all of the juice is subjected to the RO process, a pre-treatment that is aimed at increasing the filtration efficiency and reducing the fouling of the membrane is necessary. These pretreatments may include clarification, centrifugation or enzymatic depectinization [20].

The clarifications conducted in membrane processes, particularly ultrafiltration (UF) and microfiltration (MF), are replacing other conventional forms of clarifying fruit juices. These processes have the advantages of eliminating fining agents and their associated problems [8].

The application of membrane processes for fruit juices were carried out by several researches, however, few works were developed for acerola juice [21–24].

The aim of this study was to obtain a concentrated clarified acerola juice through the integration of the processes of MF, RO and OE.

2. Materials and methods

The concentration experiments were preceded by the clarification and pre-concentration of the integral acerola juice. The clarification step was carried out by MF and then the clarified juice was pre-concentrated by RO according to Pagani et al. [25]. The juice was then frozen and stored at −18°C until its use as raw material for the OE concentration processes.

Tests of OE were conducted for 30 h, under an inert atmosphere (N_2), in a laboratory system consisting of two independent circuits connected by a hydrophobic membrane composed of a thin PTFE (polytetrafluoroethylene) layer supported by a PP (polypropylene) porous support. The temperature of the brine, a solution of calcium chloride and the acerola juice concentrates were pre-maintained at 15°C and 35°C, respectively. The brine was constantly maintained close to the saturation value (6.5 mol/l) by adding calcium chloride to the brine. In both circuits, juice and brine, the pressure was maintained at 0.2 bar, i.e., the transmembrane pressure was kept equal to zero, preventing mass transfer by convection.

The efficiency of the process was evaluated by the behavior of the permeate flux (J) and the concentration factor (CF):

$$J = \frac{V}{A * t}$$

$$CF = \frac{[X]_{\text{concentrated juice}}}{[X]_{\text{feed juice}}}$$

where V is the volume permeated during a determined time t, A is the membrane surface and $[X]$ is the concentration of a specific quality evaluated parameter in the concentrated stream and in the feed stream.

Samples of the feed and final product obtained in the OE process were characterized by pH, titrable acidity, soluble solids [26].

The quantification of vitamin C was carried out using high performance liquid chromatography (HPLC) with ion exchange column [27]. The samples were weighed, extracted with 0.05 M sulfuric acid in ultrasound for 10 min, swell in amber volumetric flask, filtered through quantitative filter paper and transferred to amber vial with screw cap and septum silicone. In the chromatographic analysis it was used a high-efficiency gas-waters alliance 2695 with a detector array of photodiodes Waters 2996.

The anthocyanins were extracted with an acidic ethanol solution, 95% ethanol:1.5 N HCl (85:15) for 12 h at 4°C. The quantification was performed by spectrophotometry at 535 nm, according to Lees and Francis [28], used by De Rosso and Mercadante [29], Lima et al. [30], and Vendramini and Trugo [31].

The total antioxidant activity was determined by an improved version of the ABTS assay in which the radical cation ABTS⁺ is reduced to ABTS (2,20-azinobis-3-ethylbenzothiazoline-6-sulfonic acid) [32]. The radical was generated by reaction of a 7 mm solution of ABTS in water with 2.45 mm potassium persulphate (1:1). Absorbance measurements at 734 nm were made after 15 min of reaction time. The results were expressed in μmol of Trolox Equivalent Antioxidant Activity (TEAC), using the relevant calibration curve.

Data were analyzed by analysis of variance (ANOVA) followed by Tukey test, using the software Statistica 7.0. p values < 0.05 were considered significant.

3. Results and discussion

Through the coupling of RO and OE, the concentrated values obtained for acerola juice ranged to almost 55° Brix with a similar nutritional quality to the original juice maintaining its main thermolabile component (vitamin C) These values were similar to those obtained by conventional thermal processes. In classical juice industries, the concentration levels of the fruit juices range from 42° Brix to 65° Brix [12].

The acerola juice concentrated by OE presented an increase in the concentration of all components.

The results of the degree of concentration of total soluble solids (TSS), vitamin C, total anthocyanins and antioxidant activity are shown in Table 1. In this study, the results showed that the concentration process increased the total soluble solids content from 28.5° Brix in the

Table 1
Concentration factor of soluble solids, vitamin C, total anthocyanins and antioxidant activity of the pre-concentrated juice (feed) and concentrated juice by osmotic evaporation

	Soluble solids (°Brix)	Vitamin C (mg/100 g)	Total anthocyanins (mg/100 g)	Antioxidant activity (µmol TEAC/kg)
Pre-concentrated juice	28.50	2147.53	29.60	166.03
Concentrated juice	54.93	4742.49	41.59	379.29
Concentration factor	1.93	2.21	1.41	2.28

pre-concentrated juice to 54.9° Brix in the concentrated juice which represented 1.9 folds. The antioxidant activity and vitamin C content increased 2.28 and 2.21 folds, respectively. Similar results for vitamin C content were observed by Matta et al. [21] when evaluated the use of RO and MF associated to an enzymatic hydrolysis to produce a clarified and concentrated acerola juice. The RO concentrated the clarified juice from 7° Brix to 29.2° Brix. The final product obtained had its vitamin C content improved in 4.2 folds, according to the concentration factor of TSS.

Anthocyanins content was not maintained after OE. The concentrated juice had its anthocyanin content improved only in 1.41 folds reaching 41.59 mg/100 g. The observed loss of anthocyanins in this process condition could be explained by the great instability of this pigment, which may be readily convert to colorless derivatives and subsequently to insoluble brown pigments. It is also rapidly degraded by the action of light, oxygen, enzymes, ascorbic acid, sugars, sulfur dioxide or sulfite salts, metal ions and copigments and its instability increases with the increasing of the temperature [33]. In Table 2 are presented the results of the instrumental colour measurements of the pre-concentrated juice and concentrated juice by OE. It can be observed a decrease in both a and b color parameters corresponding to losses of red and yellow colors, respectively.

In the analysis of physical properties, pH remained around 3.2 in pre-concentrate and concentrate juices, while the acidity was observed the same concentration factor obtained from the TSS (CF = 1.9), from 3.72 g citric acid/100 g juice to 7.08 g citric acid/100 g juice.

During the OE process, a decrease in permeate flux was observed, probably due to the increase in soluble solids (TSS) and thus the viscosity of the juice (Fig. 1). This observation agreed with the results obtained for passion fruit juice at pilot scale [34] and pineapple juice at a laboratory unit [18]. To minimize the decay of the permeate flux, the water activity (A_w) of the brine was adjusted by the addition of salt to the brine tank because it was diluted over the juice concentration, decreasing the driving force process.

Table 2
Color evaluation of the pre-concentrated juice (feed) and concentrated juice by osmotic evaporation

	Luminosity	a_{Hunter}	b_{Hunter}
Pre-concentrated juice	42.78	36.60	29.25
Concentrated Juice	8.02	13.84	4.65

L – luminosity (0 = black and 100 = white); a – (−80 to 0 = green, from 0 to +100 = red); b – (−100 to 0 = blue, from 0 to +70 = yellow).
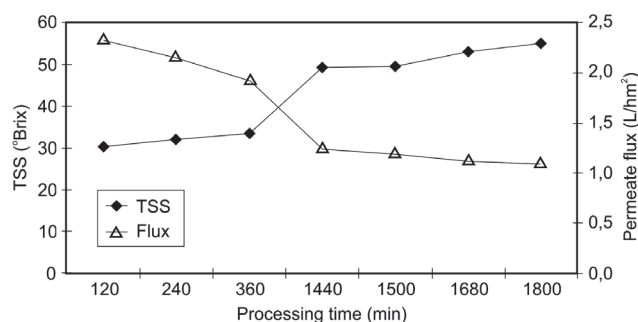

Fig. 1. Permeate flux and total soluble solids (TSS) concentration during the osmotic evaporation of acerola juice.

4. Conclusions

Acerola juice was successfully concentrated by an integrated membrane separation process. The obtained juice achieved a total soluble solids up to almost 55° Brix and maintained its nutritional quality, with no losses of vitamin C content and antioxidant activity.

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