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Integrated membrane separation processes aiming to concentrate and purify lycopene from watermelon juice

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ABSTRACT

The increasingly consumer demand for ingredients obtained from natural sources and sustainable processes represents for the industry the challenge to place on the market innovative products with high added value. Watermelon is known for its high lycopene content, the red pigment with recognized antioxidant properties. This work investigated the integration of microfiltration, diafiltration and reverse osmosis processes to obtain a low sugar lycopene-rich extract from watermelon juice. Permeate flux, lycopene and sugars content, the antioxidant capacity and color parameters were used to evaluate the performance of the integrated membrane processes. Average permeate fluxes of microfiltration/diafiltration and reverse osmosis processes were 69.6 and 19.1 kg h^{-1} m^{-2}, respectively. An increase up to 17 and 11 times in lycopene content and antioxidant capacity as well as a decrease in sugars concentration were achieved. The final product showed a dark red color, as highlighted by the brightness value (L*) of 37.06.

Industrial relevance: Watermelon juice concentration can be an alternative to produce lycopene-rich products, especially colorants and antioxidants. Membrane processes are a good alternative to the conventional thermal concentration once they operate at milder temperature conditions avoiding the undesirable losses of heat-sensitive compounds as well as sensorial characteristics as color and flavor. The integration of microfiltration, diafiltration and reverse osmosis can be useful to obtain a lycopene-rich extract from watermelon juice, with low sugar content.

1. Introduction

Watermelon is a plant of great economic and social importance around the world. The estimative for its global production was about 98.2 million ton in 2009, being China, Turkey, Iran and Brazil the main producing countries in the last 15 years (FAO, 2014).

Due to its pleasant sensory characteristics of flavor, sweetness, succulence and freshness the watermelon production is destined almost entirely to fresh consumption. Nonetheless, factors such as the fungi attack and diseases, seasonality of consumption and deformities can lead to the occurrence of losses and a productivity drop of suitable fruits for direct consumption, so that the industrial use of these may be relevant in the economic and environmental point of view.

The red color of watermelon pulp is due to lycopene, a carotenoid that has significant antioxidant properties. Lycopene levels in the range of 47–68 μg/g fresh fruit have been reported in watermelon (Perkins-Veazie, Collins, Pair, & Roberts, 2001; Rodriguez-Amaya, 2001).

Therefore, the high productivity and the specific chemical composition of watermelon make it a promising raw material for the production of ingredients, especially natural colorants and antioxidants.

In addition, in the last years, the consumer's growing concern about maintaining a healthy lifestyle has been outlining changes in the people habits with regards to a healthier, natural and equilibrated diet so that the search for natural ingredients and additives also follow this trend. For consumer, such products can be seen as distinct options for many special purposes, while for the industry it represents an opportunity to put on the market innovative products and ingredients of high added value. Therefore, watermelon emerges as an important alternative source for the development of industrial products or lycopene-rich food supplements.

It is not usual finding watermelon industrialized products. Juice concentration is a process that can produce lycopene-rich products to meet the growing market of natural ingredients, especially colorants and antioxidants, to foods and beverages and, to a lesser extent, cosmetics and medicine, as well as functional supplements presenting an average

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growth of 15% per year in Brazil (Brasilink, 2014). In particularly regarding the global food colors market it is projected to reach $2.5 billion by 2020 (Research and Markets, 2016).

Compared to conventional thermal concentration processes, membrane technology seems to be a good alternative to minimize the adverse effects of heat (Balyan & Sarkar, 2016; Bahçeci, Akillioğlu, & Gökmen, 2015; Jiao, Cassano, & Drioli, 2004). In general, membrane filtration does not involve phase transition or high temperatures, favoring the maintenance of sensory and functional characteristics of the product and depending on the selectivity of the membrane, the selected process can fractionate or concentrate different compounds. Futhermore, membrane processes are reduced in direct energy consumption, requires a lower footprint area occupied by the processes plants, are lower in waste generation, do not use organic solvents and provides a high-quality compound production, providing maximization of raw materials for economic sustainability. Such characteristics respond well to green technology requirements that frame membrane technology as an efficient and clean process (Rombaut, Tixier, Bily, & Chemat, 2014; Szekely, Jimenez-Solomon, Marchetti, Kim, & Livingston, 2014).

Due to its molecular weight (536.87 $gmol^{-1}$) and the fact that it in vegetable tissues can be tightly bound to proteins and other plant cell structures such as fibers and polysaccharides (Hurst, 2002), lycopene does not permeate microfiltration, ultrafiltration or reverse osmosis membranes, thus, the concentration of this compound from fruit juices by means of membrane separation processes has been shown to be a viable process and represents a good alternative for industrial purposes (Gomes, Costa, Campos, Couri, & Cabral, 2011; Das Gupta & Jayarama, 1996). Gomes et al. (2013), studying the watermelon juice concentration by microfiltration, achieved a lycopene concentration factor higher than 5.0 using tangential velocity values above 6.0 m/s at 30 °C.

The membrane processes can still be operated in a diafiltration mode. In this type of process it is possible to obtain a higher purity level of the compound in the same concentration ratio due to the removal of impurities smaller than the membrane porosity. Although it was first studied in 1968, few papers in the literature applied this technique for the purification of bioactive compounds from juice fruits (Sluková et al., 2016; Simon, Vandanjon, Levesque & Bourseau, 2002; Jaffrin & Charrier, 1994).

The objective of this study was to evaluate the feasibility of concentration and purification of lycopene from watermelon juice by coupling microfiltration, diafiltration and reverse osmosis processes in order to obtain a rich lycopene concentrated extract with high antioxidant capacity.

2. Material and methods

2.1. Raw material and watermelon juice

Watermelons of the variety Crimson Sweet were purchased from the local market of Rio de Janeiro. Fruits were washed, sanitized by immersion in chlorinated water (200 ppm) for 20 min, manually cut and then depulped in a horizontal depulper (model Bonina 0.25 df, Itametal, Itabuna, Brazil) equipped with a 0.6-mm sieve. The juice was packed in polyethylene containers and stored at −18 °C for a maximum of 3 days.

2.2. Pre-concentration and purification

Initially, the juice was subjected to microfiltration in order to pre-concentrate lycopene. Cross-flow microfiltration was performed in a pilot unit comprising four tubular modules of α-Al_2O_3 membranes T1–70 with a mean pore size of 0.2 μm (Pall Corporation, Membralox® Ceramic Membrane Products, Port Washington, NY, USA), arranged in a series configuration, resulting in an effective permeable area of 0.022 m^2. The processes were performed at 35 °C and transmembrane pressure of 2 bar (Gomes et al., 2013). Temperature was kept constant by using an external heat exchanger (±0.5 °C). Microfiltration was firstly conducted in concentration mode with the permeate being collected in a beaker placed on an electronic balance (±0.01 g) (Marte, model MS 20 K, São Paulo, Brazil) and the concentrate returned to the feed tank. The experiment was ended when the concentration factor (CF) reached the value of 6. The concentration factor (CF) was defined by Eqs. (1) and (2).

$$VCF = Vf/Vr \tag{1}$$

$$Vr = Vf - Vp \tag{2}$$

where: *VCF* is the volumetric concentration factor; *Vf* is the feed juice volume; *Vr* is the retentate volume and *Vp* is the permeate volume.

The permeate flux was determined by the ratio between the permeate flow and the membrane area as shown in Eq. (3):

$$J\left(Lh^{-1}m^{-2}\right) = Mp/(A \times t) \tag{3}$$

In which: *Mp* is the permeate mass, *A* is the membrane area and *t* is the time.

After reaching the desired concentration factor, using the same operating conditions, the microfiltration process was conducted in diafiltration mode in order to purify the pre-concentrated extract. The juice solutes, primarily sugars, were progressively removed by the convective flow of the added distilled used as the washing fluid. Amount of water was added to the feed tank that contained the concentrated juice in order to dilute it to 50%, and then the juice was microfiltred to its original volume. This was repeated until the juice soluble solids content was equal or lower than 1°Brix. The permeate flux was measured during processing and samples were collected for analysis.

2.3. Reverse osmosis

The reverse osmosis process was carried out in a pilot plant unit model Lab Unit M-20 (DDS Danish Separation System, Denmark), with polyamide composite membranes (98% NaCl solution rejection at 25 °C and 60 bar). The membranes were arranged in a plate and frame module, totalizing 0.396 m^2 of permeation area. The concentration was carried out in a fed batch mode at 35 °C, 60 bar transmembrane pressure and 650 Lh^{-1} recycle flow rate. The processes were finished when the volumetric concentration factor (CF) was equal to 5.

2.4. Analytical methods

Samples of the watermelon juice and of the retained fractions of microfiltration (MF), diafiltration (DF) and reverse osmosis (RO) processes were analyzed for pH, soluble solids content (°Brix) and total titrable acidity (g100 g^{-1}) according to AOAC (2000).

The lycopene content was determined according to the procedure described by Sadler, Davis, and Dezman (1990) and modified by Perkins-Veazie et al. (2001). The pigment was extracted with a mixture of hexane/acetone/ethanol (2:2:1; v:v:v). After extraction, the absorbance of the hexanic phase was measured at 503 nm. The results were expressed as μg lycopene/g sample (Eq. 4).

$$Lycopene\ (\mu g/g) = \frac{\frac{A_{503}}{\varepsilon \times b} \times MW \times V}{W} \times 10^3 \tag{4}$$

Where: A_{503} is the Absorbance at 503 nm; ε is the molar extinction coefficient ($L \cdot mol^{-1} \cdot cm^{-1}$) = 17.2×10^4 (Zechmeister, Lerosen, Schroeder, Polgar, & Pauling, 1943); *b* is the optical path length cuvette (cm); *MW* is the molecular weight of lycopene (536.9 g mol^{-1}) and *W* is the sample weight (g).

Antioxidant capacity was quantified according to Re et al. (1999) using the hexanic extracts obtained in the determination of the