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Ultrasound assisted extraction and nanofiltration of phenolic compounds from artichoke solid wastes

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ABSTRACT

Artichoke wastes from the canning industry are rich in phenolic compounds, which can be used as food additives. This study aims to evaluate the potential of sequential process based on the use of ultrasound extraction and membrane technology for phenolic recovery. In the extraction step, solvent composition and ultrasound power were evaluated to understand their impact on phenolic content and antioxidant capacity. The highest yields were observed for extracts with higher ethanol content (50 and 75%). Therefore, these extracts were selected for concentration by nanofiltration in a tangential module, using differents membranes (NF270, DK and DL). The flux decrease and the phenolic retention were evaluated. Hermia's models and membrane surface characterization were used to investigate the fouling. The highest flux was observed for extracts with 50% of ethanol with a retention of chlorogenic acid higher than 95%. DK membrane showed to be less susceptible to fouling, although the cake formation occurred in all evaluated membranes. The most suitable process condition to obtain the highest phenolic yields was extraction with 50% ethanol and an ultrasound power of 240 W and extracts nanofiltration using DK membrane.

1. Introduction

The artichoke (*Cynara scolymus* L.) is a perennial herb belonging to the family *Asteraceae*. This plant is native from subtropical regions and its inflorescences are consumed widely in Mediterranean countries (Pandino et al., 2012; Pistón et al., 2014).

Besides being a good source of inulin, fiber and minerals, artichoke is rich in phenolic compounds (Ruiz-Cano et al., 2014). These compounds have been associated with scavenging capacities of artichoke extracts against ROS (reactive oxygen species) and RNS (reactive nitrogen species) (Pistón et al., 2014), and anti-obesity effects (Cho et al., 2010), that are some of the reasons for the high popularity of artichoke products around the world. A recent paper showed that extracts obtained from artichoke waste have a remarkable delaying effect against canola oil oxidation (Claus et al., 2015).

The artichoke processing main residues are the inner and outer bracts. The phenolic composition of this waste is similar to the edible parts of the plant (Fratianni et al., 2007; Lombardo et al., 2012; Pandino et al., 2011; Sihem et al., 2015), and according to Zuorro et al. (2015) it is higher than that those found on grape pomace (Louli et al., 2004), carrot peels (Chantaro et al., 2008) and spent coffee grounds (Ranic et al., 2014).

The canning industry discards around 70% of the harvested inflorescence (López-Molina et al., 2005). The world production of this vegetable grows an average of 6% annually, and in 2012 was around 1.6 million tonnes (FAO, 2012); the amount of waste currently generated exceeds one million tons. Therefore, it is important to search for alternatives to recover phenolic compounds from artichoke wastes.

Among the extraction processes, the one assisted by ultrasound emerged as being the simplest and the most inexpensive technique; it allows the use of various solvents, low temperatures, does not have restrictions on the polarity of the compound of interest nor to the moisture of the matrix; it has also good reproducibility and a high potential for scale-up (Ghitescu et al., 2015; Rastogi, 2011). The efficiency of the ultrasound, relative to conventional extraction methods, is attributed to the cavitational effect which facilitates the release of extractable compounds and enhances the mass transport by diffusion or by disrupting the plant cell walls (Chemat et al., 2011; Esclapez et al., 2011; Gaete-Garretón et al.,

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2011; Luque de Castro et al., 2011). But like most conventional methods of extraction, one of the disadvantages of this method is that does not obtain solvent-free extracts, and a concentration step is required after extraction.

To concentrate phenolics, the use of nanofiltration membranes shows higher fluxes than the reverse osmosis and higher retentions than ultrafiltration (Conidi et al., 2012), since artichoke phenolic acids have a molar mass between 300 and 600 g/mol (Abu-reidah et al., 2013). This technology allows concentration at mild temperatures, not involving a phase change, preserves the biological activity of the compounds and enables the solvent recycling by capturing the permeate, which can be reused in further extractions enabling a sustainable process of extraction and concentration.

The use of different fractions of GRAS (Generally Regarded as Safe) solvents such as water and ethanol in the extraction and concentration processes allow the application of the final product in foods, drugs and cosmetics, contributes to selective extraction of bioactive compounds (Ghitescu et al., 2015) and, due to the membrane-solvent interactions, significantly change the permeation features of the membranes (Firman et al., 2013; Labanda et al., 2013). Thus, the importance to investigate different ratio of these solvents in sequential processes.

The concentration of extracts obtained from different ratios of solvent can lead to different interactions between the extract compounds. In hydroalcoholic systems these interactions have not yet been deeply analysed, but they can influence membrane permeation. The flux decrease caused by concentration polarization and membrane fouling is a major limitation for the industrial application of membrane technology. In previous investigations (Grenier et al., 2008; Hwang et al., 2007; Ng et al., 2014), a number of mathematical models were utilized to explain fouling mechanisms. When particle size present in extract is smaller than or comparable to the membrane pore size, the membrane blocking model is commonly used to explain how and when the particle blocking occurs (Hwang and Liao, 2012). Based on this model, four different fouling mechanisms (complete blocking, intermediate blocking, standard blocking, and cake formation) were proposed by Hermia (1982) to characterize the membrane fouling. These models can be a useful tool for selecting membranes less susceptible to fouling, especially when it comes to the filtration of vegetable hydroalcoholic extracts, due to the sample complexity.

The aim of this work was to (1) evaluate the effect of solvent composition and ultrasound power in the extraction of phenolic compounds and (2) to concentrate the best extracts by three different nanofiltration membranes. Flux decrease, coefficient retention and membrane characterization were carried out. At last, we select the most suitable sequential system of extraction and concentration of phenolic compounds from artichoke solid waste.

2. Methods

2.1. Extraction process

Artichoke wastes (external and internal bracts) were donated by Bonsucesso factory (São Roque/SP, Brazil). This material was stored in a freezing chamber at −18 °C and thawed according to the quantity required for each extraction. All trials were carried out with the same lot of raw material.

Initially, the wastes were crushed and placed in a jacketed reactor (6.5 cm of internal diameter and maximum volume of 250 mL). For extraction, an ultrasonic cell disruptor at 20 kHz, equipped with a titanium alloy 13 mm diameter flat tip probe (UNIQUE, São Paulo, Brazil) was fitted into the reactors. The w/v ratio was fixed at 1:10 (g/mL). The ultrasonic power evaluated was 0, 240, 480 and 720 W. The solvent compositions studied were 0, 25, 50 and 75% ethanol in water (v/v). After 60 min of extraction, the extracts were filtered with filter paper, and characterized. A total of 16 experiments were carried out, each done in duplicate. The experimental conditions that showed the best yields of phenolic compounds were selected, and kinetic studies (5, 10, 20, 30, 40 50 and 60 min) were performed in order to reduce extraction time. Finally, a new extraction time was fixed, and the experimental conditions selected were used as feed in the extract concentration step. All extractions were performed in batches of 100 mL at 25 ± 1 °C.

2.2. Concentration process

The tests were performed in a tangential filtration system (INVICT, MENTEST, Brazil) using flat sheet membranes (NF270, DK and DL), presented in Table 1. This system had 2 L capacity, an effective permeation area of 7.7×10^{-3} m^2, and the maximum liquid recirculation flow rate was 60 L/h.

A new membrane was used in each test to assure the same initial conditions. Conditioning of the membranes consisted of their immersion during 12 h in solutions with the same alcoholic concentrations of the extracts. During concentration, the system pressure was maintained at 20 bar and temperature was 25 °C. The initial feed volume was 900 mL and the concentration process was carried out to a volume reduction factor of 2.5.

2.2.1. Evaluated parameters

The volumetric flux of permeate (J_v) was calculated by Equation (1), and the average permeate flux (J_s) was obtained from the straight line inclination described by the function $V_p = f(A_p \times t)$, according to Tylkowski et al. (2010).

$$J_v = \left(\frac{m_p}{\rho t A_p}\right) \quad [1]$$

Where J_v is the volumetric flux of the permeate (L/m^2h); m_p is the permeate collected mass (g); ρ is the density (g/L), t is the time (h), and A_p is the membrane permeation area (m^2).

The flux decrease (D_f) was calculated according to Equation (2).

$$D_f = \left(\frac{J_i - J_s}{J_i}\right) \cdot 100 \quad [2]$$

Where J_i is the initial and J_s is the average permeate flux (L/m^2h).

The retention coefficient (R) was calculated by Equation (3):

$$R(\%) = \left(1 - \frac{C_P}{C_A}\right) \cdot 100 \quad [3]$$

Where C_p and C_A are the concentration of solute in the permeate and in feed, respectively.

The volumetric concentration factor (*VCF*) was determined by Equation (4), where V_i and V_f are the initial and the final feed volume (L), respectively.

$$VCF = \left(\frac{V_i}{V_f}\right) \quad [4]$$

2.2.2. Fouling mechanisms

The models proposed by Hermia (1982) were used to identify the predominant fouling mechanism in the evaluated processes; these models incorporate four mechanisms of fouling (cake formation, intermediate and complete blocking of the pores, and the