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Recovery of bioactive compounds from artichoke brines by nanofiltration

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ABSTRACT

In this work a membrane-based process for the fractionation of artichoke brines was investigated in order to separate flavonoids and caffeoylquinic acids from salt compounds. Therefore, the performance of different spiral-wound nanofiltration (NF) membranes in the treatment of clarified artichoke brines was evaluated in terms of productivity and selectivity towards bioactive compounds in selected operating conditions. Membranes with different polymeric material (polyethersulphone, polyammide) and molecular weight cut-off (MWCO) (from 200 to 1000 Da) were tested. NF membranes of 200 Da produced better results in terms of recovery and concentration of compounds of interest. A better separation of salt compounds from caffeoylquinic acid derivatives was reached by using Filmtec-Dow NF 200 and Desal DL membranes. For these membranes a low rejection towards dry residue (between 14% and 18%) was observed, while rejections towards total caffeoylquinic acids, flavonoids and cynarin were higher than 92%.

According to the obtained results the NF permeate, enriched in salt compounds, can be reused in the working cycle for the preparation of new acidulated brines through the adjustment of the standard salt concentration; the concentrated stream, enriched in phenolic compounds, is a good source of possible ingredients to functionalize foodstuffs.

1. Introduction

Globe artichoke (*Cynara scolymus* L.) is a traditional component of the Mediterranean diet. According to FAO estimation, Italy was the world's largest artichoke producer in 2011, with a production of 474,550 metric tons (MT), followed by Egypt, Spain and Perù (FAO, 2014).

The artichoke has many nutritional qualities being rich in water (91% of edible portion) and minerals, but also of vitamins, carotenoids and polyphenols (Christaki et al., 2012). The phenolics include cynarin (1,3-di-O-caffeoylquinic acid), luteolin, cynaroside (luteolin-7-O-glucoside), scolymoside (luteolin-7-rutinoside); phenolic acids such as caffeic, coumaric, hydroxycinnamic, ferulic, caffeoylquinic acid derivatives; mono- and dicaffeoylquinic acids, including chlorogenic acid; alcohols and flavonoid glycosides, among others (Abu-Reidah et al., 2013; Chen and Ho, 1997; Lattanzio et al., 2009; Mulinacci et al., 2004). These substances exhibit an important scavenging activity against reactive oxygen species (ROS) and free radicals, and perform as a protective shield against oxidative damage to biological molecules, such as proteins, lipids and DNA. Several studies have demonstrated

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their health-protective potential in terms of hepatoprotective (Adzet et al., 1987; Gebhardt and Fausel, 1997), antimicrobial (Kukić et al., 2008), hypocholesterolemic (Clifford and Walker, 1987; Rondanelli et al., 2013) and anticarcinogenic (Clifford, 2000) activity.

In the course of artichoke processing and packaging a large amount of wastes and residues (leaves, stems, water blanching) is produced, which can reach up to 60% of the weight of the vegetable crop. In particular, the production of canned artichoke is based on the use of acidulated brines at pH values lower than 4.6 in order to limit the growth of *Clostridium botulinum* and make a pasteurization treatment at temperatures lower than 100 °C possible to obtain the microbiological stability. On average the brine is composed of water, citric acid (0.2%), ascorbic acid (0.05%) and salt (22–23%). Artichokes are preserved and stored in this solution for 50–60 days; after that they are removed from the brine and submitted to the blanching step before packaging.

The production of exhausted acidulated brines represents a serious environmental problem for the processing industry that must withstand high treatment costs and disposal. Some applications have been studied for animal foodstuff and fiber production (Femenia et al., 1998; Martínez Teruel et al., 1998). However, considering their content of health-promoting antioxidant compounds (Llorach et al., 2002), researches are oriented in obtaining phenolic-rich extracts from artichoke byproducts.

Membrane filtration processes offer very interesting perspectives and key advantages, in terms of low energy consumption, greater separation efficiency and improved product quality, over conventional technologies in the treatment of wastewaters from food processing industries. Pressure-driven membrane operations, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), are well-known established technologies for the treatment of high strength wastewaters aimed at the production of purified water for recycle or reuse and the recovery of valuable compounds (Galanakis et al., 2010, 2014; Muro et al., 2012; Suárez et al., 2006; Tylkowski et al., 2011). Among these processes NF can also applied for applications involving fractionation rather than purification. Its potential in the food industry related to the production of high quality food, water softening, wastewater treatment, vegetable oil processing, beverage dairy and sugar industry has been recently reviewed (Salehi, 2014).

In a previous work an integrated membrane process has been investigated in order to recover from separated fractions enriched in sugar and phenolic compounds from artichoke wastewaters (Conidi et al., 2014). To the best of our knowledge, the extraction of phenolic compounds from artichoke brines has not been previously reported.

In this work a membrane-based process for the fractionation of artichoke brines was investigated in order to separate flavonoids and caffeoylquinic acids from salt compounds. Therefore, the performance of different commercial spiral-wound nanofiltration (NF) membranes in the treatment of clarified artichoke brines was evaluated in terms of productivity and selectivity towards bioactive compounds in selected operating conditions. Membranes of different polymeric material (polyethersulphone, polyammide) and molecular weight cut-off (MWCO) (from 200 to 1000 Da) were tested.

2. Materials and methods

2.1. Artichoke brines

Artichoke brines were supplied by Indena SpA (Milan, Italy). They were stored at room temperature and prefiltered with a nylon cloth before ultrafiltration.

2.2. Pretreatment of artichoke brines

Artichoke brines were submitted to a preliminary UF process in order to remove suspended solids and macromolecular compounds and to reduce fouling phenomena in the subsequent NF process. UF experiments were performed by using a laboratory pilot unit equipped with a cellulose triacetate hollow-fiber membrane module (FUC 1582, Microdyn-Nadir, Germany) having a molecular weight cut-off (MWCO) of 150 kDa and a membrane surface area of 0.26 m^2.

The UF system was operated at a transmembrane pressure (TMP) of 0.5 bar, an axial feed flow rate (Q_f) of 430 L/h and a temperature (T) of 20 ± 2 °C, according to the batch concentration mode (recycling the retentate stream and collecting the permeate separately) up to a weight reduction factor (WRF) of 14.8.

The weight reduction factor is defined according to Eq. (1):

$$\mathrm{WRF} = \frac{W_f}{W_r} \tag{1}$$

where W_f and W_r are the initial weight of the feed solution and the residual retentate weight, respectively.

2.3. NF set-up and procedures

The clarified brine was used as feed solution for the NF experimental runs. The NF process was performed by using a laboratory plant supplied by Matrix Desalination Inc. (Florida, USA). The equipment consists of a feed tank with a capacity of 20 L, a stainless steel housing for 2.4 × 21 inches spiral wound membrane module, a high pressure pump, two pressure gauges (0–40 bar) for the control of the inlet and outlet pressures, a pressure control valve and a coiling cool fed with tap water used to maintain the feed temperature constant. A schematic representation of the NF plant is presented in Fig. 1.

Five commercial membranes were studied: NP010, NP030, TFC-S, NF200, Desal DL and Desal DK. Their properties and composition, as specified by manufacturers, are reported in Table 1.

Experimental runs were performed according to the batch concentration configuration in which the permeate stream is collected separately and the retentate is recycled back to the feed reservoir. The NF system was operated at a TMP of 6 bar and at a temperature of 20 ± 2 °C up to a WRF of 3.5.

For the Desal DK membrane experiments were also performed in total recycle configuration (in which all concentrate and permeate streams were flowed back to the feed tank) in order to evaluate the effect of TMP and temperature on the permeate flux and the selectivity of the membrane towards the compounds of interest.

The permeate flux was measured gravimetrically from the permeate weight collected at fixed time intervals by using a digital balance and expressed as kg/m^2 h.

The fouling index (FI) of NF membranes was calculated by comparing the pure water permeability before and after the