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Valorization of artichoke wastewaters by integrated membrane process

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ABSTRACT

In this work an integrated membrane system was developed on laboratory scale to fractionate artichoke wastewaters. In particular, a preliminary ultrafiltration (UF) step, based on the use of hollow fibre membranes, was investigated to remove suspended solids from an artichoke extract. The clarified solution was then submitted to a nanofiltration (NF) step. Two different 2.5 × 21 in. spiral-wound membranes (Desal DL and NP030) with different properties were investigated. Both membranes showed a high rejection towards the phenolic compounds analysed (chlorogenic acid, cynarin and apigenin-7-O-glucoside) and, consequently, towards the total antioxidant activity (TAA). On the other hand, the Desal DL membrane was characterized by a high rejection towards sugar compounds (glucose, fructose and sucrose) (100%) when compared with the NP030 membrane (4.02%).

The performance of selected membranes in terms of permeate flux, fouling index and water permeability recovery was also evaluated.

On the base of experimental results, an integrated membrane process for the fractionation of artichoke wastewaters was proposed. This conceptual process design permitted to obtain different valuable products: a retentate fraction (from the NP030 membrane) enriched in phenolic compounds suitable for nutraceutical, cosmeceutical or food application; a retentate fraction (from the Desal DL membrane), enriched in sugar compounds, of interest for food applications; a clear permeate (from the Desal DL membrane) which can be reused as process water or for membrane cleaning.

1. Introduction

The artichoke (*Cynara scolymus* L.) processing industry generates large amounts of agricultural solid wastes (leaves, stems, bracts of the artichoke plant) and wastewaters, such as blanching waters, which are not suitable for human consumption. These wastes are generally used as animal feedstuff and for fibre production or directly discarded, with additional waste treatment costs in compliance with environmental laws (Llorach et al., 2002; Megias et al., 1999). In the search for new applications of artichoke wastes, it has been confirmed that they contain a large amount of bioactive compounds. Different studies have demonstrated their health-promoting potential, especially their hepatoprotective

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(Adzet et al., 1987), antioxidative (Gebhardt, 1997), anticarcinogenic (Clifford, 2000), and hypocholesterolemic (Clifford and Walker, 1987) activities.

The pharmacological properties of artichoke are well documented in vivo and in vitro studies for the treatment of hepato-biliary dysfunction, dyspeptic syndromes, gastric diseases, as well as for the inhibition of cholesterol biosynthesis and low lipoprotein (LDL) oxidation, agents responsible for arteriosclerosis and coronary heart disease (Lattanzio et al., 2009). Artichoke leaf extracts decreased serum lipids, as well as hepatic and cardiac oxidative stress in rats fed on a high cholesterol diet (Kucukgergin et al., 2010).

The biological activity of artichoke by-products, and in particular their marked antioxidative effects, are linked to their special chemical composition, which includes high levels of phenolic compounds with a wide range of caffeoylquinic acid derivatives (with chlorogenic acid as the most important of these derivatives) and flavonoids such as apigenin-7-O-glucoside and luteolin (Abu-Reidah et al., 2013; Christaki et al., 2012; Mulinacci et al., 2004; Negro et al., 2002; Sanchez-Rabaneda et al., 2003).

In addition, artichoke wastewaters contain inulin, a plant-derived carbohydrate which has been associated with enhancing the gastrointestinal and immune systems, increasing the absorption of calcium and magnesium and reducing the levels of cholesterol and serum lipids (Niness, 1999; Saengkanuk et al., 2011).

Due to these characteristics artichoke by-products represent a very useful source of high added value compounds of potential interest as food additives and nutraceuticals (Ceccarelli et al., 2010; Lattanzio et al., 2009).

Different methods to obtain purified extracts containing phenolic compounds from fruit or vegetable by-products have been evaluated including solvent extraction, γ-irradiation assisted extraction, hot water extraction, resin-based extraction, ultrasound-assisted extraction, enzyme-assisted extraction, and supercritical fluid extraction (Calvarano et al., 1996; Kim et al., 2008; Li et al., 2006; Xu et al., 2008). However, these extraction methods may either cause the degradation of the targeted compounds due to high temperature and long extraction times as in solvent extractions, or pose some health-related risks due to the unawareness of safety criteria during irradiation (Azmir et al., 2013). Furthermore, enzymes in enzyme-assisted extraction are easy to denature.

Therefore, efficient extraction methods, able to guarantee the stability of phenolic compounds are needed.

Pressure driven membrane processes, such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), have been successfully employed for the purification and concentration of bioactive compounds from natural products. These processes offer particular advantages in terms of absence of phase transition, mild operating conditions, possibility to avoid the use of additives, low energy requirement, separation efficiency and easy scaling up when compared with conventional methodologies. Successful applications related to the concentration and fractionation of grape phenolics (Crespo and Brazinha, 2010; Kalbasi and Cisneros-Zevallos, 2007; Nawaz et al., 2006), the concentration of coffee extract (Pan et al., 2013), the fractionation of bioactive compounds extracted from propolis (Tsibranska et al., 2011) and the concentration of bioactive compounds from vegetable sources (Tylkowski et al., 2011) have been reported.

In this work, an integrated membrane process based on the use of UF and NF processes was investigated in order to fractionate artichoke wastewaters in high added value compounds, such as phenolic compounds and sugars. In particular, an aqueous artichoke extract was submitted to a preliminary cross-flow UF process devoted to the removal of suspended solids. The UF permeate was then processed by two different NF membranes in order to identify a suitable membrane able to separate phenolic compounds from sugars. The performance of both processes was evaluated in terms of productivity, fouling index, recovery of hydraulic membrane permeability and selectivity towards compounds of interest.

2. Material and methods

2.1. *Artichoke wastewaters*

Artichokes were purchased from a local open market (Cosenza, Italy). The vegetables were manually washed in water and cut in pieces. The aqueous extract of artichoke was obtained by heating the vegetable material (leaves, stems and fruits) in water at 85 °C for about 30 min, avoiding boiling.

2.5 kg of fresh vegetable material were placed in 10 L of tap water. The decoction solution was separated from the vegetable material by filtering it with a nylon cloth. The obtained liquor was stored at −17 °C and defrosted at room temperature before use.

2.2. *Membrane filtration set-up and procedures*

2.2.1. *Ultrafiltration of artichoke wastewaters*

Artichoke wastewaters 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 supplied by Verind SpA (Milano, Italy). The UF system was operated at a transmembrane pressure (TMP) of 0.31 bar, an axial feed flow rate (Q_f) of 556 L/h and a temperature (T) of 24 ± 2 °C, according to the batch concentration mode (recycling the retentate stream and collecting the permeate separately) up to a volume reduction factor (VRF) of 5.67.

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

$$VRF = \frac{V_f}{V_r} \tag{1}$$

where V_f and V_r are the initial volume of the feed and the retentate volume, respectively.

2.2.2. *Nanofiltration of clarified artichoke wastewaters*

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