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Purification of artichoke polyphenols by using membrane filtration and polymeric resins

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ABSTRACT

The present study aimed at evaluating the potential of an integrated process based on the use of membrane technology and adsorbent resins for the recovery, concentration and purification of phenolic compounds from artichoke wastewaters.

In particular, artichoke wastewaters coming from the blanching step were pre-treated by ultrafiltration (UF) in order to remove suspended solids and macromolecular compounds. The UF permeate was submitted to a nanofiltration (NF) process producing a concentrated fraction enriched in phenolic and sugar compounds.

Three different macroporous resins were tested through adsorption/desorption methods to produce purified phenolic fractions with high antioxidant activity. Samples produced in UF, NF and adsorption–desorption tests were assayed for phenolic composition (chlorogenic acid and apigenin 7-O-glucoside), sugar composition (fructose, glucose and sucrose) and antioxidant activity.

Among the three different tested resins, the S 7968 offered the best performance in terms of adsorption/desorption ratio for chlorogenic acid, with a total adsorption/desorption yield (TADY) of 63.39%; for the apigenin 7-O-glucoside the S 7968 and the S 2328 resins showed a TADY in the range 68.31–78.45%.

1. Introduction

The artichoke (*Cynara scolymus* L.) is an ancient herbaceous perennial plant typically cultivated in the Mediterranean area with the main producers being Italy and Spain, where its commercial production contributes substantially to the agro-economy [1].

The results of different clinical investigations have widely demonstrated the health-protective potential of artichoke extracts in terms of hepatoprotective, anticarcinogenic, antibacterial, anti-HIV and hypocholesterolemic activity [2,3]. These properties are linked to their special composition which includes high levels of phenolic compounds and inulin. In particular, mono- and di-isomers of caffeoylquinic acids (chlorogenic acid and cynarin) and flavonoid O-glycosides (luteolin and apigenin derivatives) have been identified as the main responsible compounds for the biological properties of artichoke extracts and their marked antioxidant activity [4–8].

The artichoke-based industry generates huge amounts of agricultural waste (up to 60% of the harvested product) consisting mainly of the leaves, stems and the external parts of the flower which are not suitable for human consumption. Blanching waters represent additional residues of the canning artichoke industry.

The management of artichoke processing wastes is a serious environmental issue due to their perishable character. The common disposal of artichoke byproducts is as organic mass, animal feedstuff [9], ensilage [10], fiber and fuel production [11].

There is a considerable interest in preventive medicine and in the food industry in the development of natural antioxidants from botanic sources. Therefore, research efforts have been intensified to discover and utilize methods for the extraction, separation and purification of these compounds from artichoke by-products. The recovery of polyphenols is nowadays conducted in distinct steps following the so-called "5-Stages Universal Recovery Processing" [12]. Feasible protocols based on the use of methanol and water extractions to obtain phenolic-rich extracts [13] and inulin [14] from artichoke agroindustrial wastes have been proposed. Separation methods for the enrichment of phenolic compounds from plant-based materials, including liquid–liquid extraction,

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ultrasound-assisted extraction, heat treatment, enzyme-assisted extraction, supercritical fluid extraction and chromatography have been recently reviewed by Azmir et al. [15]. Unfortunately, most of these methodologies 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. The requirement of costly and high purity solvents with low selective extractions are additional drawbacks for large scale productions.

Membrane processes offer several advantages (low temperature, absence of phase transition and low energy consumption) when compared with conventional technologies for concentrating and/or fractionating bioactive phenolic compounds from different vegetable sources. In particular, pressure-driven membrane technologies, such as ultrafiltration (UF) and nanofiltration (NF), have been widely investigated for the recovery and concentration of bioactive compounds from natural products and by-products of their industrial transformation [16,17]. Successful applications include the concentration by NF of biologically active compounds from mate (*Ilex paraguariensis*) [18], *Sideritis* ssp. L. (an endemic plant of the Balcan Peninsula) [19] and coffee extracts [20], the fractionation of proanthocyanidins from winery extracts [21], the recovery of phenolic compounds from bergamot juice [22] and orange press liquor [23].

The integration of UF and NF units have been also proposed for the production of soy-protein hydrolysate with high antioxidant capacity [24], for the concentration of anthocyanin extracts from aronia fruits (black chokeberry) [25] and for the enrichment of polyphenolic compounds relatively to other compounds such as carbohydrates in ethanolic extracts of *Eucalyptus globulus* bark [26].

The combination of membrane operations with other conventional separation technologies (i.e. adsorption, precipitation, crystallization) offers new and interesting perspectives in order to increase the selectivity of the process [27]. For example, the combination of adsorption/desorption with UF and UF–NF coupled processes, have been applied to isolate total polyphenols and caffeic acid from *Green tea leaves* [28] and to purify phenolics compounds in distilled grape pomace press liquors in order to increase the antioxidant capacity of the final products [29].

In a previous work the combination of two different NF membranes was proposed in order to obtain two enriched fractions containing phenolic compounds and sugars, respectively, from ultrafiltered artichoke wastewaters [30].

This work was aimed at evaluating the potential of an integrated system based on the combination of membrane processes and polymeric resins for the selective purification of polyphenols with desirable biofunctional properties from artichoke wastewaters. In particular, artichoke wastewaters were clarified by UF in order to remove macromolecular compounds and suspended solids. The UF permeate was then submitted to a NF process in order to obtain concentrated fractions of phenolic compounds and sugars and a water permeate stream which can be reused in the artichoke processing industry. The NF retentate was submitted to an adsorption/desorption treatment by using three different macroporous resins in order to purify phenolic compounds, such as chlorogenic acid (CA) and apigenin 7-O-glucoside (AOG) from sugars. Fractions coming from the membrane processes (UF and NF) were analyzed for their content in total antioxidant activity (TAA), low molecular weight polyphenols and sugars, while fractions from adsorption/desorption process were analyzed in terms of low molecular weight polyphenols and sugars in order to evaluate the selectivity of each step toward compounds of interest. The performance of UF and NF membranes was also evaluated in terms of productivity (permeate fluxes) in selected operating conditions.

2. Material and methods

2.1. Artichoke wastewaters

Artichoke wastewaters coming from the blanching step were supplied by Conservas Manuel Mateo Candel S.L. (Rafal, Alicante, Spain). Before use, they were filtered through a cotton fabric filter in order to remove most of suspended solids and foreign materials. The prefiltered solutions were stored at −17 °C and defrosted before membrane processing. The physico-chemical composition of the UF feed solution is provided in Table 1.

2.2. Ultrafiltration

Artichoke wastewaters were clarified by using a pilot plant consisting of a 100 L stainless steel feed tank, a pre-filter system equipped with a 10 μm filter cartridge, a centrifugal pump, a feed flow meter, a thermometer, two manometers for the measure of the inlet and outlet pressures and a membrane module. The feed flow-rate and the transmembrane pressure (TMP) values were regulated by a pressure control valve, on the retentate side, and by regulating the pump velocity. A tube and shell heat exchanger, placed after the feed pump, was used to maintain the feed temperature constant.

The plant was equipped with a tubular UF membrane module supplied by Tami Industries (Nyons, France) whose characteristics are reported in Table 2.

Artichoke wastewaters were clarified in selected operating conditions according to a batch concentration configuration (permeate is collected separately and retentate is recycled to the feed tank). In particular, the UF system was operated at a transmembrane pressure (TMP) of 430 kPa, an axial feed flow rate of 4 m^3/h and a temperature of 25 °C. Experimental runs were performed in triplicate. Permeate flux data were expressed as mean ± SD.

After each experiment the membrane was cleaned by using a 0.2% NaOH solution at 40 °C for 1 h. Then the system was rinsed with tap water for 30 min.

Table 1
General composition of artichoke wastewaters before and after the UF process.

Parameters	Feed	Permeate	Retentate
pH	4.18 ± 0.03	4.12 ± 0.12	4.16 ± 0.60
TSS (°Brix)	2.3 ± 0.1	2.3 ± 0.1	2.6 ± 0.1
Suspended solids (%)	3.08 ± 0.08	n.d.	3.17 ± 0.07
TAA (mM Trolox)	13.2 ± 0.2	13.0 ± 0.2	13.1 ± 0.1
Chlorogenic acid (ppm)	560.1 ± 1.3	555.4 ± 1.2	556.20 ± 3.0
Apigenin-7-O-glucoside (ppm)	80.0 ± 1.3	75.0 ± 0.2	81.0 ± 2.1
Glucose (ppm)	1422.0 ± 2.5	1400.0 ± 3.2	1450.0 ± 1.7
Fructose (ppm)	614.0 ± 2.1	600.0 ± 2.3	627.0 ± 2.7
Sucrose (ppm)	350.0 ± 2.4	320.0 ± 3.1	365.0 ± 3.7

Table 2
Characteristics of UF and NF membranes.

Membrane type	Inside ceram	NF 270
Manufacturer	Tami industries	Dow-Filmtec
Material	TiO_2	Polyamide
Configuration	Tubular	Spiral-wound
MWCO (Da)	15,000	200–300
Membrane surface area (m^2)	0.1	2.6
Maximum operating pressure (kPa)	1000	4100
Maximum operating temperature (°C)	350	45
$MgSO_4$ retention (%)	–	>97
pH range	0–14	3–10