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Single and interactive effects of process variables on microwave-assisted and conventional extractions of antioxidants from vegetable solid wastes

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ABSTRACT

The aim of this work was to study the single and interactive effects of process variables in microwave-assisted and conventional extraction of antioxidant compounds from asparagus, cauliflower, celery, and chicory wastes using water as solvent. The following variables were investigated: water/sample ratio, extraction time in microwave-assisted extraction; water/sample ratio, extraction time, temperature in conventional extraction. Concerning the microwave-assisted extraction, the highest phenolic recoveries and the highest antioxidant activity were obtained at a solid-to-liquid ratio of 1:2 (w/w) and prolonging the time of treatment up to 4 min. In the conventional extraction system, the highest yields were generally obtained at a solid-to-liquid ratio of 1:2 (w/w) and with the combination high temperature-low time of treatment. Cauliflower and chicory wastes showed the highest extraction yields when submitted to microwaves and conventional extraction, respectively. Catechin, ascorbic acid, and quercetin 3-O-glucopyranoside were the main phenolic compounds identified in wastes. The application of conventional extraction system gave higher extraction yields than the microwave-assisted one.

1. Introduction

In the last few decades, as a consequence of the increased interest in healthy foods, a growing number of researches have been performed on the recognition of molecules of plant origin (mostly, antioxidants) that seem to play a role in the prevention of many diseases (Hamid et al., 2010; Pandey and Rizvi, 2009; Vladimir-Knežević et al., 2012).

Among bioactive substances, polyphenols play an important role in humans, since they are unable to synthetize these compounds and need to satisfy their phenolic requirements through a daily consumption of fruits and vegetables. Phenolic compounds are known to be effective in prevention of chronic and acute diseases such as cancer, cardiovascular disorders, inflammations (Linseisen and Rohrmann, 2008).

Food products obtained from plants are important sources of phenolic compounds. However, a significant percentage of the population in Western and developing countries are not consuming sufficient quantities of dietary polyphenols as a result of inadequate intakes (Martin and Appel, 2010). Furthermore, remarkable amounts of phenolic compounds are lost during processing. Fresh-cut fruits and vegetables are submitted to a series of technological operations responsible for physical, enzymatic, and chemical changes that affect their nutritional and sensorial quality. Operations like sorting, cleaning, washing, peeling and cutting/chopping can induce different types of stress and parameters such as the phenolic compounds can suffer noticeable losses (Amarowicz et al., 2009).

The term 'minimally processed vegetable' is applied to any fresh vegetable that has been physically altered from its original form, but remains in a fresh state (Gomez-Lopez et al., 2009). Consumers are increasingly demanding convenient, ready-to-use, and ready-to-eat fruits and vegetables, having fresh-like quality, and containing only natural ingredients. In Europe, particularly in France but also in the UK, the market for minimally processed fruit and vegetable grew explosively in recent decades (Barry-Ryan et al., 2007). Since the increasing demand for processed plant products led to a substantial increase in solid wastes, solutions for their recovery must be found. In fact, these residues contain bioactive compounds with potential application in foods, cosmetic and pharmacologic formulations. Peels, skins, seeds, stems and other lignocellulosic fractions, usually discarded, are attractive sources of antioxidants (Laroze et al., 2008). Utilization of by-products could be a source

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of revenue for the company, as these extracts may be sold to pharmaceutical companies and cosmetic manufacturers, or used by food producers to obtain functional products.

These compounds can be extracted from the vegetable matrix. Extraction with solvents is the technique most frequently used to obtain crude extracts of antioxidants of plant origin. The most common solvents are water, ethanol, methanol, acetone and ethyl acetate, used pure or in mixture. The structural diversity of antioxidant compounds extracted affects both the returns of extraction and the activity of the extracts in relation to the solvent used (Marinova and Yanishlieva, 1997). Also the extraction protocols are quite different and include conditions ranging from room temperature to boiling or reflux. The antioxidant efficacy is related to the nature of the extracted compounds and also to the type of solvent used. Consequently, for each vegetable matrix, it is necessary to select solvents and conditions able to maximize yield and the antioxidant activity of the extracts.

The conventional methods for extraction of antioxidant compounds include fluid extraction and *soxhlet* extraction, which are used for many decades but have the disadvantages to be very time consuming and to require relatively large quantities of solvents (Proestos and Komaitis, 2008). Microwave-assisted methods have a range of advantages, including: rapidity; reductions in solvent consumption; better chance of control, automation, and coupling extraction on-line with analysis of the extracts. Microwave-assisted extraction also is more environmental friendly, since it requires less energy and can efficiently use a wide range of solvents, including non-toxic and low environmentally hazardous solvents ones.

The present study was aimed to investigate the single and interactive effects of selected process variables on yield and antioxidant activity of aqueous extracts obtained through conventional and microwave-assisted extraction from vegetable solid wastes. The experiments were focused on matrices such as cauliflowers, celery, chicory and asparagus because the production of the corresponding minimally processed products gives high amounts of solid waste (an average of 50%). The choice of the variables to be studied (water/sample ratio, extraction time, and temperature in conventional extraction; water/sample ratio and extraction time in microwave-assisted extraction) depended on their impact on both efficacy/efficiency and energy cost of the process (Spigno et al., 2007). Authors applied the conventional and microwave-assisted extraction using water as a solvent because this solvent shows several advantages, including reduction of environmental hazards and possibility to use the aqueous extracts to fortify bread and other products whose process include the formation of a dough.

2. Materials and methods

2.1. Plant materials

The solid wastes originating by the production of ready-to-use vegetables were supplied by Futuragri Soc. Coop. Agric. (Foggia, Italy). They included: defective spears and parts of shoots (asparagus, *Asparagus officinalis*, cv. UC 157), external leaves and stems (cauliflower, *Brassica oleracea*, cv. Vedis e Mildis), external leaves and stems (chicory, *Cichorium intybus* L., cv. Puntarelle di Galatina), external leaves and stems (celery, *Apium graveolens*, cv. Darklet). The moisture contents were very high for all the types of solid wastes. In a decreasing order: celery 92.5%, chicory 92.4%, asparagus 91.8%, and cauliflower 89.6%.

2.2. Pretreatment

Before extraction, the solid wastes were finely chopped (5–8 mm-size) by a 30 s-treatment in a domestic cutter (Philips HR 1396/55, Milano, Italy).

2.3. Extraction systems

Microwave-assisted and conventional extraction systems were applied according the experimental conditions reported below.

2.4. Microwave-assisted extraction of the antioxidant fraction

The extractions were performed with a domestic microwave oven (JT 366, 6th sense Whirlpool Europe, Comerio, Italy).

Antioxidants were recovered from the solid waste using water as a solvent. Three solid-to-water ratio were tested: 1:1, 1:2, and 1:4 (w/w). The final standard mass was always equal to 300 g. The resulting mixtures were treated by microwaves at 750 W for 2 or 4 min, according to the methods of Pan et al. (2003) and Proestos et al. (2008). The temperatures of the mixtures were measured at the end of each treatment through a Pt100 temperature probe. The mixtures were filtered through a common Whatman paper and stored at −20 °C until analysis.

2.5. Conventional extraction of the antioxidant fraction

The extractions were performed with by using a heating system consisting of a heating magnetic stirrer, a hemispheric bowl that allowed an uniform distribution of the heat, a digital thermoregulator, a Pt100 temperature probe (Velp Scientifica, Usmate, Italy).

Antioxidants were recovered from the solid wastes using water as a solvent. Three solid-to-water ratios were tested: 1:1, 1:2, and 1:4 (w/w). The final standard mass was always equal to 300 g. The resulting mixtures were treated at a temperature of 50 and 70 °C (the solvent was previously heated to the desired temperature) respectively for 35 and 20 min. These conditions were selected after an accurate study of the available literature (Marete et al., 2009; Spigno et al., 2007). The mixtures were filtered through a common Whatman paper and stored at −20 °C until analysis.

2.6. Determination of the total phenolic content

The total phenolic compounds were determined according to the Folin–Ciocalteau method (Gorinstein et al., 2000). In a test tube, 100 mL of phenolic extract or phenolic standard were mixed with the Folin–Ciocalteau reagent (2 M, 100 mL) and, after 4 min, with an aqueous solution of Na_2CO_3 (5%, 800 mL). The mixture was kept for 20 min in a water bath set at 40 °C, then the total phenol content was determined colorimetrically at 765 nm. Quantification was based on a standard curve built with 50–100–200–400–600–800–1000 mg/L gallic acid (ExtraSynthese, Genay, France) aqueous solution. The total phenolic content was expressed as milligrams of gallic acid equivalents per kilogram of fresh material.

2.7. HPLC antioxidant profile

The HPLC analysis of the extracts was carried out according to Yildiz et al. (2008), using a HPLC binary system consisting of a degasser mod. G1322A, a binary pump mod. G1312A, an autosampler mod. G1329A equipped with a 20-μL loop, and a diode array detector mod. G1315D (Agilent, Santa Clara, CA, USA).

The stationary phase was a Gemini C18 110A analytical column (250 mm × 4.6 mm i.d., 5 μm, Phenomenex, Castelmaggiore, Italy). The mobile phases for chromatographic analysis were (A) methanol and (B) 0.2% of *o*-H_3PO_4 in bidistilled water at constant flow rate of 1 mL/min. The gradient program of solvent was as follows: 7% A for 8 min, 7–30% A in 5 min, 30–66% A in 35 min, 66–75% A in 7 min. Identification of the antioxidant compounds was performed by comparing the spectra and the relative retention times of the sample peaks with those obtained by injection of 30 pure standards. Quantification was made on the basis of calibration curves