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Potential use of pulsed electric technologies and ultrasounds to improve the recovery of high-added value compounds from blackberries

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A B S T R A C T

A better knowledge of the effect of non-conventional extraction technologies, which can avoid the use of high temperatures and toxic solvents, on the antioxidant compounds recovery from blackberries, is necessary. Thus, high voltage electrical discharges (HVED), pulsed electric fields (PEF), and ultrasounds (USN) treatments were applied in order to evaluate the effects of processing on protein, total phenolics and anthocyanins extraction from blackberries. Moreover, two-stage extraction involving the use of HVED, PEF and USN as pre-treatments and supplementary extraction during 5 h with hot water at mild temperature (50 °C) or an hydroalcoholic solution (30% ethanol, w/w) was evaluated. The impacts of both hot water (50 °C) and ethanol had a positive influence in total phenolics and anthocyanin recovery, although the yield was clearly influenced by the treatment applied and the targeted compound. The highest protein (37.95 ± 1.30 mg/100 g) and TPC (932.69 ± 33.45 mg/100 g) yields were obtained after HVED and supplementary extraction during 5 h, using ethanol and hot water at 50 °C, respectively. However, the maximum anthocyanin yield (98.46 ± 4.92 mg/100 g) was found after applying PEF treatment and supplementary extraction with hot water at 50 °C. These promising findings open the doors to a potential multi-stage green recovery, which can improve the selectivity and the amount of high-added value compounds recovered.

1. Introduction

Blackberries are known to contain appreciable levels of bioactive plant constituents like phenolic compounds, anthocyanins, flavonols, chlorogenic acid and procyanidins, that have high biological activity and may provide health benefits as dietary antioxidants (Mi et al., 2004, 2005). These compounds exist in plants enclosed in complex insoluble structures (i.e. the vacuoles of plant cells or lipoproteins bilayers) that complicate their extraction. Anthocyanins are very important for food industry as a natural alternative to replace synthetic food colorants. Recently, increased attention has been given to their potential health benefits in preventing heart diseases and cancers due to their powerful antioxidant properties (Hannum, 2004).

The recovery of valuable compounds from natural sources such as blackberries, is nowadays conducted with the so-called "5-Stages Universal Recovery Process". The latest process is based on the following stages: (i) macroscopic pretreatment, (ii) separation of macro- and micro-molecules, (iii) extraction, (iv) purification and (v) product formation (Galanakis, 2012). Extraction (typically liquid–solid) is the third and most important step of downstream processing. This process can be defined as a mass transport phenomenon in which insoluble solids (contained in a matrix) migrate into a solvent brought into contact with the matrix (Galanakis et al., 2013). The concentration gradient, diffusion coefficients or boundary layer clearly influence mass transport phenomena. Moreover, heating also increases mass transfer, however, it can deteriorate the matrix or diminish the functionality of targeted compounds such polyphenols and anthocyanins, when heat treatment at high temperatures (>60 °C) is used (Buckow et al., 2010; Kechinski et al., 2010; Skrede et al., 2000).

At this stage of development, there is a need to study the potential of new technologies that can reduce extraction time and solvent consumption, allowing the use of green solvents. For instance, pulsed electric technologies including pulsed electric fields (PEF) and high voltage electric discharges (HVED) promise to enhance secondary metabolites extraction from different food

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samples (Boussetta and Vorobiev, 2014; Corrales et al., 2008; Soliva-Fortuny et al., 2009).

PEF technology may cause lethal damage to cells or induce sublethal stress by transient permeabilization of cell membranes and electrophoretic movement of charged species between cellular compartments (Toepfl, 2006; Vorobiev and Lebovka, 2010). Different aspects of PEF application for disintegration of soft cellular tissues were intensively discussed in literature (Mastwijk, 2006; Toepfl, 2006; Vorobiev and Lebovka, 2010). The technique in its lethal version (i.e. at moderate or very high field strength) has been used for the inactivation of microorganisms in foods (El Zakhem et al., 2007; Toepfl et al., 2007). On the other hand, it could be used for the improvement of the extraction yield. Increasing the extraction of juice from different plant food materials by permeabilization of the cell membranes using high electric field pulse has been studied (Ade-Omowaye et al., 2003; Fincan et al., 2004; Lebovka et al., 2007). The application of pulsed electric fields (PEF) can facilitate the selective recovery of valuable compounds without deteriorating the treated matrix, thus favoring the subsequent separation and purification stages (Vorobiev and Lebovka, 2010).

HVED is based on both chemical and reaction processes that are generated when high voltage electrical discharges are produced directly in water (electrohydraulic discharge). It injects energy directly into an aqueous solution through a plasma channel formed by a high-current/high voltage electrical discharge between two submersed electrodes (Boussetta and Vorobiev, 2014).

On the other hand, ultrasound processing is one of the most industrially used methods to enhance mass transfer phenomena. Its feasibility for the extraction of secondary metabolites such as tea, mint, chamomile and ginseng has been highlighted in many research works (Knorr et al., 2004), including berries (Chen et al., 2007; Herrera and Luque De Castro, 2005).

During processing of cellular foodstuffs, attention needs to be given to the degree of disintegration of the initial tissue structure because of its impact on food quality, functionality and deterioration. Besides, in order to obtain the contents of blueberry tissue, the membrane must first be ruptured or permeabilized. To quantify the amount of cells in a tissue sample affected by treatment, an index for cell disintegration (Z) has been shown to be effective. This index comprises of the extent of the cell membrane damages relative to the initially intact cells and is based on electro-physical properties of cell materials before and after treatment (Vorobiev and Lebovka, 2010).

To the best of our knowledge, the influence of HVED, PEF and ultrasounds for the recovery of valuable compounds from blackberries has not been reported yet. Thus, the main aim of the present research was to evaluate the impact of two-stage extraction including HVED, PEF, or USN pre-treatment combined with (1) water extraction at mild temperature (50 °C) or (2) hydroalcoholic extraction (ethanol 30%, w/w) on the recovery of total phenolic compounds, anthocyanins and proteins from blackberries.

2. Materials and methods

2.1. Plant materials and chemicals

Blackberries (*Rubus fruticosus*, harvested in France) were purchased at a local supermarket (Compiègne, France). The fruits were washed and drained.

Folin–Ciocalteu reagent, potassium hydroxide, sodium and disodium phosphate, magnesium hydroxide carbonate and tetrabutyl ammonium hydrogen sulfate were obtained from Fluka (Steinheim, Germany). Gallic acid was purchased from UCB (Brussels, Belgium). Ethanol, methanol and sodium chloride (special grade) were obtained from Merck (Darmstadt, Germany).

2.2. Treatment by pulsed electric energy (PEF and HVED)

A pulsed high voltage power supply 40 kV–10 kA, frequency 0.5 Hz (Tomsk Polytechnic University, Tomsk, Russia) was used for the electrical treatments, 1-L cylindrical batch treatment chamber and different types of electrodes were used. Blackberry suspension (250 g) was introduced between the electrodes before treatment. The initial temperature before PEF or HVED treatment was 20 °C and the temperature elevation after electrical treatment never exceeded 35 °C. Suspension temperature was controlled by K-type thermocouple (±0.1 °C), connected to a data logger thermometer Center 305/306 (JDC Electronic SA, Yverdon-les-Bains, Switzerland) and a 1 min pause was made after each 100 pulses to maintain the temperature at 20 °C.

For PEF treatments, the two parallel stainless disks were used like electrodes. The distance between electrodes was fixed to 3 cm. Consequently, the corresponding electric field strength was 13.3 kV/cm. The total treatment duration t_t ($t_t = n \times t_i$) was changed by increasing the number of pulses n from 0 to 1550.

The exponential decay of voltage $U \propto \exp(-t/t_i)$ with effective decay time $t_i \approx 10.0 \pm 0.1$ μs were observed. The distance between pulses was $\Delta t = 2$ s. The specific energy input E (kJ/kg) was obtained from Eq. (1):

$$E = \frac{\sum_{i=1}^{n} W_{\mathrm{PEF}}}{m} \tag{1}$$

where W_{PEF} is the pulse energy (kJ/pulse), n is the number of pulses and m is the product mass (kg). W_{PEF} was calculated as follows (Rajha et al., 2014):

$$W_{\mathrm{HVED}} = \int_0^t UIdt \tag{2}$$

where U is the voltage (V) and I is the current strength (A).

For HVED, the treatment chamber was equipped with needle-plate geometry electrodes. The distance between the electrodes was 5 mm. Energy was stored in a set of low-inductance capacitors, which were charged by the high-voltage power supply. The electrical discharges were generated by electrical breakdown in water at the peak pulse voltage (U) of 40 kV. Damped oscillations were thus obtained over a total duration t_i of ≈10 μs. The voltage (Ross VD45-8.3-A-K-A, Ross Engineering Corp., Campbell, California, USA) and current (Pearson 3972, Pearson Electronics Inc., Campbell, California, USA) measurement units were connected with a 108 Hz sampling system via an oscilloscope (Tektronix TDS1002, Beaverton, Oregon, USA). The software HPVEE 4.01 (Hewlett–Packard, Palo Alto, USA) was used for data acquisition.

The energy input of HVED treatment was calculated as shown in Eqs. (1) and (2). The total treatment duration ($t_t = nt_i$) was changed by increasing the discharge number n from 0 to 600. The discharge pulse duration t_{HVED} was approximately 10 μs. The discharges were applied with a repetition rate of 0.5 Hz, which was imposed by the generator.

2.3. Ultrasound treatment

Ultrasounds (USN) treatment was done using an USN processor UP 400S (Hielscher GmbH, Germany) connected to an USN probe placed in the treatment chamber (190 × 200 × 130 mm). The titanium USN probe (H14 Hielscher GmbH, Germany) has a diameter of 14 mm and the maximum length that can be submerged is 90 mm (total length: 100 mm). The probe was immersed in the narrow-necked glass flasks of 1000 mL containing the blackberries