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High voltage electric discharges assisted extraction of phenolic compounds from grape stems: Effect of processing parameters on flavan-3-ols, flavonols and stilbenes recovery

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ABSTRACT

This work aimed at providing some novel aspects pertaining to flavan-3-ols, flavonols and stilbenes extraction from grape stems using high voltage electrical discharges (HVED). Treatment time, pH and ethanol concentration affecting the extractability of these compounds were optimized through response surface methodology. The results from the optimized extraction technique (pH = 2.5; Time = 4.0 ms: Ethanol = 50%) were compared to a conventional hydro-alcoholic extraction.

HVED improved significantly the extraction of flavan-3-ols and flavonols but was less efficient on stilbenes. The efficiency of HVED is directly correlated with the other processing conditions (pH, ethanol concentration). Prolonged HVED treatment at low pH value was a positive combination for flavan-3-ols. The proposed procedure (pH = 2.5; Time = 4.0 ms; Ethanol = 50%) allowed the release of almost 35% of additional phenolic compounds, which can be attributed to a better extractability of flavan-3-ols (+21%) and of flavonols (+12%), compared to conventional hydro-alcoholic extraction.

1. Introduction

Over the last years, several studies highlighted the potential health benefits of phenolic compounds in preventing heart diseases and cancers (Baur & Sinclair, 2006; Quideau, Deffieux, Douat-Casassus, & Pouysegu, 2011; Spigno & De Faveri, 2007). The phenolic content of grape stems reaches around 5.8% on a dry weight basis (Makris, Boskou, & Andrikopoulos, 2007), thus making these winery by-products of special interest for the production of extracts for different food applications (e.g. antioxidants, functional foods, nutraceuticals) (Joana Gil-Chávez et al., 2013).

High Voltage Electrical Discharges (HVED) in water (underwater arc discharges) is an effective method for the cell structure damage and extraction of valuable cell compounds (Boussetta, 2011; Boussetta et al., 2011; Boussetta, Vorobiev, Le, Cordin-Falcimaigne, & Lanoisellé, 2012; Rajha, Boussetta, Louka, Maroun, & Vorobiev, 2014). The first step of HVED is the formation and the propagation of a streamer from a needle electrode (pre-breakdown phase) and the formation of gaseous cavities. The second phase occurs when the streamer reaches the plate electrode (breakdown phase). HVED are accompanied by different secondary phenomena such as propagation of pressure shock waves in the surrounding media and gas bubble cavitation. The physical phenomena are accompanied by chemical reactions generating reactive species (Joshi, Locke, Arce, & Finney, 1995). HVED technology can be used in different applications, including water purification (Malik, Ghaffar, & Malik, 2001), inactivation of microorganisms (Sato, Ohgiyama, & Clements, 1996), and extraction of valuable compounds from plant materials (Boussetta & Vorobiev, 2014).

The extraction of polyphenols assisted by HVED has been the subject of several studies that have demonstrated its potential as an alternative to conventional solvent extraction. HVED is an efficient technology for the enhancement of mass transfer of bio-compounds in water at lower temperatures and shorter times (Boussetta, Lanoisellé, Bedel-Cloutour, & Vorobiev, 2009; Boussetta, Reess, Vorobiev, & Lanoisellé, 2012; Boussettaet al., 2011; Howard & Sturtevant, 1997; Liu, Vorobiev, Savoire, & Lanoisellé, 2011). The HVED treatment has been successfully employed for the recovery of total phenolic compounds (TPC) from different plant materials including grape by-products (Boussetta, 2011; Boussetta et al., 2011; Boussetta, Vorobiev, Le, et al., 2012; Rajha et al., 2014). For instance, the amount of total polyphenols was increased by 11.2 folds comparing to control when

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unfermented grape pomace was treated by HVED in water (liquid-to-solid ratio of 5), at 80 kJ/kg (150 pulses), followed by 30 min of diffusion in water/ethanol solution (30% of ethanol) at 20 °C (Boussetta et al., 2011). However, the choice of effective HVED treatment time should be accurately evaluated, as excessively prolonged treatment may deteriorate phenolic compounds (Boussetta et al., 2011).

Most of the reported studies particularly focused on the HVED-assisted extraction of total phenolic compounds. The literature clearly lacks of information about the effect of electrical discharges on particular families of polyphenols. Furthermore, the information about interactions between HVED and the solvent on the extraction of specific families of phenolic compounds are scarce. Phenolic compounds of grape stems mainly consist of flavonoids (Makris, Boskou, Andrikopoulos, & Kefalas, 2008; Souquet, Labarbe, Le Guernevé, Cheynier, & Moutounet, 2000; Spatafora, Barbagallo, Amico, & Tringali, 2013) and stilbenes (Anastasiadi, Pratsinis, Kletsas, Skaltsounis, & Haroutounian, 2012; Bavaresco, Cantù, Fregoni, & Trevisan, 1997; Püssa, Floren, Kuldkepp, & Raal, 2006). These phenolic classes proved to have different behaviors in terms of extractability, which is depending on the solvent composition and particularly the pH and the concentration of ethanol (Du, Xiao, & Li, 2007; Karvela, Makris, Kalogeropoulos, & Karathanos, 2009; Karvela, Makris, Kalogeropoulos, Karathanos, & Kefalas, 2009; Sun, Ribes, Leandro, Belchior, & Spranger, 2006; Wang, Dong, & Xiu, 2008). While the composition of the alcohol/water solutions has been intensively studied to extract these compounds, their extractability by HVED remains questionable.

This work intends to give answers about the effect of HVED processing conditions on the recovery of each individual polyphenol class, particularly flavan-3-ols, flavonols that occur as glycosylated forms, and stilbenes from grape stems. A response surface methodology obtained from multivariate study (full factorial design) was used to investigate the relevance of the parameters required for the extraction of each class of phenolic compounds and to develop predictive models for their recovery. The combined effects of HVED treatment time, pH, and ethanol concentration in water on the recovery of TPC, flavan-3-ols, flavonols, and stilbenes are investigated.

2. Materials & methods

2.1. Chemicals

All solvents (water, acetonitrile, trifluoroacetic acid) used for chromatographic purposes were HPLC grade. Catechin, epicatechin, quercetin, quercetin-3-glucuronide, quercetin-3-glucoside, rutin (quercetin 3-O-rutinoside), trans-resveratrol and piceatannol were purchased from Sigma-Aldrich (St. Quentin Fallavier, France). Procyanidin B1 and B2 and piceid (resveratrol-3-O-beta-D-glucopyranoside) were obtained from Extrasynthèse (Genay, France).

2.2. Raw material

Grapes of *Vitis vinifera* L. cv. Cabernet Franc were harvested at their enological maturity in a Swiss vineyard in 2012. Stems were collected after destemming of grapes, thoroughly rinsed, dried inside in a well ventilated room and stored at room temperature in plastic pockets under vacuum during 2 months until processing. In order to avoid complications with repeatability due to the heterogeneity of the raw material, the small (diameter (Ø) < 0.63 mm) and large fractions (Ø > 2.0 mm) were removed after separation by sieving (Retsch GmbH, Germany). The dry matter was determined by the measurement of the mass of grape stems before and after drying the samples at 105 °C overnight and was equal to 88.3 ± 2.2%.

2.3. HVED-assisted extraction

2.3.1. HVED treatment

HVED experiments were performed in a laboratory treatment chamber of 1 L (inner diameter = 10 cm, wall thickness = 2.5 cm), equipped with needle-plate geometry electrodes, and connected to a pulsed high-voltage power supply of 40 kV and 10 kA (Tomsk Polytechnic University, Russia), as previously described (Boussetta et al., 2009). The stainless steel needle electrode of 10 mm in diameter and the grounded stainless plate electrode of 35 mm in diameter were separated by a distance of 5 mm. The treatment chamber was initially filled with 40.0 ± 0.1 g of dried grape stems (Cabernet Franc, Switzerland). An optimum liquid-to-solid ratio of 7.5 (v/w) was chosen based on preliminary experiments (data not shown) that have shown the extraction of total phenolic compounds assisted by HVED increasing up to this liquid-to-solid ratio and then reaching a constant value. The methodology used for these preliminary experiments was based on a previous study on the optimization of HVED parameters (Boussetta et al., 2011).

The pH of the treatment medium was adjusted to the desired value using aqueous solvents at different pH (CONSOR C931, Bioblock Scientific, France) prepared from mother solutions of 1N KOH and 1M HCl. A positive peak pulse voltage (U) of 40 kV was applied to the needle electrode and the electrical discharges with a repetition rate of 0.5 Hz, which was imposed by the generator. HVED treatment consisted in applying n = 0–400 pulses of total duration t_i of 10 μs, corresponding to an effective treatment time ranging from 0 to 4 ms and to W = 0–188 kJ/kg of energy input. The specific energy input W (kJ/kg) was obtained from Eq (1).

$$W = \frac{\sum_{i=1}^{n} W_{HVED}}{m} \quad (1)$$

where W_{HVED} is the discharge energy (kJ/pulse), n is the number of discharges and m is the product mass (kg). W_{HVED} was determined from Eq (2) where U and I are respectively the voltage (V) and the current strengths (A).

$$W_{\mathrm{HVED}} = \int_0^t U \times I \times dt \quad (2)$$

Temperature was measured with a Teflon-coated thermocouple (measurement precision ±0.1 °C) (Thermocoax, Suresnes, France). The initial temperature of the suspension was 20 ± 0.5 °C. HVED were interrupted regularly (each 50 discharges) in order to control the temperature during the treatment. The increase of the temperature remains lower than 5 °C on the overall treatment.

2.3.2. Extraction procedure

The subsequent diffusion was performed after adjustment of the final liquid-to-solid ratio at 15 (v/w) by addition of hydro-alcoholic solvents at different pH (CONSOR C931, Bioblock Scientific, France) prepared from mother solutions of 1N KOH and 1M HCl. KOH and HCl were used at the maximal concentrations of 0.04% and 0.07% in the extraction medium, respectively. At these concentrations, acidic as well as alkaline hydrolyses of the phenolic compounds are rather limited. A gentle agitation at 160 rpm was provided using a round incubator shaker (Infors HT Aerotron, Bottmingen, Switzerland) at 20 °C, during 120 min. At this temperature, increasing the time of diffusion did not lead to a further increase of phenolic compound extraction yield. At the end of the extraction, the supernatant was separated from the residues by centrifugation (Model 3-16P, Sigma Laborzentrifugen GmbH, Germany) at 3076 *g* during 10 min, and stored at −18 °C for spectrophotometric and HPLC analyses.