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Valorisation of tomato wastes for development of nutrient-rich antioxidant ingredients: A sustainable approach towards the needs of the today's society

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ABSTRACT

Nutrient-rich antioxidant ingredients were produced from tomato fruit wastes using a microwave-assisted extraction (MAE) process. Different conditions of extraction time (t), temperature (T), ethanol concentration (Et) and solid/liquid ratio (S/L) were combined in a circumscribed central composite design and optimized by response surface methodology. The model was statistically validated and used for prediction in the experimental range. Under the global optimal MAE conditions (t = 20 min, T = 180 °C, Et = 47.4% and S/L = 45 g/L), it was possible to obtain an extraction yield of 75.5% and ingredients with high levels of sugars, proteins, phenolics, and flavonoids, and interesting antioxidant properties measured *via* $ABTS^{\bullet+}$ scavenging activity and oxidative haemolysis inhibition assay (OxHLIA). The antioxidant capacity of the extracts was lower compared to the one of commercial food additives. However, the sustainably developed ingredients may be used in the fortification and functionalisation of food, as well as for incorporation in feed products.

Industrial relevance: This study addresses current needs of the agri-food sector, namely the recycling of plant wastes and production of valuable extracts for the food/feed industry. A MAE process was developed and optimized to maximize the recovery of nutrients and antioxidants from tomato fruit wastes. The optimum processing conditions established in this study allowed a high extraction yield and reduced solvent consumption. MAE can be considered as a sustainable alternative to conventional extraction methods. These findings will contribute to promote a more sustainable bioeconomy in the agro-food sector.

1. Introduction

The strict legislation for human health and environmental safety implemented today, and the emergence of novel methodologies for the extraction, fractionation, and recovery of biomolecules have caused great interest in plant-derived waste valorisation. Different kinds and amounts of agri-food wastes are produced within the food-supply chain, representing a disposal problem for the industry (FAO, 2013), but promising sources of nutrients and phytochemicals (Ravindran & Jaiswal, 2016; Riggi & Avola, 2008). Thus, the sustainable use of plant-derived wastes for recovery of added-value compounds with potential application in the food, feed, biotechnological, and pharmaceutical industries may help to tackle the societal challenges of the 21st century.

The recovery of valuable molecules from agri-food wastes and its recycling inside the food chain as food ingredients can be carried out following the so-called "5-stages universal recovery process" (Galanakis, 2012, 2013). This holistic approach includes: (1) macroscopic pretreatment; (2) separation of macro- and micromolecules; (3) extraction; (4) purification/isolation; and (5) encapsulation or product formation (Galanakis, 2012). Recent trends on extraction, one of the most important steps of the recovery process, have focused on finding more efficient and green technologies that minimize the extraction time and solvent consumption. Among them, microwave-assisted extraction (MAE) (Albuquerque et al., 2017; Pinela, Prieto, Carvalho, et al., 2016b), ultrasound-assisted extraction (Albuquerque et al., 2017;

Abbreviations: t, extraction time; T, temperature; Et, ethanol concentration; S/L, solid/liquid ratio; PROT, total protein content; RS, reducing sugars; TFC, total flavonoid content; TPC, total phenolic content; TS, total sugars.

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Heleno et al., 2016), and extraction with electrotechnologies (such as pulsed electric fields, high-voltage electrical discharges and pulsed ohmic heating (Barba, Galanakis, Esteve, Frigola, & Vorobiev, 2015; Galanakis, 2012, 2013; Roselló-Soto et al., 2015)) and pressurized liquids (Galanakis, 2013; Setyaningsih, Saputro, Palma, & Barroso, 2016) generally meet these requirements. In the case of MAE, the microwaves energy heat the solvent and interacts directly with the free water molecules present inside the plant material, resulting in a rapid build-up of pressure within cells and a pressure-driven enhanced mass transfer of compounds into the solvent. This hot-spot technique has been indicated to achieve high yields of specific phytochemicals (Deng et al., 2015) and to minimize its degradation and the energy consumption (Strati & Oreopoulou, 2014; Zhang, Yang, & Wang, 2011).

Extraction processes are significantly affected by several factors (Albuquerque et al., 2017; Heleno et al., 2016; Pinela et al., 2016b; Wong et al., 2015). For its optimization, one-factor-at-a-time approaches do not evaluate interactive effects among variables and demand an increased number of experimental trials. However, these problems can be overcome using the response surface methodology (RSM), a collection of statistical and mathematical techniques based on the fit of a polynomial equation to the experimental data, which must describe the behaviour of a data set, with the aim of making statistical previsions (Bezerra, Santelli, Oliveira, Villar, & Escaleira, 2008). When planning MAE experiments, it is also necessary to choose an appropriate experimental design. The circumscribed central composite design (CCCD) is a common RSM used and consists of a design with centre points and a group of axial points, also called star points, to estimate the process curvature (Box & Hunter, 1957). It is also important to carry out preliminary studies to select relevant variables and centre the experimental domain.

Currently, there are large amounts of fresh tomato wastes resulting from the crop growing, as well as during packaging, processing, storage, and sale, which consist of plant remains, green fruits, turning fruits, red unmarketable fruits, and miscellaneous materials (Riggi & Avola, 2008). In addition, losses resulting from a surplus production of this crop can also occur. The fruit contains large amounts of bioactive compounds (Barros et al., 2012; Pinela, Barros, Carvalho, & Ferreira, 2012), which are involved in the reduced risk for chronic degenerative diseases induced by oxidative stress and inflammation, such as cardiovascular diseases and various types of cancer (Kim, Nam, & Friedman, 2015; Li, Deng, Liu, Loewen, & Tsao, 2014; Pinela, Oliveira, & Ferreira, 2016c; Stajčić et al., 2015; Vilahur et al., 2014). Additionally, there is a growing demand by the food industry and consumers for the use of natural functional and nutritional ingredients in foods instead of chemically synthesized molecules (Carocho, Morales, & Ferreira, 2015). Because of this, the tomato wastes are promising cheap resources to be recovered and recycled inside the food chain, in order to implement a sustainable strategy that addresses the current challenges of the industrialized world.

In this sense, this study aims the valorisation of fresh tomato fruit wastes by establishing a MAE protocol for production of nutritionally valuable ingredients with antioxidant properties based on a CCCD. In this approach, the levels of total sugars, reducing sugars, proteins, total phenolics, and total flavonoids were determined and used as dependent variables; as well as the antioxidant activity, evaluated through the ABTS and OxHLIA *in vitro* assays, which was compared with the results of typical commercial antioxidants used in the food industry.

2. Material and methods

2.1. Equipment, standards and reagents

Equipments: Microwave apparatus (Biotage® Initiator^{+}, Uppsala, Sweden) using closed high precision glass vials. Multiskan Spectrum Microplate Photometer (Thermo Fisher Scientific, Inc., Shanghai, China) using 96-well polypropylene microplates.

Standards and reagents: ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)), AAPH (2,2′-azobis(2-methylpropionamidine) dihydrochloride), trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), BHA (butylated hydroxyanisole), BHT (butylated hydroxytoluene), PG (propyl 3,4,5-trihydroxybenzoate), TOC ((2*R*)-2,5,7,8-tetramethyl-2-[(4*R*,8*R*)-(4,8,12-trimethyltridecyl)]-6-chromanol or α-tocopherol), ETX (6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline or ethoxyquin) and TBHQ (*tert*-butylhydroquinone), with a purity higher than 98%, were purchased from Sigma S.A. (St. Louis, MO, USA). All other chemicals and solvents were of analytical grade and purchased from common sources. Water was treated in a Milli-Q water purification system (Millipore, model A10, Billerica, MA, USA).

2.2. Preparation of the extracts

2.2.1. Plant material

Unmarketable ripe red tomato (*Lycopersicon esculentum* Mill.) surpluses from a farmers' variety (locally known as “tomate redondo”) were directly obtained from a local producer in Miranda do Douro, North-eastern Portugal. Pericarps without seeds, corresponding to most common tomato wastes, were lyophilized (Free Zone 4.5, Labconco, Kansas City, MO, USA), reduced to a fine dried powder (20 mesh) and kept at −20 °C until analysis.

2.2.2. Microwave-assisted extraction

The MAE process was performed in a microwave apparatus using closed vials of 20 mL (final volume). The powdered dried samples were extracted at different time (t), temperature (T), ethanol concentration (Et) and solid/liquid ratio (S/L) ranging as defined by the RSM experimental design presented in Table A1. During extraction, samples were stirred at 600 rpm and irradiated at 200 W. After that, the reaction mixture in the closed vial was quickly cooled in the processing chamber and then centrifuged at 6000 rpm for 10 min. The supernatant was carefully collected, evaporated under reduced pressure to remove the solvent and finally re-suspended in distilled water for further analysis. A full diagram of the process performed is presented in Fig. A1.

2.3. Evaluation of the extraction yield

The extracted residue (%) was evaluated gravimetrically in crucibles by partially evaporating the water at 60 °C followed by a treatment at 105 °C during 24 h.

2.4. Evaluation of compositional parameters

Total sugars (TS) were evaluated by the phenol-sulphuric acid method using glucose as standard (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956) and expressed in mg per g of extract (mg/g E).

Reducing sugars (RS) were evaluated by the 3,5-dinitrosalicylic acid (DNS) reaction using glucose as standard (Bernfeld P, 1951) and expressed in mg per g of extract (mg/g E).

The total protein content (PROT) was calculated by multiplying the total nitrogen content by the conversion factor of 6.25 (Havilah, E.J., Wallis, D.M., Morris, R., Woolnough, J.A., 1977) and expressed in mg per g of extract (mg/g E).

The total phenolic content (TPC) was determined by the Folin-Ciocalteu method with some modifications (Pereira, Barros, Carvalho, & Ferreira, 2011) using gallic acid as standard and expressed as mg of gallic acid equivalents (GAE) per g of extract (mg GAE/g E).

The total flavonoid content (TFC) was determined by the colorimetric method as described by the authors (Barros, Carvalho, Morais, & Ferreira, 2010) using catechin as standard, and expressed as mg of catechin equivalents (CE) per g of extract (mg CE/g E).