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On-line process for pressurized ethanol extraction of onion peels extract and particle formation using supercritical antisolvent

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ABSTRACT

This paper brings forward a novel process for particle production named extraction and particle formation on-line (EPFO). The process comprises the hyphenated on-line association of pressurized liquid extraction (PLE) with supercritical antisolvent (SAS) precipitation performed in the same multipurpose equipment. The highlight of EPFO process stands for using the pressure energy applied in the extraction step as a useful energy for spraying and producing microparticles in the precipitation step. Performing EPFO process also prevents degrading bioactive compounds because the extract directly flows to the precipitation vessel, avoiding light and oxygen exposure. Then, we obtained dried microparticles as a fine powder from onion peels. After studying some different extraction conditions using ethanol, the more suitable one was found: 40 °C/120 bar for extraction step and 40 °C/100 bar for precipitation step. In such condition, we obtained 4.1 ± 0.6 g microparticles/100 g of dried onion peels, the highest quercetin content in the microparticles (26 ± 2 wt.%) and the smallest mean particle diameter ($d_{[3,4]}$ = 119 ± 1 μm). Analysis of morphology showed lengthened microparticles with rod-like structures. We presented the microparticles characteristics obtained between EPFO process and conventional process (rotary evaporation), whereas EPFO process produced smaller microparticles more concentrated with quercetin.

1. Introduction

Production of natural extracts containing bioactive compounds has gained notoriety because of their functional properties. The most recent and relevant applications found in the scientific literature include the extraction of anthocyanins [1,2], tocotrienols [3], capsaicinoids [4], terpenoids [5,6], carotenoids [7], flavonoids [8,9] and phenolic terpenes [10,11]. Such bioactive compounds are preferable against the synthetic ones, because the consumers are increasingly attempting to have healthy habits. In this scenario, green processes using pressurized fluids (CO_2, water and ethanol, for instance) are emerging as promising alternatives for recovering these target compounds.

One of the target compounds with nutraceutical properties is the quercetin. Such flavonoid is a prominent naturally occurring antioxidant that is exploited in the food, pharmaceutical and cosmetics fields. Quercetin is a potential agent against pulmonary and cardiovascular diseases, osteoporosis, certain forms of cancer and aging [12]. Quercetin is mostly found in onion peels and apple skins [13]; this flavonoid is also found in grape bagasse [14]. Flavonoids content in onion peels is expressively higher than that identified in onion bulbs [15]. Unfortunately, a high amount of peels is discarded around the world as waste material. One strategy is using such waste as a rich source of natural extracts before the waste reaches its final destination as animal feed or composting.

Commonly, natural extracts are commercialized in the liquid form. However, this aggregation state presents some drawbacks, because liquid extracts need large storage spaces and some susceptible active substances might be degraded. Trying to overcome these drawbacks, some researchers formed powders and studied their characteristics in different production conditions [16–21]. The conditions include testing temperature, pressure, flow rate, injector type, solvent characteristics, as well as different methods, like spray–drying, freeze–drying, spray–chilling, crystallization, spray–cooling, rapid expansion of supercritical solutions, gas antisolvent and so on [22–25]. One of the methods is the supercritical antisolvent (SAS), which uses a supercritical fluid (generally CO_2) to change the solubility of target compounds in the solvent. SAS method uses mild temperatures and allows obtaining submicrometric particles with controlled size, being applied to several substances [18,20,23,26,27].

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Micronization using SAS method in semi-continuous mode with CO_2 is generally performed between 80 bar and 150 bar. Above 80 bar and 40 °C, CO_2 is completely miscible with several organic solvents, regardless molar composition [23]. However, some bioactive compounds show limited solubility in such conditions and, consequently, they precipitate. One example is quercetin: its solubility in CO_2 + 5% of ethanol (molar basis) is reduced eight times when pressure is reduced from 120 bar to 80 bar, at 40 °C [28]. Thus, we could change quercetin content in the solution mentioned before by changing the pressure of the system. It suggests that it is possible to obtain a bulk extract and immediately precipitate the particles by designing and performing a hyphenated on-line process. A great effort on developing this on-line process was reported by some recent studies [16,18].

The on-line process can be considered a process intensification. Stankiewicz and Moulijn [29] define process intensification as the result of taking some initiatives such as to increase the production capacity within a given equipment volume, a step decrease in energy consumption per ton of product and a reduction or even a marked cut in residues formation.

However, a few processes follow the process intensification concept. Furthermore, some bioactive compounds used for producing food-related and pharmaceutical-related products can be degraded when handled at light and oxygen exposure, which includes the steps for their extraction and concentration. One of the compounds susceptible against oxidation is quercetin [30]. For solving such problems, we proposed a process for particle production named extraction and particle formation on-line (EPFO) based on the process intensification concept. Then, the objective of carrying out EPFO process in this study stood for using the energy of pressure in the extraction step as a useful energy for spraying the onion peels microparticles in the precipitation step, as well as reducing light and oxygen exposure of the extracts. We evaluated the effects of extraction temperature and pressure on the microparticles characteristics, as mean diameter, morphology, size distribution, microparticles yield and quercetin content.

2. Material and methods

2.1. Material

Onion (*Allium cepa* L.) peels (agroindustrial residue) were donated by a local market. We comminuted the peels in a knife mill (Marconi, MA-340, Piracicaba, Brazil); the mean diameter (d_p) of the raw material was determined using a vibratory system (Bertel, 1868, Caieiras, Brazil) with sieves of 8–80 mesh sizes (Tyler series, Wheeling, USA); d_p was calculated according to ASAE standards [31]. The comminuted raw material was packed in air impermeable bags and stored at −18 °C. Moisture was determined by drying the raw material at 105 °C until obtaining a constant weight [32]. We also used ethanol (Chemco, Hortolândia, Brazil), dimethyl sulfoxide (DMSO, purity > 99%, Sigma Aldrich, St. Louis, USA), methanol (Dinâmica Química, Diadema, Brazil), acetonitrile (J. T. Baker, Phillipsburg, USA), formic acid (Dinâmica Química, Diadema, Brazil), quercetin (purity ≥ 95%, Sigma Aldrich, St. Louis, USA), Tween 80 (Sigma Aldrich, Steinhein, Germany) and ultrapure water supplied by a Milli-Q Advantage water purifier system (Millipore, Bedford, USA).

2.2. Brief equipment description

The home-made multipurpose equipment used for extraction and particle formation on-line was designed and assembled using the structure described by Santos and Meireles [20]. Commonly, extraction and micronization processes are developed in distinct equipment. For performing this operation, at least three pumps are required. Aiming to reduce energetic expenses and to increase the quality of products, our purpose stood for reusing the energy of pressure in the extraction step as useful energy for spraying the extract in the micronization step. Then, we suggested the on-line (extraction + micronization in sequence) intensified process, where two pumps are sufficient for obtaining the microparticles because extraction and micronization take place in the same system. We present the schematic flowchart of the apparatus (Fig. 1). Extraction

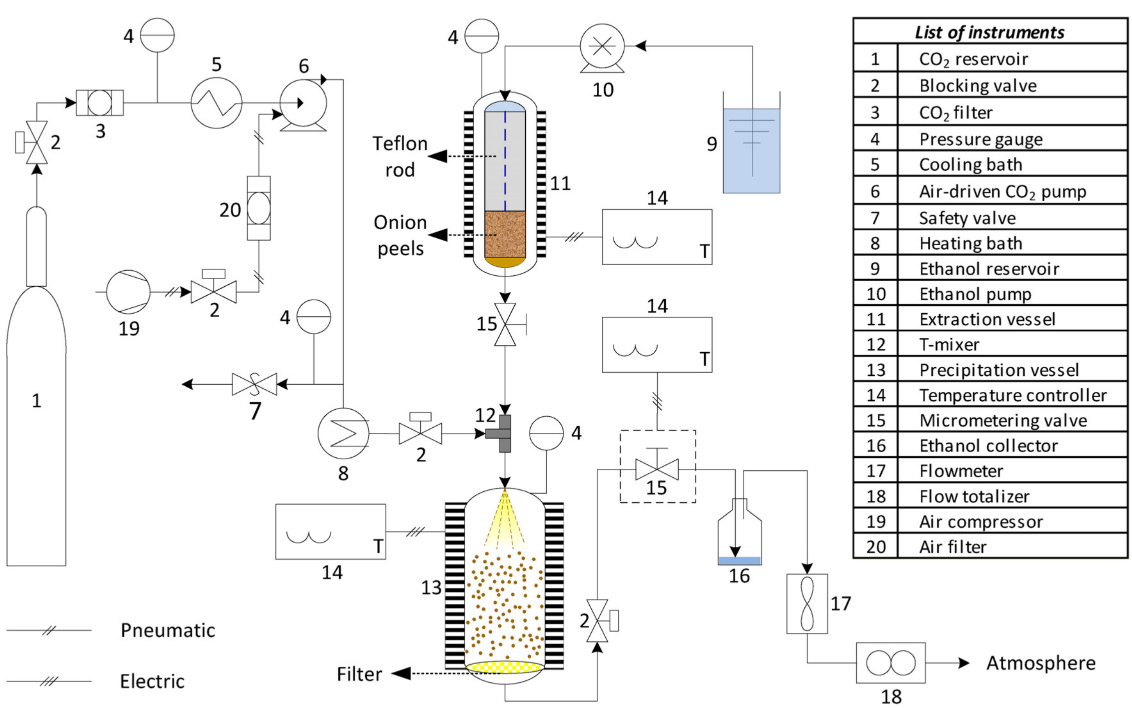

Fig. 1. Schematic drawing of the equipment designed for performing the EPFO intensified process.