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Precipitation of curcuminoids from an ethanolic turmeric extract using a supercritical antisolvent process

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ABSTRACT

This study examined the precipitation of curcuminoids from an ethanolic extract using a supercritical antisolvent process (SAS). The ethanolic extract was obtained from deflavored turmeric using pressurized liquid extraction (PLE). A Split-Plot experimental design was used to evaluate the effects of process parameters, such as nozzle type (T-mixer and coaxial), temperature (313 and 333 K), pressure (10 and 12 MPa) and CO_2 flow (500 and 800 g/h), on the curcuminoids precipitation process. The results indicate that the T-mixer nozzle obtained a higher yield and a lower particle size than the coaxial nozzle. Particles of curcuminoids were precipitated with a global yield of solids of 69% and a curcuminoid content of 554 mg/g. This corresponds to a precipitation efficiency of 97%. The particles precipitated via SAS contained a curcuminoid content 2 and 31 times higher than the extracts obtained by rotary evaporation and the ethanolic extract, respectively, obtained by PLE. Depending on experimental conditions, the particles were characterized as polydispersed and agglomerated into larger structures (by up to 100 μm) with different morphologies.

1. Introduction

Turmeric (*Curcuma longa* L.) is a plant widely cultivated in countries and regions with tropical and subtropical climates. Turmeric is known for its aromatic rhizomes and is commonly used as a condiment, preservative, flavoring and coloring agent, or in folk medicine [1]. Turmeric has been investigated for its biological activity associated with the presence of phenolic compounds classified as curcuminoids. Curcuminoids are responsible for the yellow coloration of the rhizomes and exhibit anticancer [2], antibacterial [3], chemopreventive and chemotherapeutic [4] activities. Curcuminoids are mainly used as colorants due to their coloring ability and the interest in replacing synthetic additives by natural compounds. The color tone of curcuminoids is comparable with tartrazine, and it is possible obtain a bright yellow color using low doses (5–20 ppm) [5]. According to Gomez-Estaca et al. [6] certain properties of curcuminoids could limit their use in foods: low water solubility, which may limit their dispersion in food matrices; low bioavailability, which negatively affects biological efficacy; and rapid degradation under neutral or alkaline pH conditions or when exposed to light. However, curcuminoids are commonly used in the preparation of several products, such as chutneys, pickles, mustard, butter and cheese [7].

Generally, natural extracts are marketed in the form of liquid, viscous preparations or as powders resulting from the drying of the liquid extract. Nevertheless, dried extracts have some advantages over liquid extracts, including lower storage costs and a higher concentration and stability of active substances [8]. Diverse techniques, such as spray drying, spray chilling, spray cooling, lyophilization, crystallization solvent or dry/milling processes, have been studied and employed to obtain powdered extracts and produce particles. However, these methods have several disadvantages, such as the degradation of the product, contamination with organic solvents, and the production of large sized particles [9].

As an alternative to conventional processes, precipitation and particle formation through a supercritical antisolvent process (SAS) is proposed. In the SAS process, a liquid solution of a solvent and a solute is injected into a supercritical fluid, which acts as an antisolvent. This leads to supersaturation of the solute, which is compensated by nucleation and particle growth [10]. In the SAS process, the properties of the particles produced can be strongly

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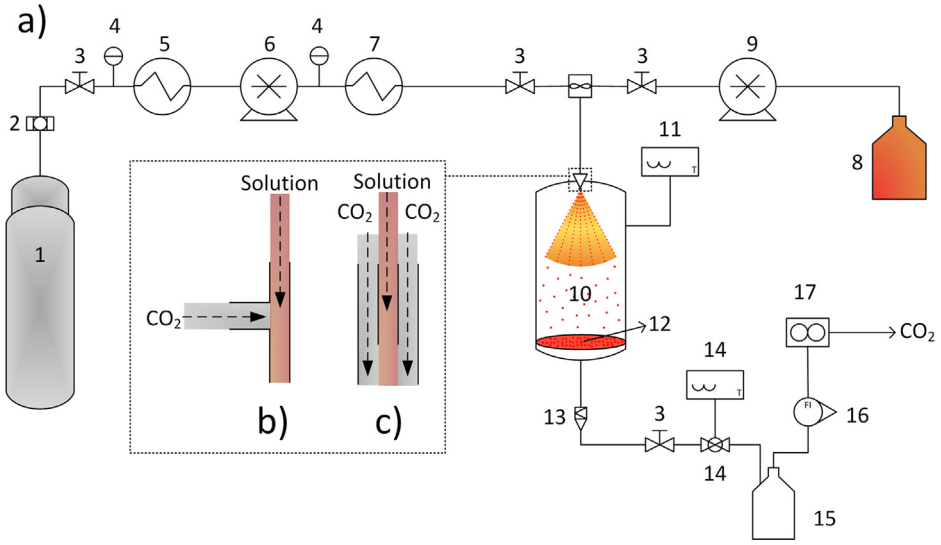

Fig. 1. (a) Schematic diagram of the SAS apparatus and types of nozzles. (1) CO_2 cylinder; (2) CO_2 filter; (3) blocking valves; (4) manometers; (5) thermostatic bath; (6) CO_2 pump; (7) heating bath; (8) solution (solute/solvent) reservoir; (9) HPLC pump; (10) precipitation vessel; (11) temperature controllers; (12) filter; (13) line filter; (14) micrometric valve with a heating system; (15) glass flask; (16) glass float rotameter; (17) flow totalizar. (b) T-mixer and (b) coaxial nozzle.

influenced by varying process parameters such as pressure, temperature, solvent type, solute concentration, and the flow-rate ratio of the solution and the antisolvent [11]. In SAS process, carbon dioxide (CO_2) is the supercritical fluid most widely used because it is considered nontoxic and nonflammable. Moreover, due to its relatively low critical point (304.2 K and 7.38 MPa), CO_2 allows for operation at a moderate temperature, providing conditions suitable for maintaining the integrity of the bioactive compounds [12]. These features, combined with very low solubility of curcuminoids in CO_2 and acceptable solubility of ethanol in CO_2, makes CO_2 a suitable antisolvent for the precipitation process. Although much research has been published on the precipitation and encapsulation of curcuminoids using different techniques [13–17], further research is necessary in order to better understand the precipitation of curcuminoids from an ethanol extract using supercritical fluids.

This work corresponds to the third step of an integrated process. In the first step, the rhizomes were deflavored using supercritical CO_2 according to work done by Carvalho et al. [19], obtaining volatile oil rich in ar-turmerone. In the second step, curcuminoids were extracted by pressurized liquid extraction (PLE), obtaining ethanolic curcuminoid-rich extracts from deflavored turmeric rhizome [18]. Subsequently, in the third step (this work), curcuminoids were precipitated by SAS. Therefore, the objective of this work was to study the precipitation of curcuminoids from an ethanolic extract obtained by PLE using supercritical fluids. The effects of temperature, pressure, type of nozzle and CO_2 flow rate on the SAS process were evaluated.

2. Materials and methods

2.1. Preparation of curcuminoid extract

The extract was obtained using pressurized liquid extraction (PLE) according to Osorio-Tobón et al. [18]. Approximately 332 g of turmeric were placed inside the extraction cell (415 cm^3) to fill the entire volume. According to the work of Carvalho et al. [19], the turmeric rhizomes were initially subjected to supercritical fluid extraction (SFE) pretreatment to remove volatile oils. This pretreatment was performed at 333 K and 25 MPa. The static period was 20 min, and the CO_2 (99.9% CO_2, White Martins Praxair, Campinas, Brazil) flow was 8.6×10^{-3} kg/min, with a solvent (S) to feed (F) mass ratio of 2.5. Without removing the sample from the equipment, the ethanolic extract, which was rich in curcuminoids, was then obtained by PLE. Ethanol (99.5%, Dinâmica, Sao Paulo, Brazil) was used as an extraction solvent at 333 K and 10 MPa. The static period was 20 min, and solvent flow was 1.22×10^{-4} kg/s, with a solvent (S) to feed (F) mass ratio of 2.4. After PLE, the curcuminoid extract was vacuum filtered (MF-Millipore^{TM}, pore size 0.45 μm) at 8×10^{-2} MPa. The liquid phase was recovered and stored at 275 K before use.

2.2. SAS: Precipitation experiments

A schematic diagram of the homemade SAS equipment used in this work is shown in Fig. 1a. Further details and a description can be found in previous work by Santos and Meireles [20]. The procedure was similar to that performed by Santos et al. [21]. The process began with the cooling of CO_2 (99.9% purity, White Martins Praxair, Campinas, Brasil) to 263 K in a thermostatic bath (Marconi, MA-184, Piracicaba, Brazil) to ensure the liquefaction of the gas. Next, CO_2 was pumped by an air-driven liquid pump (Maximator, M111 CO2, Germany) and heated using a second thermostatic bath (Marconi, MA-126, Piracicaba, Brazil) before entering the precipitation vessel (volume of 500 cm^3; 6.8-cm inner diameter). The precipitation vessel was fitted with an electric heating jacket (Autic, Campinas, Brazil). The desired conditions of pressure, temperature and CO_2 flow rate were achieved and stabilized by holding them constant for 10 min. Then, the ethanolic extract was injected into the precipitation vessel by a high-performance liquid chromatography (HPLC) pump (Jasco, PU-2080, Japan) at a flow rate of 0.5 cm^3/min. Once the extract was injected to 40 cm^3, 4 cm^3 of pure ethanol was injected to wash the tubes to avoid obstruction of the nozzles. The HPLC pump was then stopped and a minimum of 625 g of CO_2 was fed at the same operating conditions to ensure drying of the particles and complete removal of the ethanol from the precipitation vessel. The particles were collected using a stainless steel porous filter (AISE, 316, screen size of 2 μm) fixed at the bottom of the precipitation vessel. Two types of nozzles were used to mix the ethanolic extract and the CO_2. The T-mixer nozzle (Fig. 1b) is a 1/8 in. tube (inner diameter (i.d.): 317 mm) through which the ethanolic extract and the CO_2 entered simultaneously. The coaxial nozzle is a 1/16 in.