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Spray dried microparticles of chia oil using emulsion stabilized by whey protein concentrate and pectin by electrostatic deposition

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ABSTRACT

Chia seed oil has a high content of α-linolenic acid (60%) and linoleic acid (20%). Use of this oil in different products is limited due to its liquid state, and the presence of insaturation is a trigger for oxidation. In this context, to facilitate the incorporation of chia oil in food products and increase its protection against oxidation, the aim of this work was to produce chia oil microparticles by spray drying using emulsions stabilized by whey protein concentrate (ζ-potential +13.4 at pH 3.8) and pectin (ζ-potential −40.4 at pH 3.8) through the electrostatic layer-by-layer deposition technique and emulsions prepared with only whey protein concentrate. Emulsions stabilized by whey protein concentrate and stabilized by whey protein concentrate-pectin were prepared using maltodextrin (10 DE) and modified starch (Hi-Cap® 100). They were characterized in relation to stability, droplet size, ζ-Potential and optical microscopy. The microparticles were characterized in relation to moisture content, water activity, particle size, microstructure and oxidative stability by the Rancimat method. Emulsions stabilized by whey protein concentrate-pectin with added maltodextrin 10 DE and emulsions stabilized by whey protein concentrate with added modified starch (Hi-Cap® 100) were stable after 24 h. Emulsions stabilized by whey protein concentrate and by whey protein concentrate-pectin showed droplets with mean diameter ranging from 0.80 to 1.31 μm, respectively and ζ-potential varying from −6.9 to −27.43 mV, respectively. After spray drying, the microparticles showed an mean diameter ranging from 7.00 to 9.00 μm. All samples presented high encapsulation efficiency values, above 99%. Microparticles produced with modified starch showed a smoother spherical surface than particles with maltodextrin 10 DE, which presented a wrinkled surface. All microparticles exhibited higher oxidative stability than chia oil in pure form.

1. Introduction

Chia oil is a rich source of polyunsaturated omega 3 fatty acids, and it has recently been used in animal and bakery product enrichment. It presents low stability to light and oxygen and is also applied as nutraceutical capsules consumed by athletes, for weight loss, appetite suppression, and other uses (Martínez-Cruz & Paredes-López, 2014).

Chia oil is comprised of about 60% α-linolenic acid and 20% linoleic acid, polyunsaturated fatty acids (PUFAs) omega 3 and 6, respectively. The main reason for the inclusion of foods rich in ω-3 PUFAs in the diet is because the human body does not possess the enzyme responsible for producing this compound (Guiotto, Ixtaina, Nolasco, & Tomas, 2014; Porras-Loaiza, Jiménez-Munguía, Sosa-Morales, Palou, & López-Malo, 2014). The high content of polyunsaturated fatty acids present in this oil is responsible for low oxidative stability when in contact with oxygen, light, moisture and heat (Rodea-González et al., 2012).

The incorporation of chia oil in foodstuffs can be made by particles containing this oil, such as particles produced by spray drying. For this reason it is necessary to prepare emulsions, that are basically formed from two immiscible liquids, and may be the oil-in-water (O/W) or water-in-oil (W/O) type (McClements, 2007).

Other emulsion production processes are known, such as the addition of polysaccharide in emulsions obtained from oil and protein, a technique called electrostatic deposition, resulting in increased emulsion stability. The electrostatic deposition consists of homogenization of an emulsifier with ionic character with an oil phase to form oil droplets surrounded by an emulsifier. In this system, one oppositely charged polyelectrolyte is added which will aggregate oil droplets coated by protein, thus forming a second layer (Guzey & McClements, 2006). There are various interactions that have been used for the formation of protein-polysaccharide complexes. In this study, the interaction between whey protein concentrate and pectin was evaluated because the addition of pectin in emulsions obtained by oil and whey protein concentrate can generate higher droplet density, which reduces the density

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difference between the oil and aqueous phase, decreasing the driving force that causes phase separation, thus generating stable emulsions that can be spray dried.

Spray drying is a good alternative for the conversion of liquids into powders. The microencapsulation process is the inclusion of an active material, which may be liquid or solid, within a wall material forming a particle, which provides high protection against external agents (moisture, heat, light and oxygen) and the possibility of controlled release active (Gharsallaoui, Roudaut, Chambin, Voilley, & Saurel, 2007). The microencapsulation process of chia oil is intended to form powdered particles to enrich dehydrated foods, such as whole cereal bars and cookies, with omega 3.

Some works about spray dried emulsions stabilized by lecithin-chitosan are available in the literature (Carvalho, Silva, & Hubinger, 2014; Klinkesorn, Sophanodora, Chinachoti, McClements, & Decker, 2005; Serfert et al., 2013). However, we have not found articles that describe emulsions stabilized by whey protein concentrate and pectin, followed by spray drying of chia oil. Therefore, it is important to evaluate the process for obtaining chia oil emulsions stabilized by whey protein concentrate and pectin. After that, evaluating the interaction between different kinds of wall materials in the emulsion formations and production of microparticles by spray drying is still required.

The aim of this work was to produce chia oil emulsions stabilized by whey protein concentrate and pectin and those stabilized only by whey protein concentrate followed by the spray drying process. Emulsions were prepared using rotor-stator and high pressure homogenization. Emulsions characterization was performed in relation to ζ-potential, droplet size, viscosity and stability and microparticles were analyzed according to encapsulation efficiency, moisture content, water activity, particle size, microstructure and lipid oxidation.

2. Material and methods

2.1. Material

Chia seeds oil (*Salvia hispanica* L.), food grade, was provided by R & S Blumos Comercial de Produtos Alimentícios Ltda. (Campinas, Brazil), and used as active material with the following fatty acid composition: 0.06% 14:0; 0.03% 15:0; 7.19% 16:0; 0.07% 16:1; 0.04% 17:0; 0.04% 17:1; 3.42% 18:0; 7.46% 18:1; 0.22% 18:2; 20.21% 18:2; 0.25% 18:3; 60.21% 18:3; 0.30% 20:0; 0.19% 20:1; 0.19% 22:0 and 0,12% 24:0. Wall materials were maltodextrin 10 DE (ζ-potential pH 3,8 is −3.79) and Hi-Cap® 100, which is the chemically modified octenyl succinic anhydride (OSA) starch derived from waxy maize (ζ-potential of pH 3.8 is −3.37) supplied by Ingredion Brasil Ingredientes Industriais Ltda (Mogi Guaçu, Brazil). Whey protein concentrate (WPC) was supplied by Fonterra Co-operative Group Limited (Auckland, New Zealand) and pectin by Danisco Brasil LTDA (Cotia, Brazil). Milli-Q water was used for the dispersion preparation.

2.2. Emulsion formation

Emulsions stabilized by WPC/pectin or WPC were prepared according to Fig. 1. The wall materials WPC, maltodextrin 10 DE and Hi-Cap® 100 were dispersed into Milli-Q water and to complete dissolution, were kept under magnetic stirring overnight at room temperature. Pectin was dispersed in Milli-Q water and subjected to magnetic agitation at 70 °C for 30 min, and maintained under magnetic stirring at room temperature overnight. pH of all dispersions was adjusted to 3.8 with HCl at 10 $mol \cdot L^{-1}$ before emulsions production.

At first, chia oil and WPC emulsion was prepared by blending 18% (w/w) of chia oil with 82% (w/w) aqueous WPC dispersion (1.8% w/w) with a rotor-stator homogenizer (ULTRA-TURRAX MA-102, Marconi, Piracicaba, Brazil) for 1 min operating at 12,000 rpm, followed by three passes through a high-pressure valve homogenizer (PANDA 2K – NS1001L, Niro Soave, Parma, Italy), at 250 bars.

The primary emulsion (66.67% w/w) was diluted with 33.33% (w/w) of aqueous pectin (3% w/w) to form a secondary emulsion (12% chia oil, 1% WPC and 1% pectin) and homogenized using a rotor-stator (ULTRA-TURRAX MA-102, Marconi, Piracicaba, Brazil) for about 1 min at 12,000 rpm, followed by one pass through a high-pressure valve homogenizer (PANDA 2K – NS1001L, Niro Soave, Parma, Italy), at 250 bars.

Finally, this emulsion was diluted with 50% (w/w) of each dispersion of Maltodextrin 10 DE and Hi-Cap® 100 and homogenized in a rotor-stator (ULTRA-TURRAX MA-102, Marconi, Piracicaba, Brazil) for 4 min at 16,000 rpm. The final emulsion was composed of 0.5% (w/w) WPC, 0.5% (w/w) pectin, 6% (w/w) chia oil and 23% (w/w) wall material.

Following the same procedure, emulsions stabilized by WPC without the addition of the pectin dispersion were produced. Chia oil and WPC emulsion were prepared by blending 12% (w/w) chia oil with 88% (w/w) aqueous emulsifier dispersion (1.14% w/w) using a rotor-stator homogenizer (ULTRA-TURRAX MA-102, Marconi, Piracicaba. Brazil) for 1 min at 12,000 rpm, followed by one pass at 250 bars through a high pressure homogenizer (PANDA 2K – NS1001L, Niro Soave, Parma, Italy). Subsequently, the final emulsion was prepared by blending 50% (w/w) of the initial emulsion with maltodextrin 10 DE and Hi-Cap® 100 at 47% (w/w) dispersions, by a rotor-stator (ULTRA-TURRAX MA-102, Marconi, Piracicaba, Brazil) homogenizer, for 4 min at 16,000 rpm. The final emulsion composition was 0.5% (w/w) WPC, 6% (w/w) chia oil and 23.5% (w/w) wall material.

2.3. Emulsion characterization

2.3.1. ζ-Potential measurements

To determine the electrical charge on the surface of the oil droplets, freshly prepared emulsions were diluted to the concentration of 0.01% (v/v) in water pH 3.8, acidified with HCl 10 $mol \cdot L^{-1}$. The measurement was performed in a microelectrophoresis chamber of a Nano ZS Zetasizer (Malvern Instruments Ltd., Worcestershire UK). The measurements were performed in triplicate, at room temperature.

2.3.2. Emulsion droplet size ($D_{3,2}$)

Droplet size distribution was measured by a laser light diffraction instrument, Mastersizer 2000 (Malvern Instrument Ltd., UK). The emulsion droplet size was express ed as $D_{3,2}$ ($D_{[3,2]} = \sum n_i d_i^3 / \sum n_i d_i^2$), where n_i is the number of the droplets of diameter d_i. Span, parameter related to the width of a distribution was expressed as Span (Span = $((d_{90} - d_{10})/d_{50})$), where d10%, d50% and d90% are the equivalent volume diameters at 10, 50 and 90% of cumulative volume, respectively.

2.3.3. Emulsion viscosity

Emulsion viscosity was obtained using a controlled stress rheometer (Physica MCR 301 Rheometer, Anton Paar, Ostfildern, Germany) at 25 °C, through the determination of steady-shear flow curves. The cone plate of 6 cm diameter and angle 2° was used for the measurements with a 67 mm gap. Analyses were performed at least in triplicate. Flow curve measurements were carried in three sweeps (up, down and up-cycles), out with a shear rate ranging from 0 to 1000 s^{-1}. Viscosity was calculated as the instantaneous ratio of shear stress and shear rate.

2.3.4. Optical microscopy

A small portion of the emulsions was poured onto microscopes slides, covered with a glass cover slip and observed using a Carl Zeiss AG optical microscope (Model Axio Scope A1, Gottingen, Germany), with 1000× of magnification.

2.3.5. Interfacial tension

The interfacial tension between the chia oil and the WPC suspensions (1.8% w/w) was measured using a Tracker-S tensiometer (Teclis, Longessaigne, France) using the rising (O/W) drop method. An oil drop was generated in the needle tip and immersed in the WPC suspension (1.8% v/v). The experiments were performed in triplicate at 25 °C.