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Assessment of physicochemical characteristics, thermal stability and release profile of ascorbic acid microcapsules obtained by complex coacervation

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ABSTRACT

The aim of this study was to determine the physicochemical characteristics, thermal stability and release profile of ascorbic acid (AA) microcapsules obtained by complex coacervation. Gelatin and gum arabic were used as wall materials in concentrations of 2.5, 5.0 and 7.5 g% (w/v). The coacervate microcapsules were freeze-dried and assessed for physicochemical characteristics, thermal behavior and stability during 60 days of storage. The release profile was evaluated at different pH values (1.1, 2.2, 5.4, 7.4, 9.6 and 12). The encapsulation efficiency ranged from 27.3 to 93.8%. The microcapsules of AA presented good characteristics for application in food matrices, such as average diameter below 12.4 μm, low solubility and low hygroscopicity. The AA had its thermal stability significantly improved by the encapsulation process, which extends its application in the food industry. The release of AA was slower at pH near neutrality, with release of 97, 96 and 99% of encapsulated AA at 240, 300 and 270 min at pH 5.4, 7.4 and 9.6, respectively. Different mathematical models were successfully fitted to the release kinetics: $R^2 > 0.94$, absolute deviations < 16% and RMS deviations < 0.09. A mathematical model for a two-step release was proposed, resulting in very high correlations with the experimental data observed: $R^2 > 0.99$, absolute deviations < 3.5% and RMS deviations around 0.02.

1. Introduction

Ascorbic acid (AA) has been used as an ingredient or additive in foods due to its antioxidant and reducing properties, as well as its nutritional function as a source of vitamin C. In the food industry, AA is widely applied in meat curing and inhibition of enzymatic browning of fruits and vegetables. The degradation of AA is influenced by factors such as the presence of heat, light, high pH values, high oxygen concentration, high water activity and reactions catalyzed by transition metal ions, such as Cu^{2+} and Fe^{3+} (Fennema, Damodaran, & Parkin, 2010). In aqueous solutions and in foods, their stability is directly related to the storage conditions and composition of the solution or matrix. A variety of methods has been proposed in order to increase the AA's shelf-life, including encapsulation. Encapsulation is defined as a process in which small particles or droplets (the active material) are surrounded by a coating with the main purpose of protecting them from adverse conditions of the medium, such as light, moisture, oxygen and interaction with other compounds, in addition to providing controlled release of the active compound (Abbas, Wei, Hayat, & Xiaoming, 2012; Fereidoon Shahidi & Xiao-Qing Han, 1993; Gharsallaoui, Roudaut, Chambin, Voilley, & Saurel, 2007; Gibbs, Kermasha, Alli, & Mulligan, 1999).

Several methods of microencapsulation may be employed to improve the stability of AA, such as spray drying (Alvim, Stein, Koury, Dantas, & Cruz, 2016; Desai & Park, 2005; Trindade & Grosso, 2000), spray congealing (Matos-Jr, Di Sabatino, Passerini, Favaro-Trindade, & Albertini, 2015), microfluidic technique (Comunian, Abbaspourrad, Favaro-Trindade, & Weitz, 2014), solvent evaporation (Uddin, Hawlader, & Zhu, 2001), spray chilling (Sartori, Consoli, Hubinger, & Menegalli, 2015) and the complex coacervation (Comunian et al., 2013). Coacervation is the separation of one or more hydrocolloids from an initial solution followed by deposition of the coacervate phase around an active ingredient suspended or emulsified in the reaction medium (Doublier, Garnier, Renard, & Sanchez, 2000; Nori et al., 2011). Complex coacervation is an alternative encapsulation method for sensitive and unstable compounds, which produces a true capsule, completely protecting the active material within the wall material. The capsules produced by complex coacervation are insoluble in water,

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resistant to high temperatures and have favorable characteristics for controlled release (Dong et al., 2011).

Some studies have been carried out with the aim of overcoming the problems related to stability and accordingly to facilitate the application of AA in food matrices. Alvim, Souza, Koury, Jurt, and Dantas (2013) produced AA microcapsules by spray-drying and by spray-chilling. The characteristics of the microparticles were compared when added in the production of biscuits. Gum arabic was used as wall material for the spray-drying, and stearic acid and hydrogenated vegetable fat for the spray-chilling. Uddin et al. (2001) encapsulated AA using different techniques, such as melt dispersion, solvent dispersion, and spray-drying. Matos-Jr et al. (2015) used spray-congealing with hydrogenated palm oil and glycerol monostearate as wall materials to encapsulate AA. Pierucci, Andrade, Baptista, Volpato, and Rocha-Leão (2006) encapsulated AA by spray-drying using concentrated pea protein as wall material. Comunian et al. (2013) used complex coacervation to encapsulate AA with gum arabic and gelatin as wall materials. Although all these studies have shown that encapsulation increases the stability of AA when compared to free AA, it is necessary to study the behavior of the microcapsules against conditions that affect the stability of the active material.

The aim of this study was to assess the physicochemical characteristics, thermal stability and release profile of AA microcapsules obtained by complex coacervation.

2. Material and methods

2.1. Material

Pure ascorbic acid (AA) (Biotec, Pinhais, Brazil) was used as the active ingredient, while the wall materials were food grade bovine gelatin type B (Gelita South America, Mococa, Brazil) and arabic gum (Biotec, Pinhais, Brazil). For the production of the simple emulsion, corn oil (Cargill, Mairinque, Brazil) and the surfactant polyglycerol polyricinoleate (PGPR 90) (SGS Agricultura e Industria Ltda, Ponta Grossa, Brazil) were used.

2.2. Methods

2.2.1. Preparation of microcapsules

The production of the microcapsules followed the method described by Comunian et al. (2013), with some modifications. The simple W/O emulsion was prepared using a 30% (w/w) solution of AA and corn oil at a 1:1 mass ratio (1 g of AA solution:1 g of oil), and the lipophilic surfactant polyglycerol polyricinoleate (PGPR 90) at a concentration of 0.8% (w/w) in relation to the total mass of the emulsion. The formulation of the simple emulsion was established according to preliminary trials (results not shown), when the AA:oil proportion, time and homogenization velocity were optimized.

In order to form a simple W/O emulsion, the blend was homogenized with a high performance homogenizer (Ultra-Turrax® T-25, Ika, Germany) at 22,000 rpm for 4 min. This emulsion was considered the core and used in the calculations of the wall:core ratios. The simple W/O emulsions were emulsified with gelatin solutions at concentrations of 2.5, 5.0 and 7.5 g% (w/v) at 14,000 rpm for 3 min to obtain the double W/O/W emulsions. Gum arabic solutions at concentrations of 2.5, 5.0 and 7.5 g% (w/v) were slowly added to the double emulsions under constant magnetic stirring at 45 °C for 5 min. The pH was adjusted to 4.4 by addition of NaOH (1 mol/L) to promote the complex coacervation. This pH was chosen based on preliminary tests in which liquid-liquid phase separation occurred resulting in a limpid supernatant. The solution was slowly cooled to 10 °C in an ice bath, and the coacervate material was stored for 24 h at 7 °C to promote phase separation. After 24 h, the water was discarded and the samples were centrifuged at 3600 rpm for 15 min. The coacervates were transferred to vials coated with aluminum foil and then were frozen (−18 °C) for 24 h and freeze-dried (LIOBRAS, LIOTOP model L101) at −52 °C for 48 h. After freeze-dried, the samples were added into glass vials coated with aluminum foil and stored in a desiccator.

Table 1
Encapsulation efficiency of the microparticles produced by complex coacervation.

Sample	Wall concentration g% (w/v)[a]	Core (%)[b]	Wall:core (w/w)	EE (%)
S1	2.5 (−1)[c]	25 (−1)	1:0.25	49.0^{e} ± 4.40
S2	2.5 (−1)	50 (0)	1:0.5	55.1^{de} ± 2.98
S3	2.5 (−1)	75 (+1)	1:0.75	56.8^{d} ± 2.55
S4	5.0 (0)	25 (−1)	1:0.25	27.3^{f} ± 4.46
S5	5.0 (0)	50 (0)	1:0.5	67.5^{c} ± 1.16
S6	5.0 (0)	75 (+1)	1:0.75	78.4^{b} ± 2.85
S7	7.5 (+1)	25 (−1)	1:0.25	60.1^{d} ± 3.02
S8	7.5 (+1)	50 (0)	1:0.5	93.8^{a} ± 2.23
S9	7.5 (+1)	75 (+1)	1:0.75	56.3^{d} ± 2.29

[a] The ratio of gelatin:gum arabic was fixed at 1:1.
[b] Percentage of simple emulsion (core) in relation to the total amount of polymers (w/w).
[c] The numbers in parentheses represent the coded variables of experimental planning.

The concentrations of the wall and core materials, the proportions between wall material and core (payload) and the proportions of emulsifier and corn oil in relation to the AA solution were based on the literature (Alvim et al., 2016; Comunian et al., 2013; Sartori et al., 2015). To select the best ratio between the core and the polymer pair, a 3^2 full-factorial design coupled with response surface methodology (RSM) was applied according to Table 1.

2.2.2. Characterization of the microcapsules

2.2.2.1. Encapsulation efficiency (EE). The total AA amount was determined based on the methodology described by Alvim et al. (2016), with some modifications. One hundred mg of the freeze-dried microcapsules were completely melted in oxalic acid solution (0.03%) at 40 °C for 5 min. The resulting solution was transferred to a 100 mL volumetric flask. After preparation of the samples, the AA content present in the solution was determined according to the AOAC 967.21 (2010) method, with the modifications described by Benassi and Antunes (1988). The encapsulation efficiency was calculated by subtracting the amount of superficial ascorbic acid ($AA_{superficial}$) in the total ascorbic acid (AA_{total}) found in the sample, as shown in Equation (1):

$$EE\ (\%) = \frac{AA_{total} - AA_{superficial}}{AA_{total}} \times 100 \quad (1)$$

The amount of superficial AA was determined according to the methodology described by Ribeiro, Arellano, and Grosso (2012), with some adaptations. One hundread mg of sample and 10 ml of Tween 80 surfactant solution (0.1%) were added in 125 ml of residues and stirred at 100 rpm for 5 min in an orbital shaking incubatorIn summary, 100 mg of sample and 10 mL of Tween 80 (0.1%) surfactant solution were added into 125 mL erlermeyers and shaken at 100 rpm for 5 min in an incubator with orbital shaking. The suspension was then filtered on filter paper and the amount of AA in the filtrate was determined according to the AOAC 967.21 (2010) method.

2.2.2.2. Mean diameter and morphology. The mean diameter of the freeze-dried microcapsules was determined by the AxioVision LE - Observer D1 (Carl Zeiss® Group, Aalen, Jena, Germany) inverted optical microscope coupled to an AxioCam MR3 camera and connected to a computer. The images obtained by the AxioVision SE64 software (Carl Zeiss® Microscopy, Tornwood, New York, United States) were used to calculate the mean diameter of the particle with the aid of ImageJ free software. The diameter of 150 microparticles from each different