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Calcium-alginate beads loaded with gallic acid: Preparation and characterization

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ABSTRACT

Electrospray technique was used to prepare alginate beads with controllable size from about 200 μm to 1.3 mm by adjusting the working voltage. The encapsulation ability of alginate beads for gallic acid, a model hydrophilic phenolic compound, was investigated. Loading amount of gallic acid varied from 7 g/100 g–12 g/100 g among alginate beads samples. Fourier-transform infrared and differential scanning calorimetry result confirmed the inclusion of gallic acid. Moreover, no autoxidation of gallic acid was observed in the formulated alginate beads. Release profile result indicated that in simulated intestinal fluid the release was faster than that in gastric fluid. The release pattern was influenced by both loading amount of gallic acid and size of alginate beads. Our results suggest that alginate beads fabricated by electrospray method is a promising delivery system for water soluble phenolic compound like gallic acid.

1. Introduction

Gallic acid (3,4,5-trihydroxybenzoic acid) is a well-known natural antioxidant agent widely available from food such as tea leaves, bearberry, mango and many others (Karamaæ, Kosińska, & Pegg, 2006; Soong & Barlow, 2006). In the food analysis, gallic acid is commonly used as a reference standard material in the conventional Folin–Ciocalteau assay to determine the total phenol concentration. Apart from its strong antioxidant ability, gallic acid has also been demonstrated to possess various physiological functions such as antiaging, anti-inflammatory, and anticarcinogenic activity (Arunkumar, Ilango, Manikandan, & Ramalakshmi, 2009; Manosroi, Jantrawut, Akihisa, Manosroi, & Manosroi, 2010). However, gallic acid has strong astringency and bitterness which may decrease its preference and limit its potential applications in the functional food. Moreover, gallic acid, when dissolved in aqueous solution, has the tendency to autoxidize into dimer and oligomer structure (Neo, Ray, et al., 2013; Neo, Swift, et al., 2013).

The properties of gallic acid require certain delivery system to mask its unfavorable flavor as well as prevent autoxidation. Encapsulation is a promising approach to deliver bioactive compounds like gallic acid. In recent decades, micro and nano-delivery systems have been investigated for various applications in functional food and related areas. Gallic acid loaded zein submicron fiber was fabricated to prepare an active packaging material (Neo, Ray, et al., 2013; Neo, Swift, et al., 2013). The authors concluded that gallic acid loaded zein fiber mats have strong antibacterial activity and is a suitable food package material. On the other hand, inorganic nanoparticles such as Fe_3O_4 and silica nanoparticles were also exploited to deliver gallic acid for controlled release (Dorniani et al., 2012; Hu, Nie, Feng, & Suo, 2013).

To prompt its applications in food system, various biopolymer based hydrogel beads were developed to encapsulate, protect and deliver gallic acid. In previous studies, chitosan, β-cyclodextrin, xanthan, acetylated starch and inulin have been used to encapsulate gallic acid (Robert, Garcia, Reyes, Chavez, & Santos, 2012; da

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Rosa et al., 2013). Meanwhile, gallic acid was encapsulated in the carriers through various formulation techniques such as spray drying, lyophilization, emulsification and electrospinning (da Rosa et al., 2013; Medina-Torres et al., 2013; Nagpal, Singh, & Mishra, 2013; Neo, Ray, et al., 2013; Neo, Swift, et al., 2013).

As a natural polysaccharides isolated from brown algae, alginate acid possesses several advantages compared with other commonly used biopolymers for formulating hydrogel beads. It is a biocompatible, biodegradable, non-toxic biomaterial which has a broad spectrum of applications in both food and pharmaceutical industry due to its gelling properties when crosslinked with divalent ions like calcium and ferrous cation (Ribeiro, Afonso, Vila-Real, Alfaia, & Ferreira, 2010). The 'egg-box' structure of alginate bead is the basis for trapping targeted materials, either it be aqueous herbal extract or drug (Alborzi, Lim, & Kakuda, 2014; Stojanovic et al., 2012). In the food matrix, the size of the hydrogel beads has significant impact on parameters including texture, stability and mouthfeel, and thus should be carefully manipulated before incorporated into food for different end-use applications. Electrospray is a versatile device that use electrostatic force to prepare bioactive compound encapsulated particles or fibers with tunable size (Alborzi et al., 2014). Its basic structure is composed of a syringe pump, a spinneret and a high voltage direct-current (DC) supply as illustrated in our recent publication (Lee, Li, Chen, & Park, 2015). Compared with other encapsulation techniques, electrospray requires no harsh working conditions and toxic organic solvent. The size of fabricated carrier could be optimized by fine tuning the nozzle size, voltage, collection distance, as well as the spraying speed (Tapia-Hernández et al., 2015).

In the present study, gallic acid was encapsulated as a model water soluble phenolic compound in alginate beads via the electrospray technique. Size of alginate beads could be adjusted by changing the working voltage. Encapsulation of gallic acid was verified by FTIR, DSC as well as Folin–Ciocalteau test. The impacts of beads size and loading amount of gallic acid on the release profile in simulated digestion fluid were also investigated.

2. Materials and methods

2.1. Materials

Sodium alginate with molecular weight around 22 kDa was purchased from Junsei Chemical (Tokyo, Japan). Gallic acid monohydrate, sodium carbonate, sodium chloride, sodium hydroxide, potassium dihydrogen phosphate, hydrogen chloride and calcium chloride dihydrate were provided by Duksan Pure Chemical (Ansan, Korea). Folin–Ciocalteu's reagent (FCR) was obtained from Sigma–Aldrich (St. Louis, MO, USA). Distilled water was produced from a Milli-Q system of Millipore (Milford, MA, USA).

2.2. Preparing alginate bead

Sodium alginate was dispersed in distilled water at the concentration of 1 g/100 mL. After full hydration with the aid of magnetic stirring, the sodium alginate solution was left to stand for about 2 h to remove any air bubbles in the solution. Collection solution was prepared by dissolving $CaCl_2$ in distilled water (5 g/100 mL). A syringe pump was applied to deliver sodium alginate solution through a hose the other end of which was connected with a 30 gauge blunt-end stainless steel needle (outer diameter: 0.3112 mm, inner diameter: 0.159 mm). The voltage between the tip of the needle and the collection solution was modulated by a DC power supply. After preliminary studies, the extrusion speed was set at 10 mL/h, and the distance between the tip of the needle and the surface of the collection solution was set at 20 cm. Voltage was varied from 0, 5, 7.5 and 10 kV. To prepare gallic acid loaded alginate beads, gallic acid was first dissolved in distilled water (1 g/100 mL and 0.5 g/100 mL) and then sodium alginate (1 g/100 mL) was dispersed into the solution. The collection solution for gallic acid loaded alginate beads contained the same level of gallic acid (at 1 g/100 mL and 0.5 g/100 mL respectively) to reduce the loss of gallic acid during gelling period. All other parameters for electrospray were the same. The beads sample was soaked in the $CaCl_2$ solution for about 10 min before collection by paper filtration. Lyophilization at −60 °C for 48 h was applied to prepare the dried form of alginate beads. All lyophilized bead samples were stored in a refrigerator at −20 °C until use.

2.3. Water content

The water content of both wet alginate beads and the freeze dried ones were measured gravimetrically on a moisture analyzer (MX-50, A&D Company, Tokyo, Japan). Sample was weighted to the analyzer and heated at 105 °C until no weight change can be observed. The difference between the original weight and the final weight was considered as the water content.

2.4. Gallic acid content measurement

Gallic acid content was examined by the Folin–Ciocalteau assay according to our previous study (Li, Shin, Chen, & Park, 2015). Briefly, the sample was added to 2 g/100 mL sodium citrate solution to disintegrate the alginate beads. After fully dissolved, 0.4 mL of the solution along with 1.6 mL of sodium carbonate (7.5 g/100 mL in distilled water) was pipetted into 2 mL of 0.2 mol/L Folin–Ciocalteau reagent solution. The mixture was left for 1 h before the absorption at 765 nm was recorded on a UV–vis spectrophotometer (Optizen Pop, Daejeon, Korea). The concentration of gallic acid was calculated based on a calibration curve using gallic acid as the standard reference under the same conditions.

2.5. Loading ability and loading efficiency

Loading ability of alginate beads was calculated by the weight ratio of gallic acid and the weight of dried alginate beads using the following formula:

Loading ability = gallic acid weight/weight of dried alginate beads × 100.

While the loading efficiency was expressed as the gallic acid determined in the beads divided by the initial amount of gallic acid using the following formula:

Loading efficiency = amount of gallic acid in the beads/original amount of gallic acid × 100.

2.6. Size and morphology study

Photographs were acquired on a microscope equipped with a digital camera Olympus DP 22 (Tokyo, Japan). The mean size of the beads was calculated by the diameters provided in the images. For each sample group, at least 10 beads were measured and recorded.

2.7. Attenuated total reflecting-Fourier-transform infrared (ATR-FTIR) investigation

The interaction between gallic acid and alginate bead matrix was investigated by ATR-FTIR which was recorded on a PerkinElmer Spectrum 100 spectrophotometer (Waltham, MA, USA). Powder of freeze dried sample was sandwiched between the ATR accessory and the diamond crystal. Spectra of samples were recorded in the wavelength region between 400 and 4000 cm^{-1}.