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Impact of delivery system type on curcumin stability: Comparison of curcumin degradation in aqueous solutions, emulsions, and hydrogel beads

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ABSTRACT

The impact of molecular environment on the chemical stability of curcumin was determined. Equal amounts of curcumin were incorporated into different kinds of delivery system: aqueous dimethyl sulfoxide (DMSO) solutions; oil-in-water emulsions; or filled hydrogel beads. Two types of filled hydrogel beads were fabricated by injecting solutions containing curcumin-loaded lipid droplets and gelling polysaccharides (alginate or chitosan) into ionic gelling solutions (calcium or tripolyphosphate) using an extrusion device. The delivery systems were then incubated under acidic (pH 3) and neutral (pH 7) conditions at 55 °C for 14 days. The initial rate of curcumin degradation, determined by measuring the color change (b^* value) over time, depended on storage pH and delivery system type. At pH 7, the curcumin degradation rate increased in the following order: chitosan beads < emulsion < aqueous solution < alginate beads, but at pH 3 it increased in a different order: emulsion < aqueous solutions < chitosan beads < alginate beads. Overall, our results showed that curcumin was more stable under acidic than neutral conditions. Interestingly, encapsulation of curcumin in alginate beads promoted its degradation at both acidic and neutral pH, but encapsulation in chitosan beads enhanced its stability at pH 7 by reduced it at pH 3. These effects may be related to the different charge status of the polysaccharides used to fabricate the hydrogel beads: alginate is anionic, whereas chitosan is cationic. Overall, our results provide valuable information for the design and development of emulsion-based delivery systems to encapsulate and protect curcumin for functional food applications.

1. Introduction

Turmeric, a member of the ginger family, has been used as a dietary spice, yellow colorant, preservative and traditional medicine in the south and southeast of Asia for thousands of years (Gupta et al., 2013). Turmeric consists of three major curcuminoids with related structures: curcumin; demethoxycurcumin; and, bisdemethoxycurcumin (Heger, van Golen, Broekgaarden, & Michel, 2014). Curcumin is the most bioactive constituent in turmeric and has been reported to have various pharmaceutical functions, including antioxidant, antibacterial, anti-inflammatory, anti-tumor and anti-cancer activities (Aggarwal & Harikumar, 2009; Epstein, Sanderson, & MacDonald, 2010; Heger et al., 2014). Curcumin is generally regarded as safe (GRAS) by the United States Food and Drug Administration (FDA) due to its low toxicity even when ingested at relatively high levels (Cheng et al., 2001). For these reasons, curcumin has been widely investigated for its potential application as a bioactive agent in functional foods, supplements, and pharmaceuticals (Singh, Arseneault, Sanderson, Murthy, & Ramassamy, 2008; Yang, Sang, Lambert, & Lee, 2008). Moreover, curcumin has a desirable yellow color that makes it suitable for use as a natural colorant in some food products (Sharma, Gescher, & Steward, 2005).

The effectiveness of curcumin as a nutraceutical or natural colorant in foods depends on its ease of use, chemical stability, and bioavailability. Curcumin is a hydrophobic substance that has low water-solubility, poor chemical stability (especially in alkaline

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solutions), and low oral bioavailability (Heger et al., 2014). Under alkaline conditions, hydroxyl ions convert curcumin (diferuloylmethane) into *trans*-6-(4′-hydroxy-3′-methoxyphenyl)-2,4-dioxo-5-hexanal, ferulic acid, feruloylmethane, and vanillin, which leads to a reduction in its desirable yellow color (Schneider, Gordon, Edwards, & Luis, 2015; Tønnesen, Másson, & Loftsson, 2002b). Therefore, there is a need for delivery systems to improve the water-dispersibility, chemical stability and bioavailability of curcumin (Bansal, Goel, Aqil, Vadhanam, & Gupta, 2011; Patel & Velikov, 2011; Sun et al., 2012).

Previous studies have demonstrated that the functional attributes of curcumin can be improved by encapsulating it within emulsion-based delivery systems, such as emulsions or nanoemulsions (Ahmed, Li, McClements, & Xiao, 2012; Joung et al., 2016; Pinheiro, Coimbra, & Vicente, 2016; Vecchione et al., 2016; Zou et al., 2016). Encapsulation of the hydrophobic curcumin molecules within lipid droplets improves their dispersion in aqueous solutions, and helps protect them from chemical degradation by limiting their interactions with reactive substances in the aqueous phase (such as hydroxyl ions). Moreover, the presence of a digestible lipid within the delivery system can increase curcumin bioavailability by forming mixed micelles in the gastrointestinal fluids that solubilize and transport the curcumin to the epithelium cells (McClements & Li, 2010; Zou et al., 2015). An advantage to using nanoemulsions rather than emulsions for curcumin encapsulation is that they have better physical stability and a higher bioavailability (McClements and Li, 2010). Conversely, an important limitation of using nanoemulsions is that they have a large specific surface area, and so curcumin is more exposed to reactive substances in the aqueous phase that may promote their degradation (Zou et al., 2015). This problem may be overcome by encapsulating curcumin-loaded lipid droplets inside hydrogel beads (Jones & McClements, 2010; McClements, 2017; Schmitt, Sanchez, Desobry-Banon, & Hardy, 1998). The hydrogel beads should be designed to protect the curcumin from degradation in foods and the gastrointestinal tract, but then release it at an appropriate location where it can be absorbed and exhibit its bioactive effects. A number of previous studies have examined the impact of curcumin encapsulation on its bioavailability and bioactivity (Heger et al., 2014; Zou et al., 2015), but there have been few studies on the impact of encapsulation on its storage stability.

The objective of the current study was to determine the impact of delivery system type on the chemical stability of curcumin when stored under either neutral or acidic conditions so as to represent different kinds of foods. Two different types of food-grade delivery system were investigated: emulsions (curcumin-loaded lipid droplets) and filled hydrogel beads (curcumin-loaded lipid droplets trapped in microgels). The efficacy of these delivery systems was established by comparing them to a system consisting of curcumin dispersed in an aqueous solution. Hydrogel beads with different characteristics were fabricated using two types of ionic polysaccharide: alginate and chitosan; These two polysaccharides were selected because they have opposite charges (George & Abraham, 2006). Alginate is an anionic polysaccharide composed of 1,4′-linked β-D-mannuronic acid and α-L-guluronic acid units, whose negative charge comes from de-protonated carboxylic groups (Gombotz & Wee, 2012; Tønnesen & Karlsen, 2002a). Chitosan is a cationic polysaccharide that consists of D-glucosamine and *N*-acetyl glucosamine units, whose positive charge comes from protonated amino groups (Mohammadian & Madadlou, 2016; Schipper, Olsson, Hoogstraate, Vårum, & Artursson, 1997). The results of this study may be useful for the rational formulation of foods, supplements, and other products containing curcumin.

2. Materials and methods

2.1. Materials

Corn oil was purchased from a local supermarket (Mazola, ACH Foods, Cordova, TN). The following chemicals were purchased from the Sigma-Aldrich Chemical Company (St. Louis, MO): curcumin powder (C 1386, purity 76% assayed by HPLC); alginic acid (A2033) (sodium salt extracted from brown algae, medium viscosity, viscosity of 1% dissolved in water = 15–20 mPa s); chitosan (448,877, medium molecular weight, viscosity of 1 wt % dissolved in 1% acetic acid = 200–800 mPa s); Tween 80 (P1754); Nile Red (N3013). All other chemicals were of analytical grade and were purchased from the Fisher Chemical Company (Thermo Fisher Scientific). Double distilled water, obtained from a water purification system (Nanopure Infinity, Barnstead International, Dubuque, IA), was used to prepare all solutions, emulsions, and hydrogels.

2.2. Preparation of curcumin in different delivery matrices

2.2.1. Aqueous solutions

Curcumin powder (9 mg) was dissolved in 30 ml dimethyl sulfoxide (DMSO) solution. Aqueous solutions of curcumin with different pH values were prepared by pouring 90% (v/v) phosphate buffer solution (5 mM, pH 3.0 or 7.0) into 10% curcumin solution. The final systems contained 3 mg of curcumin per 100 mL of 10% DMSO solution.

2.2.2. Emulsions

A stock emulsion was prepared from 10% (w/w) oil phase (corn oil) and 90% (w/w) aqueous phase (1% w/w Tween 80, 10 mM Phosphate Buffer, pH 6.5). Initially, the oil and aqueous phases were blended together for 2 min using a high shear mixer to form a coarse emulsion (M133/1281-0, Biospec Product, Inc., ESGC, Switzerland), and then they were passed five times through a high-pressure homogenizer at an operating pressure of 12,000 psi (Microfluidizer M-110Y, Microfluidics, Newton, MA USA). The resulting emulsions were stored at 4 °C before being used.

Curcumin powder (0.3 mg/ml) was added to the stock 10% w/w oil-in-water emulsion and the resulting system was stirred for 2 h at 85 °C to fully dissolve the curcumin (SWB-10L-2, Major Science, Inc., CA, USA). This emulsion was then diluted 10-fold using either pH 3 or pH 7 phosphate buffer solution (5 mM), and the resulting systems were adjusted back to the required pH. The final systems therefore contained 1% w/w oil phase and 3 mg of curcumin per 100 mL of emulsion.

2.2.3. Curcumin-loaded filled alginate beads

An aqueous alginate solution was formed by dispersing 1.6% (w/v) alginate in double distilled water and then stirring overnight. A 1% (w/w) curcumin emulsion was then mixed with this alginate solution (1:1 v/v) and then stirred for 1 h in the dark. Curcumin-loaded filled alginate beads were formed by injecting the mixture of curcumin-loaded lipid droplets and alginate into a 10% (w/v) calcium chloride solution using an encapsulation device (Encapsulator B-390, BUSHI, Switzerland). This device had a vibrating nozzle with a diameter of 120 μm, an operating frequency of 1400 Hz, and an electrode potential of 1000 V. The beads were kept in the calcium chloride solution for at least half an hour with constant stirring to ensure crosslinking. The beads were then washed three times with double distilled water to remove any residual crosslinking agent, and then filter dried by placing them in a glass funnel containing filter paper overnight in a refrigerator. The resultant filled alginate beads were stored at 4 °C in the dark before use.