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Curcumin-loaded nanoemulsions stability as affected by the nature and concentration of surfactant

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ABSTRACT

Nanoemulsions containing 0.5% *w/w* corn oil enriched with 0.4% *w/w* curcumin, sodium-alginate (1.0% *w/w*) and 0.5, 1.0 or 2.0% *w/w* of surfactant, were assessed, including particle size (nm), ζ-potential (mV) and turbidity over time. Furthermore, nanoemulsions encapsulation efficiency (EE), antioxidant capacity (AC) and release kinetics were studied. Nanoemulsions showed particle sizes $\leq 400 \pm 3$ nm and effectively reduced droplets interfacial tension with negative ζ-potential values (≤ -37 mV), regardless the concentration of surfactant. Nanoemulsions with 2.0% *w/w* lecithin did not suffer destabilization phenomena during almost 86 days of experiment, whereas those containing Tween 20 or SMP at the same concentrations were destabilized after 5 days or along 24 h, respectively. Despite EE of nanoemulsions was above 75%, just in lecithin-stabilized nanoemulsions it was directly correlated to AC. Therefore, this work contributes to elucidate the influence of lecithin, Tween 20 and SMP on curcumin encapsulation and stabilization of curcumin-loaded nanoemulsions.

1. Introduction

Curcumin is a natural polyphenolic flavonoid obtained from *Curcuma longa*, which is known to be an effective bioactive compound to prevent several diseases like cancer, obesity, infectious disease, and cardiovascular illnesses (Aditya, Shim, Yang, Lee, & Ko, 2014). Moreover, since curcumin, considered as a potential antioxidant and antimicrobial agent, does not show toxicity even at high concentrations, its incorporation to food matrices as natural flavoring additive, yellow colorant and preservative is of great interest for the food industry (Borrin, Georges, Moraes, & Pinho, 2016).

Curcumin, as the majority of natural pigments, presents high instability under external conditions such as physiological pH, high temperature and light (Schneider, Gordon, Edwards, & Luis, 2015). Moreover, a direct addition of curcumin may cause undesirable changes in the organoleptic properties of some food products providing color, spicy flavor and odor thus decreasing their acceptance by consumers (Borrin et al., 2016). And lastly, the hydrophobic nature of curcumin hinders its incorporation in non-fatty foods and causes the fast elimination of curcumin from the body after its intake, with little absorption in the gastrointestinal tract (Aditya et al., 2014).

Nanostructured delivery systems, however, are useful tools to on one hand, protect, carry and release bioactive compounds; and on the other hand, enhance the bioavailability of lipophilic compounds in aqueous media (Sari et al., 2015). Nanoemulsions, defined as colloidal dispersions with average diameters lower than 500 nm can contain lipophilic ingredients as curcumin in the oil phase and be directly added to aqueous or non-fatty food matrices in liquid state (Otoni, Avena-Bustillos, Olsen, Bilbao-Sáinz, & McHugh, 2016).

Nonetheless, the encapsulation and release of bioactive compounds may be influenced by the type of emulsifiers, structural and compositional properties of the emulsion system and other ingredients present within the food matrix (Lee, Liu, Wong, & Liu, 2017). Therefore, the election of the appropriate surfactant has to be related with the chemical nature of the bioactive compound that will be encapsulated and with the desirable characteristics of the resultant nanostructured system. Regarding the lipophilic nature of curcumin, surfactants with a high hydrophilic-lipophilic balance (HLB) are the most suitable for the formation of stable oil-in-water (O/W) emulsions (Lee et al., 2017).

Non-ionic polyoxyethylene sorbitan esters, also called Tweens have been frequently used as surfactant due to their ability to rapidly adsorb to the surface of oil droplets and reduce interfacial tension to prevent droplet coalescence (Degner, Chung, Schlegel, Hutkins, & Mcclements, 2014).

Similarly, sucrose esters resulted efficient in encapsulating lipid compounds when surfactant-oil ratios are high due to their surface-tension-reducing capacity, dispersion, and exceptional detergent power (Sadtler, Guely, Marchal, & Choplin, 2004). Actually, sucrose monoesters such as sucrose monopalmitate, whose chemical structure consists of a lipophilic hydrocarbon tail group (C16:0) and a hydrophilic sucrose

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head group, are non-ionic emulsifiers that are increasingly utilized by the food and beverage industry as they are biodegradable, non-toxic, with good taste and aroma profile (Szuts & Szabó-Révész, 2012).

Furthermore, there is an increasing interest in using surfactants from natural sources as it is the case of lecithins. Lecithins are amphiphile molecules, which consist of a mixture of phospholipids with adherent glycolipids and oil. They have the capacity of acting as good emulsifiers since their polar head groups, which are bound to lipophilic side chains of esterified fatty acids, contain phosphate and nitrogen moieties that can be ionized. This allows lecithin to form a mechanical barrier around the droplets protecting them against destabilization phenomena such as coalescence or flocculation (Klang & Valenta, 2011).

Therefore, the aim of the present work was to assess the role of three molecularly different surfactants and their concentration on the stability of curcumin-loaded nanoemulsions and evaluate their encapsulation efficiency, antioxidant capacity and physicochemical properties.

2. Materials and methods

2.1. Materials

Corn oil (Koipesol Asua, Deoleo, Spain) enriched with curcumin (from *Curcuma longa*, Sigma-Aldrich, Darmstadt, Germany) was used for preparing all the emulsions. Tween 20 was purchased from Panreac (Barcelona, Spain), whereas L-α-Soybean Lecithin and Sucrose Palmitate (90%) were acquired from Alfa Aesar (Thermo Fisher Scientific, Massachusetts, USA). Sodium alginate (MANUCOL®DH) was obtained from FMC Biopolymer Ltd (Scotland, U.K.). Information provided by the manufacturer indicates that viscosity and pH of a 1% solution is 40–90 mPa·s and 5.0–7.5, respectively. Ultrapure water obtained from a Milli-Q filtration system was used to the preparation of all solutions.

2.2. Methods

2.2.1. Nanoemulsions preparation

Nanoemulsions aqueous phase was prepared by solving 1% *w/w* sodium alginate in ultrapure water at 70 °C for 3 h. After reaching room temperature, the corresponding quantity of Tween 20, lecithin or sucrose monopalmitate at concentrations of 0.5, 1.0 or 2.0% *w/w* was mixed with the aqueous phase until complete dissolution. Secondly, corn oil was enriched with 0.4% *w/w* of curcumin solving the pigment in the oil by magnetic stirring overnight at room temperature in dark conditions. Afterwards, 0.5% *w/w* curcumin-enriched corn oil constituting the lipid phase was added to the aqueous mixture and blended with a high-shear homogenizer (T25 digital Ultra-Turrax, IKA, Staufen, Germany) at 11,000 rpm for 2 min, leading to the formation of coarse emulsions. Lastly, nanoemulsions were formed passing their respective coarse emulsions through a microfluidizer (M110P, Microfluidics, Massachusetts, USA) at 150 MPa for 5 cycles. At the outlet of the interaction chamber of the microfluidizer, the product was refrigerated through an external coil immersed in a water bath with ice maintaining the temperature of the samples below 20 °C. Nanoemulsions were prepared avoiding the direct contact with light. Besides, pH of all the blends, which remained constant during microfuidization with values around 6.5, was controlled by a pH-meter (Eutech pH 700, Thermo Scientific, Waltham, Massachusetts, USA).

2.2.2. Physicochemical characterization of emulsions and nanoemulsions

2.2.2.1. Droplet size, size distribution and ζ-potential. Particle size distributions and mean droplet diameter (nm) of emulsions and nanoemulsions were measured by a Zetasizer Nano-ZS laser diffractometer (Malvern Instruments Ltd, Worcestershire, UK) working at 633 nm and 25 °C, equipped with a backscatter detector (173°) (Salvia-Trujillo, Rojas-Graü, Soliva-Fortuny, & Martín-Belloso, 2014).

The ζ-potential (mV), was measured by phase-analysis light scattering (PALS) with a Zetasizer Nano-ZS laser diffractometer (Malvern Instruments Ltd, Worcestershire, UK). It determines the electrical charge at the interface of the droplets dispersed in the aqueous phase.

In both determinations, samples were prior diluted in ultrapure water using a dilution factor of 1:9 sample-to-solvent.

2.2.2.2. Whiteness index. A colorimeter (CR-400, Konica Minolta Sensing Inc., Osaka, Japan) set up for illuminant D65 and 10° observer angle was used to measure the CIE L^*, a^* and b^* parameters of emulsions and nanoemulsions at room temperature. The device was calibrated with a standard white plate (Y = 94.0; x = 0.3133; y = 0.3194). The whiteness index (WI) was calculated with Eq. (1) (Salvia-Trujillo et al., 2014):

$$WI = 100-((100-L^*)^2 + (a^{*2} + b^{*2}))^{0.5} \quad (1)$$

2.2.2.3. Apparent viscosity. Viscosity measurements (mPa·s) were performed by using a vibro-viscometer (SV-10, A&D Company, Tokyo, Japan) vibrating at 30 Hz, with constant amplitude and working at room temperature. Aliquots of 10 mL of each emulsion and nanoemulsion were used for determinations.

2.2.2.4. Turbidity tests. Nanoemulsions turbidity is related to destabilization phenomena such as coalescence, creaming or flocculation among others and was monitored by a Turbiscan Classic (Formulaction, Toulouse, France) during a maximum of 86 days of storage at room temperature. Tests were performed in duplicate.

2.2.2.5. Encapsulation efficiency (%EE) and curcumin rate release. Curcumin-loaded nanoemulsion aliquots of 10 mL were placed inside a dialysis tubing cellulose membrane of 43 mm × 27 mm (Sigma-Aldrich, Darmstadt, Germany) and submerged in 20 mL of food grade ethanol. After centrifuging (2000 rpm, 10 min) with a Hettich® Universal 320 centrifuge (Sigma-Aldrich, Darmstadt, Germany) the non-encapsulated curcumin content (free curcumin) was quantified spectrophotometrically with a V-670 spectrophotometer (Jasco, Tokyo, Japan) at 425 nm. Encapsulation efficiency (%) of the obtained nanoemulsions was calculated by Eq. (2) (Surassmo, Min, Bejrapha, & Choi, 2010):

$$\%EE = \frac{\text{Total amount of curcumin} - \text{Free curcumin}}{\text{Total amount of curcumin}} \times 100 \quad (2)$$

where the total amount of curcumin is the initial concentration of this bioactive compound added to the mixture and the free curcumin is the concentration of compound that was not loaded in nanoemulsions.

All the measurements were performed in triplicate.

In order to monitor the curcumin rate release, aliquots of the samples were taken at times 0, 3, 6 and 24 h and quantified spectrophotometrically with a V-670 spectrophotometer (Jasco, Tokyo, Japan) at 425 nm. The curcumin release was calculated with Eq. (3) according to Surassmo et al. (2010) and fitted to a rectangular hyperbolic curve according to Eq. (4):

$$\%CR = \left(100 - \frac{Total\ amount\ of\ curcumin(t=0) - Released\ curcumin(t=t)}{Total\ amount\ of\ curcumin(t=0)}\right) \times 100 \quad (3)$$

$$CR = \frac{at}{b+t} \quad (4)$$

where CR is the curcumin release expressed in %, t is the time (h), a is the maximum curcumin release (%) and b is a kinetic constant (h).

2.2.2.6. Antioxidant capacity of curcumin. The antioxidant capacity of