Effect of sodium alginate incorporation procedure on the physicochemical properties of nanoemulsions.

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ABSTRACT

The aim of this work was to evaluate the effect of sodium alginate incorporation procedure on the physicochemical properties of nanoemulsions formed by microfluidization. Emulsions prepared consisted of corn oil and Tween 20 as dispersed phase and sodium alginate solution as continuous phase. In order to obtain nanoemulsion A (N_A), both phases were microfluidized together. On the other hand, coarse emulsion without sodium alginate was microfluidized and mixed with a microfluidized (MA) or non-microfluidized (N-MA) sodium alginate solution leading to nanoemulsions B(MA) and B(N-MA), respectively. N_A exhibited the smallest particle size (261 nm) and monomodal distributions with a polydispersity index of 0.25. The ζ-potential, viscosity and WI of N_A were −37 mV, 22.7 mPa s and 57.28, respectively. Spectroscopic, chromatographic and electron microscopic techniques were used to evaluate changes in microfluidized alginate molecules when they were within emulsions. After microfluidization, alginates suffered depolymerization and further rearrangement, changing the disposition of polymer chains around oil droplets and nanoemulsions characteristics. Thus, these results evidence the significant impact of sodium alginate incorporation procedure on the physicochemical properties of nanoemulsions and how it can affect to the stability of the resulting systems which are going to be used as functional ingredients in food matrices.

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1. Introduction

Nanoemulsions are described as colloidal dispersions consisting of oil droplets, with a diameter in the nano-range scale, dispersed into an aqueous phase (Rao & McClements, 2011). Moreover, the presence of a surfactant capable of adsorbing at the oil/water interface of droplets is required to reduce the surface tension and lead to emulsion formation. Oil-in-water nanoemulsions have shown some advantages compared to conventional emulsions. Nanoemulsions present higher physical stability against gravitational processes like flocculation, creaming, sedimentation and coalescence and enhance functionality due to the increase of the surface area of droplets (Guerra-Rosas, Morales-Castro, Ochoa-Martínez, Salvia-Trujillo, & Martín-Belloso, 2016). Moreover, the use of nanoemulsions let diminish the concentration of each component added to the systems minimizing the alterations in the sensorial properties of the food matrix, and also strong light scattering (McClements, 2011). The incorporation of active compounds like certain vitamins, antioxidants or antimicrobials into food matrices represents a challenge due to their low water solubility and high degradability when they are exposed to external factors such as pH, temperature or light (Borrin, Georges, Moraes, & Pinho, 2016). Nanoemulsions appear as systems that could be able to encapsulate, protect and release these compounds effectively (Salvia-Trujillo & McClements, 2015).

On the other hand, the addition of texture modifiers such as biopolymers to the aqueous phase might be useful to improve nanoemulsions stability by reducing droplets movement. Some of these macromolecules, as it is the case of alginates, are capable to interact with surfactant chains disposed around the oil droplets. Hence, they may cause steric and/or electrostatic repulsions between droplet interfaces avoiding destabilization phenomena such as droplets coalescence or gravitational separation (Salvia-Trujillo, Rojas-Graü, Soliva-Fortuny, & Martín-Belloso, 2014a,b). Alginates are linear polysaccharides, which consist of β-D-mannuronic (M) acid and α-L-guluronic (G) acid linked by 1 → 4 bonds that are able to absorb large quantities of water leading to the formation of hydrogels and hence, facilitating the solubility of the alginate chains in the aqueous phase (Lee & Mooney, 2012; Wang, Sun,

Raddatz, & Chen, 2013). In addition, alginates contain functional groups such as carboxylates, which can easily dissociate in the aqueous phase and as a result, provide negative charge to the emulsions (Pereira et al., 2013). Therefore, in presence of multivalent ions, alginates can form polymer networks by a process known as ionic gelation due to their high "gel-forming" capability (Liling et al., 2016). In these networks, linear chains of alginate are connected by ionic interactions resulting in crosslinks called "egg-box". Taking advantage of this property, nanoemulsions containing alginates could be used as films or edible coatings for food matrices (Strobel, Scher, Nitin, & Jeoh, 2016).

The addition procedure of alginate could cause either the increase of nanoemulsions stability or the destabilization of the blends resulting in the loss of functionality. Moreover, it is thought that polysaccharides suffer modifications after microfluidization process due to high shear stress, impact force and hydrodynamic cavitation, which increase the porosity of the biopolymer molecules extending their superficial area (Laneuville, Turgeon, & Paquin, 2013). In this regard, changes in alginate molecules disposed around oil droplets may alter the physicochemical characteristics of nanoemulsions. Therefore, it is necessary to understand the interactions among the alginate and the rest of the components of the nanostructured systems to obtain nanoemulsions with the most appropriated properties according to their further applications.

Thus, the aim of this work was to assess the effect of the incorporation procedure of alginate on the physicochemical properties of nanoemulsions formed by microfluidization to ensure the stability of the resulting systems during the time. And in turn, what changes may cause microfluidization in sodium alginate structure.

2. Materials and methods

2.1. Materials

Corn oil (Koipesol Asua, Deoleo, Spain) and ultrapure water, obtained from a Millipore Milli-Q filtration system (Merck, Darmstadt, Germany) were used for the preparation of all emulsions. Tween 20 was purchased from Panreac (Barcelona, Spain). Sodium alginate (MANUCOL® DH) was provided by FMC Biopolymers Ltd (Scotland, U.K.). Information provided by the manufacturer indicates that viscosity and pH of a solution 1% is 40—90 mPa s and 5.0—7.5, respectively.

2.2. Methods

2.2.1. Nanoemulsions formation

All the oil-in-water emulsions showed a final formulation consisting of 1% w/w lipid phase (corn oil) with 1% w/w of surfactant (Tween 20) and 98% w/w aqueous phase (1% w/w sodium alginate, 99% w/w water). Sodium alginate solutions were prepared by dissolving the sodium alginate in water at 70 °C for 2 h and then cooling it to room temperature. Concerning nanoemulsions preparation, two different procedures were performed in order to evaluate the effect of the sodium alginate incorporation in the properties of nanoemulsions. After characterizing nanoemulsions in terms of particle size, ζ-potential, viscosity, whiteness index and morphology, those nanoemulsions with the most suitable properties, such as lower particle sizes and ζ-potential values, were more deeply studied to assess the effect of microfluidization in sodium alginate structure.

2.2.1.1. Sodium alginate incorporation before coarse emulsion formation. A coarse emulsion (C_A), was prepared by mixing both lipid and aqueous phases and the surfactant using a high-speed blender (T25 digital Ultra-Turrax, IKA, Staufen, Germany) at 11.000 rpm for 2 min, at room temperature. C_A was treated with a microfluidizer (M110P, Microfluidics, Massachusetts, USA) at 150 MPa and 5 cycles, in order to obtain nanoemulsion A (N_A). 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.

2.2.1.2. Sodium alginate incorporation after coarse emulsion formation. The lipid phase, surfactant and ultrapure water were homogenized with the high-speed blender (T25 digital Ultra-Turrax, IKA, Staufen, Germany) at 11.000 rpm for 2 min, at room temperature. The coarse emulsion (C_B) was passed across the microfluidizer (M110P, Microfluidics, Massachusetts, USA) at 150 MPa for 5 cycles to produce a fine emulsion. This fine emulsion was stirred together with a microfluidized alginate solution (MA) (5 cycles and at 150 MPa) or with a non-microfluidized alginate solution (N-MA), both in the corresponding concentration to obtain a final blend with 1% w/w of sodium alginate, during 1 h at room temperature; this led to nanoemulsion B(MA) ($N_{B(MA)}$) or nanoemulsion B(N-MA) ($N_{B(N-MA)}$), respectively.

2.2.2. Physicochemical characterization

2.2.2.1. Particle size and size distributions. The particle size distribution, polydispersity indexes (PdI) and mean droplet diameters (nm) of coarse emulsions and nanoemulsions as well as the particle size of alginate solutions were measured using a laser diffractometer (Nano-ZS Zetasizer, Malvern Instruments, Worcestershire, U.K.) working at 633 nm, 25 °C and equipped with a backscatter detector (173°). Samples were prior diluted in ultrapure water using a dilution ratio of 1:9 sample-to-solvent.

2.2.2.2. ζ-potential. The ζ-potential (mV) of oil droplets in emulsions and nanoemulsions was measured by phase-analysis light scattering (PALS) with a Zetasizer NanoZS laser diffractometer (Malvern Instruments Ltd, Worcestershire, UK). Samples were prior diluted in ultrapure water using a dilution ratio of 1:9 sample-to-solvent.

2.2.2.3. Apparent viscosity. Apparent viscosity measurements (mPa·s) of 10 mL aliquots of coarse emulsions, nanoemulsions and alginate solutions were performed by using a vibro-viscometer (SV-10, A&D Company, Tokyo, Japan) vibrating at 30 Hz and constant amplitude (0.4 mm). The device can detect accurate temperature immediately because the fluid and the detection unit (sensor plates) with small surface area/thermal capacity reach the thermal equilibrium in only a few seconds. Therefore, the measurements were performed at controlled room temperature.

2.2.2.4. Whiteness index. The optical properties of coarse emulsions and nanoemulsions were measured using a colorimeter (Konica Minolta CR-400, Konica Minolta Sensing Inc., Osaka, Japan) at room temperature set up for illuminant D65 and 10° observer angle. The device was calibrated with a standard white plate (Y = 94.0; x = 0.3133; y = 0.3194). Once determined the values of CIE L^*, a^* and b^*; the Whiteness Index (WI) was calculated with Equation (1) (Salvia-Trujillo, Rojas-Graü, Soliva-Fortuny, & Martín-Belloso, 2013):