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Fabrication of oil-in-water nanoemulsions by dual-channel microfluidization using natural emulsifiers: Saponins, phospholipids, proteins, and polysaccharides

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Nanoemulsions are utilized within the food, pharmaceutical, and personal care industries because of their unique physicochemical properties and functional attributes: high optical clarity; prolonged stability; and, enhanced bioavailability. For many applications, it is desirable to utilize natural ingredients to formulate nanoemulsions so as to create “label-friendly” products. In this study, we compared the effectiveness of a number of natural emulsifiers at fabricating corn oil-in-water nanoemulsions using dual-channel microfluidization. These emulsifiers were either amphiphilic biopolymers (whey protein and gum arabic) or biosurfactants (quillaja saponin and soy lecithin). Differences in the surface activities of these emulsifiers were characterized using interfacial tension measurements. The influence of emulsifier type, concentration, and homogenization pressure on the efficiency of nanoemulsion formation was examined. The long-term stability of the fabricated nanoemulsions was also monitored during storage at ambient temperature. For all of the natural emulsifiers, nanoemulsions could be produced by dual-channel microfluidization, with the mean particle diameter decreasing with increasing emulsifier concentration and homogenization pressure. Whey protein isolate and quillaja saponin were more effective at forming nanoemulsions containing fine droplets than gum arabic and soy lecithin, with a lower amount of emulsifier required and smaller droplets being produced. This effect was attributed to faster emulsifier adsorption and a greater reduction in interfacial tension leading to more efficient droplet disruption within the homogenizer for saponins and whey proteins. This study highlights the potential of dual-channel microfluidization for efficiently producing label-friendly nanoemulsions from natural emulsifiers.

1. Introduction

Emulsion-based delivery systems are being increasingly investigated for their potential applications within the food, supplement and pharmaceuticals industries to encapsulate, protect, and release non-polar bioactive compounds, such as polyunsaturated (ω-3) oils, flavonoids, carotenoids, vitamins, and hydrophobic drugs (Ganta, Talekar, Singh, Coleman, & Amiji, 2014; McClements, Decker, & Weiss, 2007; Solans, Izquierdo, Nolla, Azemar, & Garcia-Celma, 2005). Oil-in-water nanoemulsions are particularly promising candidates for the efficient delivery of lipophilic bioactive compounds due to their ease of fabrication, small particle size, and high surface-to-volume ratio (McClements, 2012; Sonneville-Aubrun, Simonnet, & L'alloret, 2004). These attributes can result in high optical clarity, prolonged physical stability, and enhanced bioavailability of encapsulated compounds (McClements, 2012; Sonneville-Aubrun et al., 2004). Oil-in-water nanoemulsions are non-equilibrium, heterogeneous systems containing small oil droplets (diameter < 200 nm) dispersed within an aqueous phase (Wooster, Golding, & Sanguansri, 2008). Emulsifiers play a key role in the development of successful nanoemulsion formulations because they facilitate the formation of small droplets during homogenization by adsorbing to the oil-water interface and reducing the interfacial tension (Schubert & Engel, 2004), and also protect the droplets from aggregation after their formation by generating

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repulsive interactions (usually steric or electrostatic) between the droplets (Tadros, Izquierdo, Esquena, & Solans, 2004; Wooster, Labbett, Sanguansri, & Andrews, 2016). A large number of emulsifiers are available for the formulation of edible emulsions and nanoemulsions, such as polysaccharides, proteins, phospholipids, natural extracts, and synthetic surfactants (Guerra-Rosas, Morales-Castro, Ochoa-Martínez, Salvia-Trujillo, & Martín-Belloso, 2016; Mirhosseini, Tan, Hamid, & Yusof, 2008). The selection of an emulsifier for a particular application depends on its molecular and physicochemical properties, as well as its ease of utilization, legal status, and cost (Kralova & Sjöblom, 2009). Consequently, it is necessary to compare the functional properties of emulsifiers under similar conditions so that manufacturers can select the most appropriate one for a specific product.

Recently, consumers have been demanding products that contain "label friendly" ingredients. Therefore, identifying, developing, and utilizing natural emulsifiers that can be successfully used in edible emulsion products to replace synthetic alternatives has attracted considerable attention (Ozturk & McClements, 2016). Natural biopolymer-based emulsifiers (such as proteins and polysaccharides) have been shown to be effective high molecular weight surface-active agents for forming and stabilizing oil-in-water nanoemulsions (Charoen et al., 2011; Teo et al., 2016). In addition, biosurfactants (such as phospholipids and saponins) have also been shown to be effective low-molecular weight emulsifiers (Ozturk, Argin, Ozilgen, & McClements, 2014; Yang, Leser, Sher, & McClements, 2013).

In this study, we compared the ability of four natural emulsifiers to form and stabilize nanoemulsions prepared using a dual-channel microfluidizer: whey protein isolate (WPI); gum arabic; quillaja saponins; and, soy lecithin. WPI is a protein-based natural emulsifier that is widely used in the food industry (Adjonu, Doran, Torley, & Agboola, 2014). WPI contains a mixture of globular proteins that typically form a relatively thin coating around lipid droplets, and so the steric repulsion between them is relatively short range. As a consequence, the main mechanism inhibiting the aggregation of WPI-coated oil droplets is usually electrostatic repulsion (rather than steric repulsion), which means this type of emulsion is particularly sensitive to pH and ionic strength (McClements, 2004). Moreover, WPI-coated oil droplets are also highly sensitive to temperature because irreversible thermal denaturation of the adsorbed proteins increases the surface hydrophobicity of the droplets, thereby increasing the hydrophobic attraction between them (Kim, Decker, & McClements, 2002; Lam & Nickerson, 2013). Gum arabic is a glycoprotein derived from the acacia Senegal tree that contains three major fractions (Williams & Phillips, 2009). It is one of the most widely used amphiphilic biopolymers to stabilize food emulsions, particularly soft drinks (Ozturk, Argin, Ozilgen, & McClements, 2015). The emulsifying ability of gum arabic can be attributed to a hydrophobic protein fraction that is covalently linked to hydrophilic carbohydrate fractions (Chanamai & McClements, 2001; Williams & Phillips, 2009). The hydrophobic part penetrates into the oil phase and therefore anchors the gum arabic molecules to the oil droplet surfaces, whereas the hydrophilic part protrudes into the surrounding aqueous phase inhibiting droplet aggregation through a combination of steric and electrostatic repulsion (Chanamai & McClements, 2002). Quillaja saponin is a natural extract isolated from the bark of the *Quillaja saponaria* Molina tree (Mitra & Dungan, 1997). The major surface-active components within this extract have been identified to be saponins, which are a kind of glycoside consisting of a sugar moiety attached to a triterpene or steroid aglycone (Mitra & Dungan, 1997). Quillaja saponin is an effective emulsifier because it contains hydrophobic parts (such as triterpenoid rings) that anchor it to oil droplet surfaces and hydrophilic parts (such as carbohydrate groups) that protrude into the aqueous phase and generate a steric repulsion (Pagureva et al., 2016; Stanimirova et al., 2011; Yang, Leser, Sher, & McClements, 2013). Soy lecithin is a natural emulsifier derived from the cell membranes of soybeans (Klang & Valenta, 2011). Naturally, soy lecithin contains a polar head group and two non-polar tails, which means that it is good for forming bilayers and vesicles, but not particularly good at forming emulsions (Kralova, & Sjöblom, 2009; Weete, Betageri, & Griffith, 1994). However, it can be chemically, physically, or enzymatically modified to improve its ability to stabilize oil-in-water nanoemulsions (Weete et al., 1994).

Microfluidization is a widely used and highly efficient method of producing nanoemulsions containing small droplets (Lee & Norton, 2013; McClements, 2011). Conventional microfluidizers typically use a two-step procedure to produce nanoemulsions: (i) a coarse emulsion is created using a high shear mixer; (ii) this coarse emulsion is passed through the microfluidizer to reduce the particle size (Galooyak & Dabir, 2015; Håkansson et al., 2011; Mahdi Jafari, He, & Bhandari, 2006; McClements, 2015; Schultz, Wagner, Urban, & Ulrich, 2004). Studies have shown that the mean particle size and polydispersity index produced by a two-step microfluidizer tend to be smaller when synthetic surfactants are used rather than natural ones (Perrier-Cornet, Marie, & Gervais, 2005; Zhang, Peppard, & Reineccius, 2015). In addition, higher levels of natural emulsifiers are typically required to produce small droplets (He et al., 2011), which often increases formulation costs. This effect can be attributed to two main physicochemical phenomena. First, the slower adsorption rate of some natural emulsifiers provides less inhibition against the re-coalescence of oil droplets after they are disrupted inside the microfluidizer (Jafari, Assadpoor, He, & Bhandari, 2008). Second, oil droplets coated by some natural emulsifiers are more difficult to break down within a homogenizer because they give a higher interfacial tension and elasticity (Mackie, Ridout, Moates, Husband, & Wilde, 2007). In particular, molecular rearrangements and cross-linking of emulsifiers may occur at the droplet surfaces between preparing the initial coarse emulsion premix, and then passing it through the microfluidizer, which may reduce the efficiency of droplet disruption during homogenization. Therefore, it is important to develop an efficient method to manufacture natural emulsifier-stabilized nanoemulsions containing small droplets.

In this study, a one-step dual-channel microfluidization method (Bai & McClements, 2016) was utilized to produce natural emulsifier-stabilized oil-in-water nanoemulsions by separately feeding oil phase and aqueous phase (containing emulsifiers) into the microfluidizer (Fig. 1a). An advantage of this method is that the premix step required to form a coarse emulsion is not required, which reduces the possibility of forming natural emulsifier-coated oil droplets that are resistant to droplet disruption inside the homogenizer. In addition, this technique only requires a single pass of material through the microfluidizer (rather than multiple passes for two-step microfluidizers), which would make it more energy efficient (Stang, Schuchmann, & Schubert, 2001).

The objective of this study was therefore to manufacture oil-in-water nanoemulsions utilizing natural emulsifiers using a dual-channel microfluidization method. The information obtained from this study is important for the design and manufacture of "label friendly" nanoemulsions suitable for utilization within the food, supplement, pharmaceutical, and personal care industries.

2. Experimental

2.1. Materials

Corn oil (Mazola) was purchased from a local grocery store.