Food Chemistry 263 (2018) 283–291

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Effect of spray-drying with organic solvents on the encapsulation, release and stability of fish oil

Cristian Encina[a], Gloria Márquez-Ruiz[b], Francisca Holgado[b], Begoña Giménez[c], Cristina Vergara[d], Paz Robert[a,*]

[a] Departamento de Ciencia de los Alimentos y Tecnología Química, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santos Dumont 964, Independencia, Santiago, Chile
[b] Instituto de Ciencia y Tecnología de Alimentos y Nutrición (ICTAN-CSIC), José Antonio Novais 10, 28040 Madrid, Spain
[c] Departamento de Ciencia y Tecnología de los Alimentos, Facultad Tecnológica, Universidad de Santiago de Chile, Av. Ecuador 3769, Estación Central, Santiago, Chile
[d] Fundación Fraunhofer Chile Research, Av. Mariano Sánchez Fontecilla 310 piso 14, Las Condes, Santiago, Chile

ARTICLE INFO

Keywords:
Microencapsulation
Fish oil
Oxidation
Solvent spray-drying

ABSTRACT

Fish-oil (FO) was encapsulated with hydroxypropylcelullose (HPC) by conventional spray-drying with water (FO-water) and solvent spray-drying with ethanol (FO-EtOH), methanol (FO-MeOH) and acetone (FO-Acet) in order to study the effect of the solvent on the encapsulation efficiency (EE), microparticle properties and stability of FO during storage at 40 °C. Results showed that FO-Acet presented the highest EE of FO (92.0%), followed by FO-EtOH (80.4%), FO-MeOH (75.0%) and FO-water (71.1%). A decrease of the dielectric constant increased the EE of FO, promoting triglyceride-polymer interactions instead of oil-in-water emulsion retention. FO release profile in aqueous model was similar for all FO-microparticles, releasing only the surface FO, according to Higuchi model. Oxidative stability of FO significantly improved by spray-drying with MeOH, both in surface and encapsulated oil fractions. In conclusion, encapsulation of FO by solvent spray-drying can be proposed as an alternative technology for encapsulation of hydrophobic molecules.

1. Introduction

Long-chain omega-3 polyunsaturated fatty acids (LCw3-PUFA), especially eicosapentaenoic (EPA) and docosahexaenoic (DHA) fatty acids are well-known for their health benefits (Yashodhara et al., 2009; Arab-Tehrany et al., 2012). The most important natural sources of EPA and DHA are marine organisms such as fish, seafood and algae. Other omega-3 sources are plant rich in α-linolenic acid (ALA) but, in the human body, the conversion of ALA into EPA and DHA is low (5–10% for EPA and 1–5% for DHA; Kralovec, Zhang, Zhang & Barrow, 2012).

Recommendations from the World Health and North Atlantic Treaty Organizations are 0.3–0.5 g/d of EPA + DHA. Nevertheless, the worldwide average consumption is below these recommendations (Arab-Tehrany et al., 2012). Therefore, healthy foods supplemented with LCw3-PUFA are gaining importance in the food market. However, one of the major drawbacks of oils containing a high amount of LCw3-PUFA, such as fish oils (FO), is their non-desirable off-flavours and high susceptibility to oxidation. Microencapsulation of FO with polymers (Desai & Park, 2005; Gharsallaoui, Rouaut, Chambin, Voilley, & Saurel, 2007) has been proposed as a strategy to retard lipid oxidation, improving the oil stability, prolonging its shelf life, limiting off-flavours and controlling release into food (Arab-Tehrany et al., 2012; Kralovec et al., 2012; Pothakamury & Barbosa-Cánovas, 1995). Recently, Bakry et al. (2015) have summarized the studies on microencapsulation of oils (marine, vegetable and essential oils), and Encina, Vergara, Giménez, Oyarzun-Ampuero, & Robert (2016) have reviewed the studies on conventional spray-drying for the microencapsulation of FO, which is the most common method for encapsulation of FO. Other methods for FO encapsulation have been also reported, such as freeze drying, gelation method, complex coacervation, inclusion complexation, emulsification and nanoencapsulation (Encina et al., 2016).

The conventional method of encapsulation of fish oil by spray drying has been undertaken by preparing o/w emulsions (Aghbashlo, Mobli, Madadlou, & Rafiee, 2013a; Drusch, 2007; Drusch, Serfert, Van Den Heuvel, & Schwarz, 2006), multilayer emulsion (Shaw, McClements, & Decker, 2007) or nano-emulsion of fish oil (Jafari, Assadpoor, Bhandari, & He, 2008). The disadvantages of feed emulsion preparation include the use of high shearing forces such as microfluidization, ultrasonication (von Staszewski, Pizones Ruiz-Henestrosa, & Pilosof, 2014; Ilyasoglu and Nehir, 2014), and high-pressure

* Corresponding author.
E-mail address: proberts@uchile.cl (P. Robert).

https://doi.org/10.1016/j.foodchem.2018.05.026
Received 28 October 2017; Received in revised form 15 April 2018; Accepted 3 May 2018
Available online 04 May 2018
0308-8146/

Table 1
Experimental design for the microencapsulation of fish oil by spray-drying.

Run/System	Ratio FO/HPC [X_1]	Gas inlet temperature (°C) [X_2]	X_1	X_2	FO-MeOH EE (%)	FO-EtOH EE (%)	FO-Acet EE (%)
1	1:1	80	−1	−1	51.9 ± 0.9	47.5 ± 3.3	28.5 ± 0.2
2	1:1	130	−1	+1	57.3 ± 1.0	55.9 ± 5.0	31.5 ± 5.5
3	1:4	80	+1	−1	83.1 ± 1.5	82.0 ± 2.1	95.8 ± 1.7
4	1:4	130	+1	+1	75.0 ± 1.5	89.5 ± 0.7	89.7 ± 1.1
5	1:2.5	75	0	−1.21	75.8 ± 1.4	75.5 ± 0.3	78.2 ± 1.7
6	1:2.5	135	0	+1.21	74.3 ± 1.3	78.0 ± 1.5	75.0 ± 2.0
7	1:0.7	105	−1.21	0	29.4 ± 0.5	40.8 ± 5.5	27.9 ± 4.6
8	1:4.3	105	+1.21	0	82.7 ± 1.5	87.3 ± 2.5	97.7 ± 2.7
9	1:2.5	105	0	0	81.8 ± 1.4	79.9 ± 6.5	79.7 ± 3.6
10	1:2.5	105	0	0	78.9 ± 1.3	71.9 ± 3.0	72.2 ± 4.7
11	1:2.5	105	0	0	72.7 ± 1.3	71.5 ± 0.1	85.2 ± 8.0
12	1:2.5	105	0	0	74.7 ± 1.4	74.0 ± 0.3	79.0 ± 1.8

FO: Fish oil; HPC: Hidroxypropyl cellulose; MeOH: methanol; EtOH: ethanol; Acet: Acetone; EE: Encapsulation efficiency.

homogenization, to diminish the droplet size and to increase the emulsion stability. Solvent spray-drying has been used for drug encapsulation by pharmaceutical industry, where hydrophobic molecules are dissolved in an organic solvent and dried in a closed loop mode at low temperatures using nitrogen as drying medium (Duan, Vogt, Li, Hayes, & Mansour, 2013; Encina et al., 2016). In the case of fish oil microencapsulation, solvent spray-drying could be as a strategy which would avoid the preparation of a fish oil-in-water emulsion and hence minimize lipid oxidation during spray-drying (Serfert, Drusch, Schmidt-Hansberg, Kind, & Schwarz, 2009). In this context, our group recently addressed microencapsulation of fish oil with ethanol as organic solvent (Encina et al., 2018). However, to the best of our knowledge, this is the first study focused on the effect of the type of organic solvent on the FO microparticles properties.

A high number of variables affect oxidation in microencapsulated oils, such as matrix components, drying procedure, water activity, oil globule size and lipid distribution (Márquez-Ruiz, Velasco, & Dobarganes, 2003). Specifically, lipid distribution between surface and encapsulated fractions and heterogeneity of oil globules encapsulated are key factors influencing oxidation in multiphase complex food systems such as microencapsulated oils. Therefore, it is essential to determine the oxidation state separately in surface and encapsulated fractions (Márquez-Ruiz, Velasco, & Dobarganes, 2000; Velasco, Dobarganes, & Márquez-Ruiz, 2000; Márquez-Ruiz, et al., 2003; Velasco, Marmesat, Dobarganes, & Márquez-Ruiz, 2006). The understanding of the supramolecular chemistry of lipid oxidation in multiphase complex food systems has advanced lately with the recognition of the role of micro or nanoemulsions wherein the oxidation and antioxidation sites are the interfaces between lipids and water (Budilarto & Kamal-Eldin, 2015; Ghnimi, Budilarto, & Kamal-Eldin, 2017). In this context, we proposed recently a new antioxidant protection strategy through formation of channels within microencapsulated antioxidants that will aid their diffusion to the lipid medium (Morelo, Márquez-Ruiz, Holgado, Giménez & Robert, 2017). Accordingly, Kamal-Eldin & Ghnimi suggested that such an engineered system could be used to encapsulate PUFA in combination with antioxidants and/or synergists (Kamal-Eldin & Ghnimi, 2017).

The oxidative stability of the microencapsulated FO has been usually evaluated by several methods such as peroxide value, anisidine value, volatile oxidation markers, thiobarbituric acid reactive substances (TBARS) and conjugated dienes (Encina et al., 2016). The measurement of the formation of different groups of oxidation compounds by a combination of adsorption and size exclusion chromatographies is an analytical approach that has been applied to microencapsulated oils and proven to be more complete and sensitive than other methods traditionally used such as peroxide value or TBARS (Márquez-Ruiz et al., 2000; Márquez-Ruiz et al., 2003; Márquez-Ruiz & Dobarganes, 2005).

The aim of this work was to study the influence of the solvent type used in spray-drying for fish oil microencapsulation on the encapsulation parameters, powder properties and fish oil release pattern in an aqueous model. Hydroxypropyl cellulose (HPC), a partially substituted poly(hydroxypropyl) ether of cellulose, was selected as encapsulating agent since this polymer is soluble in both water and organic solvents. Also, oxidative stability of microencapsulated fish oil was determined through separate analysis of surface and encapsulated oil fractions.

2. Material and methods

2.1. Materials

Fish oil (FO) was donated by Spes S.A. (Santiago, Chile). The major fatty acids were 18.3 ± 0.0% (EPA, C20:5 ω3), 11.7 ± 0.1% (DHA, C22:6 ω3), 15.5 ± 0.0% (C16:0), 8.8 ± 0.1% (C16:1 ω9 cis), 7.6 ± 0.1% (C18:1 ω9 cis) and 7.6 ± 0.0% (C14:0). The initial values of oxidation compounds and peroxide value were 5.7 ± 0.2% and 0.7 ± 0.03 mEq O_2/kg oil, respectively. Hydroxypropyl cellulose (KLUCEL®, HPC) was obtained from Laboratorios Saval S.A. (Santiago, Chile). Soy lecithin (Epikuron 145V) was supplied by Blumos Ltda. (Santiago, Chile). Ethanol, acetone, methanol, hexane, chloroform, diethyl ether, petroleum ether, anhydrous sodium sulfate and acetic acid were of analytical grade and were purchased from Merck (Santiago, Chile). Silica cartridges for solid-phase extraction (SPE) were Sep-Pack Vac Silica (6 cc/1g) columns were supplied by Waters (Milford, USA). Tricosanoic acid and monostearin (purity > 99%) were purchased from Nu-Check-Prep (Elysian, USA). Tetrahydrofuran (HPLC grade) was supplied by Merck (Santiago, Chile).

2.2. Methods

2.2.1. Preparation of fish oil microparticles by solvent spray-drying

FO microparticle systems with HPC in either ethanol (FO-EtOH), methanol (FO-MeOH) or acetone (FO-Acet) were performed using a central composite + star design with 12 runs (4 experimental points, 4 star points, and 4 central points) for each system (Table 1). The FO/HPC ratio (X_1) (1:0.7–1:4.3) and the air inlet temperature (X_2) (75–135 °C) were evaluated as independent variables. These experimental conditions were selected according to previous studies (Encina et al., 2016; Encina et al., 2018). FO encapsulation efficiency (EE) was the response variable. The data were fitted to a second-order regression model (Eq. (1)). All of the experiments were conducted randomly to avoid systematic bias.

$$EE = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 + \varepsilon \quad (1)$$

where EE is the dependent variable predicted by the model (FO encapsulation efficiency); β0 the constant coefficient of the intercept; β_1