ENCAPSULATION OF CAROTENOID-RICH PAPRIKA OLEORESIN THROUGH TRADITIONAL AND NANO SPRAY DRYING

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ABSTRACT

The objective of this research was to evaluate the physicochemical properties and stability during controlled storage of the particles of oleoresin paprika (*Capsicum annuum* L.) produced by Micro and Nano spray dryer. Micro and Nano spray dryer produced micro and submicron particles, respectively. Micro and submicron particles exhibited similar values of solubility, but showed significant differences in all parameters of colour and in the moisture content and water activity. At the end of spray dried process, both powders presented significant differences in the carotenes recovery. Micro- particles showed higher content of carotenes on the surface than the submicron particles. However, both particles showed similar protection to the carotenes at the end of storage. The best storage condition for both particles was around water activity (a_w) of 0.529 with about 50% carotenes retained at 30 days.

Keywords: carotenes, encapsulation, microcapsules, oleoresin, powder

1. INTRODUCTION

Oleoresin paprika (*Capsicum annuum* L.) is a lipophilic matrix obtained by pepper fruit processing and is mainly used as a natural food colourant due to its carotenoid pigments (RASCÓN *et al*., 2011). However, carotenes are highly susceptible to degradation during the processing and storage of foods (RODRÍGUEZ-AMAYA, 2016). The polyenic structure of carotenoid pigments is responsible for their colourant properties, antioxidant activities and biological functions. It also makes them very sensitive to heat, light and prooxidant conditions, promoting isomerisation and oxidation reactions, which diminishes their activities (RASCÓN *et al*., 2015). So, it is necessary to implement a strategy to prevent carotenoid degradation in paprika oleoresin and minimise their contact with oxygen. Nanoemulsions are used as vehicles for the encapsulation of various compounds (MEHRNIA *et al*., 2017). Encapsulation of the paprika emulsions is a technique may be used to protect the principal components of paprika and to improve their stability during processing and storage. The formation of micro- particles was the main focus of research and development efforts in the 1980s, whereas the formation of submicron and nano particles had been the focus of more recent efforts (JAFARI *et al*., 2017). Micro- and submicron particles have been incorporated into many types of food and beverage products, having a wide range of food applications (MIHINDUKULASURIYA and Lim, 2013). There are several methods for producing micro- and submicron particles, such as the spray drying is a widely available and low-cost technique that has been used extensively to transform liquids into solid powders, facilitating the handling of sensitive food ingredients and providing high storage stability powders (LI *et al*., 2010). The speed of the process and consequently, the short drying time, enables the drying of temperature-sensitive products without degradation (SCHUCK *et al*., 2008). Several spray dryers have been used in the production of microcapsules. In the typical spray drying process a liquid feedstock is atomized into a spray of fine droplets and then brought into contact with the hot drying gas at sufficient temperature for the moisture evaporation to take place (LEE *et al*., 2011) and it regularly encompasses four fundamental steps: atomization of feed into a spray, spray–air contact, drying of spray, and separation of dried product from the drying air (MASTER, 1976). However, traditional atomizers do not allow the generation of solid particles in the submicron range (ARPAGAUS *et al*., 2018). In addition, Buchi® has introduced a laboratory scale spray dryer that is able to generate submicron particles in the size range of 300 nm to 5 μm for milligram sample quantities at high yields (ARPAGAUS *et al*., 2018; BUCHI, 2018; SCHMID *et al*., 2010). This equipment had a vibrating mesh technology for fine droplets generation and a piezoelectric crystal driven spray head is incorporated with a small spray cap that contains a thin perforated membrane (spray mesh) having an array of precise micron-sized holes. However, it is important to know the properties and advantages of the particles developed by Micro and Nano spray drying to select the most appropriate equipment for a specific application. Therefore, the objective of this work was to evaluate the physicochemical properties and stability during the storage of particles of paprika oleoresin rich in carotenes obtained by the Büchi Micro and Nano Spray Dryer.

2. MATERIAL S AND METHODS

2.1. Material, chemicals and reagents

Paprika oleoresin with carotenoid content of 67560 $\mu g/g$ was obtained from AMCO (Xalapa, Veracruz, Mexico city, Mexico). Maltodextrin (10 dextrose equivalents, DE) was purchased from INALMALT (Mexico), Acetone and distillated water was HPLC grade.

2.2. Preparation of micro- and submicron particles by spray drying

To preparation of particles, nanoemulsion was prepared by combining paprika oleoresin (1 g), canola oil (9 g), surfactant (6 g; Tween 20, hydrophilic-lipophilic balance, HLB = 16.7), distilled water (54 g) and the wall material, maltodextrin 10 DE (30 g). The mixture was allowed to stand for 24 h and then 50 g of sample were ultrasonicated (Digital Sonifier 250D, Branson, USA) at 35% amplitude with pulsations of 5 x 5 s during 5 min, in an ice bath to keep the temperature constant (<40°C). Finally, the mixture was microfluidized at 30 MPa (microfluidizer M110PII, Microfluidics, USA) for 11 cycles, to achieve a particle size less than 100 nm.

Micro- particles were prepared from the selected emulsion using a mini Büchi 290 Spray Dryer (Flawil, Switzerland). The operating conditions for the dryer were: inlet air temperature of 150 °C and outlet air temperature of 90 °C. The spray flow rate of the feed solution was 6.66 x 10^{-4} L/s and the atomization pressure of the air gas was 543.80 kg/m^2. A 4 x 10^{-4} m diameter nozzle was used, the aspirator was set at 70% of the maximum capacity and the volumetric flow of the drying air was about 28 m^3/h. The feed rate was 2.5 mL/min. The micro- particles were recovered from the collecting chamber, weighed into amber bottles and maintained under a nitrogen atmosphere until analysis.

Submicron particles were prepared from the selected diluted nano-emulsion (1:20 v/v) using a B-90 Nano Spray Dryer (Flawil, Switzerland). The input temperature was 110 °C, the feed rate ranged from 5–35 mL/min, the volumetric flow of the drying air was 6 m^3/h and a spray mesh of 5.5 μm pore diameter was used. The fine droplets were dried into solid particles, which were collected by electrostatic charging and deflected to the collecting electrode (LI *et al*., 2010).

2.3. Retention and encapsulation efficiency of carotenes after spray drying

The retention of the carotenes after spray drying was evaluated by yield, non-encapsulated (superficial) carotenes content and encapsulation efficiency for both processes (micro- and submicron particles). The yield encapsulation percentage was defined as the ratio of total carotenoid in the final dried micro- particles to that in the emulsion. Carotenes concentration in the emulsion and particles was determined spectrophotometrically, as proposed by HORNERO and MÍNGUEZ (2001) using following equations:

$$C^R = \frac{A_{508}x\ 2144.0 - A_{472}\,x\ 403.3}{270.9}\ (\mu g/mL)$$

$$C^Y = \frac{A_{472}\,x\ 1724.3 - A_{508}\,x\ 2450.1}{270.9}\ (\mu g/mL)$$

$$C^T = C^R + C^Y (\mu g/mL)$$

Where A represents the absorbance at specific wavelength, C_R represents the red isochromatic fraction content, C_Y represents the yellow isochromatic fraction content, and C_T represents total carotenoid content.
Quantification of carotenes in the emulsion (control experiment) prior to encapsulation was necessary for determination of yield and encapsulation efficiency. Both particles (0.025 g) were dissolved in a volumetric flask containing 100 mL of acetone, and then filtered and the absorbance measured in a diode array spectrophotometer (Agilent model 8453, USA) at 454 nm. Surface carotene in both powders was assessed using the method described by WAGNER and WARTHESEN (1995). Briefly, triplicate samples (50 mg) of powder were weighed into test tubes and extracted with 25 mL hexane. After shaking (100 rpm) for 15 s, the powder particles were centrifuged at 1000 × *g* for 1 min and the carotenes concentration in the supernatant measured at 454 nm. The percentage of surface carotenes was determined by dividing the surface concentration by the total carotenes concentration in the powder. Encapsulation efficiency was calculated considering the total carotenes in the capsules, including carotenes on the surface of the capsules and non-encapsulated (superficial) carotenes.

2.4. Physicochemical properties of the particles

The moisture content was determined gravimetrically using vacuum oven-drying at 60 °C to constant weight. The a_w of the spray-dried powders was measured using an a_w meter (AquaLab, 3TE, Decagon, USA). The solubility of the particles was determined by a gravimetric method, which involved adding 0.5 g of the sample to an Erlenmeyer flask containing 50 mL of distilled water and homogenising at 6 *x g* at room temperature for 30 min. Then, the solution was centrifuged at 3000 × *g* for 5 min before a 25-mL aliquot of the supernatant was transferred to a previously weighed Petri dish and maintained in an oven at 105 °C until complete evaporation of the water. The dishes were weighed and the solubility was calculated from the weight difference (CANO-CHAUCA *et al*., 2005). The colour was analysed using a ColorFlex V1-72 colourimeter (Hunter Lab, Reston VA, USA) by measuring the L*, a* and b* parameters and subsequently calculating the secondary hue angle (H°) and Chroma (C*). The range of diameter of the particles was determined using image analysis with the image j 7.50i software.

2.5. Physical properties of the particles

Bulk density, tapped bulk density, particle density, compressibility, and the angle of repose were determined. The particle density was measured by a pycnometric method using toluene. Bulk density was determined in 2 g of powder, which was loosely weighed into a 10-mL graduated cylinder. The final volume was recorded and the bulk density was calculated by dividing the sample weight by the volume. The compact density was determined by the method of "Tappin" in which 2–5 g of particles was placed in a 10-mL test tube. The probe was hit on a flat surface until constant volume. The percentage compressibility was determined as the ratio of the compression volume to the initial volume. For the angle of repose test, 5 g of sample was weighed and added to a dropping funnel which was placed at 10 cm above a flat surface. The height of the cone formed and its radius was measured.

2.6. Antioxidant activity by the linoleic acid method

The total antioxidant activity in the extract of the microcapsules was performed by the linoleic acid method. First a solution of β-carotene in chloroform (3.34 mg/mL) was added

to a flask containing 40 mg of linoleic acid and 400 mg of Tween 20 and mixed. Then, the chloroform was then removed by rotary evaporation at 40 °C for 5 min before 100 mL of distilled water was slowly added to the residue, with vigorous stirring, to form an emulsion.
By other hand, both particles (0.025 g) were dissolved in a volumetric flask containing 100 mL of acetone, and then filtered and prepared to tubes containing 0.2 mL at 200 mg/mL of the antioxidant solution (sample). Then, aliquots of the emulsion (5mL) were transferred into different test tubes containing 0.2 mL of samples to different concentration. The tubes were placed in a water bath at 40 °C and absorbance at 470 nm was recorded at initial time (t=0) and each 15 min intervals for 120 min. A blank consisting of an emulsion without β-carotene and 0.2 mL of ethanol in 5 mL of emulsion was used as the control. The antioxidant activity by using the following equation:

$$AA = \left(1\ \frac{A_0 - A_t}{A_0^0 - A_t^0}\right) x\ 100$$

Where, A_0 and A_0^0 are the absorbance values measured at initial time for sample and control, respectively, while, A_t and A_t^0 are the absorbance values measured in the samples and control, respectively at t=120 min.

2.7. The carotenes degradation kinetics

The spray-dried powders were placed in desiccators equilibrated to various a_w (0.108, 0.318, 0.515 and 0.743) using saturated salt solutions, and temperatures (25, 35 and 45 °C) during 30 days. The degradation kinetics of the total micro- and submicron particles carotenes was respectively evaluated according to HATEGEKIMANA *et al.* (2015). A first-order model was used to fit the thermal degradation data of the carotenes (CHEN *et al.*, 2009), using the following equations:

$$\ln\left(\frac{C_t}{C_0}\right) = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

Where, C_0 and C_t are the quality parameters at time zero and time t (days), respectively, k is the first-order kinetic constant and $t_{1/2}$ is the time (days) required for the total carotenoid content to decrease by 50%.

2.8. Moisture sorption isotherms of the particles

Moisture sorption isotherm of the micro- and submicron particles were determined by the dynamic dew point isotherm (DDI) method in a vapour sorption analyser (AquaLab VSA, Decagon Devices Inc., Pullman, WA, USA) within the a_w range of 0.1–0.850 at 25 °C. The samples used in each analysis were first dried over phosphorus pentoxide (P_2O_5) until the weight variation at 25 °C was less than 0.01%. Then, one gram of each sample was placed in the equipment to make the isotherm. The equipment was programmed so that the sample was maintained in each relative humidity until reaching equilibrium, that is, the

weight variation was less than 0.01%. The moisture sorption isotherm data were correlated to the a_w (relative humidity) using the Guggenheim–Anderson–de Boer (GAB) equation according to WEISSER (1985).

$$M = \frac{M_0 C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$$

Where a_w is water activity; M is water content of the sample on dry basis; M_0 is the monolayer water content; C is the Guggenheim constant; and *K* is the constant correcting properties of multilayer molecules with respect to bulk liquid. The parameters values of GAB equation (M0, C and k) were estimated by fitting the mathematical model to the experimental data, using non-linear regression using the Kaleidagraph 4.0 package (Synergy Software, 2457 Perkiomen Avenue Reading, PA 19606-2049, USA).

2.9. Scanning Electron Microscopy

For visualising the outer topography of the micro- and submicron particles, the particles were equilibrated at 0.529 a_w using a supersaturated solution of magnesium nitrate and then the specimen was mounted on a holder with double-sided adhesive tape. The structure of the particles was observed after coating the specimens with gold and examining under a Quanta FEG 250 scanning electron microscope.

2.10. Statistical analysis

All experiments were performed on triplicate samples and were repeated at least twice. Differences between means were determined by Tukey's test ($P < 0.05$) using one-way analysis of variance (ANOVA) followed by the multiple comparison procedure (Hol-Sidak method) with Minitab release 12 software.

3. RESULTS AND DISCUSSION

3.1. Micro- and submicron particles properties

According with image analysis Micro and Nano spray dryer produce micro- particles and submicron particles with a range of diameters of 1-250 μm and 0.5-10 μm, respectively. The evaluation of the micro- and submicron particles immediately after spray drying revealed that the micro- particles had a higher ($P \leq 0.001$) moisture content (1.40 versus 0.50 g/100g) and a_w (0.465 versus 0.011) compared to the submicron particles (Table 1). Similarly, submicron particles resulted in higher carotenes retention (71.40 mg/mL) than micro- particles (46.37 mg/mL) at the end of the drying process, which was reflected in the submicron encapsulation yield (63.46%), based on the carotenes concentration. The submicron particles also showed higher encapsulation efficiency (98.50%) than the micro-particles (81.15%), indicating a higher concentration and better protection of carotenes within the submicron particles, which was reflected in the colour parameters. The micro-particles had colour parameter values (a* = 29.30, b* = 59.71, L* = 66.13) significantly different ($P \leq 0.05$) from the submicron particles (a* = 0.06, b* = 13.74, L* = 92.20), possibly due to the comparably lower concentration of carotenes on the surface of the submicron

particles. The difference in physicochemical properties between micro- and submicron particles may be due to the different drying temperature used by each of the spray dryers.

Table 1. Physicochemical properties of micro- and submicron particles the oleoresin of paprika obtained by Micro and Nano spray drying technology.

Property	Micro- particles	Submicron particles
Moisture content (g/100 g)	1.40±0.11^{b}	0.50±0.00^{a}
Solubility (g/100 g)	7.08±1.15^{a}	9.88±1.68^{a}
a_w	0.465±0.00^{b}	0.011±0.01^{a}
Total carotenes (mg/mL)	46.37±0.05^{a}	71.40±0.01^{b}
Antioxidant activity (%)	80.00±0.01^{a}	78.26±0.01^{a}
Encapsulation Yield (%)	41.21±5.20^{a}	63.46±4.50^{b}
Surface carotenes (%)	19.30±2.50^{b}	1.49±0.05^{a}
Encapsulation Efficiency (%)	81.15±2.20^{a}	98.50±2.10^{b}
Colour parameters		
L	66.13±0.12^{a}	92.20±0.17^{b}
a	29.30±0.28^{b}	0.06±0.16^{a}
b	59.71±0.12^{b}	13.74±0.27^{a}
Hue angle (°)	63.85±0.17^{a}	87.37±0.75^{b}
Chroma	66.51±0.24^{b}	13.75±0.26^{a}
Bulk density (kg/m^3)	350.25±0.00^{b}	240.50±0.00^{a}
Tapped density (kg/m^3)	480.30±10.50^{b}	330.40±20.00^{a}
Particle density (kg/m^3)	250.10±30.25^{a}	200.15±32.40^{a}
Angle of repose (°)	28.89±2.02^{a}	24.70±0.57^{a}
Compressibility (%)	27.36±3.23^{a}	29.56±0.58^{a}
Haussner index	1.37±0.06^{a}	1.34±0.12^{a}

Results are expressed as the mean (n=3)±SD. Means followed in same row are significantly different by Tukey's test (p<0.05).

Since, higher moisture content and some physicochemical properties of the micro particles is associated to lower outlet temperature (GOULA and ADAMOPOULOS, 2005) and the higher temperature used in this process of drying, which was slightly higher during micro- than submicron encapsulation (GOULA and ADAMOPOULOS, 2005). Drying outlet temperature used in the traditional Micro and Nano spray dryers was 90 and 110°C, respectively. The micro- particles had a high concentration (around 19%) of superficial carotenes, whereas the submicron particles presented only 1.49% non-encapsulated carotenes, which helps explain why the micro- particles had a relatively lower encapsulation efficiency. Similar results were reported when pure β-carotene was microencapsulated using traditional spray drying (DESOBRY *et al*., 1999). These results on surface oil coincide with those reported by JAFARI *et al*. (2007), who found that large particles contain more un-capsulated oil on their surface than the smaller particles. These differences in performance and encapsulation efficiency between the micro- and submicron particles have been explained by other authors, who mention that the performance of the encapsulation during the drying process depends of equipment design differences, while the retention rate of the core is associated with the physicochemical properties and characteristics of both the core and the wall material used in the

encapsulation (NUNES and MERCADANTE, 2007). The outlet temperature of the Nano Spray Dryer was higher than that exhibited by the Micro Spray Dryer, possibly resulting in faster crust formation (or solidification) of the particles which may be associated with lower levels of superficial carotenes (JAFARI *et al*., 2008). Despite the difference in carotene retention, both particles showed a similar antioxidant activity (about 80%), suggesting that in the micro- particles, components other than the carotenes present in paprika oleoresin, such as polyphenols, might confer certain antioxidant activity (MUDRIĆ *et al*., 2017). ABBEDDOU *et al*. (2013) explained that the degradation of carotenes did not imply a decrease in the antioxidant activity of the processed product.
On the other hand, the flow properties were evaluated to help characterize the particles obtained for both methods. Micro- and submicron particles showed significant differences ($P \leq 0.05$) in the bulk and tapped density. The bulk density was 350 and 240 kg/m^3 whilst tapped density was 480.30 and 330.40 kg/m^3 for the micro- and submicron particles, respectively. Instead, micro- and submicron particles no showed significant differences ($P > 0.05$) in the angle of repose, compressibility percentage and Haussner index. The mechanical properties of the micro- and submicron particles are influence their stability during transport, storage and packaging design (FERY and WEINKAMER, 2007) and differences in the values of bulk density between micro- and submicron particles suggest a high tendency to brittle fracture, which may influence the flow properties (KAGAMI *et al*., 2003). The bulk density values for both particles are in the range of reported for folic microcapsules (ASSADPOUR and JAFARI, 2017). There was no significant difference between the micro- and submicron particles in the angle of repose, compressibility and Haussner index, suggesting that both capsules have poor flow and strong cohesiveness of the powder (ABDULLAH and GELDART, 1999). These properties are possibly due to the high hygroscopicity of the maltodextrin used as the wall material. The particle density is an important parameter because it considers the volume occupied by the capsules, without considering the volume of the pores of the capsule. According to the results obtained, the micro- and submicron particles had similar values of particle density explaining their similar solubility.

3.2. Degradation of carotenes in controlled storage conditions

The use of mathematical models for the release of bioactive compounds provides information on the processes of mass transfer and the influence of parameters such as the morphology and distribution of encapsulated compounds (ASSADPOUR *et al*., 2017). Table 2 shows the degradation kinetics of carotenes degradation of micro- and submicron particles during storage at various temperatures and water activities. The micro-particles presented two stages of degradation. A first stage with a rapid degradation rate with *k* values ranging from 0.039 to 0.087 days^{-1} and a second stage with a lower degradation rate with *k* values of 0.009 to 0.030 days^{-1} derived from retention of the carotenes inside the capsule. In the first stage the highest percentage of retained carotenes is degraded. It can be observed that the half-life varied from 7.96 to 19.80 days, being smaller when the micro-particles were stored at higher water activities. The time corresponding to the change in the slope between two stages was longer in micro- particles stored at 25 °C and 0.529 a_w. The submicron particles presented a single stage of degradation with higher degradation of carotenes when the samples were stored at 0.729 of water activity and 45 °C. The carotenes degradation in submicron particles showed a good fit to a first-order reaction.
Micro- and submicron particles showed higher carotenes retention when the samples were stored at 0.529 a_w at 25 °C, and under these conditions, a 40 and 50% retention of the carotenes was estimated by micro- and submicron particles, respectively at the end of 30 days of storage (Fig. 1).

Table 2. Kinetic parameters of the degradation of carotene micro- and submicron particles under different water activity and temperature storage conditions.

T(°C)	a_w	Submicron particles (Single stage)		Micro- particles First stage		Second stage	
		k (days^{-1})	$t_{1/2}$ (days)	k (days^{-1})	$t_{1/2}$ (days)	k (days^{-1})	$t_{1/2}$ (days)
25	0.328	0.023	29.61	0.047	17.74	0.012	57.75
	0.529	0.021	33.00	0.035	19.80	0.009	77.00
	0.753	0.022	31.50	0.054	12.83	0.014	49.50
35	0.321	0.028	24.06	0.067	10.34	0.018	38.50
	0.515	0.024	28.87	0.039	17.76	0.021	33.00
	0.743	0.029	23.89	0.060	11.55	0.025	27.72
45	0.309	0.037	18.72	0.055	12.60	0.024	28.87
	0.496	0.032	21.65	0.075	9.24	0.020	34.65
	0.729	0.039	17.76	0.087	7.96	0.030	23.10

Coefficient of determination (R^2) of the degradation of carotene was higher than 0.80 was in all case. Data are mean of three determinations (n=3).

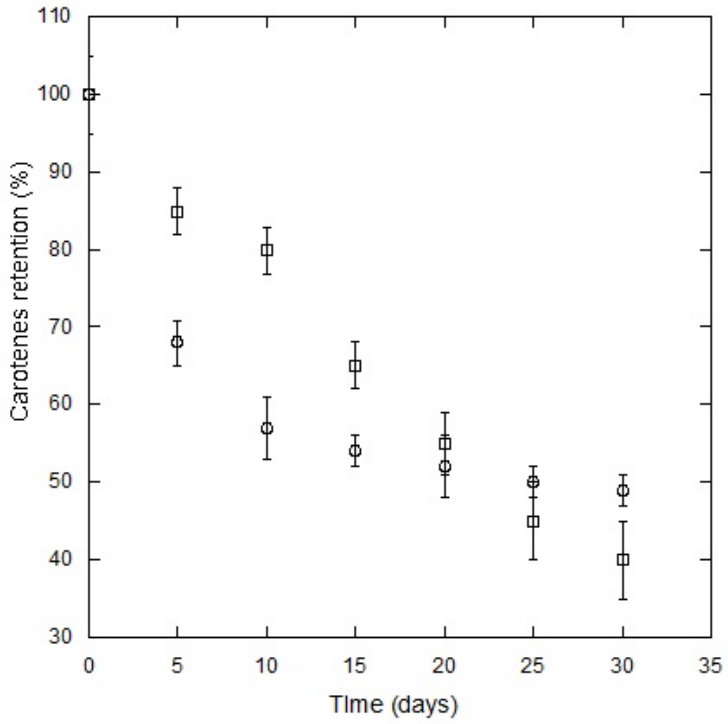

Figure 1. Carotenes retention (%) in micro- (○) submicron (□) particles obtained by spray drying and stored at 0.529 water activity at 25 °C during 30 days.

In both particles, the retention of carotenes depended on water activity and storage temperature, being higher in the range of water activities from 0.496 to 0.529 and at 25 °C. The differences in the kinetics of degradation between micro and submicron particles may be due to the fact that micro- particles have a higher concentration of carotenes on the surface compared to submicron particles, which is mostly exposed to environmental

conditions (light, oxygen and moisture) favouring the degradation of carotenes present on the surface. This same behaviour has previously been reported for the degradation of carotenes microencapsulated using maltodextrin as wall material (DESOBRY *et al*., 1999). Possibly, the lower retention of the micro- particles compared to the submicron particles at the end of the storage is due to the fact that the retention of the encapsulated carotenes depends on the particle size and the carotene content on the surface of the particle, as well as the state of the material of wall used in the encapsulation. It has been reported that low water activities maltodextrin had pores on the surface of the capsules favour carotene oxidation, whereas at higher water activities, the maltodextrin collapse, causing release and degradation of the carotenes (DESOBRY *et al*., 1999). So, an intermediate water activity would favor its stability. In turn, submicron particles have a larger surface area so water can be adsorbed onto the surface of carbohydrates at their polar sites; the dissolution of carbohydrates occurs favouring the degradation of encapsulated carotenes (AYRANCI *et al*., 1990).

The isotherm showed a type III form, according to the Brunauer-Emmet-Teller classification (VALENZUELA and AGUILERA, 2015). As shown in Fig. 2 there is no effect of the size of the particle on the water adsorption isotherm possibly this is due to other factors that affect the adsorption capacity such as pore volume, number of pores, pore diameters, total area of pores, distribution and shape of the particle, among others (ZOU and REZAEE, 2016, CHEN *et al*., 2017, ABDUL-MANAP *et al*., 2018). The water absorption isotherms and the GAB parameters of the micro and submicron particles were similar, indicating that particles exhibit similar behaviour in the equilibrium. In this work, the monolayer moisture content for the submicron (4.631 g H_2O/100 g) and micro- particles (4.531 g H_2O/100 g) was very similar and, in both instances and the value of the monolayer corresponded to the water activity about 0.500, which is close to that which provides the least carotenes degradation, corroborating that the best stability conditions for both particles is in the range 0.496- 0.529 a_w when the samples are stored at 25 °C.

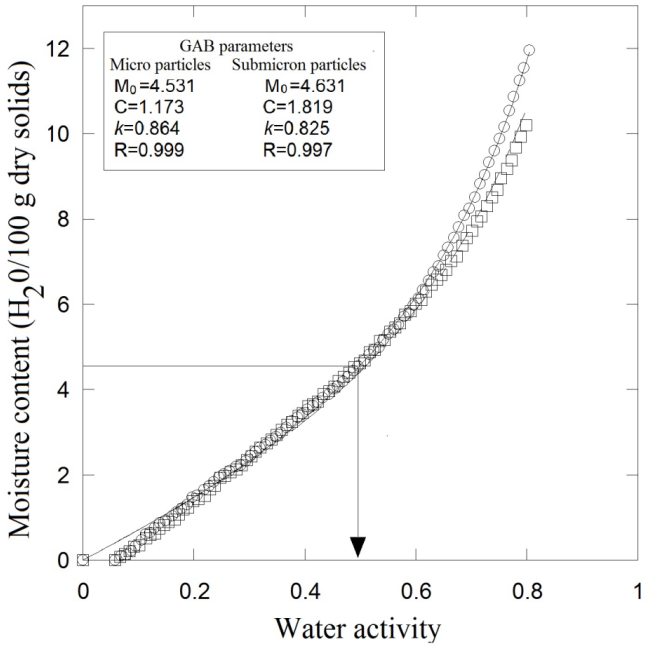

Figure 2. Water sorption isotherms of micro- (○) submicron (□) particles of paprika oleoresin with maltodextrin obtained at 25 °C.

The shape of the isotherm and the estimated GAB parameters are similar to those reported for juçara pulp microcapsules using maltodextrin as wall material (BIGETTI-GUERGOLETTO *et al*., 2017). It is well-known that the estimation of the monolayer moisture content and a_w, respectively, is important to define the conditions affording the highest stability and proper storage conditions (Kaya and Kahyaoglu, 2005). It has been reported that the monolayer moisture content corresponds to the minimum integral entropy zone, which the water molecules are best organized and less available to take part in reactions, because this humidity level, sufficient water was absorbed by the capsules to form a dough-like mass which acts as a shell opposed to oxygen diffusion into the capsule core, inasmuch as water is absorbed without initiating the wall dissolution process (BERISTAIN *et al*., 2002).

3.3. Particle morphology

The scanning electron micrographs of the particles (Fig. 3) and image analysis illustrated that the micro- particles stored at 0.529 a_w at 25 °C, were spherical with a smooth surface. In contrast, the submicron particles were spherical but much smaller with a rough.

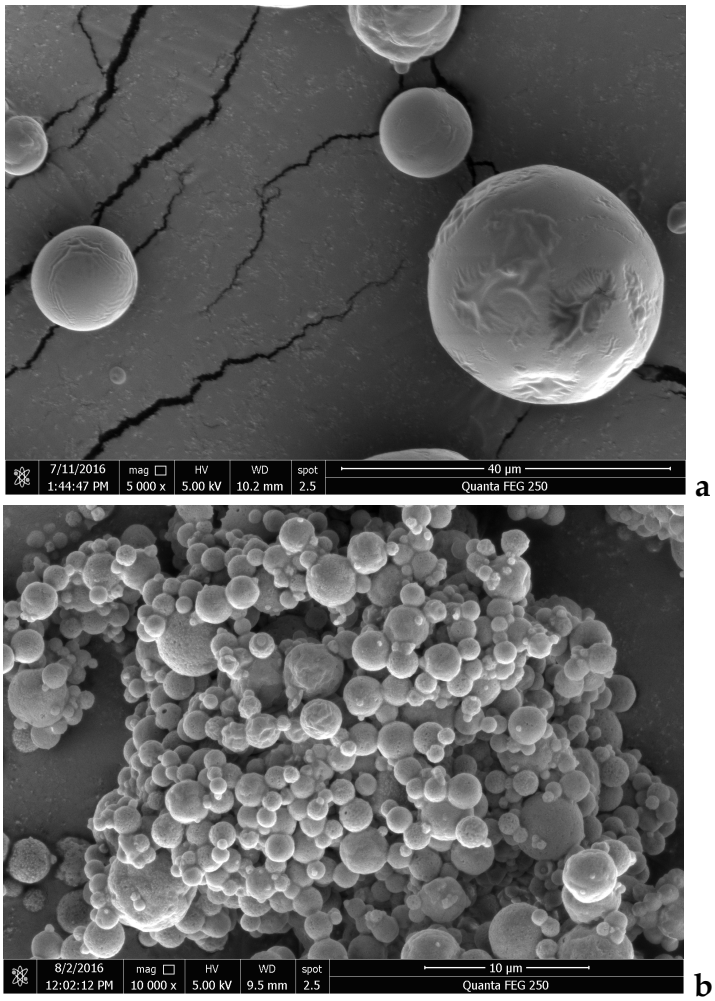

Figure 3. Scanning electron micrographs of the (a) micro- and (b) submicron particles, equilibrated at 0.529 water activity at 25 °C.

The differences in the morphology and particle size of the micro- and submicron particles are mainly due to the type of nozzle and formation of the drop during the drying process. Nano Spray Dryer uses vibration mesh technology, creating tiny droplets (before evaporation), making possible to produce powder with narrow distribution in the range of submicron particles (Li *et al*., 2010).
Particle size plays is also influenced by other factors, like shape, surface texture, and surface roughness. Similar morphology has been shown for starch capsules, displaying a smooth but depressed surface where smaller particles tended to agglomerate among themselves (HATEGEKIMANA *et al*., 2015). In addition, the powder particle size depends on the method used to obtain the capsules, the process parameters and the emulsion properties. The formation of indented surfaces of the micro- particles during spray drying is attributed to particle shrinkage during the drying process at low or high inlet temperatures. The particle shrinkage could be caused by the rapid evaporation and high pressure found inside the particles (ALAMILLA-BELTRÁN *et al*., 2005). These irregularities on the surface may favour a porous structure, in which there is a better arrangement of the water molecules and confers enhanced stability (VIVEROS-CONTRERAS *et al*., 2013).

4. CONCLUSIONS

This study showed that the carotenes present in the paprika oleoresin were successfully encapsulated through Micro and Nano spray dryer producing micro-particles and submicron particles, respectively. Submicron particles exhibited at higher yield, efficiency encapsulation and lower surface carotenes than the micro- particles. Submicron- and Micro- particles presented carotene degradation in one and two stages, respectively. However, both particles showed a similar stability to water activities of 0.529 at 25 °C after 30 days of storage. In general, the particles produced by each type of dryer exhibited differences in size, colour and encapsulation efficiency. However, they presented similarities in adsorption properties and stability. According to this, its application can be proposed in various food products, cosmetics or pharmaceutics.

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REFERENCES

Abbeddou S., Petrakis C., Pérez Gálvez A., Kefalas P. and Hornero Méndez D. 2013. Effect of simulated thermo-degradation on the carotenoids, tocopherols and antioxidant properties of tomato and paprika oleoresins. J. Am. Oil Chem. Soc. 90:1697-1703.

Abdullah E.C. and Geldart D. 1999. The use of bulk density measurements as flowability indicators. J. Powder Technol. 102(2):151-165.

Abdul-Manap N.R., Shamsudin R., Norhafsam-Maghpon M., Abdul-Hamid M.A. and Jalar A. 2018. Adsorption isotherm and kinetic study of gas-solid system of formaldehyde on oil palm mesocarp bio-char: Pyrolysis effect. J. Environ. Chem. Eng. 6:970-983.

Alamilla-Beltrán L., Chanona-Pérez J., Jiménez-Aparicio A.R. and Gutierrez-López G.F. 2005. Description of morphological changes of particles along spray drying. J. Food. Eng. 67:179-184.

Arpagaus C., Collenberg A., Rütti D., Assadpour E. and Jafari S.M. 2018. Nano spray drying for encapsulation of pharmaceuticals. Int. J. Pharm. 546:194-214.

Assadpour E. and Jafari S.M. 2017. Spray drying of folic acid within nano-emulsions: Optimization by Taguchi approach. Drying Technol. 35(9):1152-1160.

Assadpour E., Jafari S.M. and Maghsoudlou Y. 2017. Evaluation of folic acid release from spray dried powder particles of pectin-whey protein nano-capsules. Int. J. Bio. Macromol. 95:238-247.

Ayranci E., Ayranci G., and Dogantan Z. 1990. Moisture sorption isotherms of dried apricot, fig and raisin at 20°C and 30 C. J. Food Sci. 55:1591-1593.

Beristain C.I., Azuara E. and Vernon-Carter E.J. 2002. Effect of water activity on the stability to oxidation of spray-dried encapsulated orange peel oil using mesquite gum (*Prosopis juliflora*) as wall material. J. Food Sci. 67:206-211.

Bigetti-Guergoletto K., Busanello M. and Garcia S. 2017. Influence of carrier agents on the survival of *Lactobacillus reuteri* LR92 and the physicochemical properties of fermented juçara pulp produced by spray drying. LWT-Food Sci. Technol. 80:321-327.

Büchi Incorporation. 2018. Nano Spray Drier online brochure, www.buchi.com/Nano-Spray-Dryer.

Cano-Chauca M., Stringheta P.C., Ramos A.M. and Cal-Vidal J. 2005. Effect of the carriers on the microstructure of mango powder obtained by spray drying and its functional characterization. Innov. Food Sci. Emerg. 6:420-428.

Chen B., Sun W., Wang C. and Gou X. 2017. Size-dependent impact of inorganic nanoparticles on sulfamethoxazole adsorption by carbon nanotubes. Chem. Eng. J. 316:160-170.

Chen J., Shi J., Xue S.J. and Ma Y. 2009. Comparison of lycopene stability in water-and oil-based food model systems under thermal- and light-irradiation treatments. LWT-Food Sci. Technol. 42:740-747.

Desobry S.A., Netto F.M. and Labuza T.P. 1997. Comparison of spray-drying, drum-drying and freeze-drying for b-carotene encapsulation and preservation. J. Food Sci. 62(6):1158-1162.

Desobry S.A., Netto F.M. and Labuza T.P. 1999. Influence of maltodextrin system at an equivalent 25DE on encapsulated β-carotene loss during storage. J. Food Process. Pres. 23:39-55.

Fery A. and Weinkamer R. 2007. Mechanical properties of micro- and nanocapsules: Single-capsule measurements. Polymer. 48(25):7221-7235.

Goula M.A. and Adamopoulos K.G. 2005. Spray-drying of tomato pulp in dehumidified air. II. The effect on powder properties. J. Food Eng. 66:35-42.

Hategekimana J., Masamba K.G., Jianguo Ma J. and Zhong F. 2015. Encapsulation of vitamin E: Effect of physicochemical properties of wall material on retention and stability. Carbohyd. Polym. 124:172-179.

Hornero D., and Mínguez M.I. 2001. Rapid spectrophotometric determination of red and yellow isochromic carotenoid fractions in paprika y red pepper oleoresins. J. Agric. Food Chem. 49:3584-3588.

Jafari S.M., Assadpoor E., He Y. and Bhandari B. 2008. Encapsulation efficiency of food flavours and oils during spray drying. Drying Technol. 26(7):816-835.

Jafari S.M., He Y. and Bhandari B. 2007. Role of powder particle size on the encapsulation efficiency of oils during spray drying. Drying Technol. 25(6):1081-1089.

Jafari S.M., He Y. and Bhandari B. 2017. An overview of nano-encapsulation techniques and their classification. In: Jafari SM (ed). Nano-encapsulation Technologies for the Food and Nutraceutical Industries. Elsevier. Inc. New York.

Kagami Y., Sugimura S., Fujishima N., Matsuda K., Kometani T. and Matsumura T. 2003. Oxidative stability, structure and physical characteristics of microcapsules formed by spray drying of fish oil with protein and dextrin wall materials. J. Food Sci. 68:2248-2255.

Kaya S. and Kahyaoglu T. 2005. Thermodynamic properties and sorption equilibrium of pestil (grape leather). J. Food Eng. 71:200-207.

Lee S.H., Ng W.K., Chan H.K. and Tan R.B.H. 2011. Nano spray drying: A novel method for preparing protein nanoparticles for protein therapy. Int. J. Pharm. 403:192-200.

Li X., Anton N., Apargaus C., Belleteix F. and Vandamme T.F. 2010. Nanoparticles by spray drying using innovative new technology: The Büchi Nano Spray Dryer B-90. J. Control Release 147:304-310.

Masters K (1976) Spray Drying. Wiley, London.

Mehrnia M.A., Jafari S.M., Makhmal-Zadeh B.S. and Maghsoudlou Y. 2017. Rheological and release properties of double nano-emulsions containing crocin prepared with Angum gum, Arabic gum and whey protein. Food Hydrocolloids. 66:259-267.

Mihindukulasuriya S.D.F. and Lim L.T. 2013. Oxygen detection using UV-activated electrospun poly(ethylene oxide) fibers encapsulated with TiO_2 nanoparticles. J. Mater Sci. 48:5489-98.

Mudrić S.Z., Gašić U.M., Dramićanin A.M., Ćirić, I.Z., Milojković-Opsenica D.M., Popović Đorđević J.B., Momirović N.M. and Tešić Z.L. 2017. The polyphenolics and carbohydrates as indicators of botanical and geographical origin of Serbian autochthonous clones of red spice paprika. Food Chem. 217:705-715.

Nunes I.L., and Mercadante A.Z. 2007. Encapsulation of lycopene using spray-drying and molecular inclusion processes. Braz. Arch. Biol. Technol. 50:893-900.

Rascón M., Bonilla E., García H.S., Salgado M.A., Gonzalez-Arnao M.T. and Beristain C.I. 2015. *T*g and a_w as criteria for the oxidative stability of spray-dried encapsulated paprika oleoresin. Eur. Food Res. Technol. 241:217-225.

Rascón M.P., Beristain C.I., García H.S. and Salgado M.A. 2011. Carotenoid retention and storage stability of spray-dried encapsulated paprika oleoresin using gum arabic and soy protein isolate as wall materials. LWT-Food Sci. Technol. 44:549-557.

Rodríguez-Amaya B.D. 2016. Natural food pigments and colorants. Curr Opin Food Sci 7: 20-26.

Schmid K., Arpagaus, C. and Friess, W., 2010. Evaluation of the Nano Spray Dryer B-90 for pharmaceutical applications. Pharm. Dev. Technol 1-8.

Schuck P., Dolivet P.A., Méjean S., Zhu P., Blanchard E. and Jeantet R. 2008. Drying by desorption: a tool to determine spray drying parameters. J. Food Eng. 94:199-204.

Valenzuela C. and Aguilera J.M. 2015. Effects of maltodextrin on hygroscopicity and crispness of apple leathers. J. Food Eng. 144:1-9.

Viveros-Contreras R., Tellez-Medina D.I., Perea-Flores M.J., Alamilla-Beltrán L., Cornejo-Mazon M., Beristain-Guevara C.I., Azuara-Nieto E. and Gutierrez-Lopez G.F. 2013. Encapsulation of ascorbic acid into calcium alginate matrices through coacervation coupled to freeze drying. Rev. Mex. Ing. Quim. 12(1):29-39.

Wagner L.A. and Warthesen J.J. 1995. Stability of spray-dried encapsulated carrot carotene. J. Food Sci. 60:1048-1053.

Weisser H. 1985. Influence of temperature on sorption equilibria. In: Simato D. and Multon J.L. (eds). Properties of water in foods: in Relation to Quality and Stability. Springer Netherlands.

Zou J. and Rezaee R. 2016. Effect of particle size on high-pressure methane adsorption of coal. Petroleum Res. 1:53-58.

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