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Morphology and Stability of Edible Lycopene-Containing Micro- and Nanocapsules Produced Through Electrospraying and Spray Drying — Source link

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MORPHOLOGY AND STABILITY OF EDIBLE LYCOPENE-CONTAINING MICRO- AND NANOCAPSULES PRODUCED THROUGH ELECTROSPRAYING AND SPRAY DRYING

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Abstract

In this work, lycopene was encapsulated through electrospraying and spray drying (using a microporous membrane cap) within different edible biopolymeric matrices. Specifically, dextran, a whey protein concentrate (WPC) and chitosan were used as matrix materials. As a strategy to incorporate the hydrophobic bioactive within the hydrophilic matrices, emulsion electrospraying and spray drying from emulsion were carried out. Moreover and, for comparison purposes, coaxial electrospraying was also performed. The electrospraying solutions properties were studied, since they do not only affect the success of the electrohydrodynamic process, but also influence the morphology of the capsules. Apart from characterizing the morphology and molecular organization of the developed capsules, the encapsulation efficiency and the lycopene stability under moisture and heating conditions were also evaluated. Results showed that even though encapsulation structures were obtained from all the matrices assayed through both processing technologies, spray drying, as a consequence of the high temperatures needed in this process, affected lycopene stability and very poor encapsulation efficiencies were found in this case. It was also seen that WPC presented the greatest encapsulation efficiency (around 75%), probably ascribed to the interactions between the biopolymer and the lycopene. Furthermore, WPC capsules were able to better protect lycopene against moisture and thermal degradation.

Keywords: lycopene, encapsulation, electrospraying, electrospinning, spray drying

1. Introduction

Carotenoids are some of the most common pigments in nature, the most abundant being β-carotene, lycopene, lutein and zeaxanthin. These compounds are incorporated into foods, not only due to their colorant properties, but also to their nutraceutical uses. Specifically, lycopene is a natural red pigment mainly found in tomato and other red fruits, like watermelon or papaya, and it is one of the main responsible of the antioxidant capacity of these products. It has received great interest in recent years because of its activity in the prevention of chronic diseases such as atherosclerosis, skin cancer, and prostate cancer (Rao and Agarwal, 1999; Xue et al. 2013). However, lycopene presents several unsaturated bonds in its molecular structure, which makes it very susceptible to oxidants, light and heat. This fact makes that lycopene could lose its beneficial properties during processing and storage of foodstuffs. Moreover, it has a very low water solubility, which limits its industrial applicability in aqueous-based systems. A possible approach to overcome these limitations is the micro/nanoencapsulation of lycopene. Some technologies have been already used to prepare lycopene microcapsules. For instance, many authors have prepared lycopene microcapsules through the spray drying methodology. However, the resulted capsules did not present an optimum stability at room temperature (Matioli and Rodriguez-Amaya 2002; Shu et al. 2006; Rocha et al. 2012). Blanch et al. (2007) prepared lycopene microcapsules by supercritical fluid extraction method. The use of supercritical fluids in food is recommended, because it avoids the employment of large amounts of organic solvents. However, the costs of equipment and operation are too high and the technological parameters need further optimization (Guo et al. 2012). Other techniques such as complex coacervation have been used, (Rocha-Selmi et al. 2013; Silva et al. 2012) but in this case either organic solvents (not convenient for food applications), high temperature or acid conditions are needed, which could affect lycopene stability.

In this study, the use of electrohydrodynamic processing for obtaining micro/nanocapsules of lycopene was proposed as a novel encapsulation technology. This technique was compared to the spray drying methodology, since it is the most common encapsulation technology used in the food industry nowadays. Nevertheless, in this work, a novel spray drying device with a microporous membrane cap able to obtain smaller encapsulation structures was used. The electrohydrodynamic process uses electrostatic forces to produce electrically charged jets from viscoelastic polymer solutions which on drying, by the evaporation of the solvent, produce ultrathin structures (Li and Xia 2004). In particular, the technique is referred to as electrospinning when ultrathin continuous fibres are obtained. When size-reduced capsules are obtained, the technique is called electrospraying. For food and nutraceutical applications, capsules are generally preferred rather than fibres, since apart from facilitating handling and subsequent incorporation into different products, they usually present greater surface/volume ratio and, thus, are expected to have better release profiles than fibres (Hong et al. 2008). It is important to note that electrospraying does not require the use of high temperatures and, thus, temperature-sensitive ingredients, such as carotenoids, may be encapsulated using this processing technique without suffering from any activity loss (Fernandez et al. 2009). Moreover, electrosprayed capsules can be produced from some biopolymers using aqueous solutions, mainly by changing the solution properties through the addition of proper additives (Pérez-Masiá et al. 2014). This issue has special interest in food applications, where the use of organic solvents could lead to toxic effects due to the presence of remaining solvents in the structures. However, lycopene presented very low water solubility, thus electrospraying and subsequent encapsulation of this compound from water-based solutions is not simple. Nevertheless, emulsion electrospraying, as well as coaxial electrospraying can be used for the encapsulation of immiscible compounds. In the emulsion electrospraying, an immiscible liquid phase is dispersed into a polymer solution until both components form a stable emulsion. As a result, the immiscible phase forms the core material and the polymer constitutes the shell of

the capsules (Angeles et al. 2007). In the coaxial methodology, the polymer and the core material are introduced into the electrospraying equipment from separated solutions, thus the immiscibility problem is solved.

In this work, lycopene was encapsulated through electrospraying and spray drying in various food hydrocolloid matrices for potential food applications. Specifically, a whey protein concentrate from milk (WPC), and two polysaccharides (dextran and chitosan) were evaluated. It is worth noting that WPC and dextran are water dispersible polymers and, thus, emulsion and coaxial electrospraying were used in these cases. In the case of the spray drying methodology, an emulsion was also formed with these materials. For chitosan, an acetic acid solution was used, where lycopene could be easily dissolved and, thus, uniaxial electrospraying or spray drying from the acid solution were carried out. Acetic acid is allowed for food contact applications and would not generate toxicity problems in case some solvent remained within the capsules. The morphology and the molecular organization of the capsules obtained were evaluated. Moreover, the stability of encapsulated lycopene was carried out taking into account different situations that can be found in the food industry, such as the incorporation of the capsules into aqueous-based foods and exposure to thermal treatments.

2. Materials and Methods

2.1. Materials

Whey protein concentrate (WPC) was kindly donated by ARLA (ARLA Food Ingredients, Viby, Denmark). Under the commercial name Lacprodan® DI-8090, the composition per 100 g of product consisted of ~80 g of protein, ~9 g of lactose, and ~8 g of lipids, being the rest water and minerals like sodium and potassium. Dextran (Mw ~70000), low molecular weight chitosan (~50000-190000), lycopene, Tween-20 and soybean oil were supplied by Sigma-Aldrich (Spain) and they were used as received, without further purification.

2.2. Preparation of the encapsulation solutions

For the uniaxial electrospraying, 2% (w/v) of chitosan and 1.5% (w/w) of lycopene with respect to the chitosan weight were dissolved in a 90% (v/v) aqueous/acetic solution. For the coaxial electrospraying, the shell solutions were prepared by dissolving 30% (w/v) of WPC or 20% (w/v) of dextran and 5% (w/v) of Tween-20 in distilled water. The core solution was prepared by dissolving 1.25% (w/v) of lycopene in soybean oil. For the emulsion electrospraying, an aqueous surfactant solution was prepared by dissolving 10% (w/v) of Tween-20 in water. Afterwards, 16% (v/v) of lycopene/soybean oil solution [1.25 %(w/v)] was added to the surfactant solution to prepare an emulsion premix. The premix was ultrasonicated at 10% of amplitude and 20 kHz of process frequency for 120s using an ultrasonic homogenizer (Bandelin electronic, Germany). These conditions led to an oil-in-water (O/W) emulsion with an average particle size of around 150 nm. Finally, 30% (w/v) of WPC or 20% (w/v) of dextran were added to the emulsion and they were mechanically stirred until homogeneous emulsions were obtained.

For the spray drying solutions, 0.04 % (w/v) of chitosan and 1.5% (w/w) of lycopene with respect to the chitosan weight were dissolved in a 0.4% (v/v) aqueous/acetic solution. For the

preparation of the water dispersible biopolymer solutions, Tween-20 was dissolved in distilled water and afterwards, 0.3% (v/v) of lycopene/soybean oil solution [1.25 %(w/v)] was added to the surfactant solution to prepare an emulsion premix. The premix was ultrasonicated at 10% of amplitude and 20 kHz of process frequency for 120 s using an ultrasonic homogenizer (Bandelin electronic, Germany) in order to obtain an O/W emulsion with an average particle size of around 150 nm. Finally, 0.4% (w/v) of dextran or WPC was added to the emulsion and they were mechanically stirred until homogeneous emulsions were obtained.

2.3. Emulsion particle size characterization

The mean particle size and size distribution of the O/W emulsion attained were determined via dynamic light scattering (DLS) with a Zetasizer Nano-ZS 90 (Malvern Instruments Corp., UK). All measurements were performed a 25ºC in triplicate and intensity-weighted results were reported.

2.4. Characterization of the electrospraying solutions

The apparent viscosity (η_a) of the polymeric solutions at 100 s^{-1} was determined using a rotational viscosity meter Visco Basic Plus L from Fungilab S.A. (San Feliu de Llobregat, Spain). The surface tension of the solutions was measured using the Wilhemy plate method in an EasyDyne K20 tensiometer (Krüss GmbH, Hamburg, Germany). The conductivity of the solutions was measured using a conductivity meter XS Con6 (Labbox, Barcelona, Spain). All measurements were made in triplicate at 25ºC.

2.5. Encapsulation through electrospraying

The electrospraying apparatus, equipped with a variable high-voltage 0-30 kV power supply, was a Fluidnatek® L-10 assembled and supplied by Bioinicia S.L. (Valencia, Spain). Solutions were introduced in a 5 mL plastic syringe and were electrosprayed under a steady flow-rate using a stainless-steel needle. For the coaxial electrospraying, two concentrical needles were

used. The inner one was used for the core material and the outer one for the shell solution. The needle was connected through a PTFE wire to the syringe. The syringe was lying on a digitally controlled syringe pump while the needle was in horizontal towards a stainless-steel plate attached to a copper grid used as collector. More details of the electrospraying equipment and the different uniaxial and coaxial configurations can be found elsewhere (Pérez-Masiá et al. 2013). The flow rate was 0.15 mL/h, the voltage varied from 12 to 18 kV and the distance between the tip and the collector varied from 9-20 cm.

2.6. Encapsulation through spray drying

The solutions with and without lycopene were spray-dried using a Spray-dryer B-90 (Büchi, Switzerland) with a 7.0 µm spray cap. The solutions were introduced into the equipment through a silicone wire, which was connected to the spraying head of the equipment. The air flow was ~140 L/h with an inlet and outlet temperatures of 90ºC and 45ºC, respectively.

2.7. Scanning electron microscopy (SEM)

SEM was conducted on a Hitachi microscope (Hitachi S-4100) at an accelerating voltage of 10 KV and a working distance of 12-16 mm. The capsules were sputtered with a gold-palladium mixture under vacuum before their morphology was examined using SEM. Capsule diameters were measured by means of the Adobe Photoshop CS3 extended software from the SEM micrographs in their original magnification.

2.8. Attenuated total reflectance infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectra were recorded in a controlled chamber at 24°C and 40% RH using a Bruker FT-IR Tensor 37 equipment (Rheinstetten, Germany) coupled with the ATR accessory GoldenGate of Specac Ltd. (Orpington, UK) in the 4000–600 cm^{-1} range. The spectra were collected in the different materials by averaging 20 scans at 4 cm^{-1} resolution. The experiments were repeated twice to verify that the spectra were consistent between individual samples.

2.9. Encapsulation efficiency

The lycopene encapsulation efficiency was calculated by dividing the lycopene concentration found in the capsules by the initial lycopene concentration added to the different solutions. Lycopene was extracted from the capsules by dissolving the capsules in water and afterwards, adding dodecane to the solution in order to separate the lycopene from the rest of the components. The capsules' concentration was evaluated from the UV absorbance of the capsules using a SP-2000UV spectrophotometer (Spectrum, Shanghai, China). As lycopene has an absorption maximum at a wavelength of 476 nm, the bioactive concentration in the capsules was calculated according to a calibration curve obtained for different known lycopene concentrations and the corresponding absorbance at this wavenumber:

$y = 0.0187x - 0.0008$ ($R^2 = 0.99$) (Equation 1)

Where "y" was the lycopene concentration and "x" was the UV absorbance at 476 nm.

2.10. Water sorption analysis

Water sorption of different capsules was evaluated at 70%RH, by introducing petri dishes containing the materials inside a desiccator with saturated sodium chloride. Weight gain of the capsules vs. time curves at 24ºC was studied until constant weight. Afterwards, lycopene was again extracted from the capsules and the bioactive concentration was studied through the UV absorbance of lycopene at 476 nm using the previously obtained calibration curve (cf. Equation 1).

2.11. Thermal stability of lycopene

Thermal stability of lycopene in WPC capsules was studied through the exposure of the structures and the raw lycopene to heating conditions and the evaluation of the antioxidant activity of the samples before and after the heating experiment. Specifically, samples were

stored at 70ºC in darkness during 4 h, since it was observed that degradation of non-encapsulated lycopene occurred in these conditions. Antioxidant activity of lycopene was evaluated according to the ABTS radical cation ($ABTS^{\bullet+}$) methodology developed by Re et al. (1999). To this aim, $ABTS^{\bullet+}$ was produced by reacting ABTS solution with potassium persulfate and allowing the mixture to stand in the dark at room temperature for 12–16 h before use. For the study of the antioxidant activity of different samples, the $ABTS^{\bullet+}$ solution was diluted with ethanol to an absorbance of 0.70 (±0.02) at 734 nm. Afterwards, capsules and raw lycopene were dissolved in dichloromethane and an aliquot of these solutions was added into the $ABTS^{\bullet+}$ solution in order to inhibit the $ABTS^{\bullet+}$ absorbance. The percentage inhibition of absorbance at 734 nm after 4 minutes was calculated for each sample, since it was previously observed that reaction between carotenoids and $ABTS^{\bullet+}$ was complete after this time (Re et al. 1999). A Trolox curve in the same solvent was used as reference (Equation 2) and results were reported as a function of equivalent Trolox concentration.

$y = 6.7579x + 2.0433 (R^2 = 0.99)$ (Equation 2)

Where "y" was the percentage inhibition of $ABTS^{\bullet+}$ absorbance at 734 nm and "x" was the corresponding Trolox concentration (μM).

2.12. Statistical analysis

Statistical analysis of data was performed through analysis of variance (ANOVA) using Statgraphics Centurion XV (Manugistics Corp., Rockville, MD). Homogeneous sample groups were obtained by using LSD test (95% significant level).

3. Results and Discussion

As briefly mentioned in the introduction, the aim of this work was to compare between the traditional spray drying technique and the most novel electrospraying method for the encapsulation and protection of lycopene. One of the strategies used to incorporate the

hydrophobic bioactive within the hydrocolloidal-based matrices (whey protein concentrate-WPC-, dextran and chitosan) was to form O/W emulsions using a soybean oil (containing the lycopene) dispersed within the aqueous phase which had a surfactant. Later on, the encapsulating matrices were added to the solutions and the emulsions were processed using both processing techniques.

3.1. Emulsion particle size characterization and electrospraying solution properties

Initially, the emulsions obtained were characterized. Figure 1 shows the particle size distribution of the O/W emulsion attained before adding the biopolymers. From this figure it was observed that only one curve was seen with the maximum peak at ~150 nm. This result indicated that there was only one population of particles with an average size of ~150 nm. It was not possible to measure the particle size distribution of the emulsion containing the biopolymers, as upon their incorporation at the concentration used for electrospraying, the turbidity of the solution became too high for a correct characterization.

INSERT FIGURE 1 ABOUT HERE

The physical properties of the electrospraying solutions containing the biopolymers were characterized as they strongly affect the stability of the process and the successful development of structures through this technology. Moreover, capsules morphology is also influenced by solution properties. Table 1 compiles the viscosity, surface tension and electrical conductivity of the electrospraying solutions assayed. These final compositions were obtained after a previous optimization process in which the concentration of the various compounds was adjusted until stable emulsions and electrospraying jets were obtained. Nevertheless, it was seen that a phase separation always occurred in dextran emulsions after a few hours. On the contrary, lycopene-containing WPC emulsions were stable during days. From Table 1 it can be observed that the incorporation of lycopene to the dextran and WPC solutions through the emulsion process, significantly affected the solution properties. Specifically, it was seen that

viscosity considerably increased for both solutions because, in this case, lycopene was incorporated through soybean oil which was rather viscous. It is worth noting that the viscosity increase was greater for the WPC solution, which could indicate some kind of interaction between the protein and the lycopene in solution. Regarding the surface tension and electrical conductivity, it was observed that for the dextran solution these parameters slightly increased when compared to the solution without lycopene. However, in the case of WPC, the presence of the soybean oil/lycopene in the solution significantly decreased the electrical conductivity. This again could be ascribed to the interaction between the protein and the lycopene, thus, resulting in the neutralization of some of the protein charges. In contrast with the previous results, the chitosan solution properties were not modified upon lycopene incorporation. It is important to highlight that, in this case, lycopene was not incorporated through soybean oil, but it was directly added to the acid chitosan solution. Nevertheless, these data suggested that there were no interactions between chitosan and lycopene.

INSERT TABLE 1 ABOUT HERE

3.2. Morphology of the lycopene-containing capsules

SEM was used in order to analyse capsules' size and morphology. Figure 2 shows the SEM images of the different biopolymer/lycopene capsules obtained. Emulsion electrospraying of the dextran-based solution led to very homogeneous capsule sizes, while coaxial electrospraying produced more aggregated particles. This fact could be due to a worse entrapment of the soybean oil/lycopene solution when coaxial electrospraying was used, probably because of the non-continuous nature of the capsules, which complicated the incorporation of the antioxidant into the structures. In this case, part of the oil could leak from the dextran matrix, thus, causing capsules aggregation. It was also observed that spray drying gave rise to bigger structures with a broader capsule size distribution. In contrast, when WPC was used as encapsulating matrix, more heterogeneous structures were obtained through

electrospraying, while smoother and more regular size capsules were produced through spray drying. This result might be explained by the greater electrical conductivity of the protein solutions, which could destabilize the electrospraying jet, thus producing different particle sizes. In this case, aggregated particles were also seen when coaxial electrospraying was used, probably because of oil leakages. Regarding the structures made up of chitosan, from Figure 2 it can be observed that very small capsules were obtained through electrospraying and spray drying. This fact was attributed to the use of the acid solvent (pH ~ 2.5), which generated strong electrostatic repulsions along the chitosan chains. These repulsive interactions hindered the formation of chain entanglements and, thus, small capsules were attained with this polymer (Torres-Giner et al. 2008).

INSERT FIGURE 2 ABOUT HERE

3.3. Infrared spectra of the bioactive capsules

ATR-FTIR analyses were carried out in order to confirm the presence of the antioxidant in the different structures, as well as to characterize the molecular organization of the capsules and detect interactions between the matrix and the core material. Figure 3 shows the ATR-FTIR spectra of the different materials assayed. From Figure 3A it was seen that FTIR spectra of dextran encapsulation structures showed some bands attributed to both soybean oil (SBO) and lycopene (cf. arrows in Figure 3A). Specifically, it was seen that the C-H stretching vibration bands, centered around 2930 cm^{-1}, which appeared as a single broad spectral band for the as-received dextran, became narrower and better defined in the dextran capsules. These could be related to a greater molecular order due to the formation of the capsules, as well as to the presence of the SBO and lycopene in these capsules, since it was seen that both components presented sharp bands in this area. Moreover, the C=O group of the triglycerides of SBO found at 1743 cm^{-1} (Vlachos et al. 2005) and the lycopene band attributed to the C=C trans bond found at 957 cm^{-1} (Rubio-Diaz et al., 2011) also appeared in the dextran capsules, especially in

those obtained through spray drying. Therefore, FTIR results suggested that lycopene was incorporated in all the structures, but spray drying seemed to result in a greater encapsulation yield. It is also important to note that spectral bands of dextran were shifted depending on the encapsulation technology used. This shift was attributed to the process conditions, i.e. the solution preparation and subsequent drying of the carbohydrate, which could led to a rearrangement of the molecules, which was also probably influenced by the presence of surfactant. Figure 3A shows the details of the spectral region from 800 to 1200 cm^{-1}, in which the characteristic vibrational bands from carbohydrates arise, and it shows that the maximum of the most intense carbohydrate band at around 1005 cm^{-1} varied depending on the encapsulation technology used, i.e. this band arose at ~1006 cm^{-1}, ~1004 cm^{-1} and ~1012 cm^{-1} in the capsules obtained through emulsion electrospraying, coaxial electrospraying and spray drying, respectively. The shift towards higher wavenumbers has been normally related to shorter and more attractive bonds (Wolkers et al. 2004). Therefore, this result suggested that the molecular conformation of capsules was affected by the encapsulation technology and spray drying, probably as a consequence of the high temperatures used in this process, produced more compact structures.

Regarding the WPC capsules, Figure 3B shows that the C=O band of SBO at 1743 cm^{-1} and the lycopene band at 957 cm^{-1} also appeared in the spectra from all the capsules, thus confirming the encapsulation of the lycopene through all the techniques used. Moreover, it was observed that both amide bands of the WPC/lycopene capsules were shifted in comparison to the pure protein. In this case the shifts could be attributed not only to the process conditions, but also to chemical or physico-chemical interactions between the protein and the bioactive, since the previous results about the viscosity and the emulsion stabilization suggested that some kind of interaction occurred between the protein and the lycopene, as already reported in previous works (Zhang and Zhong, 2013; Mensi et al. 2013). Specifically, it was seen that amide I band (~1630 cm^{-1}) was displaced towards lower wavenumbers, indicating new β-sheets

arrangements (Eissa et al. 2006) and the amide II band (~1530 cm^{-1}) of WPC/lyc capsules was displaced towards greater wavenumbers when compared to the as-received WPC powder. This latter shift was related to changes in the in-plane N-H and C-N vibrations (Kong and Yu 2007). Again, it is interesting to highlight that these shifts were different depending on the kind of encapsulation technique, being the spray dried capsules those which again presented the most noticeable shifts.

Concerning the chitosan materials, from Figure 3C it was observed that the chitosan spectra completely changed after both encapsulation processes. This fact was attributed to the acetylation of chitosan due to the dissolution of the biopolymer in acetic acid media. Specifically, the main changes in the chitosan spectra occurred in the amide I and II regions (from 1700 to 1500 cm^{-1} aprox.). In this area the as-received chitosan shows the amide I and amide II bands at around 1650 and 1590 cm^{-1} respectively. However, after processing, the capsules presented two dominant bands centered at around 1546 and 1405 cm^{-1} associated to carboxylate ions (NH_3^+ and $COOH^-$). The amine groups in this chemical form are referred to as protonated or activated amine groups. These results suggested that capsules could exhibit antimicrobial performance (Fernandez-Saiz et al., 2006), even though the free acetic acid band at ~1706 cm^{-1} was not evident in the capsules spectra, indicating that solvent was completely evaporated during the encapsulation process. However, lycopene signal was not apparent in these capsules, suggesting that the bioactive could be degraded in the presence of the concentrated acetic acid or that it was not properly encapsulated in this case (maybe as a consequence of the smaller size of these structures). As with the other encapsulation matrices, it is interesting to note that, depending on the encapsulation technology used, the characteristic spectral bands arose slightly at different wavenumbers, thus confirming different molecular conformations depending on the technology used.

INSERT FIGURE 3 ABOUT HERE

3.4. Encapsulation efficiency

The encapsulation efficiency of the different structures developed was evaluated through UV spectroscopy. Figure 4 shows the UV spectra from 350 to 650 nm of the raw lycopene, as well as of the lycopene extracted from the capsules. It was observed that lycopene presented 3 characteristic bands at 449, 476 and 509 nm, being the band at 476 nm the most intense one. Therefore, the intensity of the band at 476 nm was used to evaluate lycopene concentration according to Equation 1 (cf. materials and methods, section 2.8). From Figure 4 it can be observed that lycopene extracted from the capsules presented a similar spectrum than that from raw lycopene. However, lycopene extracted from chitosan capsules presented very low absorbance values probably because of a greater degradation of the carotenoid in this case due to the acid conditions used in the formation of these capsules. From this figure it is also seen that the high temperature employed during spray drying also affected to the stability of the bioactive. Indeed, if comparing the spectra of extracted lycopene from the electrosprayed and spray dried capsules (cf. Figure 4A vs. 4B), it is clear that the high temperature involved in the spray drying technique led to a certain degradation of the bioactive, as reflected by the lower spectral intensity. It was previously seen that degradation kinetics of lycopene during hot air drying strongly increased at temperatures above 70ºC (Demiray et al. 2013). However, as inferred from the literature, it appears that the degradation temperature of lycopene is strongly dependent on its degree of purity and extraction method used (Goula and Adamopoulos, 2005; Shu et al., 2006). A thermal stability analysis of the lycopene used in this work was done before the spray drying experiment and it was seen that the compound was degraded after 3h at 70ºC. However, temperatures below 90ºC were not enough for completely eliminating the solvent and, thus, producing the dried capsules.

INSERT FIGURE 4 ABOUT HERE

Table 2 shows the initial lycopene concentration added to the solutions and the lycopene concentration remaining in the capsules obtained through Equation 1, expressed as the percentage of lycopene with respect to the total solids in the capsules. The encapsulation efficiency is also included in this table and it was calculated by dividing the initial lycopene concentration by the lycopene concentration found in the capsules. From this table it was seen that capsules obtained through spray drying presented very low encapsulation efficiencies for all the matrices, probably because the high temperature needed for solvent evaporation during capsule formation affected lycopene stability. This data seems to be in disagreement with FTIR results, which suggested that spray drying led to higher encapsulation yield. However, FTIR spectra showed the soybean oil (SBO) signal which was not affected by temperature. Thus, although higher amount of SBO/lycopene solution was probably encapsulated through spray drying, lycopene was possibly degraded due to heat exposure and, thus, the bioactive signal could not be detected through UV spectroscopy. This result is in accordance with previous works which have studied lycopene loss during heating or drying of tomato products (Rocha et al. 2012; Goula and Adamopoulos, 2005). Table 2 also shows that for dextran, emulsion electrospraying also led to low encapsulation efficiency, due to the unstable emulsion formed with this polymer. Therefore, for this material it was better to use the coaxial methodology, which led to an encapsulation yield around 55-60%. For WPC capsules it was seen that emulsion electrospraying led to proper encapsulation efficiency, since WPC and SBO/lycopene solution produced a stable emulsion which did not separate during the electrospraying experiment. Regarding the coaxial electrospraying very high variability was found, probably because this technique led to a worse encapsulation process with oil leakages, which made that some capsules presented very high lycopene contents, while other structures presented very low encapsulation yields. Finally, it was observed that lycopene was poorly encapsulated in chitosan capsules through uniaxial electrospraying.

Moreover, the lycopene found in these capsules was probably partially degraded due to the acid conditions used in this case.

INSERT TABLE 2 ABOUT HERE

3.5. Water sorption analysis

If considering the developed structures for food applications, and taking into account that most food products have high water activity, it is important to know the water sorption behavior of the different capsules and, what is more important, the bioactive stability in the presence of moisture. To this aim, water sorption was evaluated through the exposure of the capsules and also of the raw lycopene (for comparison purposes) at ambient temperature (T = 21 ºC) and high relative humidity (~70%). Their weight gain was evaluated until a constant value was reached. Afterwards, lycopene was extracted from the capsules and evaluated through UV spectroscopy in order to study the efficiency of the capsules for stabilizing the antioxidant compound under moisture conditions. Table 3 shows the weight gain of all the capsules developed, the initial lycopene concentration in the capsules previously obtained (cf. Table 2), the lycopene concentration after moisture exposure obtained through Eq. 1 and the total lycopene loss. From this table it can be clearly seen that after moisture exposure, in all cases, lycopene absorbance decreased. This effect was attributed to spatial rearrangements of the double bonds and partial degradation of the bioactive (Tan and Soderstrom, 1989). Specifically, it was seen that ~65% of non-encapsulated lycopene was degraded, even when the raw lycopene hardly increased its weight after moisture exposure. Nevertheless, the oxygen presence and ambient temperature (21ºC) in the moisture chambers could also alter the molecular structure of the lycopene. Regarding the capsules it was seen that water uptake of capsules was generally greater than those of raw lycopene, probably because capsules' matrices were hydrophilic materials which favoured water sorption. Specifically, it was seen that dextran capsules absorbed a greater amount of water than WPC and chitosan, ascribed to

its higher water solubility. This fact affected lycopene stability, since dextran capsules were partially dissolved and lycopene was thus exposed to moisture, oxygen and temperature conditions. Thus, it was seen that the lycopene absorbance decreased in these capsules after moisture exposure, probably because of the degradation of part of the antioxidant. On the contrary, WPC is not water soluble, but it is water dispersible, thus water sorption was lower for these capsules than for dextran capsules. In this case, it was seen that WPC capsules obtained through emulsion electrospraying and spray drying were able to better protect the bioactive, which was not considerably affected after moisture exposure. However, a considerable decrease of the lycopene content was seen for the WPC capsules obtained through coaxial electrospraying. This was probably because, as discussed above, non-continuous capsules hindered the proper incorporation of the bioactive through the coaxial methodology and, thus, there was some leakage from these capsules. Therefore, part of the lycopene could be on the surface of the structures exposed to humidity and, thus, more prone to degradation. Regarding chitosan, it is important to highlight that it was partially acetylated due to the solution preparation procedure with acetic acid as the solvent. This fact resulted in increased water solubility of chitosan, affecting the water uptake of these capsules (Pillai et al. 2009). Even though water uptake was limited in the chitosan matrices, in comparison with the other encapsulating materials, lycopene was completely degraded in these capsules, not only due to moisture exposure, but also probably because of the acid conditions needed for capsules formation, which led to a rapid degradation of the antioxidant. From Table 3 it can also be observed that water uptake was greater for electrosprayed capsules than for capsules obtained through spray drying. As it was previously seen from ATR-FTIR results, molecular organization of matrices was different in electrosprayed than in spray dried capsules. Particularly, it was seen that spray dried capsules presented more attractive bonds and, thus, more compact structures than electrosprayed capsules. This fact could be hindering water

uptake in the spray dried capsules. Moreover, the greater specific surface of the electrosprayed materials could be also favouring water sorption.

INSERT TABLE 3 ABOUT HERE

3.6. Thermal stability

Thermal treatments are commonly employed for food processing and, thus, lycopene stability under heating conditions is an important attribute to evaluate. Specifically in this work, the stability of non-encapsulated lycopene and lycopene encapsulated in WPC capsules obtained through emulsion electrospraying was studied, since it was previously seen that these structures provided the best encapsulation efficiency and protection under moisture conditions. To this end, the antioxidant activity of lycopene was evaluated according to the ABTS methodology. It is important to note that WPC capsules also contained SBO and, thus, the antioxidant activity of the solution lycopene/SBO was taken as the control value. Table 4 shows the antioxidant activity of lycopene before and after the thermal treatment (70ºC during 4h). From this data it was observed that, initially, both systems presented similar antioxidant activity, which confirmed that lycopene was not degraded after encapsulation in the WPC matrix. However, after the thermal treatment, it was seen that the ABTS inhibition percentage of the non-encapsulated lycopene/SBO solution considerably decreased, when compared to the lycopene/SBO extracted from the WPC capsules. This data indicated that lycopene lost its antioxidant activity and, thus, its beneficial effects when it was exposed to heating conditions. In contrast, WPC capsules were able to significantly reduce the bioactive degradation and, thus, while the antioxidant activity of non-encapsulated lycopene was reduced by ~80%, more than 60% of the antioxidant activity was retained when encapsulated in WPC. These promising results seem to indicate that encapsulation using adequate matrices

and encapsulation technologies would effectively have an impact in the commercial life of the antioxidant.

INSERT TABLE 4 ABOUT HERE

4. Conclusions

In this work it has been demonstrated, for the first time, that lycopene can be properly encapsulated through electrospraying using aqueous biopolymer solutions. These results are very interesting for food-related applications in which organic solvents could lead to toxicity problems. The antioxidant-containing electrosprayed capsules were compared with those obtained through spray drying and results showed that poor encapsulation efficiencies were obtained through the latter technique, probably because of the high temperature required in this case which led to a partial degradation of the antioxidant. On the contrary, emulsion electrospraying could be used for lycopene encapsulation, especially when using protein matrices which create more stable emulsions that do not phase separate during the encapsulation process. In this case, around 75% of the antioxidant was incorporated within the capsules. Coaxial electrospraying could also be used for lycopene encapsulation, although some leakages were found in this case probably because of the non-continuous nature of the structures developed which resulted in a worse entrapment of the core material. Chitosan was also used as a matrix to encapsulate lycopene through both techniques. However, the acid conditions needed in this case in order to dissolve the polymer affected lycopene stability and very poor encapsulation efficiencies were found in this case (~2%). Nevertheless, other bioactive ingredients with higher acid resistance could be potentially encapsulated using this matrix. Finally, it was seen that WPC-based capsules were able to protect lycopene from both

moisture and heating conditions and, thus, this kind of capsules could be used to increase lycopene shelf life when incorporated within different food products.

Acknowledgements

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Figure Captions

Figure 1. Particle size distribution of the O/W emulsion without the biopolymers.

Figure 2. Selected SEM images of dextran/lycopene capsules obtained through emulsion (A), coaxial electrospraying (B) and spray drying (C); WPC/lycopene capsules obtained through emulsion (D), coaxial electrospraying (E) and spray drying (F); chitosan/lycopene capsules obtained through uniaxial electrospraying (G) and spray drying (H).

Figure 3. ATR-FTIR spectra of the different materials assayed: (A) dextran-based materials, (B) WPC-based materials and (C) chitosan-based materials. Arrows point out the most remarkable spectral changes as a consequence of lycopene incorporation. Images on the left side show the complete spectra of the materials from 4000 to 600 cm^{-1}. Images on the right side show the lycopene contribution in the spectra of the different materials.

Figure 4. UV spectra from 350 to 650 nm of lycopene extracted from electrosprayed capsules (A) and spray-dried capsules (B).

Figure 1
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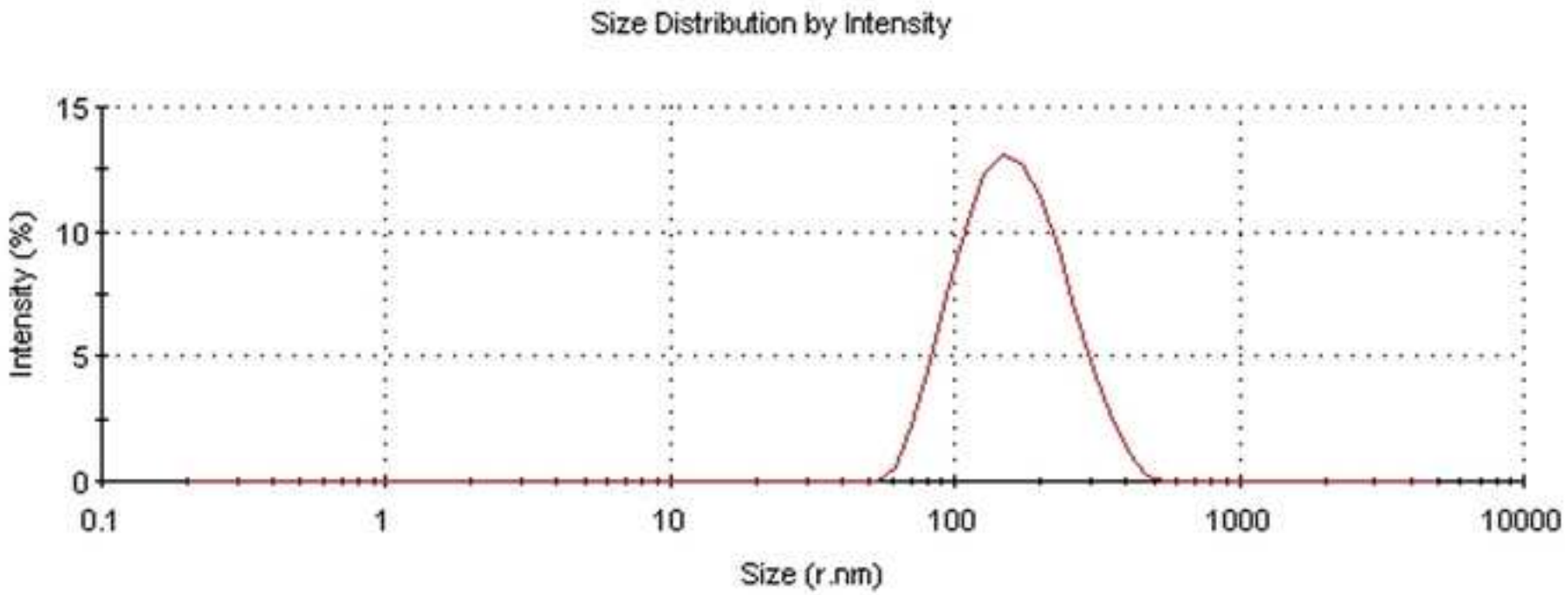

Figure 2
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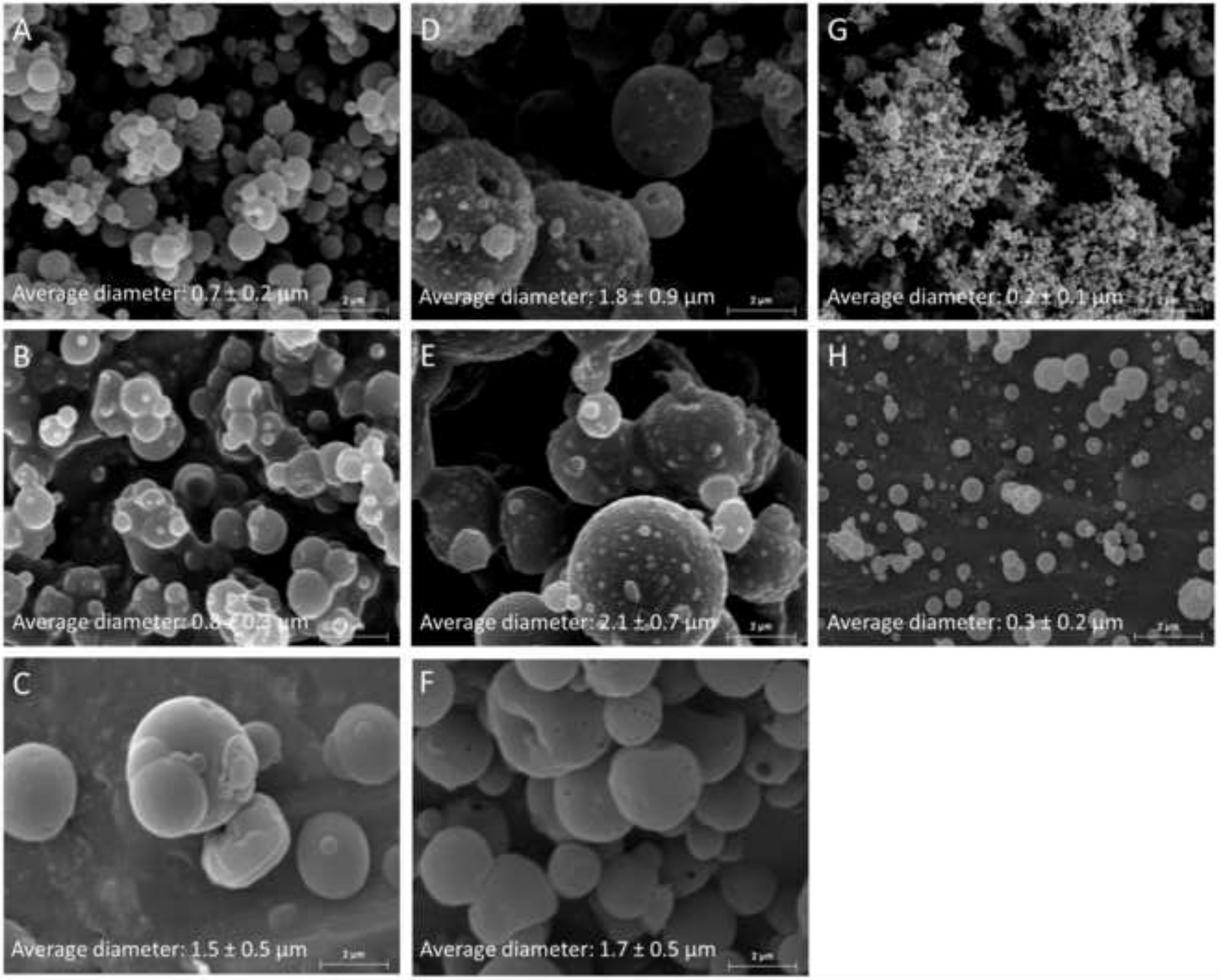

Figure 3

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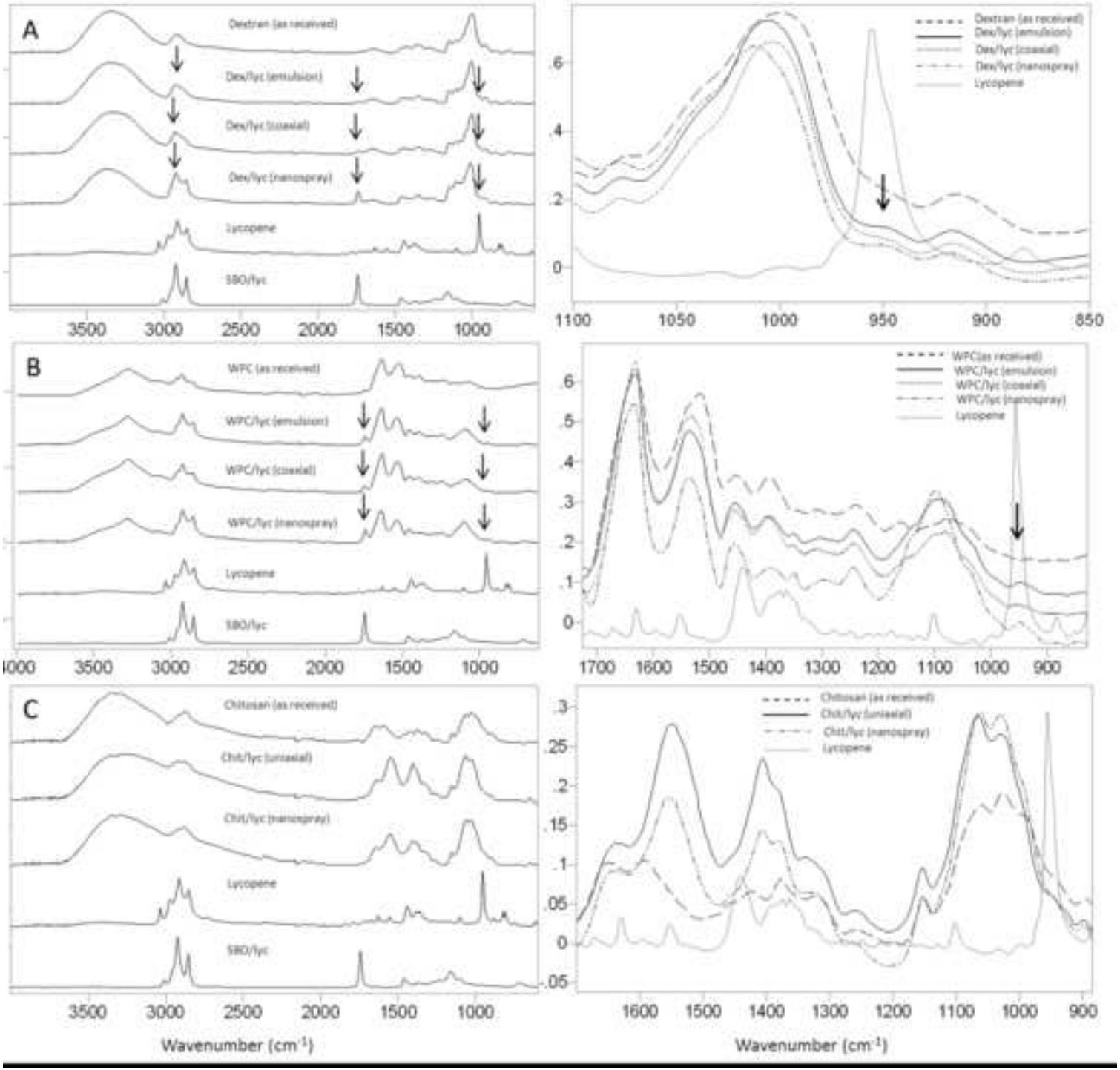

Figure 4
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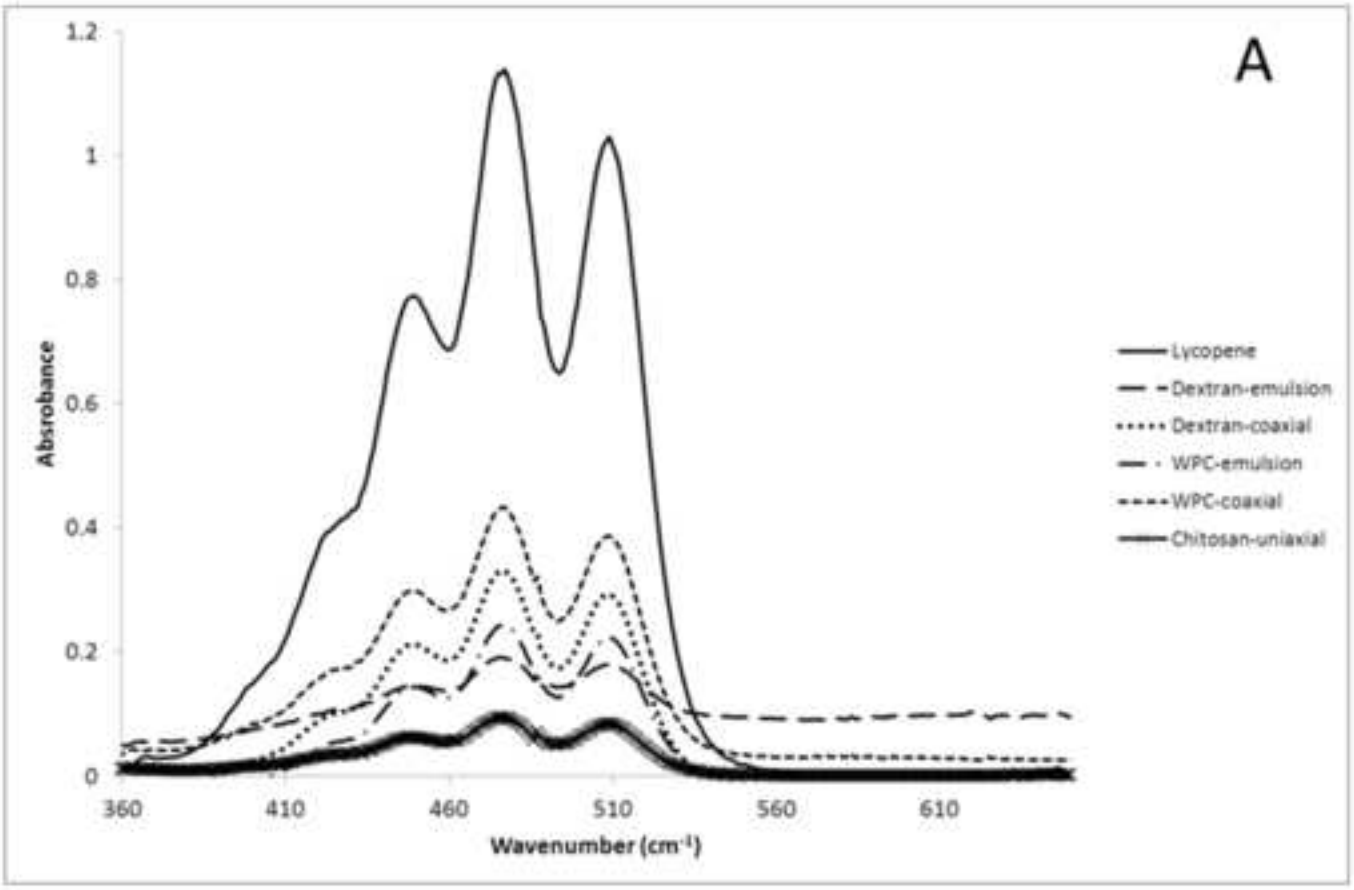

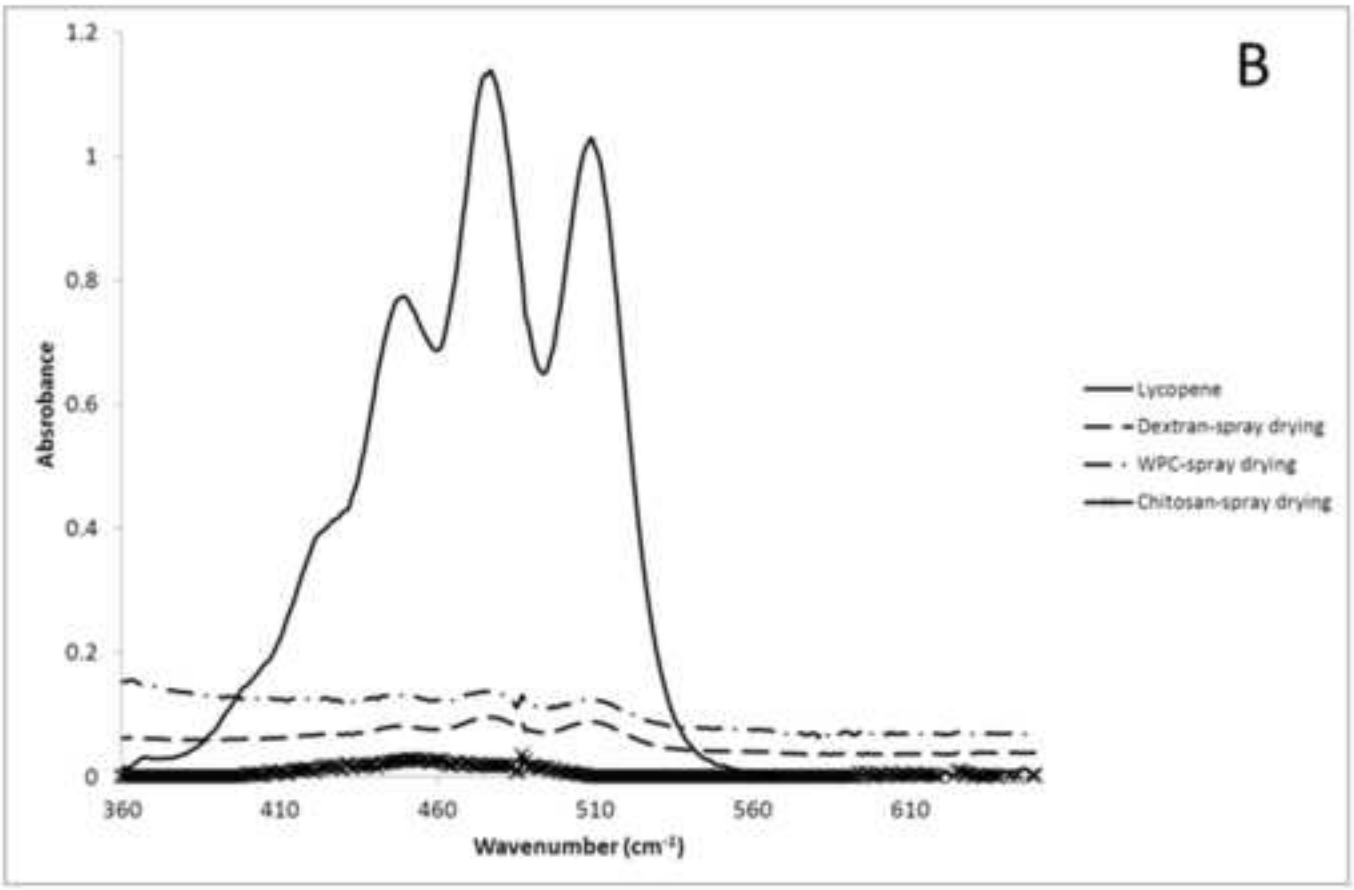

Table 1
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Table 1. Properties of the different electrospraying solutions

	Viscosity (cP)	Surface Tension (mN/m)	Electrical conductivity (μS)
Dextran	29.6 ± 0.2[a]	35.6 ± 0.2[a]	91.7 ± 0.8[a]
WPC	19.0 ± 0.9[b]	35.2 ± 0.2[a]	2056.7 ± 35.1[b]
Chitosan	49.0 ± 2.0[c]	39.9 ± 0.8[b]	392 ± 4.7[c]
Soybean Oil/lycopene	58.9 ± 0.7[d]	33.8 ± 0.1[c]	0.2 ± 0.1[d]
Dextran/lycopene	73.4 ± 1.1[e]	36.7 ± 0.5[d]	103.2 ± 1.0[e]
WPC/lycopene	110.7 ± 1.3[f]	36.7 ± 0.2[d]	1578.3 ± 11.2[f]
Chitosan/lycopene	49.3 ± 2.3[c]	39.1 ± 1.3[b]	398 ± 7.1[c]

a-f: Different superscripts within the same column indicate significant differences among different solutions ($p < 0.05$)

Table 2
Click here to download Table: Table 2. Lycopene concentration and encapsulation efficiency.docx

Table 2. Lycopene concentration and encapsulation efficiency of the different capsules developed through electrospraying (e-sp.) and spray drying.

		Lycopene concentration		
		Solution concentration (%)	Capsules concentration (%)	Encapsulation efficiency (%)
Dextran/lycopene	Emulsion e-sp.	0.5	0.13 ± 0.04^{a}	26.0 ± 8.7^{a}
	Coaxial e-sp.	0.4	0.23 ± 0.07^{b}	57.5 ± 17.7^{b}
	Spray Drying	0.5	0.08 ± 0.02^{a}	16.0 ± 4.3^{a}
WPC/lycopene	Emulsion e-sp.	0.4	0.29 ± 0.03^{b}	72.5 ± 7.1^{b}
	Coaxial e-sp.	0.3	0.23 ± 0.06^{b}	75.2 ± 33.5^{b}
	Spray Drying	0.4	0.11 ± 0.01^{a}	27.5 ± 2.1^{a}
Chitosan/lycopene	Uniaxial e-sp.	1.5	0.04 ± 0.02^{c}	2.7 ± 4.2^{a}
	Spray Drying	1.5	0.02 ± 0.01^{c}	1.3 ± 2.3^{c}

a-c: Different superscripts within the same column indicate significant differences among lycopene capsules ($p < 0.05$)

Table 3
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Table 3. Equilibrium water uptake of as-received lycopene and capsules after exposure to 70% RH, lycopene concentration before (initial) and after (final) water sorption, and total lycopene loss after water sorption.

			Lycopene concentration		
		Water uptake (%)	Initial (%)	Final (%)	Lycopene loss (%)
Lycopene	raw material	2.5 ± 0.7^{a}	100 ± 0.0^{a}	36.2 ± 10.6^{a}	63.8 ± 10.6^{a}
Dextran/lycopene	emulsion e-sp.	10.6 ± 1.4^{b}	0.13 ± 0.04^{b}	0^{b}	100^{b}
	coaxial e-sp.	15.1 ± 0.8^{c}	0.23 ± 0.07^{bc}	0.09 ± 0.02^{c}	56.6 ± 13.6^{a}
	spray drying	6.0 ± 1.8^{d}	0.08 ± 0.02^{b}	0.06 ± 0.01^{c}	19.8 ± 15.2^{c}
WPC/lycopene	emulsion e-sp.	6.1 ± 1.0^{d}	0.29 ± 0.03^{c}	0.26 ± 0.01^{d}	11.6 ± 7.3^{c}
	coaxial e-sp.	5.2 ± 0.9^{d}	0.23 ± 0.06^{c}	0.11 ± 0.06^{c}	52.1 ± 23.6^{ac}
	spray drying	2.3 ± 0.6^{a}	0.11 ± 0.01^{b}	0.10 ± 0.02^{c}	16.7 ± 23.3^{cd}
chitosan/lycopene	uniaxial e-sp.	3.3 ± 1.2^{a}	0.41 ± 0.02^{d}	0^{b}	100^{b}
	spray drying	4.8 ± 0.2^{d}	0.04 ± 0.01^{e}	0^{b}	100^{b}

a-d: Different superscripts within the same column indicate significant differences among different lycopene capsules ($p < 0.05$)

Table 4
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Table 4. Antioxidant activity, according to the ABTS methodology, of non-encapsulated lycopene/SBO and encapsulated lycopene/SBO before and after the thermal treatment (70ºC during 4 hours).

		% inhibition/µg antioxidant	µM Trolox/µg antioxidant
Lycopene/SBO	Before thermal exposure	25.6 ± 6.2^{a}	3.5 ± 0.9^{a}
	After thermal exposure	5.2 ± 0.6^{b}	0.5 ± 0.1^{b}
Lycopene/SBO from WPC capsules	Before thermal exposure	24.1 ± 1.8^{a}	3.3 ± 0.3^{a}
	After thermal exposure	14.6 ± 1.8^{c}	1.9 ± 0.3^{c}

a-c: Different superscripts within the same column indicate significant differences among antioxidant activitiy ($p < 0.05$)

MORPHOLOGY AND STABILITY OF EDIBLE LYCOPENE-CONTAINING MICRO- AND NANOCAPSULES PRODUCED THROUGH ELECTROSPRAYING AND SPRAY DRYING

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Abstract

In this work, lycopene was encapsulated through electrospraying and spray drying (using a microporous membrane cap) within different edible biopolymeric matrices. Specifically, dextran, a whey protein concentrate (WPC) and chitosan were used as matrix materials. As a strategy to incorporate the hydrophobic bioactive within the hydrophilic matrices, emulsion electrospraying and spray drying from emulsion were carried out. Moreover and, for comparison purposes, coaxial electrospraying was also performed. The electrospraying solutions properties were studied, since they do not only affect the success of the electrohydrodynamic process, but also influence the morphology of the capsules. Apart from characterizing the morphology and molecular organization of the developed capsules, the encapsulation efficiency and the lycopene stability under moisture and heating conditions were also evaluated. Results showed that even though encapsulation structures were obtained from all the matrices assayed through both processing technologies, spray drying, as a consequence of the high temperatures needed in this process, affected lycopene stability and very poor encapsulation efficiencies were found in this case. It was also seen that WPC presented the greatest encapsulation efficiency (around 75%), probably ascribed to the interactions between the biopolymer and the lycopene. Furthermore, WPC capsules were able to better protect lycopene against moisture and thermal degradation.

Keywords: lycopene, encapsulation, electrospraying, electrospinning, spray drying