processes

MDPI

Article

Storage Stability of Spray- and Freeze-Dried Chitosan-Based Pickering Emulsions Containing Roasted Coffee Oil: Color Evaluation, Lipid Oxidation, and Volatile Compounds

Elisa Franco Ribeiro [1,2,*], Tiago Carregari Polachini [1], Adilson Roberto Locali-Pereira [1], Natália Soares Janzantti [1], Amparo Quiles [2], Isabel Hernando [2] and Vânia Regina Nicoletti [1]

[1] São Paulo State University (Unesp), Institute of Bioscience, Humanities and Exact Sciences (Ibilce), Campus, São José do Rio Preto 15054-000, SP, Brazil; tiago.polachini@unesp.br (T.C.P.); a.pereira@unesp.br (A.R.L.-P.); natalia.soares-janzantti@unesp.br (N.S.J.)

[2] Food Microstructure and Chemistry Research Group, Universitat Politècnica de València (UPV), 46022 Valencia, Spain; mquichu@tal.upv.es (A.Q.); mihernan@tal.upv.es (I.H.)

* Correspondence: author: elisa.franco@unesp.br

Abstract: Drying Pickering o/w emulsions has been considered as a promising strategy to produce oil microcapsules, as long as their quality parameters can be preserved over storage. In this sense, it is shown as an interesting alternative to preserve the quality of roasted coffee oil, a valuable agroindustrial byproduct. Thus, freeze- and spray-dried chitosan-based Pickering emulsions of roasted coffee oil were evaluated over 30 days of storage at 25 °C together with the non-encapsulated oil as a control. Water sorption isotherms were determined, whereas color, oxidative stability (peroxide value and conjugated dienes) and volatile compounds were assessed over the storage period. Type II isotherms and Guggenheim–Anderson–Boer (GAB) model parameters showed that water binding was impaired by the surface oil in freeze-dried samples. Oxidation was maintained under acceptable values over the storage for all samples, with slightly higher protection also observed for volatile compounds in the spray-dried particles. The powdered emulsions were able to suitably preserve the oil's quality over 30 days of storage, enabling its commercialization and application as a food ingredient and potential flavoring.

Keywords: drying; self-aggregation; sorption isotherms; lipid oxidation; volatile compounds

Citation: Ribeiro, E.F.; Polachini, T.C.; Locali-Pereira, A.R.; Janzantti, N.S.; Quiles, A.; Hernando, I.; Nicoletti, V.R. Storage Stability of Spray- and Freeze-Dried Chitosan-Based Pickering Emulsions Containing Roasted Coffee Oil: Color Evaluation, Lipid Oxidation, and Volatile Compounds. *Processes* **2023**, *11*, 1048. https://doi.org/10.3390/pr11041048

Academic Editor: Dariusz Dziki

Received: 10 March 2023
Revised: 23 March 2023
Accepted: 28 March 2023
Published: 30 March 2023

1. Introduction

Roasted coffee oil (RCO) is a byproduct with high aggregate value that is obtained from the coffee processing industry [1]. It can be used as an interesting ingredient in the replacement of saturated fats as well as to incorporate bioactive compounds and antioxidant properties in food products [2]. Furthermore, RCO is rich in volatile compounds that are formed during the roasting process of coffee beans [3]. This lipid fraction is responsible for conferring interesting flavor to different food products as chocolates, baked goods, dairy products, and beverages such as the own coffee brew [4]. Because of the several health and flavor-promoting characteristics attributed to RCO, methods have been developed to encapsulate this byproduct in order to improve its stability and facilitate its application. One main technique is oil emulsification, which may be accomplished with the aid of natural solid particles instead of surfactants. The principle of the so-called Pickering mechanism consists in adsorbing solid particles with partial wettability at the oil droplet interface. This is carried out not only to avoid droplet coalescence (due to the high energy for detachment) but also to protect the oil against degrading external agents [5].

Many polysaccharides and/or proteins have been successfully employed to produce Pickering stabilizing particles: soy protein, whey protein, nanocellulose, nanocrystals, starch, and others [6]. Among these various solid particles, chitosan modification has been

explored in order to confer suitable emulsifying properties for the controlled release of bioactive compounds [7]. The interest in using chitosan is attributed to its biocompatibility, biodegradability, non-toxicity, and antioxidant properties, aside from being a cleaner alternative to current surfactants [8]. In fact, previous studies have demonstrated the ability of both self-aggregate and trypolyphosphate (TPP)-crosslinked chitosan to encapsulate RCO by the Pickering emulsification route [9,10]. Nevertheless, the high volume of liquid emulsions hinders their use as a delivery medium for the material of interest. In addition, their high water content has a direct effect on the long-term stability of the oil and its constituents.

Drying is a simple and effective method to reduce the water content of food products. Spray-drying is an easy and simple water removal method in which the product is aspersed in contact with a hot airflow and the dried products are collected in powdered form. On the other hand, freeze-drying is based on water sublimation under vacuum at low temperature, thus following a direct transition from the solid to the vapor phase. In spite of being more complex and slower than spray-drying, the use of low temperatures in freeze-drying prevents the degradation of thermo-sensitive compounds. Regardless of the technique, drying o/w Pickering emulsions is a novel procedure that might improve oil encapsulation and thus enhance the product quality. Ribeiro et al. [11] investigated the effects of the type of chitosan modification and drying method on the quality parameters of Pickering emulsions containing RCO. Although both self-aggregated and crosslinked chitosan showed good results, a higher oil retention was obtained for microcapsules formulated with self-aggregated chitosan.

The microencapsulation process should focus on generating final products with efficiency and quality. In addition, it is important that these quality attributes remain as less affected as possible over storage. One of the major factors affecting food preservation is the state of water, a reason by which studying sorption isotherms is encouraged. Furthermore, in lipid-rich foods such as microencapsulated oils, parameters such as lipid oxidation and color changes are indicative of deterioration [12]. Such parameters can be affected not only by the wall material used but also by the drying method [2]. In the specific case of RCO, the knowledge about how the volatile composition changes over storage may reflect the potential application and shelf life of the encapsulated oil.

This work focused on the storage stability of spray-dried and freeze-dried chitosan-based Pickering emulsions containing RCO. Sorption isotherms were experimentally determined and modeled for samples produced by the different drying methods. Lipid oxidation and volatile compounds were assessed over 30 days of storage under controlled relative humidity.

2. Materials and Methods

2.1. Microencapsulation of Roasted Coffee Oil

2.1.1. Synthesis of Chitosan Nanoparticles

Chitosan nanoparticles were synthesized by self-aggregation to formulate the Pickering emulsions. Low molecular weight chitosan (deacetylation degree of 77%, Sigma-Aldrich) was dissolved into 1% (*w*/*w*) glacial acetic acid (Dinâmica, Indaiatuba, Brazil) solution, reaching the concentration of 0.9% (*w*/*w*). The solution was kept under magnetic stirring at room temperature for 24 h until complete dissolution. Chitosan nanoparticles (CN) were obtained by deprotonating the amino groups of the D-glucosamine units, which was performed by increasing the solution pH from 3.5 up to 6.7 with NaOH 6 M (Dinâmica, Brazil).

2.1.2. Preparation of Pickering Emulsions

Roasted coffee oil, kindly supplied by Companhia Iguaçu de Café Solúvel (Cornélio Procópio, Brazil), was used to formulate emulsions with 10% (*w*/*w*) of lipid phase. RCO was dripped into the CN dispersion under homogenization (Ultra-Turrax T25, IKA, Staufen,

Germany) at 1256 rad.s^{-1}. After the total amount of oil was added to the dispersion, the samples were maintained under homogenization for an additional 5 min.

2.1.3. Microencapsulation by Spray- and Freeze-Drying

Microcapsules containing RCO were produced using the previously prepared emulsions. Maltodextrin DE 10 (Dinâmica, Brazil) was added to the emulsions as a carrier aid at the ratio of 1:5 [solids in the emulsion]:[maltodextrin] [13]. Maltodextrin was dispersed into the emulsion using an Ultra-Turrax stirrer (T25 model, IKA, Germany) at 1256 rad.s^{-1} for 5 min. For comparison purposes, a control system was elaborated by homogenizing RCO and maltodextrin under the same conditions but without CNs in the aqueous phase.

Samples were dried in triplicate using a spray dryer (B-290 model, Büchi, Switzerland). A peristaltic pump was responsible for driving the emulsion to the double-fluid spray nozzle with 0.7 mm orifice diameter. After fixing the minimum inlet air temperature at which the emulsions could be dried (160 °C), the feed flow rate was established at 2 mL.min^{-1}, atomization air rate at 742 L.h^{-1}, and aspiration rate at 35 m^3.h^{-1}. Samples were conditioned in metallized bags.

For freeze-drying, the emulsions were initially frozen at –40 °C in an ultra-freezer for 24 h, followed by drying in a freeze-dryer (model L-101, Liotop, São Carlos, Brazil) for 48 h at an approximated pressure of 200 µmHg. After freeze-drying, samples were finely ground using a mortar and stored in metallized bags. The metallized bags containing both samples of spray and freeze-dried microcapsules were placed inside desiccators at room temperature.

The resulting microencapsulation efficiency of each sample was previously reported in a recent study published by the group [11].

2.2. Storage Conditions

Spray-dried and freeze-dried microcapsules were stored in opened plastic containers at 25 °C and 54.4% of relative humidity for 30 days. Roasted coffee oil was used as a control. Samples were taken at different time intervals (0, 2, 4, 6, 10, 20, and 30 days) and the oxidation process was monitored via the analysis of color, peroxide value, conjugated dienes, and volatile composition. The amount of sample used for the analysis in the oil fraction was taken into consideration based on the oil retained in the microcapsules (85.15% for freeze-dried and 83.04%) as previously reported [11].

2.3. Water Sorption Isotherms

Water sorption behavior was evaluated by the static gravimetric method. Samples were maintained under different relative humidity and periodically weighed until constant weight was reached (<5% of weight variation), characterizing the moisture content at the equilibrium. In order to reach a wide range of relative humidity ($a_w \times 100$), saturated salt solutions of LiCl, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, NaCl, $(NH_4)_2SO_4$, and $BaCl_2$ were placed into glass desiccators, reaching a range of water activity from 0.113 up to 0.902 at 25 °C [14]. Approximately 0.3 g of each sample of the microcapsules was placed into small recipients inside desiccators accommodated in a controlled BOD-type temperature chamber (MA415, Marconi, Piracicaba, Brazil) previously set at 25 °C. The samples were weighed every week using an analytical balance (AUW220D, Shimadzu, Kyoto, Japan). The initial moisture content of the samples was determined in a vacuum oven at 70 °C [15]. After ~3 weeks, the equilibrium moisture content could be determined by the weight difference. Analyses were carried out in triplicate.

Sorption isotherms were obtained by plotting each equilibrium moisture content (X_{eq}, g of water per g of dried matter) against the corresponding water activity (a_w). The Guggenheim–Anderson–de Boer (GAB) model (Equation (1)), which is reported to accu-

rately fit sorption isotherms of food products in wide range of water activity [16], was used to model the experimental data.

$$X_{eq} = \frac{X_m C k a_w}{(1 - k a_w)(1 + (C - 1) k a_w)} \quad (1)$$

where X_m, C, and k are parameters of the model. The fitting accuracy was evaluated by the adjusted determination coefficient (R^2_{adj}) and by the root mean square error ($RMSE$).

2.4. Color Parameters

The color parameters of the microcapsules were analyzed in a colorimeter CM-5 (Konica Minolta, NJ, USA) measuring the coordinates: L (brightness) on a 0–100 scale from black to white, a (red-green), b (yellow-bluish) as well as the total color change (ΔE), given by Equation (2):

$$\Delta E = \sqrt{(L - L_0)^2 + (a - a_0)^2 + (b - b_0)^2} \quad (2)$$

where the subscript "0" corresponds to the sample before storage (time 0 days).

2.5. Peroxide Value

The oil was extracted according to the method described by Partanen et al. [17] with some modifications. Briefly, 0.5 g of microcapsules was mixed with 5 mL of acetic acid solution (1%, v/v) in a test tube and the extract was shaken for 1 min on a vortex mixer to disrupt the microcapsules. After adding 1.5 mL of iso-octane/isopropanol solution (2:1) to 400 µL of the extract, vortexed for 1 min, and centrifuged at 1000× g for 4 min, the phases were separated. The non-encapsulated oil sample was decolored according to Anese et al. [18] in order to avoid the absorbance interference of colored compounds. The peroxide value was determined spectrophotometrically according to the IDF standard method 74A:1991 [19]. The supernatant (0.4 mL) or a droplet of oil (0.1–0.3 g) in the case of the control was added to 9.6 mL of chloroform/methanol solution (7:3, v/v). Then, 50 µL of 3.9 mol/L potassium thiocyanate and 50 µL of 0.072 mol/L Fe^{2+} were added. The mixture was vortexed and reacted in the dark for 5 min. The chloroform/methanol solution was used as a blank and the absorbance was measured at 510 nm using a Multiskan Go Spectrophotometer (Thermo Fisher Scientific, Vantaa, Finland). The concentration of hydroperoxides was determined using a Fe^{3+} standard curve, as described by Frascareli et al. [4].

2.6. Conjugated Dienes

For measurement of the conjugated dienes, the oil was extracted from the microcapsules following the method described by Satué-Garcia et al. [20] with modifications. A powder sample of 1.0 g was mixed with 10 mL of acetic acid solution (1%, v/v) and the extract was vortexed for 1 min. Hexane (7 mL) was used for separating the organic phase through centrifugation at 10,000 rpm for 20 min and the supernatant was evaporated under nitrogen flow. The recovered oil was suspended with 2-propanol in order to obtain a measurable absorbance at 234 nm [21]. The results obtained spectrophotometrically were expressed as millimoles of hydroperoxides per kilogram of oil using a molar coefficient of 26,000 for methyl linoleate hydroperoxides in hexane [22].

2.7. Volatile Compounds

The volatile compound profile of the crude and microencapsulated RCO was analyzed by using headspace solid phase microextraction-gas chromatography-flame ionization detector/mass spectrometry (HS-SPME-GC-FID/MS). Samples were taken from storage at 10-day time intervals to be analyzed. The extraction of volatile compounds was carried out in 10 mL vials (hermetically sealed) containing 300 µL of RCO or 2 g of microcapsules, based on the oil retention values previously determined. The samples were heated at 70 °C for 20 min and then the SPME fiber (DVB/CarboxenTM/PDMS) was inserted into the headspace for 30 min according to the methodology described by

Freiberger et al. [23]. After that, the fiber was placed in the GC-FID injection system for 5 min and volatile compounds were desorbed at 250 °C under splitless mode into an Rtx-Wax column (30 m × 0.25 mm × 0.25 µm) using hydrogen as the carrier gas at a flow rate of 1.2 mL.min^{-1}. The separation and quantification of compounds was performed on a gas chromatograph equipped with a flame ionization detector (CF-2014, Shimadzu Scientific Corporation, Japan) according to the following oven temperature program: 40 °C for 5 min; ramp 4 °C.min^{-1} up to 60 °C, hold for 5 min; then 8 °C.min^{-1} up to 250 °C and hold 3 min. The detector temperature was 280 °C. The same chromatographic parameters described for GC-FID were used in GC-MS (GC–MS QP2010 SE, Shimadzu, Japan) for the identification of volatile compounds. For this, a fused silica capillary column SH-Rtx-Wax (30 m × 0.25 mm × 0.25 µm) was used with helium as the carrier gas at a constant flow rate of 1 mL.min^{-1}. The quadrupole mass spectrometer was operated in the electron impact mode (70 eV) and the source temperature and detector were 250 °C and 280 °C, respectively, with a mass/charge range of 35–350 *m/z*. The identification of the compounds was based on their mass spectra compared to the National Institute of Standards and Technology (NIST/2002) Library and retention indices. An alkane standard (C7-C30) (Sigma-Aldrich) diluted in hexane was employed to obtain the retention indices [24] that were also compared with those of the literature [25–28].

2.8. Statistical Analysis

Means of the experimental measurements were subjected to analysis of variance (ANOVA) using the STATISCA Software (StatSoft Inc., Tulsa, OK, USA) and the presence of significant differences was evaluated by the Tukey test at a 95% confidence level.

3. Results and Discussion

3.1. Water Sorption Isotherms

The equilibrium moisture content (X_{eq}) of the spray-dried (SD) and freeze-dried (FD) samples was determined in triplicate for the range of water activity studied. Spray-dried microcapsules showed X_{eq} varying from 0.0187 to 0.2717 g of water·g^{-1} of dry matter, whereas the freeze-dried samples had slightly higher X_{eq}, varying from 0.0312 and 0.3061 g of water·g^{-1} of dry matter. The X_{eq} values increased with increasing water activity as expected.

The sorption isotherms showed a sigmoidal shape (Figure 1) typical of type II isotherms according to the Brunauer classification [29]. The first zone of low water activity corresponded to the region where water molecules were strongly bound to the matrix, while the latter, of high a_w, was related to free water molecules [30]. The intermediate zone of almost constant X_{eq} was barely noticed for both samples. This is probably a consequence of the constituting maltodextrin, which has a trend to confer a type III isotherm (with a linear increase in X_{eq} up to a critical a_w) when incorporated in dried products [16], but also to the hydrophobicity degree of self-aggregated chitosan [9].

In addition to the mathematical estimation of the sorption behavior, the parameters of the GAB model provide important information about the microstructure and water–matrix interactions. Thus, the GAB model was fitted to the experimental data and $R^2_{adj} > 0.99$ and $RMSE < 0.01$ was observed (Table 1). These results provide insights into the model's accuracy and the reliability of the fitting parameters shown in Table 1. A requirement of $0.24 < k < 1$ and $5.4 < C < \infty$ is reported in the literature for GAB parameters to confirm type II isotherms [31], which, in fact, were satisfied in the present study.

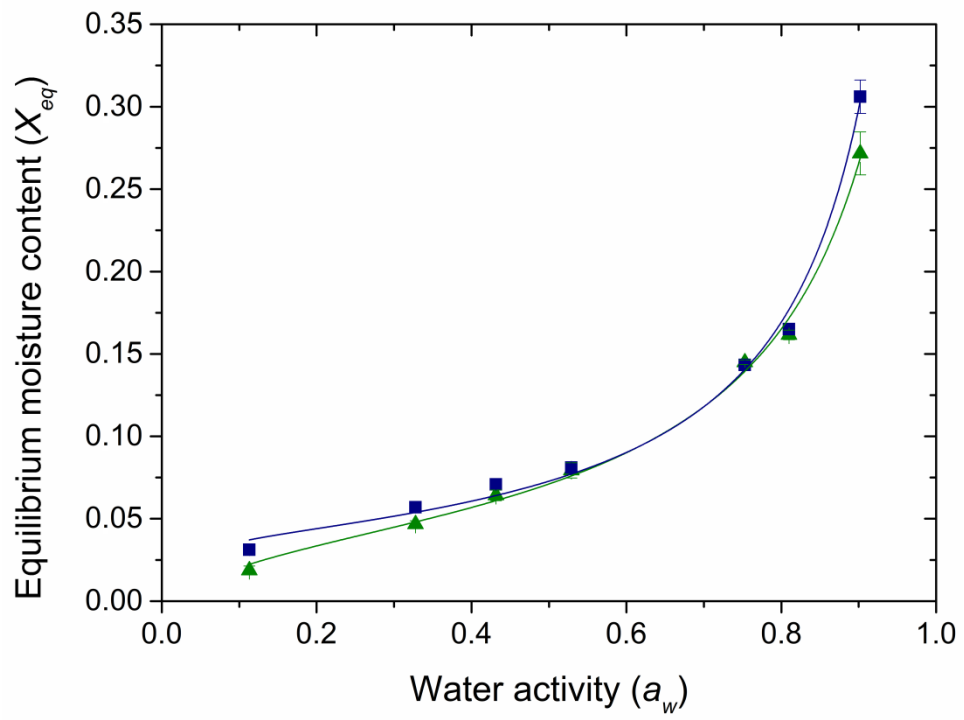

Figure 1. Water sorption isotherms at 25 °C for the spray-dried (▲, ——) and freeze-dried (■, ——) samples. Lines represent the fitted GAB model.

Table 1. Fitting parameters of the GAB model to the sorption isotherms.

Parameters	Samples	
	Spray-Dried	Freeze-Dried
X_m (g water/g dry matter)	0.044 ± 0.003 [a]	0.038 ± 0.001 [b]
C	7.04 ± 1.08 [b]	29.82 ± 4.34 [a]
k	0.931 ± 0.019 [b]	0.969 ± 0.009 [a]
R^2_{adj}	>0.991	>0.990
$RMSE$	<0.0064	<0.0072

[ab] Means and standard deviation followed by the same letter in the same line represent no significant difference among the samples by the Tukey test at 95% of confidence.

The parameter X_m represents the monolayer moisture content (i.e., the moisture content needed to cover the first layer of water molecules bound to the food matrix). Above this value, multilayer water molecules with less strong interactions are expected for the sorbent than the monolayer. In these conditions, water molecules are more available for reactions. Monolayer moisture (X_m) has a close agreement with the hydrogen bonding degree [30], which means that freeze-dried samples, presenting smaller X_m values, have less active sites for water sorption, probably due to the higher particle size (276.21 µm in comparison to 12.83 µm to spray-dried microparticles) with lower surface area [32] and to the overlapping of active sites by the higher amounts of surface oil—parameters evaluated in a previous study for the same samples [11]. On the other hand, Figure 1 showed slightly higher X_{eq} for the freeze-dried than spray-dried samples, mainly at low (<0.25) and high (>0.85) water activities. This may be a result of the capacity for entrapping water into the porous structure of freeze-dried samples, although this moisture is not strongly bound to the active site. In summary, the spray-dried microcapsules bound the water molecules in a stronger way, whereas the freeze-dried samples seemed to have cavities that were able to entrap water molecules, impairing water removal due to steric issues.

3.2. Color Parameters

The color of the microcapsules was evaluated over the 30 days of storage at 25 °C. As expected, the color parameters (Table 2) showed that the oil had brown darkened coloration with low brightness, *a*, and *b* values. These results are strongly related to the presence of compounds formed during the Maillard reaction during roasting of the beans [18]. On the other hand, both SD and FD samples were showed to be brighter than the oil, which tended toward a yellowish coloration as a consequence of the encapsulant material's incorporation. SD samples were slightly brighter and less yellowish than the FD samples, probably due to the higher oil retention in the latter [11].

Table 2. Color parameters of the roasted coffee oil (RCO) and spray- and freeze-dried microcapsules over 30 days of storage at 25 °C.

Samples	Days	Color Parameters			
		a	***b***	***L***	**Δ*E***
RCO	0	$0.02 \pm <0.01^{e}$	0.11 ± 0.09^{d}	$0.09 \pm <0.01^{d}$	-
	2	0.44 ± 0.01^{de}	0.13 ± 0.08^{cd}	0.16 ± 0.04^{cd}	$0.45 \pm <0.01^{d}$
	4	1.66 ± 0.46^{bcd}	0.42 ± 0.09^{bcd}	0.40 ± 0.10^{bc}	1.71 ± 0.44^{bcd}
	6	1.56 ± 0.71^{cd}	0.38 ± 0.21^{bcd}	0.38 ± 0.21^{bc}	1.61 ± 0.77^{cd}
	10	4.21 ± 0.38^{a}	1.15 ± 0.09^{a}	0.85 ± 0.09^{a}	4.39 ± 0.35^{a}
	20	2.60 ± 0.61^{bc}	0.65 ± 0.13^{bc}	0.58 ± 0.12^{ab}	2.69 ± 0.63^{bc}
	30	2.87 ± 1.07^{ab}	0.72 ± 0.39^{ab}	0.57 ± 0.18^{ab}	2.97 ± 1.12^{b}
Spray-dried	0	0.94 ± 0.05^{c}	12.43 ± 0.40^{ab}	86.54 ± 0.31^{ab}	-
	2	0.89 ± 0.04^{c}	11.63 ± 0.08^{c}	85.45 ± 0.05^{c}	1.35 ± 0.03^{a}
	4	0.87 ± 0.01^{bc}	11.71 ± 0.03^{c}	85.52 ± 0.04^{c}	1.25 ± 0.05^{ab}
	6	0.95 ± 0.02^{bc}	12.35 ± 0.16^{b}	86.78 ± 0.08^{a}	0.29 ± 0.02^{d}
	10	0.99 ± 0.01^{b}	12.36 ± 0.13^{b}	86.63 ± 0.07^{ab}	0.17 ± 0.04^{d}
	20	1.15 ± 0.02^{a}	12.91 ± 0.06^{a}	86.32 ± 0.16^{b}	0.59 ± 0.12^{c}
	30	1.17 ± 0.02^{a}	12.65 ± 0.23^{ab}	85.49 ± 0.13^{c}	1.11 ± 0.09^{b}
Freeze-dried	0	2.9 ± 0.01^{b}	21.63 ± 0.04^{a}	77.19 ± 0.04^{ab}	-
	2	2.75 ± 0.08^{c}	20.51 ± 0.52^{c}	76.84 ± 0.29^{c}	1.18 ± 0.58^{b}
	4	2.90 ± 0.01^{b}	21.28 ± 0.04^{ab}	77.02 ± 0.07^{bc}	0.39 ± 0.06^{c}
	6	2.93 ± 0.01^{b}	21.03 ± 0.13^{abc}	76.69 ± 0.04^{cd}	0.78 ± 0.10^{bc}
	10	2.95 ± 0.04^{b}	20.88 ± 0.10^{bc}	76.91 ± 0.08^{bc}	0.81 ± 0.12^{bc}
	20	2.86 ± 0.01^{b}	19.25 ± 0.02^{d}	77.49 ± 0.05^{a}	2.40 ± 0.02^{a}
	30	3.19 ± 0.01^{a}	20.81 ± 0.01^{bc}	76.38 ± 0.09^{d}	1.19 ± 0.07^{b}

^{abcde} Means and standard deviation followed by the same letter in the same column for the same sample represent no significant difference among the days for the same sample by the Tukey test at 95% of confidence.

Total color variation (Δ*E*) was used to evaluate possible changes in the coloration of the samples during storage. According to Wibowo et al. [33], Δ*E* between 0 and 0.5 is considered to be unnoticeable, between 0.5 and 1.5 slightly noticeable, between 1.5 and 3.0 noticeable, between 3.0 and 6.0 visible, and higher than 6.0 greatly visible. Thus, it can be stated that the majority of the changes in the coloration of microcapsules were slightly noticeable. Some slightly variations could be seen in the RCO, probably due to homogenization of the samples during measurement.

In general, the RCO tended to become slightly brighter over the storage days, which can be attributed to be more related to sedimentation of the unsaponifiable matter than to oxidation itself (see Sections 3.3 and 3.4). Regarding the dried samples, the FD samples were darker than the SD, probably due to the higher amount of surface oil [11]. Both powders became slightly darker over storage, which can be related to the moisture gain during the equilibration with the controlled relative humidity.

3.3. Peroxide Value

The formation of hydroperoxides as primary compounds of lipid degradation products was determined as indicative of the product quality and its safety. As the hydroperoxides are degraded, compounds such as aldehydes, ketones, and hydrocarbons are released and technological properties of the oil start to be affected [34]. Thus, the peroxide value of the non-encapsulated and encapsulated roasted coffee oil was determined over 30 days of storage at 25 °C (Figure 2a).

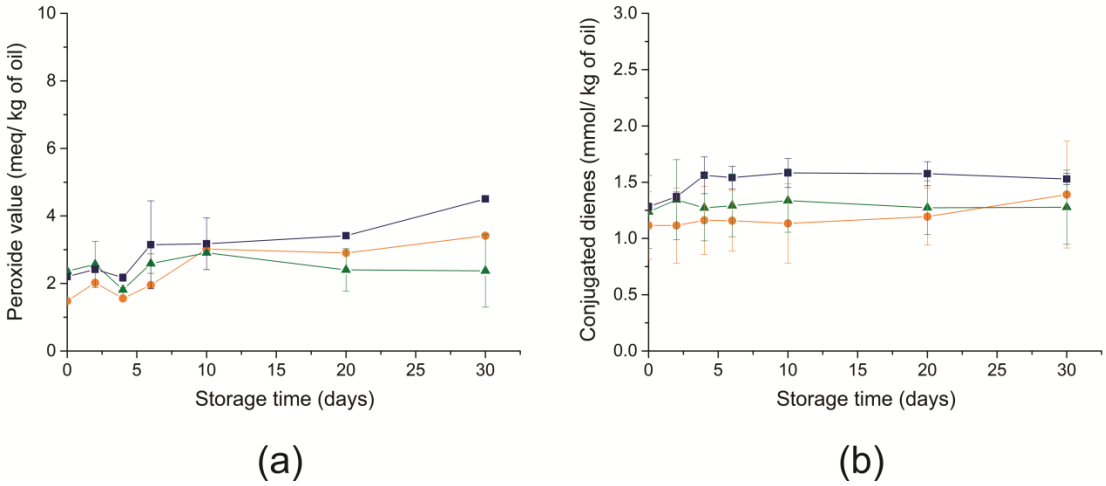

Figure 2. (**a**) Peroxide value (meq/kg of oil) and (**b**) conjugated dienes (mmol/kg of oil) for the spray-dried (—), freeze-dried (—), and non-encapsulated RCO (—) over 30 days of storage at 25 °C.

At the beginning of the storage experiments, the non-encapsulated oil showed a slightly lower peroxide (~1.5 meq/kg of oil) value when compared to the encapsulated oil by both drying methods (~2.4 meq/kg of oil). These differences can be attributed to the air incorporation into the oil during emulsification and drying, which is in accordance with the literature for other lipid sources [35,36].

Up to 10 days of storage, the samples showed an approximately similar peroxide value. After that, the oil from the SD microcapsules showed slightly lower peroxide values when compared to the non-encapsulated oil, although this difference was not significant due to the heterogeneity of the samples. The possible trend of SD samples for decreasing oil peroxide values can be attributed to the reduction in hydroperoxide precursors and secondary degradation compounds, which may occur through the steric and chitosan wall thickness hindrance against pro-oxidant penetration into the microcapsules [37]. On the other hand, the oil in the FD microparticles presented a peroxide value higher (~4.5 meq/kg of oil) than that of the non-encapsulated oil (~3.4 meq/kg of oil) and the oil in the SD microcapsules (~2.4 meq/kg of oil). Because the FD microparticles had a much higher particle size than the SD microcapsules [11], the bed porosity of the FD microparticles tended to be higher than that for the SD microcapsules. In addition to the higher amounts of external oil observed in the FD sample and its more porous structure [11], the higher bed porosity might have allowed oxygen to diffuse more easily in the FD samples, consequently causing the slightly higher lipid oxidation than in the SD samples. In fact, the bed porosity plays an important role during the storage of microcapsules due to the increased oil accessibility from the microcapsules [21]. Moreover, according to the sorption isotherms (see Section 3.1), water molecules are more freely available in the FD samples than in the SD ones, which might had an important role in accelerating the oxidation reactions.

In the non-encapsulated oil, the oxidation occurred only on the surface of the samples and the oxygen was not able to penetrate the samples, bringing the peroxide content per kg of oil to lower levels. Moreover, the roasting process led to the formation of colored Maillard reaction compounds known as melanoidins with antioxidant properties. These

compounds act against oxidation and explain the low oxidation rate of the lipid fraction of roasted coffee beans [18].

In spite of the observed differences, all of the samples showed an acceptable peroxide value with less than 15 meq/kg of oil—within the safety range recommended by the *Codex Alimentarius* for cold-pressed oils. The way that lipid oxidation proceeds in each sample should be carefully evaluated over longer periods in order to observe whether this trend remains similar over time.

3.4. Conjugated Dienes

The conjugated diene content in the samples was determined by measuring the rearrangement of the hydroperoxide double bonds during lipid oxidation. Results are shown in Figure 2b for all samples over the 30 day period of storage. The obtained data over storage time were in accordance with the peroxide value determinations, confirming the analyses' dependence [38]. At day 0, the samples had a similar concentration of conjugated dienes of 1.2 mmol/kg of oil. Nevertheless, the oil in the FD samples was slightly more affected by lipid oxidation than the non-encapsulated oil and the oil in the SD samples. It is important to highlight that at day 30, the non-encapsulated oil started to show a trend to increase up to the values of the FD samples. This may be indicative of the lower protection of non-encapsulated oil under longer storage periods, mainly after 30 days. Analogously, the presence of chitosan nanoparticles as a wall material seemed to present a protective effect that scavenged free radicals and interrupted lipid oxidation under long-term storage. Although there was a subtle distinction among the samples, conjugated dienes did not exceed 1.6 mmol/kg of oil for the whole period analyzed. These values were lower than the ones found for different oils subjected to oxidative stress [38–40], which can be attributed to the colored compounds from the Maillard reaction formed during the roasting process. Together with the results of the peroxide value, lipid oxidation during 30 days may not be a restriction for the application of microcapsules in food products.

3.5. Volatile Compounds

Changes in the content of volatile compounds during storage were observed using HS-SPME-GC-FID/MS applied to the microcapsules and non-encapsulated RCO. The 27 major compounds identified in the headspace and their respective GC-FID peak areas are shown in Table 3. Aroma description was reported based on the literature.

In addition to protecting the RCO against lipid oxidation, it is important that the microcapsules contain the desired compounds that compose the roasted coffee aroma. The SD and FD microcapsules presented similar values for the total content of volatile compounds at the end of storage. A higher impact of storing could be observed for the non-encapsulated oil, which presented a decrease of about 50% in the total volatile content (Figure 3).

Despite most of the volatile compounds present in RCO having been identified to contribute to the coffee flavor, the high presence of ketones, pyrazines, aldehydes, and furans played an important role on the aroma of the studied samples. Figure 4 shows the behavior of each group along 4 weeks of storage.

Table 3. Volatile aroma compounds of the non-encapsulated roasted coffee oil (RCO) and microcapsules of RCO produced by spray-drying (SD) and freeze-drying (FD).

Volatile Compounds	Retention Index (RI)		GC-FID Peak Area ($\times 10^4$)													Aroma Description
			t = 0			t = 10			t = 20			t = 30				
	Experimental	Literature [a]	Coffee Oil	SD	FD	Coffee Oil	SD	FD	Coffee Oil	SD	FD	Coffee Oil	SD	FD		
Pyridine	-	1194 [2]	13.4 ± 4.8 [a]	1.1 ± 0.3 [b]	0.3 ± 0.1 [c]	18.3 ± 1.8 [a]	0.5 ± 0.1 [c]	0.8 ± 0.1 [b]	7.2 ± 0.2 [a]	1.4 ± 0.3 [b]	1.3 ± 0.2 [b]	7.4 ± 0.2 [a]	0.8 ± 0.2 [b]	0.6 ± 0.0 [b]	Roasted [3]	
Pyrazine																
Pyrazine	-	-	4.5 ± 0.5 [a]	0.5 ± 0.4 [c]	2.4 ± 1.4 [b]	1.9 ± 0.8 [a]	0.4 ± 0.1 [b]	0.5 ± 0.2 [b]	1.5 ± 0.4 [a]	0.4 ± 0.0 [b]	0.3 ± 0.1 [b]	0.5 ± 0.1 [a]	0.1 ± 0.1 [b]	0.2 ± 0.0 [b]	Rancid peanuts [3]	
2,5-Dimethylpyrazine	1314	1329 [2]	15.4 ± 1.2 [a]	2.8 ± 0.9 [b]	1.4 ± 0.4 [b]	17.0 ± 0.9 [a]	1.2 ± 0.3 [b]	0.6 ± 0.1 [c]	7.8 ± 3.7 [a]	1.5 ± 0.3 [b]	2.3 ± 1.7 [b]	10.2 ± 1.3 [a]	1.9 ± 0.3 [b]	3.6 ± 2.5 [b]	Nuts [3]	
2,6-Dimethylpyrazine	1337	1335 [2]	0.1 ± 0.1 [b]	0.5 ± 0.2 [a]	0.7 ± 0.1 [a]	0.0 ± 0.0 [b]	0.1 ± 0.0 [a]	0.0 ± 0.0 [b]	0.0 ± 0.0 [c]	0.1 ± 0.0 [b]	0.3 ± 0.0 [a]	0.0 ± 0.0 [a]	0.0 ± 0.0 [a]	0.0 ± 0.0 [a]	Roasted [3]	
2-Ethyl-5-methylpyrazine	1432	1428 [2]	2.6 ± 0.1	4.8 ± 0.1	16.1 ± 1.2	1.0 ± 0.7 [c]	4.2 ± 0.8 [a]	2.7 ± 0.2 [b]	2.6 ± 2.0 [a]	0.1 ± 0.1 [b]	1.4 ± 1.2 [ab]	0.1 ± 0.0 [b]	4.6 ± 0.1 [a]	0.1 ± 0.1 [b]	Nuts, peanut [2]	
Aldehyde																
Pyrrole-2-carboxaldehyde	2040	2017 [2]	9.8 ± 0.6 [a]	6.2 ± 0.6 [b]	5.6 ± 0.4 [b]	9.0 ± 0.2 [a]	5.8 ± 0.6 [b]	5.0 ± 0.4 [b]	10.5 ± 0.4 [a]	5.3 ± 0.3 [b]	6.3 ± 0.8 [b]	8.1 ± 1.6 [a]	5.6 ± 0.4 [b]	4.1 ± 0.1 [c]	Roasted, smoky [2]	
Nonanal	1397	-	1.2 ± 0.1 [a]	0.3 ± 0.0 [c]	0.8 ± 0.2 [b]	3.2 ± 0.2 [a]	0.6 ± 0.0 [b]	0.5 ± 0.0 [b]	0.6 ± 0.0 [b]	0.4 ±0.0 [c]	0.8 ± 0.1 [a]	0.0 ± 0.0 [b]	0.2 ± 0.1 [a]	0.0 ± 0.0 [b]	-	
Furans																
2-Furancarboxaldehyde	1467	1465 [2]	1.6 ± 0.1 [a]	1.8 ± 0.1 [a]	1.6 ± 0.0 [a]	1.2 ± 0.1 [a]	0.8 ± 0.0 [b]	0.4 ± 0.0 [c]	0.8 ± 0.0 [b]	4.3 ± 0.3 [a]	3.9 ± 1.8 [a]	2.4 ± 0.1 [a]	0.9 ± 0.1 [b]	0.7 ± 0.1 [b]	Caramellic, cinnamon, almond [2]	
Furfural	1484	1485 [1]	4.8 ± 2.1 [a]	0.0 ± 0.0 [c]	0.2 ± 0.0 [b]	13.4 ± 0.9 [a]	0.2 ± 0.1 [b]	0.2 ± 0.0 [b]	1.8 ± 0.5 [a]	0.4 ± 0.0 [b]	0.5 ± 0.1 [b]	0.0 ± 0.0 [a]	0.2 ± 0.2 [a]	0.1 ± 0.1 [a]	Caramellic, woody [1]	
2-Furanmethhyl acetate	1538	1539 [2]	0.2 ± 0.0 [b]	0.3 ± 0.1 [b]	1.4 ± 0.3 [a]	0.2 ± 0.0 [b]	0.4 ± 0.1 [a]	0.4 ± 0.1 [a]	1.0 ± 0.2 [a]	0.1 ± 0.0 [c]	0.2 ± 0.0 [b]	0.2 ± 0.0 [b]	0.8 ± 0.3 [a]	0.0 ± 0.0 [b]	Roasted nut, floral [2]	
Furan-3-methanol	1677	1673 [2]	2.8 ± 0.1 [a]	2.6 ± 0.4 [a]	3.2 ± 0.3 [a]	1.8 ± 0.0 [c]	2.0 ± 0.0 [b]	2.3 ± 0.0 [a]	1.8 ± 0.0 [a]	1.6 ± 0.1 [b]	1.3 ± 0.7 [ab]	1.6 ± 0.1 [b]	1.7 ± 0.0 [b]	1.9 ± 0.1 [a]	Carmellic [3]	
Ketones																
4-Cyclopentene-1,3-dione	1574	1573	64.5 ± 2.8 [a]	40.8 ± 2.7 [b]	44.1 ± 4.0 [b]	19.6 ± 0.6 [a]	14.0 ± 0.6 [b]	19.3 ± 1.5 [a]	24.7 ± 2.1 [a]	10.2 ± 3.3 [c]	19.8 ± 2.1 [b]	5.0 ± 0.6 [c]	7.2 ± 0.3 [b]	13.6 ± 1.3 [a]	-	
1,2-Cyclopentanedione	1748	1742	123.9 ± 5.3 [c]	196.0 ± 13.9 [b]	226.5 ± 6.7 [a]	67.6 ± 1.8 [c]	172.2 ± 4.8 [b]	207.0 ± 8.5 [a]	59.7 ± 2.4 [c]	159.3 ± 0.3 [b]	210.2 ± 15.4 [a]	48.9 ± 8.8 [b]	112 ± 39.7 [a]	116.8 ± 29.3 [a]	-	
2-Hydroxy-3-methyl-2-cyclopenten-1-one	1855	1857 [1]	5.0 ± 0.2 [a]	4.1 ± 0.9 [b]	5.0 ± 1.1 [a]	4.2 ± 0.1 [a]	3.4 ± 0.3 [b]	2.9 ± 0.1 [b]	4.2 ± 0.1 [a]	2.4 ± 0.2 [b]	3.1 ± 0.1 [a]	2.7 ± 0.3 [a]	2.6 ± 0.0 [a]	2.8 ± 0.1 [a]	Caramellic [1]	
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	1920	1909 [1]	646.3 ± 50.0 [a]	152.4 ± 14.6 [b]	139.7 ± 3.2 [b]	422.0 ± 7.5 [a]	144.7 ± 7.5 [b]	130.5 ± 3.8 [c]	411.8 ± 2.0 [a]	92.9 ± 5.5 [c]	124.5 ± 1.7 [b]	207.2 ± 25.5 [a]	119.0 ± 4.4 [b]	103.3 ± 14.5 [b]	Caramellic, smoky [1]	
3-Hydroxy-2-methyl-4-pyrone	1965	1955 [2]	13.4 ± 0.9 [b]	16.3 ± 1.4 [a]	16.6 ± 2.9 [a]	12.1 ± 0.2 [c]	16.5 ± 1.3 [a]	14.1 ± 0.6 [b]	15.2 ± 0.4 [c]	17.5 ± 0.8 [b]	20.1 ± 0.3 [a]	11.3 ± 1.5 [b]	17.4 ± 0.4 [a]	16.8 ± 0.1 [a]	Caramel	
2-Pentadecanone	2143	2031	33.5 ± 1.7 [a]	32.9 ± 5.8 [a]	24.7 ± 2.2 [b]	25.2 ± 0.5 [c]	39.8 ± 3.2 [a]	32.3 ± 0.8 [b]	40.0 ± 1.0 [a]	37.4 ± 0.9 [b]	33.3 ± 4.9 [ab]	35.0 ± 6.2 [ab]	39.1 ± 2.6 [a]	34.2 ± 0.6 [b]	Waxy [2]	

Table 3. *Cont.*

Volatile Compounds	Retention Index (RI)		GC-FID Peak Area ($\times 10^4$)												Aroma Description
			t = 0			t = 10			t = 20			t = 30			
	Experimental	Literature [a]	Coffee Oil	SD	FD	Coffee Oil	SD	FD	Coffee Oil	SD	FD	Coffee Oil	SD	FD	
Acids															
3-Methyl-2-butenoic acid	1772	1777 [2]	33.4 ± 0.2 [a]	22.1 ± 0.9 [b]	24.8 ± 3.8 [b]	16.4 ± 0.6 [b]	21.8 ± 0.1 [a]	21.1 ± 1.9 [a]	23.3 ± 1.1 [b]	33.4 ± 1.9 [a]	31.4 ± 1.1 [a]	13.4 ± 1.5 [b]	23.3 ± 0.1 [a]	23.3 ± 1.4 [a]	Dairy, fermented [3]
Caproic acid	1844	1829	88.6 ± 3.5 [b]	102.4 ± 3.5 [a]	95.1 ± 11.5 [ab]	69.6 ± 2.2 [b]	83.5 ± 4.0 [a]	78.0 ± 1.7 [a]	61.8 ± 0.6 [b]	58.2 ± 2.8 [c]	63.8 ± 0.6 [a]	37.7 ± 4.9 [b]	66.9 ± 0.4 [a]	67.7 ± 1.2 [a]	Goat-like odor
Acetic acid	1451	1458 [1]	4.3 ± 0.2	4.7 ± 0.5	5.6 ± 0.5	0.8 ± 0.1 [a]	0.2 ± 0.0 [b]	0.2 ± 0.0 [b]	1.2 ± 0.0 [b]	7.8 ± 0.1 [a]	6.6 ± 4.5 [a]	0.6 ± 0.1 [c]	5.1 ± 3.6 [a]	1.9 ± 0.2 [b]	Acidic, pungent [1]
Butanoic acid	1630	1632 [1]	29.3 ± 1.1 [a]	22.8 ± 0.7 [b]	25.1 ± 1.6 [b]	16.5 ± 0.3 [a]	13.6 ± 0.1 [c]	15.5 ± 0.2 [b]	15.9 ± 0.1 [a]	8.7 ± 0.8 [c]	14.8 ± 0.2 [b]	6.5 ± 0.7 [c]	9.4 ± 0.2 [b]	13.1 ± 0.8 [a]	Sharp, buttery [1]
Benzoic acid	2443	2443 [2]	23.9 ± 4.7 [a]	4.3 ± 0.4 [b]	4.9 ± 0.8 [b]	23.1 ± 0.2 [a]	3.7 ± 0.2 [c]	7.1 ± 0.5 [b]	27.0 ± 0.4 [a]	4.2 ± 0.0 [b]	5.0 ± 0.9 [b]	25.6 ± 3.5 [a]	3.1 ± 0.1 [c]	5.7 ± 0.7 [b]	-
Palmitic acid	2900	2919	0.9 ± 0.1 [a]	0.4 ± 0.0 [b]	0.4 ± 0.0 [b]	3.0 ± 0.2 [a]	0.3 ± 0.0 [c]	0.9 ± 0.0 [b]	2.4 ± 0.0 [a]	0.3 ± 0.0 [b]	0.4 ± 0.0 [b]	1.8 ± 0.0 [a]	1.9 ± 0.1 [a]	0.7 ± 0.1 [b]	-
Phenolics															
4-Ethyl-2-methoxy-phenol	2048	2044 [2]	20.7 ± 0.7 [a]	17.3 ± 1.2 [b]	15.3 ± 0.6 [c]	8.3 ± 0.4 [a]	6.7 ± 0.9 [b]	5.3 ± 0.7 [c]	22.3 ± 0.3 [a]	15.9 ± 0.8 [b]	16.9 ± 0.7 [b]	17.2 ± 3.0 [a]	15.5 ± 0.6 [a]	15.6 ± 0.0 [a]	Spicy; smoky [1]
4-Methoxyphenol	2098	2099 [2]	17.1 ± 0.3 [a]	10.3 ± 0.7 [b]	8.8 ± 0.4 [c]	16.1 ± 0.5 [a]	9.4 ± 0.7 [b]	8.3 ± 0.8 [c]	19.4 ± 0.1 [a]	9.1 ± 0.3 [b]	9.4 ± 0.0 [b]	15.8 ± 3.1 [a]	9.7 ± 0.6 [b]	8.8 ± 0.2 [b]	-
2-Methoxy-4-vinylphenol	2215	2219 [2]	12.6 ± 1.0 [a]	7.8 ± 1.0 [b]	7.7 ± 0.0 [b]	13.2 ± 0.3 [a]	8.8 ± 0.8 [b]	8.2 ± 0.2 [b]	15.5 ± 0.3 [a]	8.4 ± 0.1 [b]	7.6 ± 0.1 [c]	14.3 ± 2.9 [a]	8.6 ± 0.8 [b]	7.3 ± 0.0 [b]	Spicy, peanut [2]
Total			1330.6 ± 83.4 [a]	735.2 ± 9.8 [b]	757.8 ± 32.8 [b]	956.0 ± 24.3 [a]	639.5 ± 0.6 [c]	668.6 ± 25.1 [b]	980.8 ± 0.1 [a]	566.8 ± 12.5 [c]	669.0 ± 6.7 [b]	654.1 ± 81.4 [a]	529.7 ± 57.6 [b]	530.9 ± 48.7 [b]	

[a] Lee et al. [25] [1]; Hurtato-Benavides et al. [26] [2]; Cincotta et al. [27] [3]. Mean ± standard deviation. Different letters in the same period and in the same line indicate significant difference ($p < 0.05$).

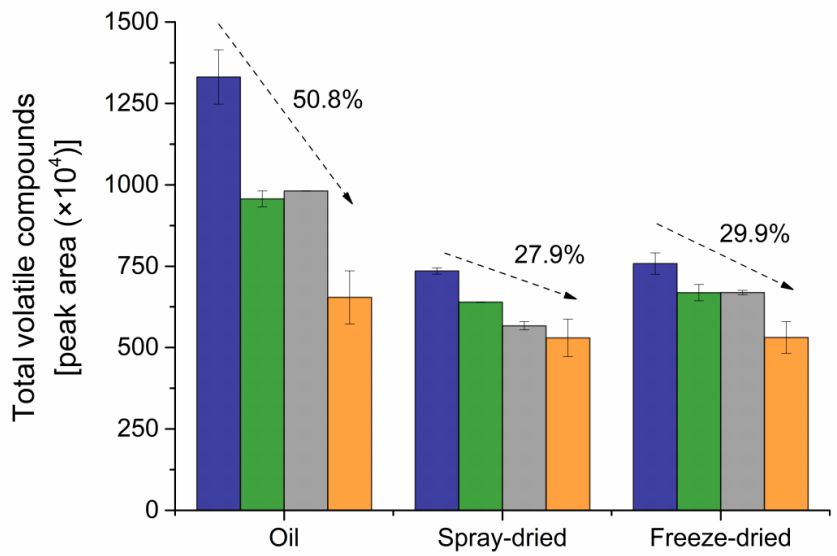

Figure 3. The effects of drying methods for the encapsulation of RCO on the peak areas of the total volatile compounds detected in the samples under storage. Analyses were carried out at day 0 (■), day 10 (■), day 20 (■), and day 30 (■).

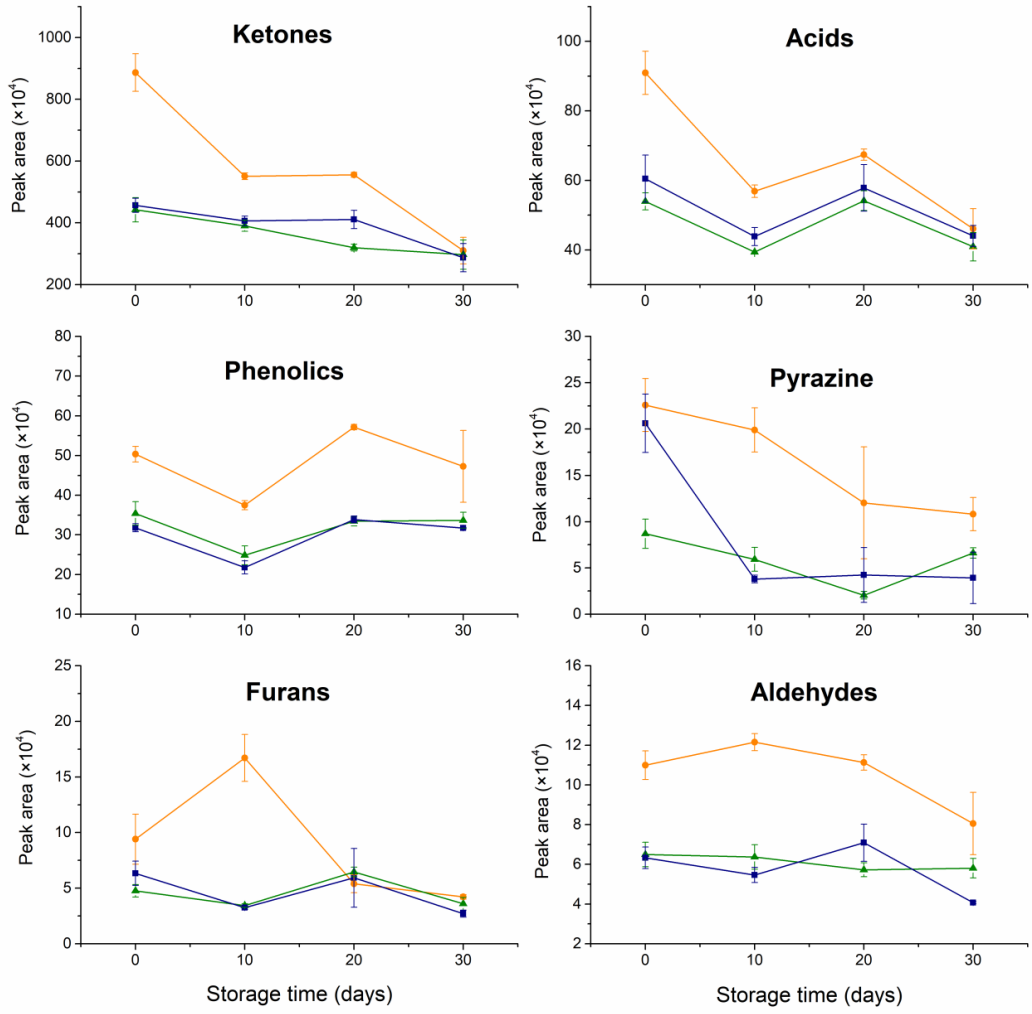

Figure 4. The effects of storage on the spray-dried (—), freeze-dried (—), and non-encapsulated RCO (—) on the peak areas of specific compounds.

According to reports by Hurtado-Benavides et al. [26], Lee et al. [25] and Akiyama et al. [41], ketones and pyrazines are the main and more potent odorants of coffee due to its caramel and nutty flavor. In the current study, ketones corresponded to approximately 60% of the total compounds present in the samples, with no significant difference between microcapsules, and the main aromatic compound responsible for the coffee flavor could be attributed to 3-ethyl-2-hydroxy-2-cyclopenten-1-one. There was a reduction of 19% in this important group throughout the storage of non-encapsulated RCO. On the other hand, both the SD and FD microcapsules showed a protective effect since more than 90% of total ketones were maintained during storage. As aforementioned for lipid oxidation, factors such as porosity and heterogeneity of the encapsulant matrix also contribute to diffusion of the core material.

Furfural is a product of the Maillard reaction, used as an identifier of heating effects and also as a component of some beverages [42]. Present in high levels after roasting coffee beans, this compound is derived from sucrose present in raw coffee beans by Maillard reactions and pyrolysis, and has a significant impact on the coffee aroma [43].

Although a higher content of compounds was found in the non-encapsulated oil, the chitosan nanoparticles demonstrated a high efficacy on the retention of volatile compounds, since the loss of compounds during storage was lower for the microcapsules than for the oil, considering the content initially present in each sample. The effect of encapsulating methods for protecting the volatile compounds of RCO was in close agreement with the oxidation parameters analyzed. Freeze-drying also accelerated the oxidation of fish oil when compared to spray-drying as reported by Anwar and Kunz [44], since the particle morphology obtained by that method enables oxygen diffusivity. In summary, spray-drying and freeze-drying are considered important drying techniques to be utilized to preserve the volatile content of RCO and prevent lipid oxidation throughout 30 days of storage.

4. Conclusions

Pickering emulsion templates of the roasted coffee oil were produced using self-aggregated chitosan nanoparticles by freeze-drying and spray-drying techniques. Storage stability of the non-encapsulated oil and the resulting powders was performed over 30 days at 25 °C under controlled relative humidity. Sorption isotherms of type II showed a better capacity for binding water molecules in the spray-dried samples than in the freeze-dried ones. The GAB model fitted the experimental data well, and the monolayer moisture content showed lower sorption sites in the freeze-dried particles. Roasted coffee oil showed a strong dark color, and as a consequence of the carrier agents, the powdered samples had a yellowish coloration. In spite of slight differences in the color parameters over the storage period, the color variation compared to day 0 was not visible. Because the freeze-dried particles were bigger than the spray-dried ones, with a higher content of surface oil and lower water binding properties, oxidation was slightly favored. However, the peroxide value and conjugated dienes were maintained under acceptable values over 30 days of storage for all of the samples, and the volatile compounds responsible for the coffee flavor were preserved in the microcapsules over the studied period.

Author Contributions: Conceptualization, E.F.R. and V.R.N.; Data curation, E.F.R. and A.R.L.-P.; Formal analysis, E.F.R., T.C.P., N.S.J., A.Q. and I.H.; Funding acquisition, V.R.N.; Methodology, E.F.R., A.R.L.-P. and N.S.J.; Project administration, V.R.N.; Supervision, I.H. and V.R.N.; Writing—original draft, E.F.R. and T.C.P.; Writing—review & editing, A.Q., I.H. and V.R.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—CAPES (Finance Code 001; grant number 88887.468140/2019-00) and the São Paulo Research Foundation—FAPESP (grant number 2016/22727-8).

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy issues.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Reddy, M.N.P.; Ishwarya, S.P.; Anandharamakrishnan, C. Nanoencapsulation of roasted coffee bean oil in whey protein wall system through nanospray drying. *J. Food Process. Preserv.* **2019**, *43*, e13893. [CrossRef]
2. Ogrodowska, D.; Tańska, M.; Brandt, W. The Influence of Drying Process Conditions on the Physical Properties, Bioactive Compounds and Stability of Encapsulated Pumpkin Seed Oil. *Food Bioprocess Technol.* **2017**, *10*, 1265–1280. [CrossRef]
3. Oliveira, A.L.; Cruz, P.M.; Eberlin, M.N.; Cabral, F.A. Brazilian roasted coffee oil obtained by mechanical expelling: Compositional analysis by GC-MS. *Food Sci. Technol.* **2005**, *25*, 677–682. [CrossRef]
4. Frascareli, E.C.; Silva, V.M.; Tonon, R.V.; Hubinger, M.D. Effect of process conditions on the microencapsulation of coffee oil by spray drying. *Food Bioprod. Process.* **2012**, *90*, 413–424. [CrossRef]
5. Atarian, M.; Rajaei, A.; Tabatabaei, M.; Mohsenifar, A.; Bodaghi, H. Formulation of Pickering sunflower oil-in-water emulsion stabilized by chitosan-stearic acid nanogel and studying its oxidative stability. *Carbohyd. Polym.* **2019**, *210*, 47–55. [CrossRef]
6. Yang, Y.; Fang, Z.; Chen, X.; Zhang, W.; Xie, Y.; Chen, Y.; Liu, Z.; Yuan, W. An Overview of Pickering Emulsions: Solid-Particle Materials, Classification, Morphology, and Applications. *Front. Pharmacol.* **2017**, *8*, 287. [CrossRef]
7. Garg, U.; Chauhan, S.; Nagaich, U.; Jain, N. Current Advances in Chitosan Nanoparticles Based Drug Delivery and Targeting. *Pharm. Bull.* **2019**, *9*, 195–204. [CrossRef]
8. Rizeq, B.R.; Younes, N.N.; Rasool, K.; Nasrallah, G.K. Synthesis, Bioapplications, and Toxicity Evaluation of Chitosan-Based Nanoparticles. *Int. J. Mol. Sci.* **2019**, *20*, 5776. [CrossRef]
9. Ribeiro, E.F.; Barros-Alexandrino, T.T.; Assis, O.B.G.; Cruz-Jr, A.; Quiles, A.; Hernando, I.; Nicoletti, V.R. Chitosan and crosslinked chitosan nanoparticles: Synthesis, characterization and their role as Pickering emulsifiers. *Carbohyd. Polym.* **2020**, *250*, 116878. [CrossRef]
10. Ribeiro, E.F.; Borreani, J.; Moraga, G.; Nicoletti, V.R.; Quiles, A.; Hernando, I. Digestibility and Bioaccessibility of Pickering Emulsions of Roasted Coffee Oil Stabilized by Chitosan and Chitosan-Sodium Tripolyphosphate Nanoparticles. *Food Biophys.* **2020**, *15*, 196–205. [CrossRef]
11. Ribeiro, E.F.; Polachini, T.C.; Alvim, I.D.; Quiles, A.; Hernando, I.; Nicoletti, V.R. Microencapsulation of roasted coffee oil Pickering emulsions using spray- and freeze-drying: Physical, structural and in vitro bioaccessibility studies. *Int. J. Food Sci. Technol.* **2022**, *57*, 145–153. [CrossRef]
12. Rodriguez, E.S.; Julio, L.M.; Henning, C.; Diehl, B.W.K.; Tomás, M.C.; Ixtaina, V.Y. Effect of natural antioxidants on the physicochemical properties and stability of freeze-dried microencapsulated chia seed oil. *J. Sci. Food Agric.* **2019**, *99*, 1682–1690. [CrossRef] [PubMed]
13. Ribeiro, M.L.F.F.; Roos, Y.H.; Ribeiro, A.P.B.; Nicoletti, V.R. Effects of maltodextrin content in double-layer emulsion for production and storage of spray-dried carotenoid-rich microcapsules. *Food Bioprod. Process.* **2020**, *124*, 208–221. [CrossRef]
14. Labuza, T. *Creation of Moisture Sorption Isotherms for Hygroscopic Materials. Sorption Isotherm Methods*; American Society of Heating, Refrigerating and Air Conditioning Engineers: Washington, DC, USA, 1963.
15. AOAC. *Official Methods of Analysis of Association of Official Analytical Chemists*; Association of Official Analytical Chemists: Washington, DC, USA, 2010.
16. Bastıoğlu, A.Z.; Koç, M.; Ertekin, F.K. Moisture sorption isotherm of microencapsulated extra virgin olive oil by spray drying. *J. Food Meas. Charact.* **2017**, *11*, 1295–1305. [CrossRef]
17. Partanen, R.; Raula, J.; Seppänen, R.; Buchert, J.; Kauppinen, E.; Forssell, P. Effect of Relative Humidity on Oxidation of Flaxseed Oil in Spray Dried Whey Protein Emulsions. *J. Agric. Food Chem.* **2008**, *56*, 5717–5722. [CrossRef]
18. Anese, M.; De Pilli, T.; Massini, R.; Lerici, C.R. Oxidative stability of the lipid fraction in roasted coffee. *Ital. J. Food Sci.* **2002**, *12*, 457–462.
19. *International Dairy Federation*; IDF-Square Vergote 41: Brussels, Belgium, 1991.
20. Satué-Gracia, M.T.; Frankel, E.N.; Rangavajhyala, N.; German, J.B. Lactoferrin in Infant Formulas: Effect on Oxidation. *J. Agric. Food Chem.* **2000**, *48*, 4984–4990. [CrossRef]
21. Drusch, S.; Schwarz, K. Microencapsulation properties of two different types of n-octenylsuccinate-derivatised starch. *Eur. Food Res. Technol.* **2006**, *222*, 155–164. [CrossRef]
22. Chan, H.W.-S.; Levett, G. Autoxidation of methyl linoleate. Separation and analysis of isomeric mixtures of methyl linoleate hydroperoxides and methyl hydroxylinoleates. *Lipids* **1997**, *12*, 99–104. [CrossRef]
23. Freiberger, E.B.; Kaufmann, K.C.; Bona, E.; de Araújo, P.H.H.; Sayer, C.; Leimann, F.V.; Gonçalves, O.H. Encapsulation of roasted coffee oil in biocompatible nanoparticles. *LWT-Food Sci. Technol.* **2015**, *64*, 381–389. [CrossRef]
24. Van Den Dool, H.; Kratz, P.D.J. A generalization of the retention index system including linear temperature programmed gas-liquid partition chromatography. *J. Chromatogr. A* **1963**, *11*, 463–471. [CrossRef] [PubMed]
25. Lee, L.W.; Liu, X.; Wong, W.S.E.; Liu, S.Q. Effects of sucrose monopalmitate (P90), Tween 80 and modified starch on coffee aroma retention and release in coffee oil-based emulsions. *Food Hydrcolloid.* **2017**, *66*, 128–135. [CrossRef]
26. Hurtado-Benavides, A.; Dorado, A.D.; Sánchez-Camargo, A.P. Study of the fatty acid profile and the aroma composition of oilobtained from roasted Colombian coffee beans by supercritical fluidextraction. *J. Supercrit. Fluid.* **2016**, *113*, 44–52. [CrossRef]
27. Cincotta, F.; Tripodi, G.; Merlino, M.; Verzera, A.; Condurso, C. Variety and shelf-life of coffee packaged in capsules. *LWT-Food Sci. Technol.* **2020**, *118*, 108718. [CrossRef]
28. Acree, T.; Arn, H. Flavornet and Human Odor Space. Available online: http://www.flavornet.org/flavornet.html (accessed on 9 October 2016).

29. Brunauer, S.; Deming, L.S.; Deming, W.E.; Teller, E. On a Theory of the van der Waals Adsorption of Gases. *J. Am. Chem. Soc.* **1940**, *62*, 1723–1732. [CrossRef]
30. Polachini, T.C.; Betiol, L.F.L.; Lopes-Filho, J.F.; Telis-Romero, J. Water adsorption isotherms and thermodynamic properties of cassava bagasse. *Thermochim. Acta* **2016**, *632*, 79–85. [CrossRef]
31. Lewicki, P.P. The applicability of the GAB model to food water sorption isotherms. *Int. J. Food Sci. Technol.* **1997**, *32*, 553–557. [CrossRef]
32. Koc, B.; Isleroglu, H.; Turker, I. Sorption behavior and storage stability of microencapsulated transglutaminase by ultrasonic spray–freeze–drying. *Dry. Technol.* **2022**, *40*, 337–351. [CrossRef]
33. Wibowo, S.; Vervoort, L.; Tomic, J.; Santiago, J.S.; Lemmens, L.; Panozzo, A.; Grauwet, T.; Hendrickx, M.; Van Loey, A. Colour and carotenoid changes of pasteurised orange juice during storage. *Food Chem.* **2015**, *171*, 330–340. [CrossRef]
34. Menin, A.; Zanoni, F.; Vakarelova, M.; Chignola, R.; Donà, G.; Rizzi, C.; Mainente, F.; Zoccatelli, G. Effects of microencapsulation by ionic gelation on the oxidative stability of flaxseed oil. *Food Chem.* **2018**, *269*, 293–299. [CrossRef]
35. Ferreira, C.D.; Conceição, E.J.L.; Machado, B.A.S.; Hermes, V.S.; Rios, A.O.; Druzian, J.I.; Nunes, I.L. Physicochemical Characterization and Oxidative Stability of Microencapsulated Crude Palm Oil by Spray Drying. *Food Bioprocess Technol.* **2016**, *9*, 124–136. [CrossRef]
36. Hoyos-Leyva, J.D.; Bello-Perez, L.A.; Agama-Acevedo, J.E.; Alvarez-Ramirez, J.; Jaramillo-Echeverry, L.M. Characterization of spray drying microencapsulation of almond oil into taro starch spherical aggregates. *LWT-Food Sci. Technol.* **2019**, *101*, 526–533. [CrossRef]
37. Chang, H.W.; Tan, T.B.; Tan, P.Y.; Abas, F.; Lai, O.M.; Wang, Y.; Wang, Y.; Nehdi, I.A.; Tan, C.P. Microencapsulation of fish oil using thiol-modified β-lactoglobulin fibrils/chitosan complex: A study on the storage stability and in vitro release. *Food Hydrocolloid.* **2018**, *80*, 186–194. [CrossRef]
38. Talón, E.; Vargas, M.; Chiralt, A.; González-Martínez, C. Antioxidant starch-based films with encapsulated eugenol. Application to sunflower oil preservation. *LWT-Food Sci. Technol.* **2019**, *113*, 108290. [CrossRef]
39. Kenari, R.E.; Amiri, Z.R.; Motamedzadegan, A.; Milani, J.M.; Farmani, J.; Farahmandfar, R. Optimization of Iranian golpar (*Heracleum persicum*) extract encapsulation using sage (*Salvia macrosiphon*) seed gum: Chitosan as a wall materials and its effect on the shelf life of soybean oil during storage. *J. Food Meas. Charact.* **2020**, *14*, 2828–2839. [CrossRef]
40. Moser, P.; Nicoletti, V.R.; Drusch, S.; Brückner-Gühmann, M. Functional properties of chickpea protein-pectin interfacial complex in buriti oil emulsions and spray dried microcapsules. *Food Hydrocoll.* **2020**, *107*, 105929. [CrossRef]
41. Akiyama, M.; Murukami, K.; Ikeda, M.; Iwatsuki, K.; Kokubo, S.; Wada, A.; Tokuno, K.; Onishi, M.; Iwabuchi and Tanaka, K. Characterization of Flavor Compounds Released During Grinding of Roasted Robusta Coffee Beans. *Food Sci. Technol. Res.* **2005**, *11*, 298–307. [CrossRef]
42. Ferreira, M.V.; Cappato, L.P.; Silva, R.; Rocha, R.S.; Guimarães, J.T.; Balthazar, C.F.; Esmerino, E.A.; Freitas, M.Q.; Rodrigues, F.N.; Granato, D.; et al. Ohmic heating for processing of whey-raspberry flavored beverage. *Food Chem.* **2019**, *297*, 125018. [CrossRef]
43. Agnoletti, B.Z.; Folli, G.S.; Pereira, L.L.; Pinheiro, P.F.; Guarçoni, R.C.; Oliveira, E.C.S.; Filgueiras, P.R. Multivariate calibration applied to study of volatile predictors of arabica coffee quality. *Food Chem.* **2022**, *367*, 130679. [CrossRef]
44. Anwar, S.H.; Kunz, B. The influence of drying methods on the stabilization of fish oil microcapsules: Comparison of spray granulation, spray drying, and freeze drying. *J. Food Eng.* **2011**, *105*, 367–378. [CrossRef]