

## Article

# Comparative Study of Encapsulation Techniques for Hibiscus Extract: Spray Drying, Co-Crystallization, and Ionic Gelation

Eleni Gesthimani Pachni, Nikoletta Solomakou , Dimitrios Fotiou and Athanasia M. Goula \* 

Department of Food Science and Technology, School of Agriculture, Forestry and Natural Environment, Aristotle University, 541 24 Thessaloniki, Greece; elenipachni5@gmail.com (E.G.P.); nsolomak@agro.auth.gr (N.S.); dmfotiou@agro.auth.gr (D.F.)

\* Correspondence: athgou@agro.auth.gr; Tel./Fax: +30-2310-991658

## Abstract

*Hibiscus sabdariffa* L. is a valuable source of phenolic compounds, including anthocyanins with recognized antioxidant and health-related properties; however, their instability under processing and storage conditions limits their direct application in food and nutraceutical systems. In this context, encapsulation offers a promising strategy for enhancing the stability and delivery of hibiscus bioactives. The present study comparatively evaluates three encapsulation techniques, spray drying, co-crystallization, and ionic gelation, for the stabilization of aqueous hibiscus extract. Each process was optimized through systematic adjustment of key operating parameters. The encapsulated products were characterized for physicochemical properties (moisture content, bulk density, wetting time, hygroscopicity, color, particle morphology), encapsulation efficiency, antioxidant capacity, anthocyanin content release behavior, and structural interactions through Fourier-transform infrared (FTIR) analysis. The encapsulation method strongly affected phenolic retention, antioxidant activity, color characteristics, and release behavior of the final products. Under the optimized conditions, encapsulation efficiency was approximately 95% for spray drying, while co-crystallization showed an apparent encapsulation efficiency of 99.96%, whereas ionic gelation showed measured values of 7.0–34.0% and a model-predicted, validated optimum of 50.83%. Spray drying better preserved antioxidant activity, anthocyanin content, and color characteristics, while co-crystallization produced low-moisture, low-hygroscopicity powders with rapid aqueous release. FTIR analysis of the spray-dried and co-crystallized samples indicated physical entrapment rather than chemical modification, confirming the successful formation of encapsulated systems. The findings highlight method-dependent differences in the technological and functional performance of the encapsulation systems, providing insight into the stabilization and controlled release of hibiscus-derived bioactive ingredients, with spray drying and co-crystallization emerging as the most promising approaches.



Academic Editor: Monika Gibis

Received: 10 June 2026

Revised: 13 July 2026

Accepted: 16 July 2026

Published: 19 July 2026

**Copyright:** © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

**Keywords:** *Hibiscus sabdariffa* extract; encapsulation; spray drying; co-crystallization; ionic gelation

## 1. Introduction

Hibiscus (*Hibiscus sabdariffa* L.), commonly known as roselle, belongs to the Malvaceae family and is widely cultivated in tropical and subtropical regions. Its fleshy red calyces are commonly used for the preparation of herbal infusions, beverages, syrups, jams, natural colorants, and traditional remedies [1]. *H. sabdariffa* has attracted considerable scientific

interest as a rich source of bioactive components, particularly phenolic acids, flavonoids, and anthocyanins, which contribute to the intense red color, antioxidant properties, and sensory characteristics of hibiscus products. Previous *in vitro* and *in vivo* studies have associated *H. sabdariffa* extracts with antioxidant, antihypertensive, anti-inflammatory, and metabolic regulatory effects [1,2]. These compounds make hibiscus extracts promising functional ingredients for food, nutraceutical, and pharmaceutical applications. However, despite their potential, practical utilization of hibiscus phenolics remains constrained by their inherent instability [3,4].

Polyphenolic compounds from hibiscus are highly susceptible to environmental and processing conditions, including oxygen, light, temperature, and pH fluctuations, which can lead to rapid degradation, loss of bioactivity, and undesirable color changes during storage and application [5–7]. Additionally, their low stability in gastrointestinal conditions and limited bioavailability further restrict their effectiveness when incorporated directly into food systems. These limitations highlight the need for protective strategies that can preserve the functional properties of hibiscus extracts throughout processing, storage, and delivery [2,8].

Encapsulation has emerged as an effective approach to address these challenges by entrapping sensitive bioactive components within protective matrices, thereby enhancing their stability, controlling their release, and improving their bioavailability [7,9]. Among the various encapsulation techniques, spray drying, co-crystallization, and ionic gelation are widely studied due to their adaptability, efficiency, and applicability in food systems.

Spray drying is one of the most commonly used encapsulation techniques in the food industry, offering advantages such as scalability, cost-effectiveness, and the production of stable powders with relatively high retention of phenolic compounds [10]. In this process, bioactive compounds are embedded within a glassy matrix formed by carrier materials such as maltodextrin or proteins, which protect them against environmental degradation despite the use of elevated temperatures [6,11,12].

Co-crystallization, on the other hand, is an emerging encapsulation method that involves the incorporation of bioactive compounds into a porous sucrose matrix during crystallization. This technique not only improves the physical properties of the encapsulated product, such as flowability, solubility, and stability, but also facilitates handling and incorporation into dry food systems [13,14]. Despite its advantages, its application to plant phenolic extract remains relatively limited and warrants further investigation.

Ionic gelation, typically using alginate as the wall material, represents a mild and solvent-free encapsulation technique based on the formation of hydrogels through ionic crosslinking with multivalent cations such as calcium. This method is particularly suitable for heat-sensitive compounds, as it operates under ambient conditions and provides high encapsulation efficiency and controlled release properties [1,15]. The resulting gel network can effectively protect phenolic compounds from degradation while enabling targeted delivery. However, each technique also presents limitations. Spray drying is scalable and widely used, but exposure to elevated temperatures may affect thermosensitive compounds, and powder stickiness can reduce product recovery. Co-crystallization can improve powder handling and solubility, but it involves heating and uses sucrose as the main carrier, which may limit its suitability for low-sugar formulations. Ionic gelation is a mild process suitable for heat-sensitive compounds, but small hydrophilic phenolic compounds may diffuse out of alginate beads during gelation, curing, and washing, leading to lower retention.

These three techniques were selected because they represent distinct encapsulation systems: spray drying produces dry amorphous powders, co-crystallization produces sucrose-based crystalline powders, and ionic gelation produces hydrated alginate beads, allowing comparison of structurally different carriers for hibiscus extract stabilization. The wall materials were selected based on their food compatibility and different structural prop-

erties. Maltodextrin was used because of its relatively high glass transition temperature, low viscosity at high solids content, and ability to improve drying performance, although it may provide limited emulsifying capacity when used alone. Whey protein isolate (WPI) was selected because of its film-forming properties and potential interactions with phenolic compounds, but its performance may be affected by pH and thermal conditions. Sucrose was used as the crystallizing matrix in co-crystallization because it can form porous crystalline structures capable of incorporating bioactive compounds, although its use may be less suitable for reduced-sugar applications. Sodium alginate was selected for ionic gelation because it forms calcium-crosslinked hydrogel networks under mild conditions, although diffusion losses of low-molecular-weight hydrophilic compounds may occur [5,14].

Despite the growing interest in *H. sabdariffa* as a source of natural phenolics and pigments, systematic comparisons of encapsulation strategies for its aqueous extract remain limited. Most available studies focus on individual encapsulation methods, making it difficult to determine which technique provides the best balance between encapsulation efficiency, phenolic retention, antioxidant stability, and final encapsulated product functionality. The present study addresses this gap by providing a direct comparative evaluation of spray drying, co-crystallization, and ionic gelation for the encapsulation of hibiscus aqueous extract. The contribution of the present study lies in the direct comparison of three different encapsulation approaches for aqueous hibiscus extract under controlled experimental conditions, providing a unified basis for assessing their relative technological and functional performance. Therefore, the objective of this study is to evaluate the influence of these encapsulation methods on the physicochemical properties, including moisture content, bulk density, wetting time, hygroscopicity, color characteristics, particle morphology or bead size, as well as encapsulation efficiency, antioxidant capacity, anthocyanin content, and release behavior of hibiscus phenolics, aiming to develop stable and value-added functional ingredients for food and nutraceutical applications.

## 2. Materials and Methods

### 2.1. Raw Materials

Gel beads were formed with sodium alginate (Na-Alg, low viscosity) and calcium chloride (Fisher Scientific, Pittsburgh, PA, USA). For the spray drying encapsulation, maltodextrin (13.5 Dextrose Equivalent-DE) (2.3% moisture), sucrose, and WPI (5.5% moisture, 0.8% lactose, 1.0% fat) were purchased commercially. Folin–Ciocalteu reagent, potassium chloride, sodium acetate, sodium carbonate, gallic acid, and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were of analytical grade and purchased from Sigma-Aldrich (Steinheim, Germany).

Dried hibiscus calyces (*H. sabdariffa*), which were harvested in 2024, were supplied by Stamos Herbs from the Kolindros region (prefecture of Katerini, North Greece). The plant material was ground immediately prior to extraction using a laboratory mill (Type A10, Janke and Kunkel, IKA Labortechnik, Staufen, Germany) and stored in dark airtight glass containers at ambient temperature until further processing. The particle size distribution of the milled berries was determined by a sieve shaker (Retax, Labor Siebmaschine, Type LS10, Nr 4082, Berlin, Germany), and the mean diameter was about 0.4 mm.

### 2.2. Preparation of Phenolic Extract

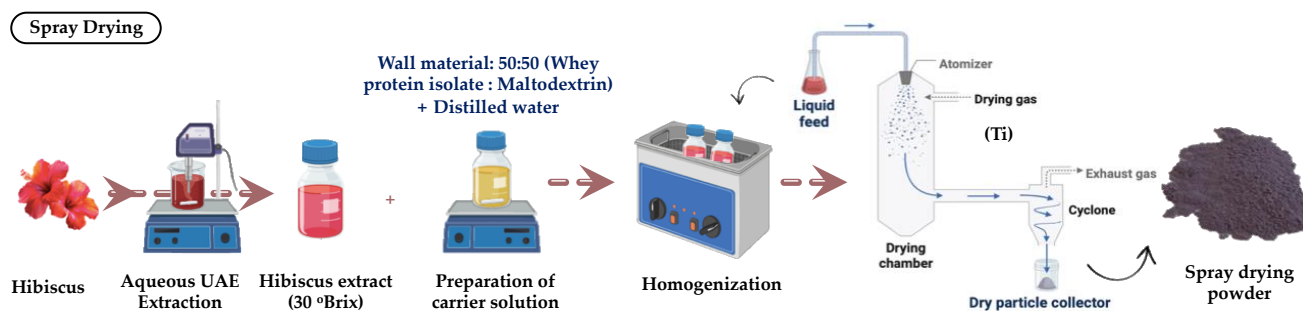
For extract preparation, 20 g of ground hibiscus material was weighed and mixed with 200 mL of deionized water. Water was selected as the extraction medium based on preliminary experiments and to obtain a food-compatible aqueous extract suitable for direct incorporation into encapsulated food ingredients. Extraction was performed by ultrasound-assisted extraction (UAE) using a Bandelin Sonoplus HD 2070 sonicator (Bandelin, Berlin, Germany), with a maximum power of 70 W, operated at 50% amplitude

for 10 min. The extraction temperature was monitored with a thermocouple and maintained using a thermostatically controlled water bath to prevent sample overheating. The resulting suspension was centrifuged at 4000 rpm for 10 min at 4 °C using an SV 11 laboratory centrifuge (Filab, Saint Apollinaire, France). The supernatant was then filtered under vacuum through a Büchner funnel, and the obtained extract was concentrated under reduced pressure at 40 °C and 150 mbar using a rotary evaporator (Rotavapor R-114, Waterbath B-480, Büchi, Flawil, Switzerland). The concentrated extract was stored at −18 °C until further use.

### 2.3. Encapsulation by Spray Drying

For each encapsulation experiment, following preliminary trials, 50 mL of feed solution was prepared. The required amounts of encapsulating material, core material, and distilled water were calculated according to the selected wall-to-core ratio ( $w/c$ ), while maintaining the total solids content of the feed at 30%  $w/w$ . A mixture of maltodextrin and WPI (50:50,  $w/w$ ) was used as the wall material [16]. The wall material was gradually dispersed in distilled water at 60 °C under magnetic stirring for 20 min in order to prevent agglomeration and promote complete dissolution. The solution was then removed from the heating system and allowed to cool to room temperature, while stirring was continued for approximately 12 h to ensure complete hydration of the encapsulating matrix.

The phenolic extract, previously concentrated to 30 °Brix, was then added to the hydrated wall-material solution immediately before homogenization and spray drying. Homogenization was performed by indirect ultrasonication for 20 min using a Bandelin ultrasonic bath, Model DL 512 H (Bandelin, Berlin, Germany). During indirect ultrasonication, the water bath temperature was maintained at 22–25 °C, and the ultrasound intensity was set at 20%, allowing complete dispersion of the wall materials without noticeable sample heating or foam formation. The resulting feed emulsions/solutions were dried using a YC-015 laboratory spray dryer (Pilotech, Shanghai, China). The system is equipped with a two-fluid nozzle atomizer, with a standard nozzle diameter of 0.5 mm, and an integrated oil-free air compressor. According to the manufacturer's specifications, the maximum inlet air temperature is 250 °C, the processing capacity is up to 1500 mL/h, and the compressed-air supply is 32 L/min at 0.2–2 bar. The drying chamber, cyclone separator, and collection vessel are made of borosilicate glass, allowing visual monitoring of the drying process (Figure 1).



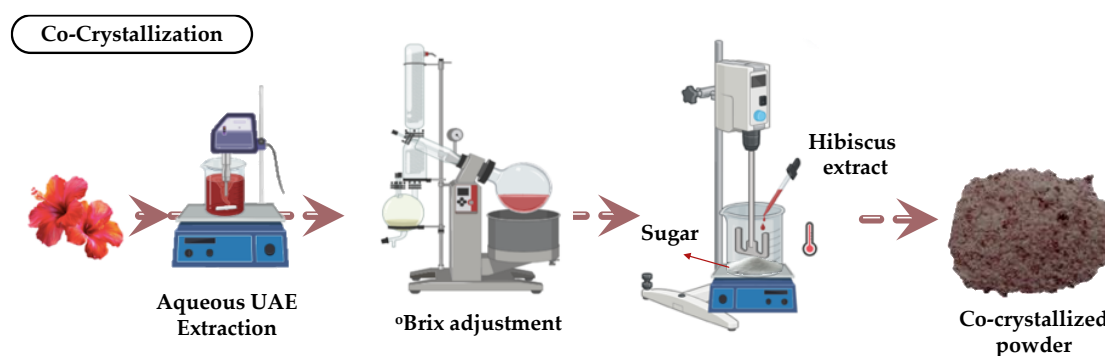
**Figure 1.** Schematic diagram of the spray drying method (UAE: ultrasound-assisted extraction; WPI: whey protein isolate;  $T_i$ : inlet air temperature).

The spray-drying encapsulation experiments were designed using Response Surface Methodology (RSM), based on central composite design (CCD). The independent variables were the inlet drying air temperature ( $T_i$ , °C) and the  $w/c$  ratio (g/g). A total of 13 experimental runs were performed. The inlet air temperature ranged from 150 to 190 °C, while the  $w/c$  ratio ranged from 2.3:1 to 9.0:1 g/g. The total solids content of the feed was kept

constant at 30% *w/w* throughout the experimental procedure, and the drying air flow rate was maintained constant at 1.44 m<sup>3</sup>/min. The obtained spray-dried powders were collected and further analyzed for their physicochemical and encapsulation-related parameters.

#### 2.4. Encapsulation by Co-Crystallization

Sucrose (75 g) was dissolved in 12.5 mL of distilled water and continuously stirred at 500 rpm using a vertical agitator (IKA Eurostar 40 digital, Staufen, Germany). The process was carried out in a cylindrical stainless-steel vessel with dimensions of 8 cm in height, 0.8 cm in wall thickness, and 6.8 cm in bottom diameter, placed on a heating plate, as illustrated in Figure 2 and described by Chezanoglou et al. [17]. The sucrose solution was heated until the target temperature of approximately 140 °C was reached. Continuous stirring during heating was applied to promote uniform crystallization, while water evaporation at elevated temperature increased the soluble solids content of the sucrose syrup from 70 to 75 to 90–95 °Brix. The onset of crystallization was indicated by the appearance of slight turbidity, attributed to spontaneous nucleation under supersaturated conditions.



**Figure 2.** Schematic diagram of the co-crystallization method.

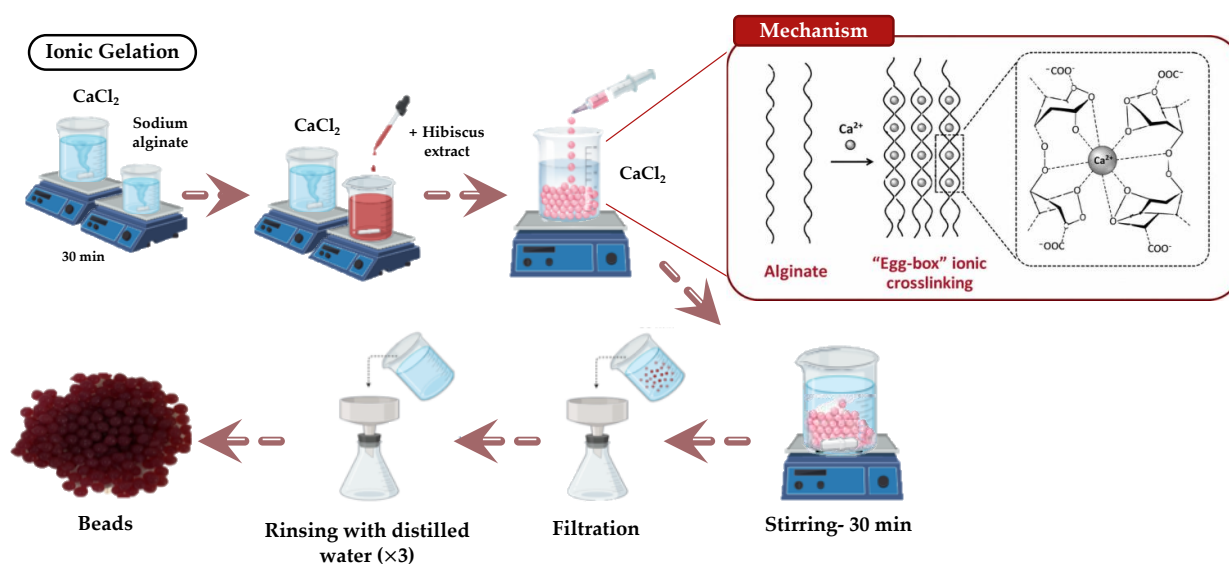
Once the target temperature was reached, heating was discontinued, and the stirring speed was increased to 700 rpm. Hibiscus extract, maintained at ambient temperature and with total soluble solids content ( $X_s$ ) ranging from 35 to 70 °Brix, was then rapidly added to the sucrose syrup at different dry extract-to-sucrose ratios ( $E/S$ ), ranging from 0.1 to 0.7 g/g, according to the experimental design presented in Table 1. The mixture was immediately transferred to a water bath maintained at 25 °C and continuously stirred until the temperature decreased below 40 °C. The overall co-crystallization process, from initial heating to final product formation, was completed within approximately 25 min. The resulting powder was collected and subsequently subjected to physicochemical characterization.

**Table 1.** Experimental values, coded levels, and optimum process conditions of the independent variables of each encapsulation method.

| Independent Variable (Symbol)                           | Unit    | Levels |      |      |      |      | Optimum Conditions |
|---------------------------------------------------------|---------|--------|------|------|------|------|--------------------|
| Encapsulation by Spray Drying                           |         |        |      |      |      |      |                    |
| Wall-to-core material ratio ( $w/c$ )                   | g/g     | 2.30   | 3.28 | 5.65 | 8.02 | 9.00 | 9.0                |
| Inlet air temperature ( $T_i$ )                         | °C      | 150    | 156  | 170  | 184  | 190  | 190                |
| Encapsulation by Co-Crystallization                     |         |        |      |      |      |      |                    |
| Solids concentration of extract ( $X_s$ )               | °Brix   | 35     | 40   | 52.5 | 65   | 70   | 35                 |
| Dry extract-to-sucrose ratio ( $E/S$ )                  | g/g     | 0.1    | 0.19 | 0.4  | 0.61 | 0.7  | 0.1                |
| Encapsulation by Ionic Gelation                         |         |        |      |      |      |      |                    |
| Concentration of sodium alginate solution ( $C_{alg}$ ) | % $w/w$ | 2      |      | 2.5  |      | 3    | 3                  |
| Concentration of extract ( $C_e$ )                      | % $w/w$ | 1      |      | 7.5  |      | 15   | 1                  |

## 2.5. Encapsulation by Ionic Gelation

Sodium alginate solutions with concentrations ranging from 2 to 3%  $w/w$  ( $C_{alg}$ ) were prepared and mixed with hibiscus extract previously concentrated to 17 °Brix. The extract concentration in the alginate mixture ( $C_e$ ) ranged from 1 to 15%  $w/w$ . According to the experimental design (Table 1), nine different formulations were evaluated, following a modified version of the method by Solomakou et al. [14]. Specifically, the mixtures were homogenized at 500 rpm for 30 min. To ensure adequate dissolution and uniform dispersion of the components, ultrasonication was applied for 10 min at 50% intensity using an ultrasonic water bath (Sonorex Digiplus, Bandelin, Berlin, Germany). The resulting mixtures were then added dropwise into a 2.5%  $w/v$  calcium chloride solution under stirring, using a 5 mL pipette with a tip diameter of  $1.43 \pm 0.03$  mm. Droplets were released from a fixed height of 20 cm to ensure consistent bead formation. The formed beads were kept in the calcium chloride crosslinking solution for 30 min to complete gelation. Subsequently, the beads were collected by filtration and rinsed three times with distilled water (Figure 3).



**Figure 3.** Schematic diagram of the ionic gelation method.

## 2.6. Encapsulation Efficiency and Encapsulation Yield

Encapsulation efficiency refers to the percentage of total phenolic compounds successfully retained within the encapsulated product. Because the three encapsulation techniques produced structurally different systems, the calculation of  $E_f$  was adapted to the physical characteristics of each product. For spray-dried samples,  $E_f$  was calculated based on the total phenolic content (TPC) and the surface phenolic content (SPC), according to the following equation:

$$E_f(\%) = \frac{TPC - SPC}{TPC} \times 100 \quad (1)$$

The TPC of the encapsulated sample was determined using the Folin–Ciocalteu assay and expressed as mg gallic acid equivalents per gram of sample (mg GAE/g wet basis (w.b.)), as described in detail by Solomakou et al. [14]. To determine the phenolic content of the extruded beads, 6 g of chopped alginate beads were extracted with 20 mL of methanol (MeOH). The extraction was carried out in an ultrasonic water bath (Sonorex Digiplus, Bandelin, Berlin, Germany) at 20 °C for 30 min and 50% intensity. The resulting extract was collected by vacuum filtration and concentrated using a rotary evaporator. For co-crystallized and spray-dried powders, 0.2 mL of the prepared sample solution was

dispersed in 10 mL of distilled water, thoroughly mixed, and filtered through a 0.45 µm membrane filter. The clear filtrate was then used for TPC determination using the Folin–Ciocalteu method. Briefly, 0.5 mL of Folin–Ciocalteu reagent was added to the filtrate, and the mixture was vigorously shaken. After 5 min, 5 mL of 5% Na<sub>2</sub>CO<sub>3</sub> solution was added under continuous mixing. The final volume was adjusted to 25 mL with distilled water, thoroughly mixed, and left to stand for 90 min. The absorbance was measured at 750 nm against the corresponding procedural blank. Phenolic concentration was calculated from a gallic acid calibration curve using the equation  $y = 0.0008x + 0.0142$ , where  $y$  is the absorbance and  $x$  is the gallic acid concentration expressed as mg/L. The calibration range was 0.10–200 mg/L gallic acid, and the results were expressed as gallic acid equivalents.

SPC was determined using a rapid rinsing procedure, lasting approximately 10 s, in order to remove non-encapsulated phenolics from the particle surface, while minimizing any structural modification of the powder. This approach has been commonly applied for SPC determination in encapsulated powders [14,16,17].

For samples produced by co-crystallization and ionic gelation, encapsulation efficiency ( $E_f$ ) was calculated based on the TPC retained in the final encapsulated products ( $B$ ) and the initial phenolic content of the loaded extract ( $A$ ), according to the equation, as described by Tzatsi and Goula [16]:

$$E_f(\%) = \frac{B}{A} \times 100 \quad (2)$$

For the spray-drying process, the encapsulation yield ( $Y$ ) was also calculated as an indicator of process performance. Yield was determined as the ratio of the dry solid mass of the recovered encapsulated product to the total solid mass initially subjected to spray drying:

$$Y(\%) = \frac{\text{dry solid mass of recovered encapsulated product}}{\text{total dry solid mass in the feed}} \times 100 \quad (3)$$

## 2.7. Characterization of the Encapsulated Products

After production, all obtained samples were collected and subjected to physicochemical and encapsulation-performance analyses. These analyses were carried out immediately after sample preparation to minimize possible changes in product characteristics before characterization.

### 2.7.1. Moisture Content (MC, %)

The moisture content of the encapsulated samples was determined on a wet basis by oven-drying at 105 °C until constant weight. The dried samples were then cooled to room temperature in a desiccator before weighing [16].

### 2.7.2. Bulk Density (BD, g/mL)

A 1 g powder sample was accurately weighed and transferred into a 20 mL graduated cylinder without compaction. Bulk density (g/mL) was calculated as the ratio of powder mass to the volume occupied in the cylinder, providing an estimate of the powder's packing behavior under gravity [16].

### 2.7.3. Solubility-Wetting Time (S, s)

Solubility performance was evaluated through the determination of wetting time. Briefly, 1 g of powder was added to 25 mL of distilled water at room temperature in a 150 mL glass beaker and continuously stirred at 900 rpm using a 2 mm × 7 mm magnetic stir bar. Wetting time was recorded as the time required for the powder particles to become completely submerged below the water surface [16].

#### 2.7.4. Hygroscopicity (H, %)

Approximately 1 g of powder was evenly distributed in a porcelain capsule to maximize the surface area exposed to air. The samples were then placed in a desiccator maintained at 23 °C and 76% relative humidity, established using a nitric acid (HNO<sub>3</sub>) solution. Moisture sorption kinetics were assessed by recording weight changes at 10 min intervals. Moisture uptake was expressed as the increase in mass per gram of powder solids, reflecting the powder's hygroscopic behavior under controlled humidity conditions [14].

#### 2.7.5. Color

The color of the encapsulated phenolic extract was measured using an automatic Minolta colorimeter (CR-400, Konica-Minolta Sensing, Tokyo, Japan). Samples were evenly spread in 5 cm-diameter Petri dishes, with a thickness of 0.5 cm. Color parameters were recorded using the CIE  $L^*a^*b^*$  uniform color space [14].

#### 2.7.6. Particle Morphology/Bead Size

The morphology and structure of the encapsulated products were examined using an XTX-5C Step stereo microscope (Hinotek, Ningbo, China) at a magnification range of 20–80 $\times$ .

The size of the alginate beads produced by the ionic gelation process was determined by randomly selecting 8–10 beads from each experimental run. The diameter of each bead was measured using a precision caliper with a resolution of 0.02 mm. For each sample, three replicate measurements were performed, and the mean diameter was calculated to obtain a representative estimate of bead size [14].

#### 2.7.7. Antioxidant Activity

The antioxidant activity (AA) of the samples was assessed based on their free radical scavenging capacity using the 1,1-diphenyl-2-picrylhydrazyl (DPPH) assay, following the protocol described by Solomakou et al. [14]. Prior to AA determination, the encapsulated products obtained under the optimum conditions were appropriately prepared to extract the antioxidant compounds from each matrix. For powder samples, 1 g of encapsulated product was dispersed in 10 mL of distilled water, thoroughly mixed, and filtered before analysis. For alginate beads, the samples were first chopped and then dispersed under the same conditions to facilitate the release of the entrapped compounds. The analysis was performed separately for all encapsulated samples, and the results were expressed as a percentage of DPPH radical inhibition (%).

#### 2.7.8. Anthocyanin Content

Total monomeric anthocyanin content (TMAC) was determined using the pH-differential method, as described by Kokkinomagoulos et al. [18]. TMAC was determined for samples produced under the optimized and experimentally validated conditions and was used as a complementary indicator of pigment retention, color-related quality, and bioactive preservation. Briefly, aliquots of the sample were appropriately diluted with 0.025 M potassium chloride buffer at pH 1.0 and separately with 0.4 M sodium acetate buffer at pH 4.5. Each mixture was vortexed and allowed to stand at room temperature for 20 min.

The absorbance of each solution was measured at 520 and 700 nm using a UV-Vis spectrophotometer (Genesis 50, Spectrophotometre, Madison WI, USA). TMAC was expressed as mg cyanidin-3-glucoside equivalents per liter (mg Cy3GE L<sup>-1</sup>) and calculated according to the following equation:

$$\text{cyanidin-3-glucoside equivalents (mg/L)} = \frac{A \times MW \times DF \times 10^3}{\epsilon \times l} \quad (4)$$

where

$$A = (A_{520\text{nm}} - A_{700\text{nm}}) \text{ pH}1.0 - (A_{520\text{nm}} - A_{700\text{nm}}) \text{ pH}4.5$$

MW is the molecular weight of cyanidin-3-glucoside, 449.2 g/mol; DF is the dilution factor;  $\epsilon$  is the molar extinction coefficient of cyanidin-3-glucoside, 26,900 L/mol·cm; and  $l$  is the optical path length (1 cm).

#### 2.7.9. Fourier-Transform Infrared (FT-IR) Analysis

Fourier Transform Infrared Spectroscopy (FT-IR) was performed to identify potential changes in functional groups and interactions between the encapsulating agents and the hibiscus extract. The spectra of the wall materials, namely sucrose, WPI, and maltodextrin, as well as the raw hibiscus extract, were compared with those of the encapsulated samples obtained after co-crystallization and spray drying.

FT-IR spectra were recorded using an FT-IR 6700 spectrometer series (JASCO, Tokyo, Japan) equipped with an Attenuated Total Reflectance (ATR) sampling accessory, MIRacle™ Universal ATR (Pike Technologies, Madison, WI, USA), fitted with a 3-reflection Diamond/ZnSe performance crystal plate. A small amount of each sample was placed directly onto the ATR crystal. Spectra were collected in triplicate at room temperature, with 64 scans per spectrum, a resolution of 4 cm<sup>-1</sup>, and a spectral range of 4000–400 cm<sup>-1</sup>.

Before each measurement, a background spectrum was recorded using a clean and dry ATR cell as a reference. The raw spectra were sequentially corrected for CO<sub>2</sub>, H<sub>2</sub>O, and ATR effects using Spectra Manager software version 2.15.01 (JASCO, Tokyo, Japan). The corrected spectra were then processed with Savitzky–Golay smoothing, using a convolution width of 11, followed by baseline correction. The final spectra were expressed as transmittance values (%) [19].

#### 2.7.10. Release Kinetics

The release of phenolics from the encapsulated products in water was evaluated according to the method described by Tzatsi and Goula [16]. Briefly, a known amount of encapsulated product, approximately 3 g, was dispersed in 50 mL of distilled water. The dispersion was agitated at 100 rpm and 25 °C. At predetermined time intervals, aliquots of the supernatant were withdrawn for TPC analysis. The volume removed at each sampling point was replaced with an equal amount of distilled water. The percentage release of phenolic compounds was calculated as  $M_t/M_0$ , where  $M_t$  represents the amount of phenolic compounds released at time  $t$  (mg), and  $M_0$  represents the initial phenolic content (mg) in the encapsulated product dispersed in water.

#### 2.8. Statistical Analysis

Analysis of variance (ANOVA) was performed to evaluate the significance of individual effects and their interactions. Differences were considered statistically significant at  $p < 0.05$ . The experimental ranges of the independent variables were selected based on preliminary trials and literature data on the encapsulation of phenolic-rich extracts from plant matrices. Experimental data were processed using Minitab statistical software, Version 15.1.20 (MINITAB Inc., Lock Haven, PA, USA) to identify optimal experimental conditions for maximizing encapsulation efficiency. For all three encapsulation methods, the model-derived optimum conditions were subsequently prepared experimentally and analyzed in triplicate to validate the predicted responses. Analytical measurements were

carried out in triplicate ( $n = 3$ ), and results are expressed as mean  $\pm$  standard deviation where applicable. Graphical outputs derived from the experimental design and model fitting are presented without standard deviation bars.

### 3. Results

#### 3.1. Encapsulation by Spray Drying

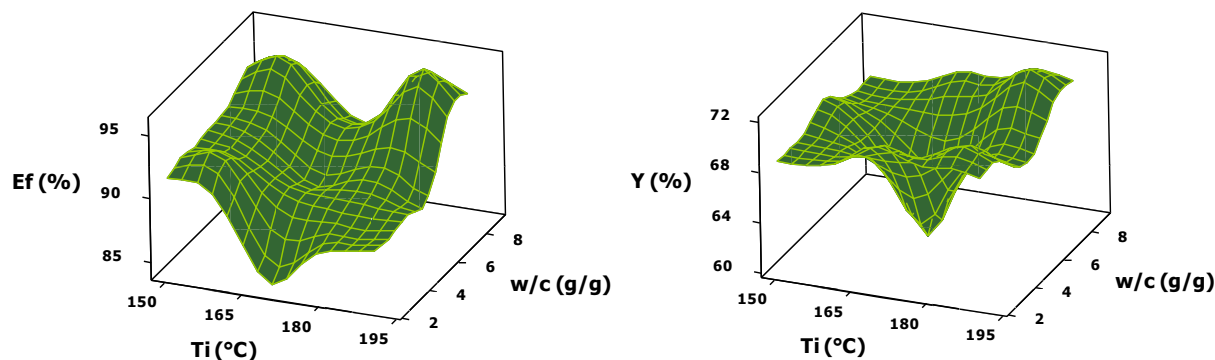
The encapsulation efficiency ( $E_f$ ) of hibiscus phenolic extract by spray drying ranged from 84.23 to 95.76%, while the process yield ( $Y$ ) varied between 60.26 and 71.73%, indicating that spray drying was highly effective for producing encapsulated hibiscus powders with high phenolic retention and satisfactory powder recovery. These results are comparable to those reported by Nguyen et al. [20] for spray-dried hibiscus roselle anthocyanins, where encapsulation efficiency ranged from 83.0 to 95.7%, depending on the carrier system used. This agreement suggests that the maltodextrin-WPI matrix used in the present study provided a level of protection similar to efficient carbohydrate-based carrier blends previously applied to hibiscus bioactives. Similarly, Vargas et al. [21] reported anthocyanin retention of 96% and solids recovery-process yield of 60.8% during spray drying of hibiscus flower anthocyanins using a starch-alginate carrier blend. Therefore, the maximum  $E_f$  obtained in the present study was closely aligned with their anthocyanin retention, whereas the process yield achieved here was within a comparable range or higher than their maximum solids recovery. In agreement with these findings, Cid-Ortega and Guerrero-Beltrán [22] reported a maximum roselle powder yield of  $73.3 \pm 3.3\%$  using a 3% maltodextrin:gum arabic carrier blend, further supporting the technological suitability of spray drying for hibiscus-derived extracts.

The high encapsulation efficiency observed in the present study can be mainly attributed to the rapid evaporation of water from atomized droplets and the consequent formation of a dry outer layer around the particles, which limits the migration of phenolic compounds, particularly anthocyanins, toward the particle surface and reduces their exposure to oxygen, heat, and light. This mechanism is also reported by Tzatsi and Goula [16], who demonstrated that spray drying can be highly effective for phenolic-rich plant extracts when the wall material,  $w/c$  ratio, and drying conditions are properly controlled. The use of maltodextrin-WPI as wall material likely contributed to this behavior, since maltodextrin improves drying performance and reduces stickiness, while WPI may enhance matrix cohesion and phenolic retention through protein-polyphenol interactions. This is consistent with the general conclusion of Nguyen et al. [20] that carrier composition plays a critical role in the retention of phenolics in roselle powders, and the mixed carrier systems can improve encapsulation performance compared with single carriers.

As shown in Figure 4, increasing the  $w/c$  improved encapsulation efficiency, although a decrease was observed at the highest ratio tested (9:1 g/g). At low  $w/c$  ratios, the amount of encapsulating material may be insufficient to fully surround the hibiscus extract, leaving a larger fraction of phenolics close to the particle surface. This increases the probability of oxidation, surface deposition, or loss during drying. In contrast, increasing the amount of wall material promotes the formation of a more continuous protective matrix and increases the diffusion path of phenolic compounds toward the surface. However, excessive wall material may increase feed viscosity and impair atomization, resulting in less uniform particle formation and explaining the decline observed at the highest  $w/c$  ratio [16,21].

The effect of inlet air temperature ( $T_i$ ) on  $E_f$  was non-linear. The maximum  $E_f$  was observed at approximately 156 °C, followed by a decrease at higher temperatures and a partial recovery within the experimental range (Figure 4). This indicates the existence of an intermediate optimum temperature. Moderate inlet temperatures may generate internal vapor pressure, leading to ballooning, cracking, or surface defects [16]. These structural

defects can facilitate premature release or degradation of thermosensitive hibiscus anthocyanins. This supports the existence of an optimum inlet temperature range, as previous studies on phenolic- and anthocyanin-rich extracts have shown that maximum retention or encapsulation efficiency is typically achieved at intermediate drying temperatures, rather than at the highest inlet temperature tested [16,21,23].



**Figure 4.** Effects of inlet air temperature ( $T_i$ , °C), and wall-to-core material ratio ( $w/c$ , g/g) on efficiency ( $E_f$ , %) and yield ( $Y$ , %) in spray drying encapsulation with a maltodextrin:WPI (50:50) carrier.

The process yield ( $Y$ ) ranged from 60.26 to 71.73%, indicating satisfactory powder recovery, which is primarily governed by particle stickiness, wall deposition, drying kinetics, and the ability of the wall material to form stable dry particles. This behavior is strongly associated with the glass transition temperature ( $T_g$ ) of the system, as particles tend to become sticky and form wall deposits or agglomerates when their temperature exceeds  $T_g$  by approximately 10–20 °C [16]. Therefore, the use of maltodextrin–WPI may have contributed to the relatively high yield by improving matrix stability and reducing stickiness, particularly since the  $T_g$  of WPI has been reported to range from 75.35 to 126.85 °C, depending on moisture content [23], whereas maltodextrin (13.5 DE) has a  $T_g$  of about 157.5 °C. As shown in Figure 4, the effect of  $w/c$  ratio on  $Y$  was non-linear. Yield increased after the intermediate  $w/c$  value of approximately 5.65:1 g/g. This may be attributed to the lower relative amount of hibiscus extract solids in the feed and the improved capacity of the wall matrix to form dry, less sticky particles. At higher wall-material levels, droplets are expected to dry more efficiently and form particles with reduced surface stickiness, limiting deposition losses inside the drying chamber and cyclone. As illustrated in Figure 4, the process yield showed a non-linear response to  $T_i$ , with a reduction around 170 °C, a subsequent increase near 184 °C, and a further decline at 190 °C. This behavior reflects the complex interaction between drying rate, crust formation, thermal stress, and particle stickiness. Increasing temperature initially enhances water evaporation and supports rapid surface solidification; however, excessive temperature can promote particle deformation, cracking, or adhesion to chamber walls. The comparable yield values reported by Vargas et al. [21] and Cid-Ortega and Guerrero-Beltrán [22] further support that the yield range obtained in the present study is technologically acceptable for hibiscus-based spray-dried powders.

The ANOVA results support the experimental trends. For  $E_f$ ,  $T_i$ , and its quadratic term were close to statistical significance, with a  $p$  value of 0.056 and 0.075, respectively, indicating that temperature was the most influential variable for  $E_f$ . However, the relatively low  $R^2 = 68.44$  suggests that other factors, such as feed viscosity, outlet air temperature, particle morphology, and drying kinetics, may also contribute to phenolic retention. In contrast, the model for encapsulation yield showed a much stronger fit, with  $R^2 = 95.30$ , indicating that powder recovery was more directly controlled by the examined process variables.

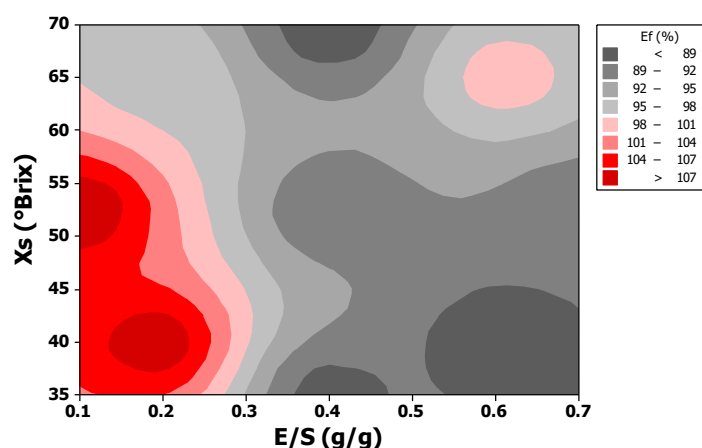
### 3.2. Encapsulation by Co-Crystallization

The apparent  $E_f$  of hibiscus phenolic extract by co-crystallization ranged from 86.25 to 109.37% across the experimental design, indicating highly effective incorporation of the extract into the sucrose-based crystalline matrix. Chezanoglou and Goula [24] described sucrose co-crystallization as a promising encapsulation technique for food bioactives, as it forms a porous crystalline structure that can incorporate active components while improving properties such as solubility, hygroscopicity, and flowability. The apparent  $E_f$  obtained in the present study can be explained by this mechanism. During co-crystallization, sucrose undergoes structural modification from regular dense crystals to irregular agglomerated crystalline structures with increased void space and surface area. This porous sucrose matrix can physically incorporate hibiscus phenolics, reducing their molecular mobility and exposure to degradation factors. The present results are also consistent with Tzatsi and Goula [16], who reported an optimum co-crystallization  $E_f$  of 96.3% for chokeberry phenolic extract at 35 °Brix extract solids and a dry extract-to-sucrose ratio of 0.7 g/g. The apparent  $E_f$  obtained in the present study is therefore comparable, although values exceeding 100% should be interpreted as apparent encapsulation efficiencies rather than absolute recoveries. The behavior may be associated, first, with the hygroscopic nature of sucrose-based co-crystallized products, which can lead to moisture uptake and small deviations in mass-based calculations. Second, the Folin–Ciocalteu assay is not specific exclusively to phenolic components, as it may also respond to other reducing substances. In the case of hibiscus co-crystallized products, naturally occurring reducing compounds or thermally formed reaction products may have contributed to the measured absorbance, resulting in apparent phenolic contents higher than the calculated initial values, as also suggested for thermally processed phenolic systems by Marpaung et al. [25]. Similar evidence was provided by Solomakou et al. [14], who applied optimized encapsulation processes to lavender distillation residues and reported that co-crystallization outperformed ionic gelation across most evaluated quality parameters. Although their co-crystallized products exhibited higher  $E_f$  values, exceeding 150%, than those obtained in the present study, both studies confirm the suitability of sucrose co-crystallization for stabilizing phenolic-rich plant extracts.

As shown in Figure 5, the effect of extract soluble solids concentration ( $X_s$ , °Brix) on apparent  $E_f$  was non-linear. Increasing  $X_s$  from 35 to 40 °Brix initially improved  $E_f$ , likely because the moderate increase in solids and viscosity supported sucrose matrix formation and extract immobilization. However, a decrease was observed at 52.5 °Brix, followed by an increase at 65 °Brix and another decrease at 70 °Brix. This fluctuation suggests that the effect of extract concentration is governed by the balance between viscosity, molecular mobility, mass transfer, and sucrose crystallization kinetics. At moderate solids concentration, the system can promote efficient incorporation of phenolic components without strongly restricting crystal growth. At excessive solids concentration, reduced molecular mobility and higher viscosity may hinder crystallization and disturb matrix uniformity.

The extract-to-sucrose ratio ( $E/S$ ) showed a pronounced effect on  $E_f$ , as the highest values were obtained at low  $E/S$  ratios, whereas a progressive decrease was observed with increasing extract loading. This behavior suggests that excessive incorporation of hibiscus extract solids may overload the sucrose matrix and interfere with the development of a coherent crystalline structure. Hibiscus extract contains phenolic compounds, anthocyanins, organic acids, sugars, and other soluble constituents, which, at high concentrations, may disturb sucrose crystallization, increase hygroscopicity, reduce matrix continuity, and consequently limit the ability of sucrose agglomerates to retain phenolic compounds. This interpretation is further supported by the contour plot shown in Figure 5, where the highest apparent  $E_f$  values, exceeding 107%, were observed at low to moderate extract solu-

ble solids concentrations, approximately 35–50 °Brix, and low  $E/S$  ratios, approximately 0.10–0.25 g/g. Under these conditions, the system appears to maintain an appropriate balance between viscosity and crystallization kinetics, allowing efficient incorporation of hibiscus bioactives into the crystalline matrix. In contrast, at  $E/S$  values above 0.40 g/g, apparent encapsulation efficiency decreased markedly, reaching values below 92%, regardless of extract soluble solids concentration, confirming that extract loading was the critical limiting factor in the co-crystallization process [26].



**Figure 5.** Effects of extract solids concentration ( $X_s$ , °Brix) and dry extract-to-sucrose ratio ( $E/S$ , g/g) on efficiency ( $E_f$ , %) in encapsulation of hibiscus extract by co-crystallization. Values exceeding 100% are interpreted as apparent Folin–Ciocalteu-based responses and not as absolute phenolic recoveries.

This interpretation is consistent with previous co-crystallization studies, which have shown that the efficiency of active-compound incorporation depends strongly on the balance between core loading and sucrose crystallization. Tzatsi and Goula [16] similarly reported that the encapsulation efficiency of chokeberry phenolic extract in a sucrose matrix was affected by the  $E/S$  ratio, confirming the importance of extract loading in determining the structural integrity of the co-crystallized product. However, excessive incorporation of core material may interfere with crystal growth and modify the crystallinity, hygroscopicity, and water sorption behavior of the final product. Therefore, the decrease in  $E_f$  observed in the present study at  $E/S$  values above 0.40 g/g can be attributed to matrix overloading and disruption of sucrose crystallization, rather than to insufficient encapsulation capacity of sucrose itself.

The ANOVA results confirmed the statistical significance of the co-crystallization model. The overall regression model was significant ( $p = 0.001$ ), with a high coefficient of determination ( $R^2 = 92.47\%$ ) and a low standard error ( $S = 2.899$ ), indicating a good agreement between experimental and predicted values. Among the examined factors,  $E/S$  had a highly significant linear effect ( $p < 0.001$ ), whereas  $X_s$  was not significant as a linear term ( $p = 0.243$ ). The quadratic term of  $E/S$  was also significant ( $p = 0.001$ ), confirming the non-linear behavior of the response with respect to extract loading. Furthermore, the interaction between  $X_s$  and  $E/S$  was statistically significant ( $p = 0.004$ ), indicating that the effect of extract soluble solids depended on the level of the extract-to-sucrose ratio.

Overall, co-crystallization was highly effective for hibiscus extract phenolics encapsulation. The extract-to-sucrose ratio was the dominant factor controlling  $E_f$ , while  $X_s$  played a secondary but interactive role. The optimum region was associated with moderate extract concentration and low extract loading, where the sucrose matrix retained sufficient structural integrity to entrap phenolic compounds effectively.

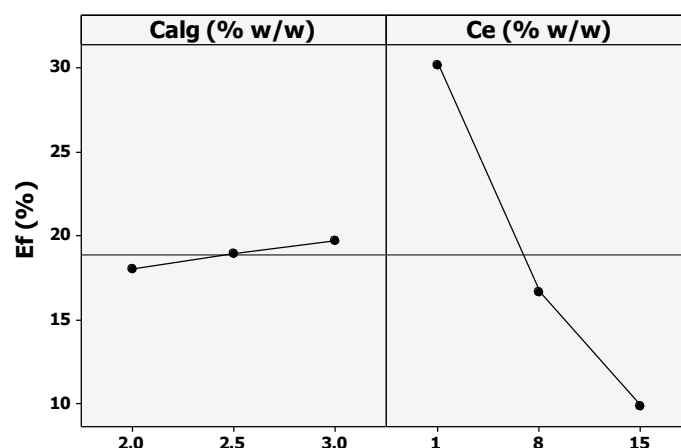
### 3.3. Encapsulation by Ionic Gelation

The  $E_f$  of hibiscus phenolic extract in calcium alginate beads ranged from 7.0 to 34.0% across the tested formulation, while response surface optimization predicted a maximum  $E_f$  of 50.83% under the optimum process conditions, indicating considerably lower retention compared with spray drying and co-crystallization. Although ionic gelation is a mild technique suitable for thermosensitive bioactive compounds, the encapsulation of small hydrophilic phenolics in alginate beads is often limited by diffusion losses during bead formation, curing, and washing. This is particularly relevant for aqueous hibiscus extracts, where phenolic compounds can migrate from the bead interior into the calcium chloride solution during crosslinking.

The low  $E_f$  values obtained here are in agreement with the lower range reported by Toprakçı et al. [27] for rosemary phenolic antioxidants encapsulated in alginate beads, where  $E_f$  ranged from 11 to 49%. Their study also showed that sodium alginate concentration was the most critical factor affecting bead quality and encapsulation performance. The range of the present study is slightly lower but comparable, suggesting that phenolic retention in alginate systems is highly dependent on extract composition, matrix density, and formulation conditions. In contrast, substantially higher  $E_f$  values have been reported when alginate systems are optimized or modified. Machado et al. [28] reported a high  $E_f$  (~89%) for a spirulina phenolic extract in alginate particles, while Tzatsi and Goula [16] reported an optimum  $E_f$  of ~94% for chokeberry phenolic extract in alginate beads. These differences indicate that the low efficiency observed in the present hibiscus systems was not due to ionic gelation itself, but rather to the specific interaction between hibiscus extract composition, alginate concentration, extract loading, and diffusion during gelation.

Calcium alginate beads are formed through ionic crosslinking between  $\text{Ca}^{2+}$  ions and the carboxylate groups of alginate chains, commonly described by the “egg-box” model. However, the resulting hydrogel network is highly hydrated and porous. Therefore, low-molecular-weight hydrophilic compounds, such as hibiscus phenolics and anthocyanins, can diffuse through the gel matrix into the surrounding aqueous medium [29]. Kopyjar et al. [30] emphasized that alginate is widely used for polyphenol encapsulation by ionic gelation, but its highly porous network may limit the retention of low-molecular-weight phenolics unless other biopolymers or fillers are incorporated. In their work, alginate/pullulan beads retained higher TPC than alginate-only beads, confirming the importance of matrix composition for improving phenolic entrapment. This diffusion-driven mechanism is also consistent with Tzatsi and Goula [16], who attributed phenolic losses during ionic gelation to the diffusion of hydrophilic phenolics through the porous calcium alginate structure during immersion in the calcium chloride solution.

As shown in Figure 6, increasing sodium alginate concentration from 2.0 to 3.0% *w/w* resulted in a slight increase in  $E_f$ , probably due to the formation of a denser and more cohesive polymeric network. The higher alginate content may provide more carboxylate groups for interaction with  $\text{Ca}^{2+}$  ions, thereby improving gel strength and limiting the diffusion of phenolic compounds. However, this improvement was limited, indicating that alginate concentration alone was not sufficient to counteract diffusion-driven losses. In contrast, hibiscus extract concentration had a more pronounced effect on  $E_f$ , as increasing  $C_e$  from 1.0 to 15.0% *w/w* markedly reduced  $E_f$ . This behavior suggests that high extract content overloaded the alginate matrix. Increasing the fraction of phenolic compounds located near the bead surface shortened the diffusion path to the calcium chloride solution and possibly interfered with  $\text{Ca}^{2+}$ -alginate interactions through the presence of soluble extract components such as organic acids, sugars, and phenolics.



**Figure 6.** Main effects plot of sodium alginate concentration ( $C_{alg}$ , % w/w), and concentration of extract ( $C_e$ , % w/w) on efficiency ( $E_f$ , %) in encapsulation of hibiscus extract by ionic gelation.

Figure 6 further confirms that  $E_f$  decreased markedly when extract concentration exceeded approximately 6% w/w, regardless of sodium alginate concentration, indicating that extract loading was the main limiting factor for phenolic retention. Similar diffusion-related limitations were reported by Silveira et al. [31], who showed that the  $E_f$  of pomegranate polyphenols in hydrogel beads could be increased from 42 to 101% by strategies designed to reduce mass transfer and improve retention. This comparison supports the interpretation that, in the present system, the main limitation was the diffusion of hydrophilic phenolics from the alginate network to the surrounding aqueous phase.

The ANOVA results were consistent with these trends, as the regression model was statistically significant ( $p = 0.016$ ) and showed a high  $R^2 = 97.15\%$ , indicating adequate description of the experimental data. Among the examined variables,  $C_e$  exerted the strongest effect on  $E_f$ , whereas sodium  $C_{alg}$  had a weaker, supportive role. The quadratic terms and interaction between the two factors were not statistically significant ( $p > 0.05$ ), suggesting that the response was mainly governed by the linear effect of extract loading. Overall, ionic gelation was less efficient than spray drying and co-crystallization for hibiscus phenolic extract encapsulation under the tested conditions, mainly due to the hydrophilic nature and low molecular weight of hibiscus phenolics and anthocyanins, which favored their diffusion through the porous alginate matrix during gelation and washing. Nevertheless, ionic gelation remains promising for applications requiring mild processing, bead-type delivery systems, and controlled release, while further improvement could be achieved by reducing extract loading, optimizing matrix compactness,  $\text{CaCl}_2$  concentration, and curing time, or applying a coating layer or mixed matrices such as alginate–pectin, alginate–chitosan, alginate–pullulan, or protein–polysaccharide systems.

### 3.4. Encapsulated Products Properties

#### 3.4.1. Moisture Characteristics of the Encapsulated Products

Moisture content (MC, %) is a critical physicochemical property of encapsulated products, as it directly affects storage stability, flowability, microbial safety, glass transition behavior, and the potential degradation of bioactive compounds during storage. In the present study, marked differences in moisture content were observed among the encapsulation techniques, reflecting the different mechanisms of particle formation and water retention involved in spray drying, co-crystallization, and ionic gelation.

For the spray-dried hibiscus powders, moisture content ranged from 4.5 to 8.1% w.b. Increasing the w/c ratio decreased the final moisture content, probably because the higher proportion of maltodextrin–WPI modified the rheological behavior of the feed

and promoted the formation of droplets and particles that dried more efficiently. At low  $w/c$  ratios, the higher relative amount of hibiscus extract increased the hydrophilic fraction of the feed and limited the availability of wall material, resulting in powders with higher residual moisture. Inlet air temperature also contributed to moisture reduction, as higher temperatures enhanced heat and mass transfer between the drying air and droplets, increasing the driving force for water evaporation [32]. Similar behavior has been reported in recent spray-drying studies, where higher inlet temperatures and optimized carrier concentrations promoted water removal and improved powder stability. Vargas et al. [21], for example, showed that hibiscus anthocyanin-rich extracts could be converted into stable powders by spray drying, with process performance strongly affected by inlet temperature and carrier concentration.

The co-crystallized hibiscus powders exhibited the lowest moisture content among all encapsulated products, ranging from 0.1 to 0.31% w.b. This very low moisture level indicates the strong capacity of sucrose co-crystallization to produce dry, physically stable matrices without requiring an additional drying step. The low residual moisture can be attributed to the formation of a sucrose crystalline network during supersaturation and crystallization, which reduces water availability and promotes the development of a solid matrix with limited free water. The effect of  $X_s$  was non-linear, suggesting that moisture retention was governed by the balance between initial water content, viscosity, supersaturation level, and crystallization kinetics. Increasing the  $E/S$  ratio generally reduced moisture content, probably due to enhanced crystalline organization and reduced water-holding capacity of the final sucrose-based structure. This agrees with the behavior described by Chezanoglou and Goula [24], who emphasized that sucrose co-crystallization forms porous crystalline structures suitable for the incorporation of food bioactives. Similar low-moisture co-crystallized products were also reported by Solomakou et al. [14], who found moisture contents below 0.5% in co-crystallized powders from lavender distillation residues.

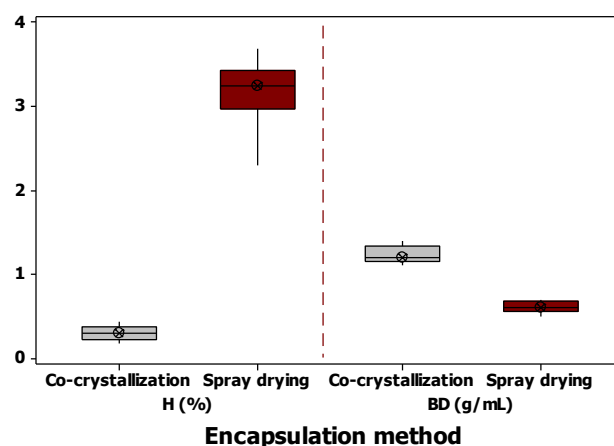
In contrast, alginate beads produced by ionic gelation showed very high moisture contents, ranging from 95.6 to 97.5% w.b. This behavior was expected, since ionic gelation produced hydrogel beads rather than dry powders. The calcium alginate network is highly hydrated and able to retain large quantities of water within its polymeric structure. Increasing the sodium alginate increased the moisture content, which may be attributed to the hydrophilic nature of alginate and its ability to bind water within the gel network. Conversely, increasing  $C_e$  reduced the bead moisture content, possibly due to interactions between extract components and alginate chains, which may reduce the number of available hydrophilic binding sites. Solomakou et al. [14] similarly reported high moisture levels, 94.0–95.4%, for extruded beads obtained by ionic gelation, confirming that high water retention is an intrinsic characteristic of hydrogel-type encapsulation systems. Therefore, among the three methods, co-crystallization produced the driest and potentially most storage-stable product, spray drying generated powders with intermediate moisture content suitable for dry ingredient applications, while ionic gelation produced hydrated beads more appropriate for aqueous or controlled-release systems.

### 3.4.2. Bulk Density

Bulk density is an important technological property for powdered ingredients, as it affects packaging requirements, transportation, storage, powder flowability, dosing accuracy, and reconstitution behavior. This property reflects not only the chemical composition of the powder, but also particle size, porosity, and surface structure.

For spray-dried hibiscus powder, bulk density ranged from 0.52 to 0.70 g/mL (Figure 7). These values are consistent with typical spray-dried fruit and plant extract powders. The bulk density was affected by both  $w/c$  ratio and  $T_i$ . Increasing  $T_i$  tended to reduce bulk

density, probably due to faster evaporation, rapid crust formation, and the development of more porous or hollow particles. At higher drying temperatures, internal vapor pressure may expand the particle structure, creating a void that reduces mass per unit volume. The effect of  $w/c$  ratio is also linked to moisture content and particle morphology. In the present study, increasing the  $w/c$  ratio reduced moisture content and affected particle packing, indicating that the matrix composition modified not only drying behavior but also particle structure.



**Figure 7.** Distribution of hygroscopicity ( $H$ , %) and bulk density ( $BD$ , g/mL) values for co-crystallized and spray-dried hibiscus extract powders obtained across all experimental conditions.

Co-crystallized powders exhibited much higher bulk density values, ranging from 1.10 to 1.40 g/mL (Figure 7). The difference reflects the denser nature of sucrose-based crystalline particles compared with spray-dried particles, which are often hollow, porous, or irregularly collapsed. In co-crystallized products, bulk density was influenced by both  $X_s$  and the  $E/S$  ratio. Higher  $X_s$  and  $C_e$  promoted denser particle packing, probably due to increased matrix cohesion and reduced internal porosity under specific crystallization conditions. This is consistent with co-crystallization studies indicating that bulk density depends on the degree of crystallization, particle size distribution, and incorporation of active compounds within the sucrose matrix. A similar relationship between extract incorporation and powder packing behavior was reported by Ali et al. [33], who encapsulated Poniol fruit extract in a sucrose matrix by co-crystallization and observed a slightly higher bulk density for the co-crystallized powder compared with recrystallized sucrose. This was attributed to the filling of interstitial spaces within the sucrose crystal agglomerates by extract solids, leading to a more compact powder structure.

For ionic gelation, direct comparison with powder bulk density is not appropriate, because alginate beads are hydrated gel particles rather than dry powders. Therefore, among the powder-based products, co-crystallization produced substantially denser particles than spray drying, indicating better packing efficiency and potentially lower packaging volume. Spray-dried powders, by contrast, were less dense, which may be advantageous for rapid dispersion but can increase packaging volume and sensitivity to powder handling conditions.

### 3.4.3. Hygroscopicity

Hygroscopicity ( $H$ ) is the key indicator of the physical stability of encapsulated products, especially in powder systems, because it reflects their tendency to absorb moisture from the surrounding environment. High hygroscopicity can accelerate caking, reduce flowability, promote structural collapse, and enhance the degradation of phenolic compounds and anthocyanins during storage. The hygroscopic behavior of encapsulated products is strongly influenced by the chemical composition of the wall material, the

amount of hydrophilic core material, the degree of crystallinity, the porosity of the matrix, and the surface characteristics of the particles.

For spray-dried hibiscus powders, hygroscopicity ranged from 2.30 to 3.69%. Increasing the  $w/c$  ratio reduced hygroscopicity (Figure 7). This behavior can be attributed to the lower relative contribution of the hydrophilic hibiscus extract and the higher proportion of maltodextrin-WPI in the matrix. Maltodextrin is commonly used to reduce stickiness and improve the physical stability of spray-dried powders, while WPI may contribute to film formation and surface stabilization. In the present system, increasing inlet air temperature also reduced hygroscopicity, indicating that more intense drying produced powders with a lower tendency to absorb moisture. Although some studies report that drier powders may exhibit higher moisture uptake during storage, this is not general and depends on particle structure, wall-material composition, and surface morphology. In the present case, the combined effect of maltodextrin and WPI likely contributed to the formation of a more stable powder matrix with reduced water sorption capacity.

The co-crystallized powders exhibited substantially lower hygroscopicity, ranging from 0.10 to 0.22%, confirming one of the main technological advantages of sucrose-based encapsulation. This behavior is associated with the crystalline nature of sucrose, which restricts water adsorption compared with amorphous carbohydrate systems. The hygroscopicity of the co-crystallized powders was governed by the combined effect of  $X_s$  and  $E/S$  ratio. At suitable extract loading, hibiscus bioactives were likely incorporated within the intercrystalline spaces of the sucrose matrix without severely disrupting crystalline organization. However, excessive extract loading may increase surface polarity, disturb crystal growth, and increase the availability of hydrophilic sites. Similarly, Irigoiti et al. [34] reported that co-crystallized sucrose powders containing propolis extract exhibited low moisture and low hygroscopicity, supporting the ability of sucrose-based co-crystallized matrices to limit moisture uptake while preserving suitable reconstitution properties.

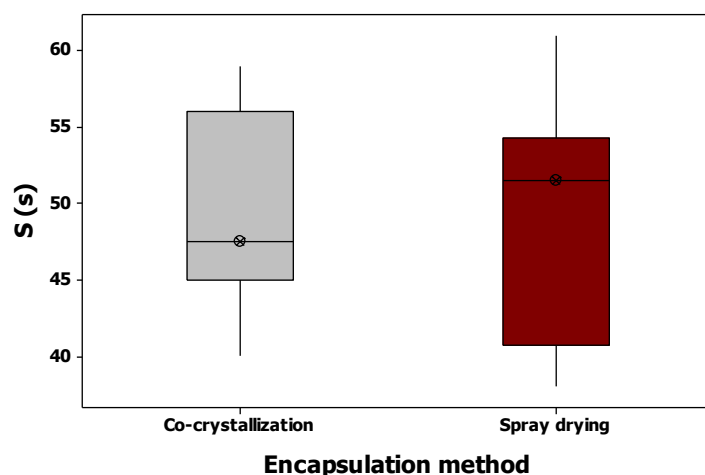
For alginate beads, hygroscopicity ranged from  $-6.05$  to  $-4.71\%$ . These negative values should not be interpreted as negative hygroscopicity, but rather as net water loss from the hydrated hydrogel beads under the applied test conditions. Unlike dry powders, calcium alginate beads contain a high amount of retained water, and their mass change during exposure to controlled relative humidity reflects the balance between water retention, evaporation, swelling behavior, and polymer network structure. The  $C_e$  had a stronger effect than  $C_{alg}$ , with higher extract levels making the  $H$  values less negative, indicating reduced net moisture loss and altered water-matrix interactions. This behavior may be associated with interactions between hibiscus phenolics and alginate carboxyl groups, which can modify the polymer network and influence water retention. Co-crystallization showed the most favorable hygroscopic behavior for dry storage. Spray drying produced moderately stable powder depending on  $w/c$  ratio and drying temperature, whereas ionic gelation generated hydrated systems whose water interactions are governed primarily by the gel structure rather than dry powder hygroscopicity.

#### 3.4.4. Solubility-Wetting Behavior

Solubility or dissolution time is a critical technological parameter for encapsulated ingredients intended for incorporation into beverages, instant products, or aqueous food systems, as it reflects the ability of the encapsulated material to wet, disperse, and dissolve in water. This property is directly related to product reconstitution and to the release of the encapsulated phenolic compounds during use. However, a direct comparison among the three encapsulation systems should be made carefully, since spray drying and co-crystallization produce dry powders, whereas ionic gelation produces hydrated calcium alginate beads that behave as hydrogel delivery systems rather than instant-soluble

particles. Therefore, in the case of alginate beads, water interaction is more appropriately interpreted in terms of swelling, diffusion, and controlled release through the gel network rather than conventional powder dissolution.

For spray-dried hibiscus powders, wetting time ranged from 38 to 61 s, indicating relatively rapid reconstitution in water. Increasing the  $w/c$  ratio increased dissolution time, suggesting slower hydration when the proportion of maltodextrin-WPI in the matrix was higher. This behavior may be associated with the formation of a more continuous encapsulating layer around the hibiscus extract, which can reduce the rate of water penetration despite the high solubility of maltodextrin. The presence of WPI may also modify surface hydration and reconstitution behavior by altering particle surface composition and matrix cohesion. Inlet air temperature also increased wetting time overall, although the trend was not fully linear, probably because higher drying temperatures modified particle morphology, porosity, density, and surface structure. This interpretation is consistent with Nguyen et al. [20], who reported high solubility in spray-dried roselle powders and attributed this partly to maltodextrin, which has high water solubility. Li et al. [35] also showed that the behavior of maltodextrin-WPI spray-dried microcapsules depends on wall-material composition and maltodextrin characteristics. In addition, Sundar et al. [36] reported that WPI-based systems exhibited favorable solubility and rehydration properties, supporting the role of WPI in modulating powder reconstitution behavior. The distribution of wetting-time values for the co-crystallized and spray-dried powders is presented in Figure 8.



**Figure 8.** Distribution of dissolution time ( $S$ , s) values for co-crystallized and spray-dried hibiscus extract powders across all experimental conditions.

For co-crystallized hibiscus powders, wetting time ranged from 40 to 59 s, showing similarly rapid reconstitution to the spray-dried powders. Their dissolution behavior was mainly governed by the crystalline structure of sucrose and the hibiscus extract within the sucrose matrix. Although sucrose is highly soluble, the incorporation of phenolic extract can modify crystallinity, compactness, porosity, and intercrystalline spaces, thereby affecting the time required for complete dissolution. Compared with spray-dried powders, co-crystallized powders are expected to show particularly favorable reconstitution behavior when a porous sucrose matrix is formed, because water can penetrate through intercrystalline voids and promote rapid disintegration. Irigoiti et al. [34] similarly reported that propolis extract, despite its poor water solubility, was successfully transformed into a co-crystallized sucrose powder with high water solubility. Ali et al. [33] reported a dissolution time of 61 s for co-crystallized Poniol fruit extract, while Tzatsi and Goula [16] reported wetting times of 60–120 s for co-crystallized chokeberry extract powders. Rai et al. [26], working with ginger oleoresin encapsulated in co-crystallized sucrose, also showed that the

transformation of sucrose into irregular agglomerates with increased void space and surface area provides a porous matrix for active-compound incorporation, while crystallinity and structural organization influence water-related properties. Solomakou et al. [14] reported wetting times below 60 s for optimized co-crystallized lavender distillation residue products, demonstrating the suitability of sucrose co-crystallization for applications requiring rapid solubility. Therefore, the present co-crystallized hibiscus powders exhibited dissolution behavior that was at least comparable, and in some cases faster than that reported for other co-crystallized plant extracts, suggesting that the sucrose matrix retained sufficient porosity and structural organization to allow rapid water penetration and reconstitution.

These findings indicate that both spray drying and co-crystallization produced encapsulated hibiscus powders with technologically favorable dissolution properties, indicating that both systems are suitable for dry ingredients applications requiring rapid reconstitution. Although spray drying offers fast dissolution combined with high encapsulation efficiency, co-crystallization appears to provide an equally favorable, and slightly more uniform, dissolution profile, likely due to the high solubility of sucrose and the porous crystalline structure of the co-crystallized matrix.

### 3.4.5. Morphology–Color Characteristics

Morphology and color are closely related quality attributes of encapsulated hibiscus products, as they determine not only the visual appearance of the final ingredient but also its technological performance, including flowability, wettability, dissolution behavior, packing properties, stability, and potential consumer acceptance. In hibiscus-based systems, color is particularly important because the extract is rich in anthocyanins, which are responsible for its characteristic red-purple coloration. Therefore, changes in CIE Lab\* parameters can provide indirect information on pigment concentration, carrier dilution, extract distribution within the matrix, thermal degradation, and structural changes induced by the encapsulation process. At the same time, morphology reflects the particle-formation mechanism of each technique, since spray drying produces dry microparticles, co-crystallization forms sucrose-based crystalline agglomerates, and ionic gelation generates hydrated calcium alginate beads. The morphology, color parameters, and phenolic content of the products obtained using the three encapsulation methods are summarized in Figure 9.

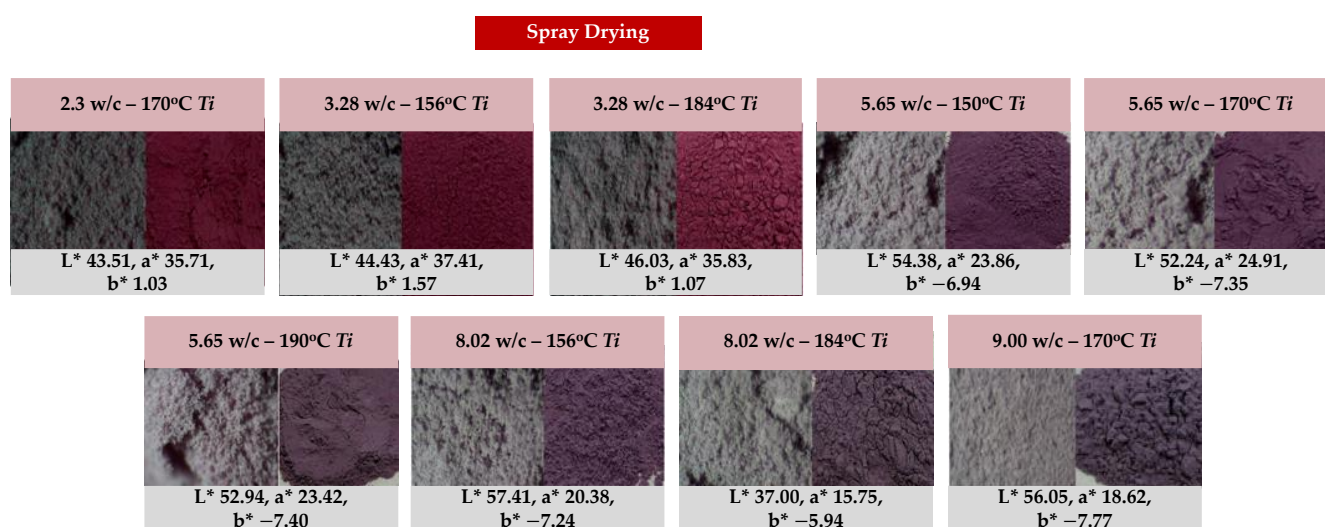
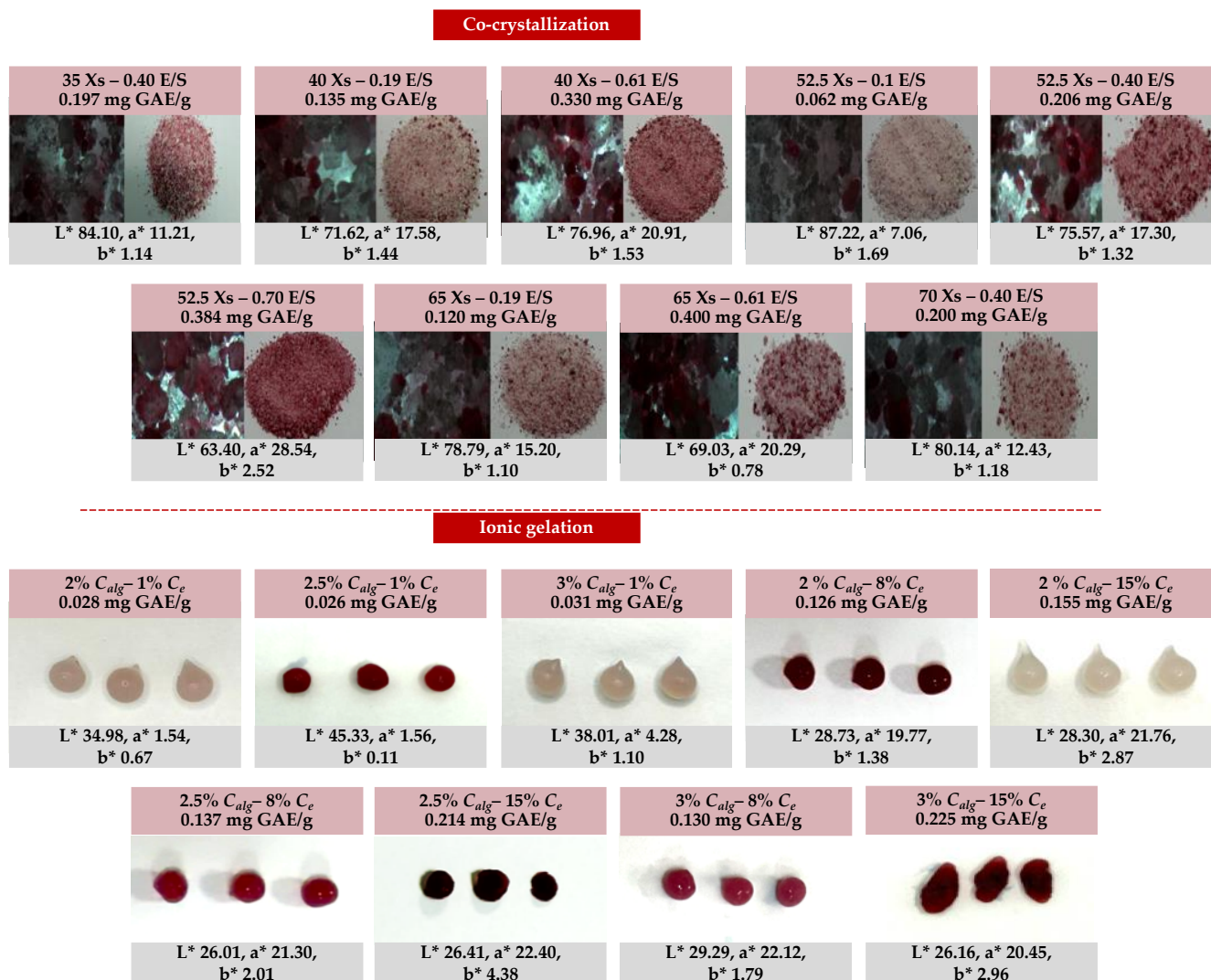


Figure 9. Cont.



**Figure 9.** Morphology, color parameters ( $L^*$ ,  $a^*$ ,  $b^*$ ), and phenolic content (in mg GAE/g) of hibiscus extracts encapsulated by spray drying, co-crystallization, and ionic gelation.

In spray-dried powders, morphology and color were strongly affected by both the  $w/c$  ratio and  $T_i$ . Specifically, increasing the  $w/c$  ratio increased  $L^*$ , indicating the formation of lighter powders due to the higher proportion of maltodextrin-WPI, which diluted the intense color of the hibiscus extract. At the same time,  $a^*$  decreased as the  $w/c$  ratio increased, reflecting the lower relative concentration of anthocyanins and, consequently, reduced redness. The effect of inlet air temperature was more complex and non-linear. Intermediate drying temperatures favored higher  $a^*$  values, suggesting better preservation of the red hue, whereas higher temperatures may have promoted partial anthocyanin degradation or structural modification affecting color perception. From a morphological perspective, spray drying probably produced particles whose structure depended on drying kinetics, feed composition, and matrix formation. Higher  $T_i$  can promote rapid crust formation, particle shrinkage, hollow-particle development, or surface deformation, depending on the balance between water evaporation and matrix solidification. The maltodextrin-WPI system likely contributed to the formation of a more stable particle wall, reducing stickiness and improving powder formation, while the hibiscus extract affected particle cohesion and surface coloration. These observations are consistent with the trends observed for moisture content, bulk density, and dissolution behavior, confirming that color and morphology are strongly linked to the structural development of spray-dried particles.

Similar effects of carrier concentration and  $T_i$  on the color and visual quality of spray-dried hibiscus powders have been reported by Nguyen et al. [20] and Vargas et al. [21], who emphasized that optimized carrier systems and moderate drying conditions are required to preserve anthocyanin-rich color during spray drying.

In co-crystallized powders, morphology and color were mainly governed by sucrose crystallization and by the amount of hibiscus extract incorporated into the crystalline matrix. Increasing the  $E/S$  ratio reduced  $L^*$ , indicating darker powders due to higher pigment loading, while the  $a^*$  parameter ranged from 7.06 to 28.54, confirming the strong red character of the co-crystallized hibiscus products. Higher extract incorporation generally increased redness, although the effect was also influenced by  $X_s$ , which may modify pigment distribution within the sucrose network. At high soluble solids levels, increased supersaturation and more intense crystal formation may entrap chromophore compounds within the internal structure of the sucrose agglomerates, reducing their surface visibility and altering perceived color intensity. The  $b^*$  values ranged from 0.78 to 2.52, indicating a limited shift toward yellow tones, which may be associated with flavonoids, minor pigment transformations, or matrix-related optical effects. Morphologically, co-crystallization produced sucrose-based agglomerated crystalline particles. Under appropriate extract loading, sucrose crystals form irregular porous agglomerates with void spaces capable of incorporating hibiscus phenolics and anthocyanins. However, excessive extract loading may disturb crystal growth, increase heterogeneity, reduce structural uniformity, and modify packing behavior. This explains the relationship between co-crystallized powder morphology, bulk density, hygroscopicity, dissolution behavior, and color intensity. Chezanoglou and Goula [24] similarly emphasized that sucrose co-crystallization produced irregular crystalline structures with increased void space and surface area, providing a suitable matrix for the incorporation of bioactive compounds. In addition, Rai et al. [26] reported that co-crystallization of ginger oleoresin in sucrose generated irregular agglomerates with modified crystallinity and surface structure, supporting the interpretation that the morphology of co-crystallized systems is closely related to active-compound loading and matrix organization.

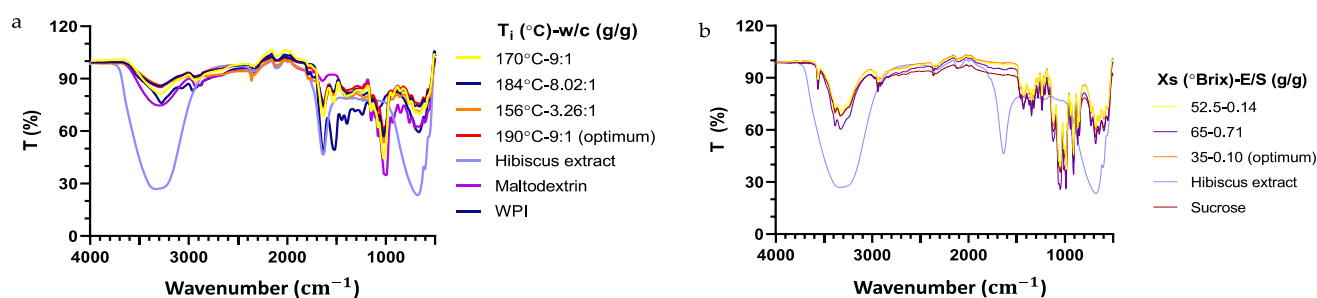
In alginate beads produced by ionic gelation, morphology and color were controlled primarily by  $C_{alg}$ ,  $C_e$ , and the extrusion-gelation mechanism. Color was strongly affected by  $C_e$ , as increasing hibiscus extract content reduced  $L^*$  and increased  $a^*$ , producing darker and redder beads due to the higher concentration of anthocyanins and other phenolic chromophores.  $C_{alg}$  exerted a weaker but still relevant effect, mainly through changes in gel density, transparency, and light scattering. Higher  $C_{alg}$  may form denser and less transparent networks, modifying the visual intensity of the entrapped pigments and influencing color perception. Unlike the two powder-based systems, ionic gelation maintained the visual identity of hibiscus in a hydrated bead form, where pigment distribution depends not only on concentration but also on diffusion within the hydrogel network. From a morphological standpoint, bead diameter ranged from 2.8 to 3.5 mm, with the largest beads obtained at the highest  $C_{alg}$  and  $X_s$  concentrations. This behavior can be attributed to the increased viscosity of the alginate-extract mixture, which promoted the formation of larger droplets during extrusion and, consequently, larger beads after contact with the calcium chloride solution. Droplet size during ionic gelation is also influenced by extrusion tip diameter, distance from the calcium chloride solution, surface tension, viscosity, and gelation kinetics. Similar observations have been reported by Ćorković et al. [37] and Toprakçı et al. [27], who highlighted the role of  $C_{alg}$  and processing conditions in controlling the morphology and encapsulation performance of alginate microbeads containing phenolic antioxidants.

Overall, the three encapsulation methods produced products with clearly different morphology-color profiles. Spray drying generated light-colored powders whose redness

decreased with increasing wall material concentration, mainly due to pigment dilution by maltodextrin-WPI and possible thermal effects at high inlet temperatures. Co-crystallization produced denser sucrose-based crystalline agglomerates with strong red coloration when extract loading was high, although excessive extract incorporation could modify crystal growth and color distribution. Ionic gelation produced large, hydrated beads with intense, extract-dependent coloration and a morphology governed by gel network formation rather than dry particle development. Therefore, spray drying and co-crystallization are more suitable for dry powdered ingredients requiring good handling and reconstitution properties, whereas ionic gelation is more appropriate for visually distinct bead-type delivery systems, controlled release, and incorporation into high-moisture food matrices.

### 3.5. FT-IR Analysis

FT-IR spectroscopy was applied to investigate interactions between hibiscus phenolic extract and the encapsulating matrices and to evaluate the effect of the encapsulation process on the structure of the systems. The spectra of the raw hibiscus extract, the wall materials, and selected encapsulated samples were compared in order to identify changes in the position, intensity, or shape of characteristic absorption bands. In the case of spray drying, FTIR spectroscopy was used to investigate possible interactions between hibiscus extract and the maltodextrin-WPI wall system and to evaluate the effect of spray-drying conditions on microcapsule structure. The selected spectra included hibiscus extract, WPI, maltodextrin, and representative spray-dried samples with different encapsulation efficiencies. The spectra of the encapsulated samples showed high similarity to those of the wall materials, indicating that the maltodextrin-WPI matrix dominated spectroscopically and that hibiscus extract was successfully incorporated without the formation of new covalent bonds (Figure 10). The observed differences were mainly related to changes in band intensity and slight shifts in characteristic absorption bands, reflecting the degree of entrapment and the interactions between bioactive compounds and the encapsulating matrix. This behavior is consistent with the literature, where spray-drying encapsulation is described as being governed mainly by non-covalent interactions, including hydrogen bonding and hydrophobic interactions [16,38].



**Figure 10.** FTIR spectra of hibiscus extract, encapsulating materials (sucrose, maltodextrin, WPI), and representative encapsulated samples obtained by (a) spray drying and (b) co-crystallization.

In the 3200–3400 cm<sup>-1</sup> region, assigned to O-H and N-H stretching vibrations, the spray-dried samples showed broadening and a slight shift toward lower wavenumbers, suggesting hydrogen-bonding interaction between hibiscus phenolic components and the biopolymers of the maltodextrin-WPI matrix. Similar changes have been reported for protein-polyphenol systems by Ren et al. [39] and Zhao et al. [40]. The sample produced at 170 °C and a *w/c* ratio of 9:1 g/g, which presented a lower *E<sub>f</sub>* (89.58%), exhibited a more intense band in this region. This suggests a higher number of free phenolic groups, probably because the lower *T<sub>i</sub>* led to less efficient moisture removal and the formation of a less compact microcapsule structure, leaving more phenolic compounds on or near the

particle surface. In contrast, samples with higher  $E_f$ , such as those produced at 184 °C and 8.02:1 g/g and 190 °C and 9:1 g/g, showed smoother spectra that more closely resembled those of the carriers, indicating more effective embedding of bioactive compounds within the maltodextrin-WPI matrix. These conditions likely promoted faster drying and the formation of a denser and more homogenous wall structure, providing better protection for the encapsulated components.

The region around  $1650\text{ cm}^{-1}$ , related to C=O stretching of peptide bonds in WPI and commonly used as an indicator of protein secondary structure, showed slight shifts and reductions in intensity in the spray-dried samples [41,42]. These changes suggest interactions between hibiscus polyphenols and protein functional groups, consistent with the formation of protein-polyphenol complexes through non-covalent mechanisms [39,43]. In the  $1540\text{--}1510\text{ cm}^{-1}$  region, differences in band intensity were associated with interactions between protein and anthocyanins, further supporting the formation of non-covalent complexes [43]. Finally, in the  $1200\text{--}900\text{ cm}^{-1}$  region, corresponding mainly to C-O and C-O-C stretching vibrations of maltodextrin glycosidic bonds, characteristic carbohydrate bands were present in all encapsulated samples. The presence of these bands, along with the reduction in characteristic hibiscus extract bands, confirmed the successful entrapment of phenolic components within the carrier matrix.

In the case of co-crystallization, FTIR analysis was used to investigate the interaction between hibiscus extract and sucrose and to assess the influence of process conditions on the structure of the final products. The spectra of the co-crystallized samples, produced at different  $X_s$  concentrations and  $E/S$  ratios, showed high similarity to that of sucrose, indicating that sucrose was the dominant structural component of the encapsulating matrix (Figure 10). The absence of new characteristic bands suggests that hibiscus extract was incorporated without the formation of new covalent bonds. This observation agrees with previous studies reporting that co-crystallization with sucrose mainly leads to physical entrapment of bioactives within the crystalline sucrose network, without substantial modification of the chemical structure of sucrose [24,44]. Tzatsi and Goula [16] also reported that co-crystallization can effectively incorporate chokeberry phenolic extracts into a sucrose matrix, with differences among the final powders being mainly associated with the degree of entrapment and the physical distribution of the extract within the carrier.

The broad absorption band in the  $3200\text{--}3400\text{ cm}^{-1}$  region was attributed to O-H stretching vibrations originating from both sucrose and hydroxyl-rich phenolics of hibiscus extract. Minor differences in the intensity and shape of this band among the co-crystallized samples may be assigned to hydrogen-bonding interactions between hydroxyl groups of sucrose and anthocyanins or other phenolic compounds. However, the absence of pronounced shifts indicates that these interactions were mainly physical and non-covalent and did not result in substantial chemical modification of the system, in agreement with Irigoiti et al. [34] and Ali et al. [33]. In the  $1600\text{--}1650\text{ cm}^{-1}$  region, where aromatic C=C and C=O vibrations of phenolic components are expected, the intensity of the extract-related bonds was reduced in the co-crystallized samples compared with the raw extract. This attenuation suggests that anthocyanins and other phenolics were incorporated within the sucrose matrix and were not fully exposed in the free form, as previously reported for co-crystallized polyphenol-rich systems [33,34]. In the  $1200\text{--}900\text{ cm}^{-1}$  region, the characteristic sucrose bands, attributed to C-O and C-O-C vibrations of glycosidic bonds, remained dominant in all co-crystallized samples, further confirming that sucrose constituted the main matrix and that extract addition did not substantially disrupt its structure [24,44].

The spectral differences among the co-crystallized samples were associated with both  $X_s$  and  $E/S$ . The effect of  $X_s$  concentration on  $E_f$  was non-linear, with an increase between 35 and 40 °Brix, a decrease at 52.5 °Brix, a subsequent increase at 65 °Brix, and a further

reduction at 70 °Brix. This behavior can be attributed to changes in viscosity, molecular mobility, supersaturation, and crystallization kinetics, which affect both the degree of entrapment and the formation of the sucrose crystalline structure. The samples produced at 65 °Brix and  $E/S$  of 0.71 g/g showed more pronounced FTIR differences compared with the other co-crystallized samples, probably because they contained the highest TPC and showed high  $E_f$ , 99.49%. However, the maximum  $E_f$  was obtained at 52 °Brix and  $E/S$  of 0.14 g/g, reaching 109.38%. This indicates that the highest phenolic content in the final product does not necessarily correspond to the highest encapsulation efficiency, since  $E_f$  also depends on initial extract loading, sucrose crystallization, and the spatial distribution of the extract within the matrix.

At high °Brix values, rapid supersaturation and fast crystal growth may favor the incorporation of a considerable amount of bioactives but not necessarily their homogenous distribution throughout the sucrose matrix. Therefore, part of the phenolics may remain in regions of higher local concentration or closer to the crystal surface, explaining the stronger differences observed in the 3200–3400  $\text{cm}^{-1}$  and 1600–1650  $\text{cm}^{-1}$  regions for the 65 °Brix and  $E/S$  of 0.71 g/g. In contrast, the lower extract loading in the 52 °Brix and  $E/S$  of 0.14 g/g probably favored more efficient and homogeneous incorporation. The visual heterogeneity of the co-crystallized products supports this interpretation, as hibiscus extract appeared locally distributed within the crystalline structure, forming regions with different concentrations of bioactive components. FTIR results indicate that co-crystallization with sucrose effectively incorporated hibiscus extract mainly through physical entrapment and weak hydrogen-bonding interactions, while the observed spectral differences reflected extract loading, °Brix, degree of entrapment, and natural heterogeneity of extract distribution rather than chemical transformation.

FTIR analysis confirmed that both spray drying and co-crystallization incorporated hibiscus phenolic extract mainly through physical entrapment and non-covalent interactions, without evidence of new covalent bond formation or chemical degradation of the bioactive components. In spray-dried powders, the predominance of maltodextrin-WPI spectral features and the attenuation of extract-related bands confirmed successful embedding of the extract within the wall matrix. The higher the encapsulation efficiency, the more closely the spectra resembled those of the carriers, whereas lower  $E_f$  was associated with more intense extract-related bands, indicating a higher fraction of phenolics remaining closer to the particle surface. In co-crystallized powders, the dominance of sucrose-related bands confirmed the formation of a sucrose-based matrix, while spectral differences were associated with  $E/S$ , °Brix, extract distribution, and encapsulation efficiency.

### 3.6. Comparative Evaluation of the Encapsulated Products Under Optimum Conditions

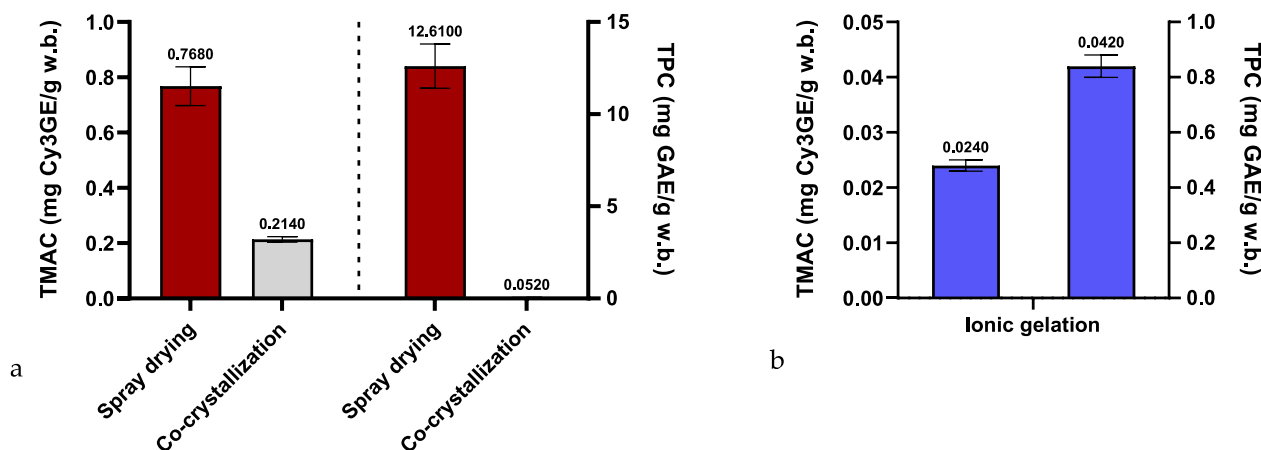
The encapsulated products obtained under the optimum conditions for each process (Table 1) were comparatively evaluated in order to identify the most suitable encapsulation strategy for hibiscus extract, considering both functional retention and technological performance. Since the three techniques produced structurally different systems, namely spray-dried powders, sucrose-based co-crystallized powders, and hydrated calcium alginate beads, the comparison was interpreted according to the technological role of each product.

Encapsulation efficiency ( $E_f$ ) is one of the most important indicators of encapsulation performance as it reflects the ability of the carrier matrix to retain and protect bioactives during processing. Under optimal conditions, co-crystallization showed the highest apparent  $E_f$ , reaching 99.96%, followed closely by spray drying, with 95.06%, whereas ionic gelation showed a considerably lower value of 50.83%. These results indicate that both dry encapsulation techniques were highly effective at retaining hibiscus bioactives within their carrier matrices, although with different mechanisms. The high  $E_f$  obtained by co-crystallization

and spray drying is consistent with previous studies showing that sucrose crystalline matrices and optimized spray-drying carrier systems can efficiently retain phenolic-rich extracts through physical entrapment and matrix protection [16,20,21,24,33,34]. Conversely, the lower  $E_f$  of ionic gelation suggests diffusion losses of hydrophilic hibiscus phenolics during bead formation, gel hardening, and washing, in agreement with studies showing that retention in alginate systems depends on gel compactness, hydrophilicity, and affinity for the polymer network [27,28,30].

Antioxidant activity provided a different ranking and, therefore, a more functional interpretation of the optimum products. Spray drying showed the highest antioxidant activity, ~37.77%, followed by co-crystallization, ~20.70%, and ionic gelation, ~9.07%. This finding shows that the method with the highest  $E_f$  did not necessarily provide the highest antioxidant performance. Although co-crystallization was very effective at incorporating the extract into the sucrose matrix, spray drying preserved a higher fraction of compounds contributing to radical-scavenging activity. This result is consistent with the high TPC and TMAC of the spray-dried product and agrees with studies showing that spray drying, when combined with appropriate carriers, can preserve the antioxidant potential of phenolic- and anthocyanin-rich extracts [20,21]. The intermediate antioxidant activity of the co-crystallized product indicates that sucrose co-crystallization can provide protection, but the final functional activity may be affected by dilution in the sucrose matrix and by the distribution of the extract within the crystalline structure. The low antioxidant activity of alginate beads is consistent with their lower  $E_f$  and suggests greater loss or lower availability of antioxidant compounds in the final hydrated system.

Because TPC and TMAC are expressed on a wet basis and may be strongly influenced by product moisture content and physical form, the optimized products are presented separately according to product type in Figure 11. The dry powder systems produced by spray drying and co-crystallization are shown in Figure 11a, whereas the hydrated alginate beads produced by ionic gelation are shown in Figure 11b, allowing the results to be interpreted according to their different applicable scenarios.



**Figure 11.** Total monomeric anthocyanin content (TMAC, mg cyanidin-3-glucoside equivalents-Cy3GE/g w.b.) and total phenolic content (TPC, mg gallic acid equivalents-GAE/g w.b.) of hibiscus extract products obtained under optimized and experimentally validated encapsulation conditions: (a) dry powder systems produced by spray drying and co-crystallization; (b) hydrated hydrogel beads produced by ionic gelation. Bars represent mean values, and error bars indicate standard deviation.

TPC, expressed as mg GAE/g w.b., further supported the superiority of spray drying in terms of functional compound retention. As shown in Figure 11a,b, the spray-dried powder exhibited the highest value, ~12.61 mg GAE/g w.b., followed by co-crystallization, ~0.052 mg GAE/g w.b., and ionic gelation, ~0.042 mg GAE/g w.b. Although ionic gela-

tion showed a higher dry-basis phenolic content than co-crystallization, its very high moisture content and lower  $E_f$  limit its practical performance as a concentrated dry ingredient. Spray drying, therefore, remained clearly superior under the selected optimum conditions, indicating that the maltodextrin-WPI matrix was more effective in retaining hibiscus phenolics. This trend is consistent with previous studies on spray-dried roselle and hibiscus products, which found that suitable carrier systems enhanced phenolic retention and reduced degradation during processing [20,21]. In contrast, the lower phenolic content of the co-crystallized product, despite its high  $E_f$ , should be interpreted in relation to the relatively low amount of extract incorporated under the optimum conditions and the dilution effect of the sucrose matrix, rather than as evidence of poor encapsulation performance.

Because *TMAC* was determined only for the optimized and experimentally validated samples, it was not used as the primary optimization response but rather as a key complementary indicator of pigment retention and bioactive quality. Anthocyanin content followed the same trend as *TPC* and antioxidant activity. As shown in Figure 11a, among the dry powder systems, spray drying resulted in the highest anthocyanin content, ~0.77 mg Cy3GE/g w.b., compared with co-crystallization, ~0.21 mg Cy3GE/g w.b. In contrast, ionic gelation, shown in Figure 11b, resulted in considerably lower anthocyanin content, ~0.024 mg Cy3GE/g w.b. Since anthocyanins are among the main pigments and bioactive compounds of hibiscus, this result confirms that spray drying was the most effective method for preserving the characteristic functional and chromatic quality of the extract [45]. The higher anthocyanin content of the spray-dried powder is also consistent with its higher redness value and antioxidant activity, indicating close consistency among the chemical, functional, and color measurements. Similar conclusions have been reported for spray-dried hibiscus and roselle powders, where carrier composition and optimized drying conditions were critical for anthocyanin stabilization [46]. The lower anthocyanin content in the co-crystallized powder may be associated with dilution within the sucrose matrix and possible pigment redistribution during crystallization, whereas the very low value observed for alginate beads may be attributed to diffusion of water-soluble pigments into the calcium chloride solution and washing medium during gelation. The higher *TMAC* compared to *TPC* in the co-crystallized powder is most likely due to methodological and matrix-related factors rather than an actual compositional inconsistency. Specifically, *TPC* was determined by the Folin–Ciocalteu method, which is a nonspecific assay and can be affected by interfering substances (e.g., sugars or other reducing compounds in the co-crystallized product), leading to underestimation or variability in phenolic quantification. On the contrary, *TMAC* was measured with the pH-differential method, which is less prone to interference from the co-crystallization carrier materials. Additionally, the co-crystallization procedure and the carrier matrix may differentially influence the extraction efficiency of total phenolics as opposed to anthocyanins, resulting in apparent discrepancies between these two measurements.

The remaining physicochemical properties, determined for the samples obtained under the optimum conditions of each encapsulation process, confirmed the different technological roles of the three systems (Table 1). Co-crystallization produced the most physically stable dry powder, with the lowest moisture content, 0.41%, very low hygroscopicity, approximately 0.2%, the highest bulk density, 1.2 g/mL, and the shortest dissolution time among the powder products, 45 s. Spray drying also produced a technologically acceptable dry powder under its optimum conditions, with 4.3% moisture, 3.5% hygroscopicity, approximately 0.7 g/mL bulk density, and dissolution time of 51 s, indicating effective reconstitution despite its more porous structure. Ionic gelation, under its respective optimum conditions, produced highly hydrated beads with 95.1% moisture, confirming that

this system is not directly comparable to dry powders in terms of storage stability or instant reconstitution, but rather represents a hydrated delivery format.

Color parameters, also determined under the optimum conditions for each encapsulation process, were consistent with the bioactive compound results. Co-crystallization produced the lightest product, with  $L^* = 84.10$ ,  $a^* = 11.21$ , and  $b^* = 1.14$ , mainly due to the dominance of the sucrose matrix. Spray drying showed intermediate lightness but the most intense red-purple character ( $L^* = 63.64$ ,  $a^* = 12.83$ , and  $b^* = -7.07$ ). Ionic gelation produced the darkest product and the lowest redness, with  $L^* = 36.82$ ,  $a^* = 4.5$ , and  $b^* = 1.09$ . The negative  $b^*$  value of the spray-dried powder indicates a shift toward bluish-purple tones, consistent with the presence of hibiscus anthocyanins. Therefore, although co-crystallization gave the most physically stable dry product under optimum conditions, spray drying better preserved the pigment-related visual quality of hibiscus extract.

Taken together, the optimum condition comparison shows a clear distinction between physical stability and functional preservation. Co-crystallization was the most favorable method for producing a physically stable dry ingredient, combining the highest  $E_f$ , the lowest moisture content and hygroscopicity, high bulk density, and rapid dissolution. Spray drying, however, was the most effective technique for preserving the bioactive and chromatic quality of hibiscus extract, as it resulted in the highest antioxidant activity, TPC, TMAC, and redness. Ionic gelation showed lower retention of phenolics and anthocyanins under the selected conditions but remains relevant for applications where hydrated bead-type delivery or controlled release is required.

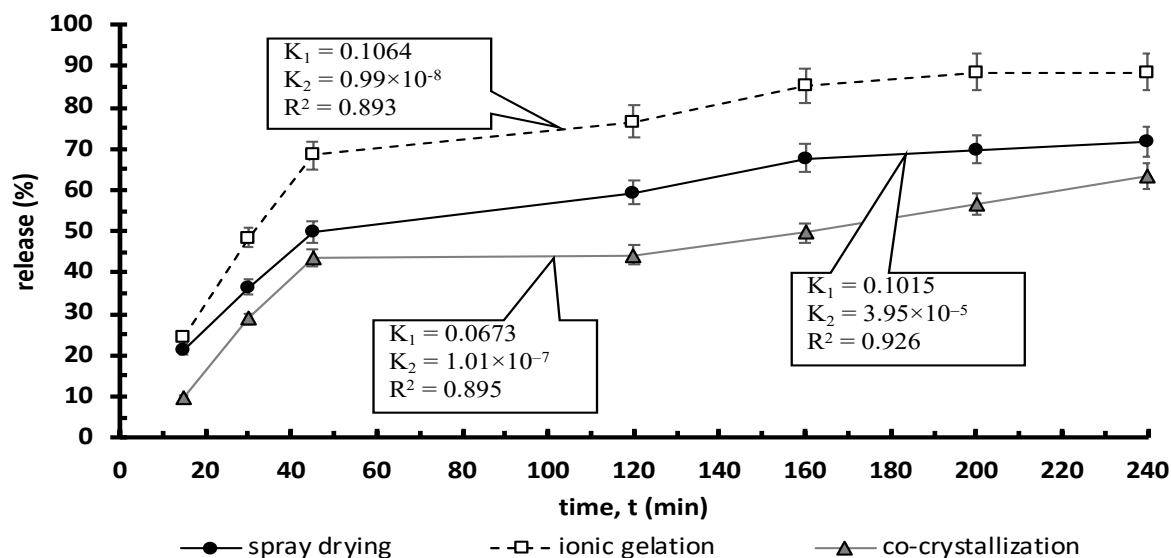
The release of the encapsulated hibiscus extract was evaluated by monitoring the relative release of bioactive compounds as a function of time for the three encapsulation techniques. For the quantitative description of release kinetics, the modified Peppas-Sahlin-type model was applied:

$$\frac{M_t}{M_\infty} = K_1 t^{0.43} + K_2 t^{0.86} \quad (5)$$

where  $\frac{M_t}{M_\infty}$  is the fractional release at time  $t$ ;  $K_1 t^{0.43}$  represents the contribution of Fickian diffusion; and  $K_2 t^{0.86}$  is associated with relaxation, swelling, and/or structural rearrangement of the encapsulating matrix. This model is particularly suitable for systems in which release is not governed by a single mechanism, but rather by the combined contribution of diffusion and matrix-related structural phenomena. Mathematical analysis of release from encapsulated systems is therefore useful for comparing encapsulation technologies and for understanding the effect of the wall material on release behavior [47]. Recent studies have also applied the Peppas-Sahlin model to describe the release of encapsulated phenolic components and other bioactives, showing that the diffusion mechanism often dominates, while matrix relaxation or swelling may also contribute depending on the carrier structure [48–50]. All encapsulated systems showed a biphasic release profile, characterized by an initial rapid release stage followed by a slower phase approaching a plateau (Figure 12). The first stage can be attributed to bioactive compounds located close to the particle surface or weakly associated with the encapsulating matrix, whereas the second stage reflects the gradual diffusion of compounds embedded deeper within the matrix. Such behavior is commonly observed in encapsulated phenolic systems, where the release profile depends on matrix hydration, porosity, swelling, dissolution, and the strength of interactions between the bioactive compounds and the carrier [51].

The maximum release was observed at approximately 150, 200, and 240 min for spray drying, ionic gelation, and co-crystallization, respectively. The corresponding release percentages were approximately 60, 85, and 55%, indicating clear differences among the encapsulation matrices. Ionic gelation showed the highest release percentage, probably due to the hydrated and porous nature of the calcium alginate network, which facilitates

water penetration, swelling, and the diffusion of hydrophilic phenolic components. Similar release behavior has been reported for alginate-based systems, where matrix composition and gel structure strongly affect the release and bioaccessibility of encapsulated phenolics and anthocyanins [49,52,53].



**Figure 12.** Release profiles of phenolic compounds in water from microcapsules of hibiscus extract encapsulated by spray drying, ionic gelation, and co-crystallization under optimum conditions.

Spray-dried powders showed an intermediate release, reaching approximately 60% after 150 min. This suggests that maltodextrin–WPI matrix allowed relatively rapid hydration and diffusion, while still providing partial retention of the encapsulated components. The release behavior of spray-dried systems is generally controlled by the solubility of the wall material, particle porosity, surface-associated bioactives, and the degree of interaction between phenolics and the carrier matrix [20,21,54].

Co-crystallized powder showed the slowest and lowest release, reaching approximately ~55% after 240 min. Although sucrose is highly soluble, the lower release may be related to the physical entrapment of hibiscus phenolics within the sucrose crystalline matrix and the heterogeneous distribution of the extract inside the co-crystallized particles [33,34]. This behavior indicates that co-crystallization can provide a more restrictive matrix for bioactive release compared with spray drying and ionic gelation.

The different release percentages can also be related to the dissolution and hygroscopic behavior of the products, as both properties influence water penetration into the matrix and the mobility of encapsulated compounds. The balance between hydrophilic and hydrophobic sites within each encapsulating system affects matrix hydration, swelling, and diffusion pathways. The relationship between the kinetic constants  $K_1$  and  $K_2$  indicated that diffusion was the dominant release mechanism in all systems, although relaxation, swelling, and structural rearrangement of the matrix also contributed to the overall release process.

#### 4. Conclusions

This study demonstrated that hibiscus phenolic extract can be successfully encapsulated by spray drying, co-crystallization, and ionic gelation, with each method producing systems with distinct technological and functional characteristics. The results clearly showed that the selection of the encapsulation technique strongly affects encapsulation efficiency, bioactive retention, antioxidant activity, color preservation, and final product applicability.

Spray drying was the most effective method for preserving the bioactive quality of hibiscus extract. Although total phenolic content was used as the primary indicator for optimization and comparison, anthocyanin content was considered an important complementary marker of pigment retention, color preservation, and bioactive quality in the optimized products. Under optimal conditions, the spray-dried powder showed high  $E_f$  and the highest antioxidant activity, *TPC*, and anthocyanin content. Co-crystallization was the most advantageous method in terms of physical stability and powder functionality, achieving the highest apparent encapsulation efficiency under the optimized conditions, together with the lowest moisture content and very low hygroscopicity, indicating the formation of a stable dry powder. Although its *TPC* and *TMAC* were lower than those obtained by spray drying, this was mainly associated with the lower extract loading under the optimum conditions and the dilution effect of the sucrose matrix, rather than with poor encapsulation performance. Ionic gelation produced hydrated alginate beads with a different technological profile; under optimum conditions, it showed lower encapsulation efficiency, antioxidant activity, *TPC*, and *TMAC*, while moisture content remained very high. Thus, ionic gelation was less suitable for producing concentrated dry ingredients but remains relevant for hydrated bead-type and controlled-release applications.

FTIR analysis confirmed that spray drying and co-crystallization incorporated hibiscus phenolics mainly through physical entrapment and non-covalent interactions, without evidence of new covalent bond formation or chemical degradation. Overall, spray drying is preferable when the main objective is the preservation of phenolics, anthocyanins, and antioxidant activity, whereas co-crystallization is more suitable for producing physically stable dry powders with low moisture and low hygroscopicity. Ionic gelation offers a complementary route for hydrated delivery systems.

Several limitations should be acknowledged. Future work should focus on storage stability, with emphasis on phenolic degradation, color retention, and antioxidant activity. Compound-specific chromatographic analysis, such as HPLC, should also be performed to further validate the retention of individual hibiscus phenolics and anthocyanins and to complement the total-phenolic-content-based encapsulation efficiency values reported in the present study. In addition, release behavior should be assessed under simulated gastrointestinal conditions to determine how the different encapsulating matrices affect the delivery and bioaccessibility of hibiscus phenolics. Scale-up performance should also be examined to confirm the reproducibility, process efficiency, and technological feasibility of the optimized conditions at a larger production scale. Finally, incorporation of the optimized products into real food systems is necessary to evaluate their practical performance as functional food additives.

**Author Contributions:** Conceptualization, A.M.G.; methodology, E.G.P., D.F., N.S., and A.M.G.; software, E.G.P. and N.S.; validation, E.G.P.; formal analysis and investigation, E.G.P. and N.S.; resources, A.M.G.; writing—original draft preparation, N.S.; writing—review and editing, A.M.G.; visualization and supervision, A.M.G.; project administration, A.M.G.; funding acquisition, A.M.G. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## Abbreviations

The following abbreviations are used in this manuscript:

|                    |                                                                             |
|--------------------|-----------------------------------------------------------------------------|
| MW                 | Molecular weight                                                            |
| DPPH               | 1,1-diphenyl-2-picrylhydrazyl                                               |
| UAE                | Ultrasound-assisted extraction                                              |
| $E_f$              | Encapsulation efficiency                                                    |
| WPI                | Whey protein isolate                                                        |
| RSM                | Response surface methodology                                                |
| CCD                | Central composite design                                                    |
| $T_i$              | Inlet air temperature                                                       |
| $C_{alg}$          | Concentration of sodium alginate solution                                   |
| $C_e$              | Concentration of extract                                                    |
| $X_s$              | Solids concentration of the extract                                         |
| $E/S$              | Dry extract-to-sucrose ratio                                                |
| TPC                | Total phenolic content                                                      |
| SPC                | Surface phenolic content                                                    |
| GAE                | Gallic acid equivalents                                                     |
| $Y$                | Encapsulation yield                                                         |
| MC                 | Moisture content                                                            |
| $BD$               | Bulk density                                                                |
| $S$                | Solubility–Wetting time                                                     |
| $H$                | Hygroscopicity                                                              |
| $HNO_3$            | Nitric acid                                                                 |
| AA                 | Antioxidant activity                                                        |
| d.b.               | Dry basis                                                                   |
| w.b.               | Wet basis                                                                   |
| $\epsilon$         | Molar extinction coefficient of cyanidin-3-glucoside                        |
| $l$                | Optical path length                                                         |
| $L^*$              | Lightness                                                                   |
| $a^*$              | Green–red color coordinate                                                  |
| $b^*$              | Blue–yellow color coordinate                                                |
| $CIE L^*a^*b^*$    | Commission Internationale de l’Éclairage color space                        |
| $CaCl_2$           | Calcium chloride                                                            |
| TMAC               | Total monomeric anthocyanin content                                         |
| $DF$               | Dilution factor                                                             |
| FT-IR              | Fourier-transform infrared spectroscopy                                     |
| ATR                | Attenuated total reflectance                                                |
| ANOVA              | Analysis of variance                                                        |
| $p$ -value ( $p$ ) | Probability value indicating statistical significance                       |
| $R^2$              | Coefficient of determination                                                |
| $S$                | Standard error of the regression                                            |
| $M_t$              | Amount of bioactive compounds released at time $t$                          |
| $M_\infty$         | Amount of bioactive compounds released at equilibrium or at infinite time   |
| $M_t/M_\infty$     | Fractional release of bioactive compounds at time $t$                       |
| $K_1$              | Diffusion-related release constant in the Peppas–Sahlin model               |
| $K_2$              | Relaxation- or swelling-related release constant in the Peppas–Sahlin model |

## References

1. Singh, M. Application of Hibiscus sabdariffa Extract to Manage Obesity. Ph.D. Thesis, RMIT University, Melbourne, Australia, 2024. [\[CrossRef\]](#)
2. Villalobos-Vega, M.J.; Rodríguez-Rodríguez, G.; Armijo-Montes, O.; Jiménez-Bonilla, P.; Álvarez-Valverde, V. Optimization of the extraction of antioxidant compounds from roselle hibiscus calyxes (*Hibiscus sabdariffa*) as a source of nutraceutical beverages. *Molecules* **2023**, *28*, 2628. [\[CrossRef\]](#) [\[PubMed\]](#)

3. M'be, C.U.; Scher, J.; Gaiani, C.; Amani, N.G.; Burgain, J. Impact of processing and physicochemical parameter on *Hibiscus sabdariffa* calyxes biomolecules and antioxidant activity: From powder production to reconstitution. *Foods* **2023**, *12*, 2984. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Hapsari, B.W.; Manikhanda; Setyaningsih, W. Methodologies in the analysis of phenolic compounds in roselle (*Hibiscus sabdariffa* L.): Composition, biological activity, and beneficial effects on human health. *Horticulturae* **2021**, *7*, 35. [\[CrossRef\]](#)
5. Bińkowska, W.; Szpicer, A.; Stelmasiak, A.; Wojtasik-Kalinowska, I.; Półtorak, A. Microencapsulation of polyphenols and their application in food technology. *Appl. Sci.* **2024**, *14*, 11954. [\[CrossRef\]](#)
6. Díaz-Montes, E. Advances in the preservation of plant-based pigments via spray drying—A systematic review. *Processes* **2025**, *13*, 663. [\[CrossRef\]](#)
7. Mehta, N.; Kumar, P.; Verma, A.K.; Umaraw, P.; Kumar, Y.; Malav, O.P.; Sazili, A.Q.; Domínguez, R.; Lorenzo, J.M. Microencapsulation as a noble technique for the application of bioactive compounds in the food industry: A comprehensive review. *Appl. Sci.* **2022**, *12*, 1424. [\[CrossRef\]](#)
8. Zannou, O.; Koca, I.; Aldawoud, T.M.S.; Galanakis, C.M. Recovery and stabilization of anthocyanins and phenolic antioxidants of roselle (*Hibiscus sabdariffa* L.) with hydrophilic deep eutectic solvents. *Molecules* **2020**, *25*, 3715. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Venkatachalam, C.D.; Damodaran, S.; Natarajan, A.; Shahulhameed, M.A.; Ravichandran, S.R.; Sengottian, M. Microencapsulation techniques: A comprehensive review. *Food Feed Res.* **2026**, *53*, 107–131. [\[CrossRef\]](#)
10. Navidad-Murrieta, M.S.; Pérez-Larios, A.; Sánchez-Burgos, J.A.; Ragazzo-Sánchez, J.A.; Luna-Bárceñas, G.; Sáyo-Ayerdi, S.G. Use of a Taguchi design in *Hibiscus sabdariffa* extracts encapsulated by spray-drying. *Foods* **2020**, *9*, 128. [\[CrossRef\]](#) [\[PubMed\]](#)
11. Mazár, J.; Albert, K.; Kovács, Z.; Koris, A.; Nath, A.; Bánvölgyi, S. Advances in spray-drying and freeze-drying technologies for the microencapsulation of instant tea and herbal powders: The role of wall materials. *Foods* **2025**, *14*, 486. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Rubio, F.T.V.; Haminiuk, C.W.I.; dos Santos, M.M.; Thomazini, M.; Moraes, I.C.F.; Martelli-Tosi, M.; Fávaro-Trindade, C.S. Development of natural pigments microencapsulated in waste yeast *Saccharomyces cerevisiae* using spray drying technology and their application in yogurt. *Food Funct.* **2021**, *12*, 8946–8959. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Potdar, S.B.; Landge, V.K.; Barkade, S.S.; Potoroko, I.; Sonawane, S.H. Flavor encapsulation and release studies in food. In *Encapsulation of Active Molecules and Their Delivery System*; Sonawane, S.H., Bhanvase, B.A., Sivakumar, M., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; pp. 293–321. [\[CrossRef\]](#)
14. Solomakou, N.; Fotiou, D.; Tsachouridou, E.; Goula, A.M. Valorization of waste from lavender distillation through optimized encapsulation processes. *Foods* **2025**, *14*, 2684. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Toprakçı, İ.; Torun, M.; Torun, F.B.; Şahin, S. Alginate-based hydrogels for trapping the polyphenols of *Hibiscus sabdariffa*: Use of a statistical experimental design approach. *Biomass Convers. Biorefin.* **2024**, *14*, 28143–28153. [\[CrossRef\]](#)
16. Tzatsi, P.; Goula, A.M. Encapsulation of extract from unused chokeberries by spray drying, co-crystallization, and ionic gelation. *Waste Biomass Valorization* **2021**, *12*, 4567–4581. [\[CrossRef\]](#)
17. Chezanoglou, E.; Kenanidou, N.; Spyropoulos, C.; Xenitopoulou, D.; Zlati, E.; Goula, A.M. Encapsulation of pomegranate peel extract in sucrose matrix by co-crystallization. *Sustain. Chem. Pharm.* **2023**, *31*, 100949. [\[CrossRef\]](#)
18. Kokkinomagoulos, E.; Nikolaou, A.; Kourkoutas, Y.; Kandyli, P. Evaluation of yeast strains for pomegranate alcoholic beverage production: Effect on physicochemical characteristics, antioxidant activity, and aroma compounds. *Microorganisms* **2020**, *8*, 1583. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Solomakou, N.; Kyriakoudi, A.; Mourtzinis, I.; Goula, A.M. Removal of phenolics from olive mill wastewater using activated spent coffee grounds: Toward an understanding of adsorption behavior. *Waste Biomass Valorization* **2025**, *16*, 6665–6678. [\[CrossRef\]](#)
20. Nguyen, Q.D.; Dang, T.T.; Nguyen, T.V.L.; Nguyen, T.T.D.; Nguyen, N.N. Microencapsulation of roselle (*Hibiscus sabdariffa* L.) anthocyanins: Effects of drying conditions on some physicochemical properties and antioxidant activities of spray-dried powder. *Food Sci. Nutr.* **2022**, *10*, 191–203. [\[CrossRef\]](#) [\[PubMed\]](#)
21. Vargas, D.A.; Vargas, N.; Osorio-Doblado, A.M.; Ruano-Ortiz, J.A.; de Medeiros, F.G.M.; Hoskin, R.T.; Moncada, M. Valorization of hibiscus flower (*Hibiscus sabdariffa* L.) anthocyanins to produce sustainable spray-dried ingredients. *Sustainability* **2024**, *16*, 5523. [\[CrossRef\]](#)
22. Cid-Ortega, S.; Guerrero-Beltrán, J.Á. Microencapsulation of *Hibiscus sabdariffa* extracts by spray drying using maltodextrin and gum Arabic as carriers. *J. Food Res.* **2020**, *9*, 53–66. [\[CrossRef\]](#)
23. Kaderides, K.; Goula, A.M. Encapsulation of pomegranate peel extract with a new carrier material from orange juice by-products. *J. Food Eng.* **2019**, *253*, 1–13. [\[CrossRef\]](#)
24. Chezanoglou, E.; Goula, A.M. Co-crystallization in sucrose: A promising method for encapsulation of food bioactive components. *Trends Food Sci. Technol.* **2021**, *114*, 546–558. [\[CrossRef\]](#)
25. Marpaung, A.M.; Lee, M.; Kartawiria, I.S. The development of butterfly pea (*Clitoria ternatea*) flower powder drink by co-crystallization. *Indones. Food Sci. Technol. J.* **2020**, *3*, 34–37. [\[CrossRef\]](#)
26. Rai, K.; Chhanwal, N.; Shah, N.N.; Singhal, R.S. Encapsulation of ginger oleoresin in co-crystallized sucrose: Development, characterization and storage stability. *Food Funct.* **2021**, *12*, 7964–7974. [\[CrossRef\]](#) [\[PubMed\]](#)

27. Toprakçı, G.; Toprakçı, İ.; Şahin, S. Alginate microbeads for trapping phenolic antioxidants in rosemary (*Rosmarinus officinalis* L.): Multivariate optimization based on bioactive properties and morphological measurements. *Gels* **2025**, *11*, 172. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Machado, A.R.; Silva, P.M.P.; Vicente, A.A.; Souza-Soares, L.A.; Pinheiro, A.C.; Cerqueira, M.A. Alginate particles for encapsulation of phenolic extract from *Spirulina* sp. LEB-18: Physicochemical characterization and assessment of in vitro gastrointestinal behavior. *Polymers* **2022**, *14*, 4759. [\[CrossRef\]](#) [\[PubMed\]](#)
29. Bevan, P.; Pastor, M.V.; Almajano, M.P.; Codina-Torrella, I. Antioxidant and antiradical activities of *Hibiscus sabdariffa* L. extracts encapsulated in calcium alginate spheres. *Polymers* **2023**, *15*, 1740. [\[CrossRef\]](#) [\[PubMed\]](#)
30. Kopjar, M.; Ćorković, I.; Šimunović, J.; Pichler, A. Encapsulation of chokeberry polyphenols by ionic gelation: Impact of pullulan and disaccharides addition to alginate beads. *Appl. Sci.* **2025**, *15*, 6320. [\[CrossRef\]](#)
31. Silveira, M.P.; Almeida, F.L.C.; Alvim, I.D.; Prata, A.S. Encapsulation of pomegranate polyphenols by ionic gelation: Strategies for improved retention and controlled release. *Food Res. Int.* **2023**, *174*, 113590. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Qadri, T.; Naik, H.R.; Hussain, S.Z.; Bhat, T.A.; Naseer, B.; Zargar, I.; Beigh, M.A. Impact of spray drying conditions on the reconstitution, efficiency and flow properties of spray dried apple powder—Optimization, sensorial and rheological assessment. *Heliyon* **2023**, *9*, e18527. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Ali, N.A.; Dash, K.K.; Pandey, V.K.; Tripathi, A.; Mukarram, S.A.; Harsányi, E.; Kovács, B. Extraction and encapsulation of phytochemicals of ponio fruit via co-crystallization: Physicochemical properties and characterization. *Molecules* **2023**, *28*, 4764. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Irigoiti, Y.; Yamul, D.K.; Navarro, A.S. Co-crystallized sucrose with propolis extract as a food ingredient: Powder characterization and antioxidant stability. *LWT* **2021**, *143*, 111164. [\[CrossRef\]](#)
35. Li, K.; Pan, B.; Ma, L.; Miao, S.; Ji, J. Effect of dextrose equivalent on maltodextrin/whey protein spray-dried powder microcapsules and dynamic release of loaded flavor during storage and powder rehydration. *Foods* **2020**, *9*, 1878. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Sundar, S.; Singh, B.; Kaur, A.; Yadav, M.P. Microencapsulation of niger seed oil: Impact of protein types, maltodextrin ratios, and drying methods on stability and functional properties. *Food Hydrocoll.* **2025**, *168*, 111553. [\[CrossRef\]](#)
37. Ćorković, I.; Pichler, A.; Ivić, I.; Šimunović, J.; Kopjar, M. Microencapsulation of chokeberry polyphenols and volatiles: Application of alginate and pectin as wall materials. *Gels* **2021**, *7*, 231. [\[CrossRef\]](#) [\[PubMed\]](#)
38. Hosseini, H.; Jafari, S.M. Introducing nano/microencapsulated bioactive ingredients for extending the shelf-life of food products. *Adv. Colloid Interface Sci.* **2020**, *282*, 102210. [\[CrossRef\]](#) [\[PubMed\]](#)
39. Ren, S.; Jiménez-Flores, R.; Giusti, M.M. The interactions between anthocyanin and whey protein: A review. *Compr. Rev. Food Sci. Food Saf.* **2021**, *20*, 5992–6011. [\[CrossRef\]](#) [\[PubMed\]](#)
40. Zhao, M.; Cao, W.; Li, L.; Ren, A.; Yang, Y.; Chen, J.; Bhandari, B.; Wang, Z.; Ren, X.; Ren, G.; et al. Effects of different proteins and maltodextrin combinations as wall material on the characteristics of *Cornus officinalis* flavonoids microcapsules. *Front. Nutr.* **2022**, *9*, 1007863. [\[CrossRef\]](#) [\[PubMed\]](#)
41. Barth, A. Infrared spectroscopy of proteins. *Biochim. ET Biophys. Acta (BBA)-Bioenerg.* **2007**, *1767*, 1073–1101. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Kong, J.; Yu, S. Fourier transform infrared spectroscopic analysis of protein secondary structures. *Acta Biochim. Biophys. Sin.* **2007**, *39*, 549–559. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Ozdal, T.; Capanoglu, E.; Altay, F. A review on protein–phenolic interactions and associated changes. *Food Res. Int.* **2013**, *51*, 954–970. [\[CrossRef\]](#)
44. Kaur, P.; Elsayed, A.; Subramanian, J.; Singh, A. Encapsulation of carotenoids with sucrose by co-crystallization: Physicochemical properties, characterization and thermal stability of pigments. *LWT* **2021**, *139*, 110861. [\[CrossRef\]](#)
45. Mohammadlinejad, S.; Kurek, M.A. Microencapsulation of anthocyanins—Critical review of techniques and wall materials. *Appl. Sci.* **2021**, *11*, 3936. [\[CrossRef\]](#)
46. Hoang, N.T.N.; Nguyen, N.N.K.; Nguyen, L.T.K.; Le, A.T.H.; Dong, D.T.A. Research on optimization of spray drying conditions, characteristics of anthocyanins extracted from *Hibiscus sabdariffa* L. flower, and application to marshmallows. *Food Sci. Nutr.* **2024**, *12*, 2003–2015. [\[CrossRef\]](#) [\[PubMed\]](#)
47. Peppas, N.A.; Sahlin, J.J. A simple equation for the description of solute release. III. Coupling of diffusion and relaxation. *Int. J. Pharm.* **1989**, *57*, 169–172. [\[CrossRef\]](#)
48. Naranjo-Durán, A.M.; Quintero-Quiroz, J.; Rojas-Camargo, J.; Ciro-Gómez, G.L. Modified-release of encapsulated bioactive compounds from annatto seeds produced by optimized ionic gelation techniques. *Sci. Rep.* **2021**, *11*, 1317. [\[CrossRef\]](#) [\[PubMed\]](#)
49. Sahin, O.I.; Uzuner, K.; Dundar, A.N.; Parlak, M.E.; Gul, L.B.; Dagdelen, A.F.; Saricaoglu, F.T.; Simsek, S. Functional properties and bioaccessibility of alginate-based phycocyanin–honey hydrogels. *LWT* **2023**, *184*, 115099. [\[CrossRef\]](#)
50. Aykın-Dinçer, E.; Dinçer, C.; Topuz, O.K. Modeling of release mechanism of sage (*Salvia fruticosa* Miller) phenolics encapsulated in alginate capsule: Physicochemical properties. *J. Food Process. Preserv.* **2024**, *2024*, 7598455. [\[CrossRef\]](#)
51. Silva, V.M.; Vieira, G.S.; Hubinger, M.D. Influence of different combinations of wall materials and homogenisation pressure on the microencapsulation of green coffee oil by spray drying. *Food Res. Int.* **2014**, *61*, 132–143. [\[CrossRef\]](#)

52. Seke, F.; Manhivi, V.E.; Slabbert, R.M.; Sultanbawa, Y.; Sivakumar, D. In vitro release of anthocyanins from microencapsulated natal plum (*Carissa macrocarpa*) phenolic extract in alginate/psyllium mucilage beads. *Foods* **2022**, *11*, 2550. [[CrossRef](#)] [[PubMed](#)]
53. More, K.S.; Kadavakollu, S.; Nigar, S.; Gul, K.; Sehwat, R.; Mir, N.A. Encapsulation of resveratrol in alginate microcapsules using internal gelation technique: Fabrication, characterization and release kinetics. *LWT* **2024**, *207*, 116663. [[CrossRef](#)]
54. Dang, Y.T.; Tran, H.; Kha, T.C. Encapsulation of w/o/w acerola emulsion by spray drying: Optimization, release kinetics, and storage stability. *Foods* **2024**, *13*, 1463. [[CrossRef](#)] [[PubMed](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.