

## Article

# Influence of the Operating Conditions on the Release of Corrosion Inhibitors from Spray-Dried Carboxymethylcellulose Microspheres

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**Abstract:** Sodium carboxymethylcellulose (CMC-Na) microparticles, containing corrosion inhibitor benzotriazole (BTA), were prepared using different spray drying processing parameters, with the purpose of future application in protective coatings for the delivery of corrosion inhibitors. The effects of the processing parameters, such as inlet temperature and spray flow rate, are discussed herein. The biopolymeric CMC-Na microparticles obtained were characterized morphologically by SEM and TEM, and their release profile studied by UV-Vis. The results show that the prepared microparticles (microspheres) were homogeneous, spherically shaped and of a matrix-type nature. Additionally, it was observed that the inlet temperature and spray flow rate significantly influenced the release profiles and process yields. From the different process parameters tested, it was found that the best conditions to achieve higher process yields, higher encapsulation efficiencies and better release properties, were an inlet temperature of 170 °C, a pump rate of 2.5 mL/min, and a drying air-flow rate of 440 L/h.

**Keywords:** carboxymethylcellulose; microencapsulation; benzotriazole; spray drying; release studies



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## 1. Introduction

The corrosion of metallic structures is still a common and serious problem [1] with great impacts in the economy [2,3]. Corrosion is the result of a metal–environment interaction, which changes the physicochemical properties of the metal, leading to failure of the function of the metal [4,5]. When the integrity of the material is affected by the external action of the environment, it may become necessary to protect it against this detrimental action. In this sense, the application of protective coatings is among the most suitable strategies to protect metallic surfaces. Coatings designed for corrosion protection must offer an effective physical barrier, hindering the access of water and ions to the metallic interface. In the past, most effective corrosion protection systems were based on the use of protective organic coatings [2,4]. However, coating degradation may occur as a consequence of external effects (temperature, UV light, scratches) [2]; therefore, in addition to the barrier effect offered by the coating, an active protection is required to inhibit corrosion when the coating is damaged, aiming at longer service time of metallic structures [2,4]. One way to achieve the active effect is via incorporation of active species capable of inhibiting the corrosion activity [2].

In the last decade, smart anticorrosive coatings have been described as an evolution from ordinary available commercial coatings for metallic material protection [4,6,7]. This

new type of protective coating is based on the use of nano/microcontainers for corrosion inhibitor storage, dispersed in organic or hybrid coating matrices. Nano/microcontainers have the ability of smart delivery of inhibitors, but also prevent the negative interactions between inhibitors and coating formulations. Thus, corrosion inhibitors are released based on a stimulus–response mechanism and are also able to avoid the degradation of the protective coating barrier properties and the inactivation of the inhibitive corrosion compounds [5,8]. This type of technology may also help to prevent spontaneous leaching of the inhibitor from the coating into the environment [2].

There are several methods described for nano/microreservoir development. Research has shown the use of chemical processes for corrosion inhibitor encapsulation, such as *in situ* and interfacial polymerization, as well as co-precipitation techniques [8–10]. Furthermore, physicochemical methods such as layer-by-layer and coacervation techniques have also been largely reported in the literature [1,11].

Although rarely used for the development of nano/microreservoirs for corrosion inhibitor storage, spray drying is one of the most common techniques to perform microencapsulation in the pharmaceutical and food industries [12,13]. Regarding the use of spray drying in corrosion applications, scarce work is available that describes the use of this technique to prepare polylactic acid microcapsules containing a corrosion inhibitor, to be used as an additive to concrete for protection against steel bar corrosion [14,15].

Spray drying is a physical process and a well-established industrial encapsulation technique that presents several advantages, mainly due to its simplicity, relatively low cost, high encapsulation efficiency, large-scale production, and the possibility of using a totally aqueous system [16,17].

With respect to the encapsulating material, synthetic organic polymers derived from petroleum—such as polyurea, polystyrene and poly (diallyldimethylammonium chloride), among others—have been gradually replaced by inorganic particles such as  $\text{CeO}_2$ ,  $\text{SiO}_2$ ,  $\text{ZnO}$ ,  $\text{TiO}_2$ , halloysite nanotubes and layered double hydroxides [6]. Another alternative, that has gained considerable attention for the encapsulation of corrosion inhibitors, relies on the use of biopolymers such as alginate, cellulose and chitosan as matrices [1,18,19]. The main advantage of these materials lies in their non-toxicity, biodegradability and in the fact that they can be obtained from renewable sources, e.g., from the exoskeletons of crustaceans (chitosan, a chitin derivative), brown algae (alginate) or plants (cellulose, and consequently its derivatives, are known as main constituents of plants) and even agro-industrial wastes such as wheat straw and sugarcane bagasse, among others [20,21].

Sodium carboxymethylcellulose (CMC-Na) is an anionic biopolymer obtained by introducing carboxymethyl groups along the cellulose chain [22]. CMC-Na is a polysaccharide hydrogel, a well-established material for the encapsulation of several compounds [23–25]. It is well known that the delivery mechanism of hydrogel reservoirs is based on erosion caused by the adsorption of water through a swelling process. That is, the trigger-release mechanism occurs due to the swelling of CMC-Na capsules in the presence of water molecules, progressively causing the diffusion of the encapsulated component out of the biopolymer network [24,26].

Greener processes and materials are aspects of great importance, especially in research targeting industrial applications. In a previous work by our group, the potential of CMC-Na microspheres containing benzotriazole (BTA), as delivery systems for the development of smart coatings, was evidenced by electrochemical impedance studies in a corrosion-prone environment [16]. The present study aims to obtain insights on the influence of different inlet temperatures and spray flow rates on the physicochemical properties of CMC-Na microreservoirs, using benzotriazole as a model of corrosion inhibitors. For this purpose, in this work, the different spray drying parameters' influence on CMC-Na microspheres was studied beyond morphology and size distribution. Microspheres' moisture content, encapsulation efficiency and process yield were assessed to evaluate whether different inlet temperatures and spray flow rates would impact the microspheres produced. Moreover, BTA loading and release from CMC-Na microspheres were also performed and discussed.

These results may provide crucial information on the behavior of the prepared material for corrosion-inhibiting applications. Considering the aforementioned points, the combination of the spray drying encapsulation technique, together with a CMC-Na encapsulating material, may contribute to the development of smart coatings by using environmentally friendly microreservoirs produced by a green aqueous process.

## 2. Materials and Methods

### 2.1. Materials

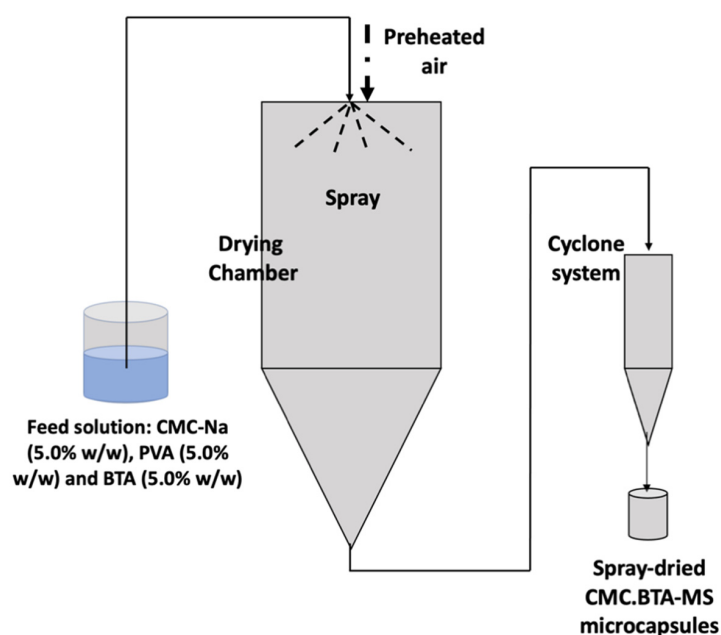
Benzotriazole (BTA), sodium carboxymethylcellulose (CMC-Na, average molecular weight: 90 kDa) and poly (vinyl alcohol) (PVA, average molecular weight: 31–50 kDa) were purchased from Sigma-Aldrich. Ethanol was supplied by Panreac.

All chemicals were of analytical grade and used without any further purification.

### 2.2. Preparation of Carboxymethylcellulose Microspheres Loaded with BTA

For the preparation of carboxymethylcellulose microspheres and encapsulation of BTA, CMC-Na was dissolved in water, at room temperature, and left under magnetic stirring overnight to give a 5.0% *w/w* solution. Then, PVA was dissolved in water at 90 °C, under magnetic stirring, until complete dissolution and homogenization to give a 5.0% *w/w* solution. A BTA alcoholic solution of 5.0% *w/w* was also prepared. The feed solution was prepared by mixing, under magnetic stirring until complete homogenization, 25 mL of CMC-Na (5.0% *w/w*), 5 mL of PVA (5.0% *w/w*) and 20 mL of BTA (5.0% *w/w*), resulting in a solid content of 5% (*w/w*). The polymer:inhibitor ratio in the feeding solution was kept at 1.25:1.

The resulting solution was sprayed in a mini spray dryer (Büchi mini spray dryer B-290) using a two-fluid pressurized nozzle (Figure 1). Experiments were carried out at the following operating conditions (Table 1): aspirator setting, 100%; pump rate, 2.5 mL/min; spray flow rate, 440 and 600 L/h; and inlet temperature, 170, 180 and 190 °C. The atomized powder was blown into the cyclone separator system and collected in the collection vessel at the bottom of the cyclone. Exhaust air was extracted out of the cyclone by a vacuum pump and filtered through a polyester textile filter. For comparison purposes, empty microspheres (CMC-MS) were prepared by the same procedure, but in the absence of BTA in the feed/sprayed solution (results not shown). Microspheres containing encapsulated BTA were named CMC.BTA-MS.



**Figure 1.** Schematic illustration of the preparation of CMC.BTA microspheres by a spray drying procedure.

**Table 1.** Experimental conditions for the preparation of CMC.BTA-MS by spray drying.

| Condition Number | Inlet Temperature (°C) | Drying Gas Flow Rate (L/h) |
|------------------|------------------------|----------------------------|
| 1                | 170                    | 440                        |
| 2                | 170                    | 600                        |
| 3                | 180                    | 440                        |
| 4                | 180                    | 600                        |
| 5                | 190                    | 440                        |
| 6                | 190                    | 600                        |

### 2.3. Characterization of Spray-Dried Microspheres

Small samples of the synthesized microparticles were used for physical and chemical characterization (moisture content, encapsulation efficiency, loading capacity, particle morphology and size distribution) as well as for release studies. Process yield was also assessed and determined according to Equation (1).

$$\text{Process Yield (PY\%)} = (M_{\text{microspheres}} / M_{\text{theoretical}}) \times 100\% \quad (1)$$

where  $M_{\text{microspheres}}$  obtained is the amount of microspheres recovered after the spray drying process, and  $M_{\text{theoretical}}$  comprises the amount of PVA, CMC-Na and BTA used in the feed solution for microsphere production.

#### 2.3.1. Moisture Content

The moisture content of the spray-dried microparticles was determined by the oven drying method. Samples, weighed in an analytical balance (Ohaus corporation AR2140-USA), were placed in a drying and sterilization oven (Odontobrás EL 1.1-Brazil), heated at 102 °C until constant weight, and then reweighed. The product's moisture content was determined from the registered weight loss by averaging three measurements.

#### 2.3.2. Microparticle Morphology and Size Distribution

Carboxymethylcellulose microspheres containing BTA were characterized by Scanning (SEM) and Transmission Electron Microscopy (TEM) on a Hitachi TM3000 (Tokyo, Japan) tabletop microscope system with an electron beam energy of 15 eV, and on a JEOL JEM 1200EX-II (Peabody, MA, USA) microscope system with an electron beam energy of 120 keV, respectively. Image J software version 1.41 (freeware) was used for image processing, analysis, and particle size distribution.

#### 2.3.3. BTA Release Studies

For the quantification of BTA, released from CMC-Na microspheres, calibration curves were performed on a Perkin Elmer LAMBDA 650 UV/Vis Spectrophotometer by measuring the absorbance of BTA standard solutions at 258 nm. The correlation coefficient, from five standards, was higher than 0.999.

BTA release profiles were performed by dispersing 10.0 mg of CMC.BTA-MS in 50.0 mL of distilled water, giving rise to a 0.2 mg mL<sup>-1</sup> suspension. At different time points (5 min–96 h), an aliquot of the capsule's suspension was extracted with a syringe, filtered through PTFE membrane filters (0.20 µm pore), and measured after appropriate dilution with distilled water (dilution factor: 10). UV-Vis measurements were performed, in triplicate, following the same time scale for all of the samples, for all of the spray drying conditions tested (standard deviation was lower than 3%). The same experimental procedure was performed with empty CMC microspheres (CMC-MS) to investigate whether CMC-Na would interfere in the quantification of BTA (results not shown).

### Encapsulation Efficiency and Loading Capacity

Encapsulation efficiency and loading capacity were calculated according to Equations (2) and (3), respectively, and estimated from the release study results, assuming a complete release of the encapsulated material at 96 h.

$$\text{Encapsulation efficiency (EE\%)} = (M_{\text{final}}/M_{\text{initial}}) \times 100\% \quad (2)$$

where  $M_{\text{final}}$  is the amount of encapsulated BTA in carboxymethylcellulose microspheres determined from the release profiles, and  $M_{\text{initial}}$  is the initial amount of BTA added in the feed solution (before the spray drying process).

$$\text{Loading capacity (LC\%)} = (M_{\text{encapsulated}}/M_{\text{microspheres}}) \times 100\% \quad (3)$$

where  $M_{\text{encapsulated}}$  is the amount of encapsulated BTA in carboxymethylcellulose microspheres determined from the release profiles, and  $M_{\text{microspheres}}$  is the total amount of microspheres obtained.

## 3. Results and Discussion

The CMC-Na microparticles were developed with the purpose of obtaining suitable microreservoirs for the encapsulation and delivery of corrosion inhibitors. Specifically, the main objective was to describe a simple and efficient process to obtain an eco-friendly system able to deliver inhibitors based on a triggered-release mechanism compatible with the required application, i.e., active anticorrosive coatings. Different experimental conditions (spray flow rate and inlet temperature, see Table 1), for the preparation of CMC-Na microspheres, were tested and optimized. All tested conditions were evaluated in terms of process yield (PY%), encapsulation efficiency (EE%), loading capacity (LC%), moisture content (MC%), release profile curves, particle morphology and size distribution.

### 3.1. Microsphere Morphological Characterization

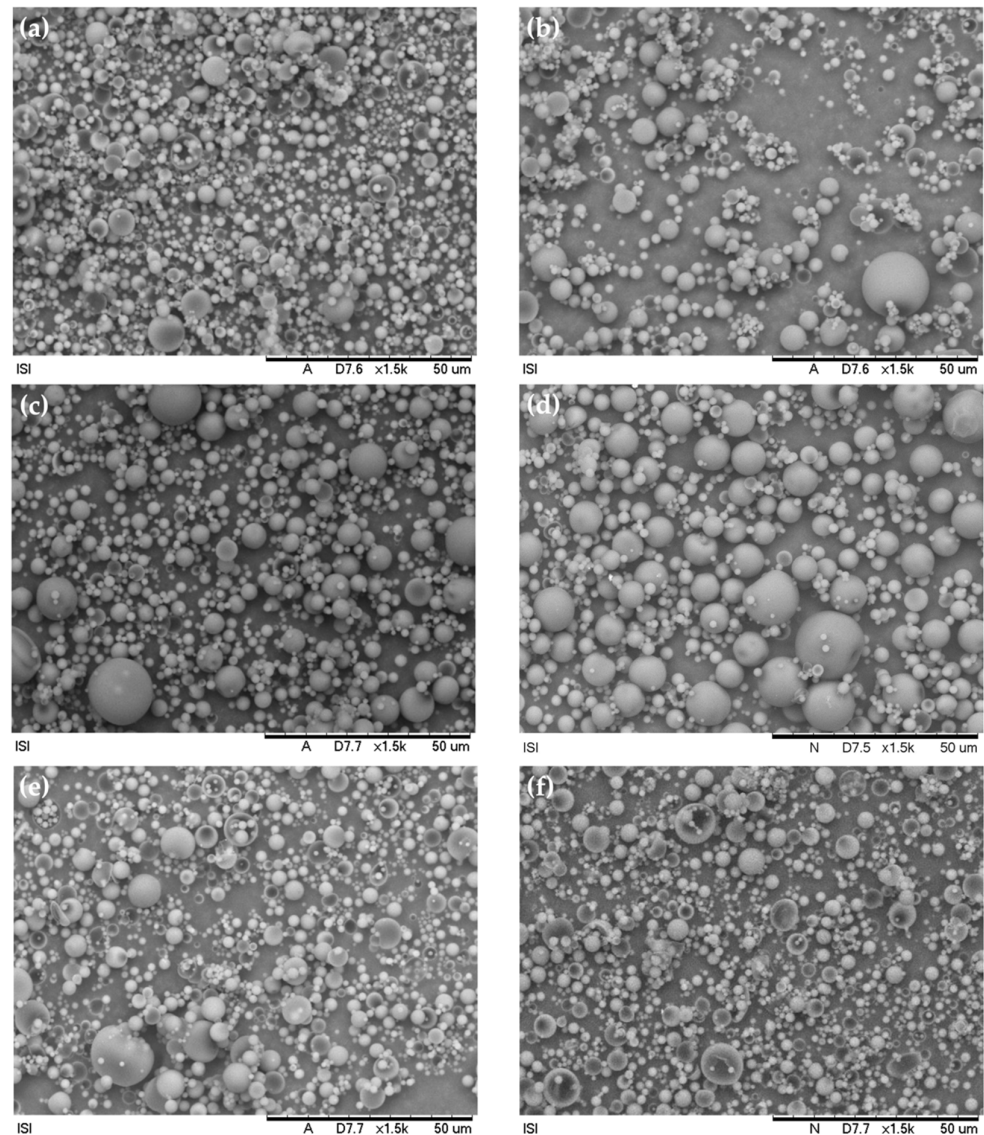
CMC.BTA microsphere morphology was examined by SEM and TEM. Figure 2 shows SEM micrographs of the spray-dried particles obtained using different experimental conditions, described in Table 1 (1 to 6). It is possible to observe that a spherical shape with a smooth surface was a predominant characteristic for all microparticles, regardless of the experimental parameters. The microspheres' surface smoothness, along with the absence of deposits or incrustations, suggests that the corrosion inhibitor is dispersed within the biopolymeric network.

Such results are in agreement with the literature. Cellulose derivatives, such as carboxymethylcellulose, are common polymeric materials used in the pharmaceutical and food industries [23,27]. The use of this class of biopolymers often results in spherically shaped particles with homogeneous surfaces [27]. Another feature that may have contributed to the formation of uniform particles, in this work, was the appropriate ratio between the encapsulated material and the encapsulating polymeric matrix (1.25:1), along with the use of poly (vinylalcohol) (PVA) as plasticizer. The addition of plasticizers is a widely used alternative to reduce fragility, and to increase the flexibility, toughness and impact resistance of polymeric films. Therefore, it is possible that PVA minimized the intermolecular interactions present in the CMC-Na network, thus increasing polymeric chain mobility and, consequently, improving the physical properties of the resulting particles [28–31].

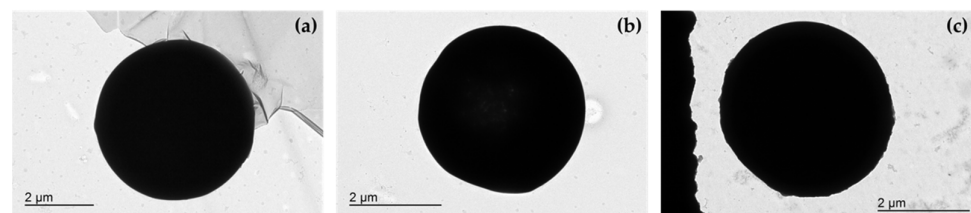
The internal morphological structure of CMC-Na microparticles containing BTA was investigated by TEM. The results are shown in Figure 3. Conditions 1, 3 and 5 were selected to represent the three inlet temperatures tested (170, 180 and 190 °C) at a constant spray flow rate of 440 L/h.

Similar to what was observed in SEM images, microcapsules with a well-defined spherical shape were found for all tested conditions. Additionally, no noticeable distinction between wall and core materials can be observed, which suggests the presence of a dense matrix-type structure (microsphere) formed by the CMC-Na polymeric network, with

BTA molecules dispersed within the solid matrix. In general, particles, formed from homogeneous solutions, produced by spray drying are, according to the literature, of the matrix type [18,32,33]. The active material (i.e., benzotriazole) should be homogeneously distributed through the carrier polymeric matrix as previously reported by our group [16].



**Figure 2.** SEM images of CMC.BTA microspheres obtained by spray drying with different experimental conditions (inlet temperature and spray flow rate): (a) 170 °C and 440 L/h; (b) 170 °C and 600 L/h; (c) 180 °C and 440 L/h; (d) 180 °C and 600 L/h; (e) 190 °C and 440 L/h; and (f) 190 °C and 600 L/h.



**Figure 3.** TEM images of CMC-Na microcapsules containing BTA obtained by spray drying with different experimental conditions: (a) condition 1: 170 °C and 440 L/h; (b) condition 3: 180 °C and 440 L/h; and (c) condition 5: 190 °C and 440 L/h.

### 3.2. Particle Size

The average diameter and size distribution range of spray-dried CMC.BTA microspheres, obtained from different SEM micrographs, are listed in Table 2, and the respective histograms are available in the supplementary information (Figure S1).

**Table 2.** Effect of the set experimental conditions on the average diameter and size distribution range of the CMC.BTA-MS obtained by spray drying.

| Condition Number | Average Diameter ( $\mu\text{m}$ ) | Size Distribution ( $\mu\text{m}$ ) |
|------------------|------------------------------------|-------------------------------------|
| 1                | $1.7 \pm 0.97$                     | 0.52–9.88                           |
| 2                | $2.0 \pm 1.2$                      | 0.12–11.4                           |
| 3                | $2.2 \pm 1.5$                      | 0.73–14.8                           |
| 4                | $1.8 \pm 1.1$                      | 0.38–11.5                           |
| 5                | $2.0 \pm 1.2$                      | 0.52–9.08                           |
| 6                | $1.8 \pm 1.0$                      | 0.67–7.67                           |

It is possible to observe that the mean average size of the microparticles produced with different inlet temperatures was not affected by the different experimental conditions. Although different size microparticles were observed, the associated standard deviations are high and the mean average size values fall within experimental error of each other. High standard deviations are most likely a consequence of the broad size distribution observed, a common and known limitation of the spray drying technique [14]. Notwithstanding, a closer analysis of the size distributions (see Figure S1) for each of the spray flow rates tested, suggests that for 440 L/h (conditions 1, 3 and 5), sizes range from 0.5 to 14.8  $\mu\text{m}$ , whereas for 600 L/h (conditions 2, 4 and 6), sizes range between 0.2 and 12  $\mu\text{m}$ ; this indicates that for a higher spray flow rate (drying air), a decrease in size occurs. Reports in the literature support this observation, since it is known that high temperatures during spray drying may cause a decrease in particle size, due to a high evaporation (volatilization) rate of the solvent from the atomized droplets [15,34,35].

In order to confirm whether these values are significantly different, an ANOVA analysis was performed on the size experimental data. The statistical analysis revealed that the mean average size values are not statistically different ( $F < F_{\text{crit}}$  with  $p\text{-value} > 0.05$ ).

When considering active anticorrosive coating development, the size of the microcontainer must be lower than the thickness of the coating layer where the microcontainers will be dispersed. Since the thickness of coatings, used in different applications, can range from a few to several hundred micrometers [4], and given the small size of the CMC.BTA-MS synthesized (Table 2), they can be readily applied in organic coatings [3,4,36].

### 3.3. Moisture Content

The moisture content (MC%) present in a powder product has an important impact on its stability and, consequently, on the durability of the material, commonly known as shelf-life. Additionally, powder products are considered the most practical type of material to employ in the industrial field. Therefore, low water contents are particularly desirable [14]. One of the major advantages of using spray drying for the microencapsulation of active materials is the fact that the particles obtained (in powder form) have a low moisture content and water activity, making them resistant to microbial and oxidative degradation and, therefore, attractive for the food and pharmaceutical industry [14].

The results of MC%, presented in Table 3, showed average values of approximately 2.0% for all obtained particles. Similar values of MC% were observed for all tested conditions, which can be associated with the high inlet temperatures.

In the food industry, low values of moisture content (0.2–5%) are desirable to maintain microbiological stability [14]. On the other hand, in the paint industry, specifically in the encapsulation of corrosion inhibitors, this parameter has not yet been discussed. Nonetheless, it is expected that a material with low water content is better for preventing corrosion,

as water molecules are involved in the electrochemical processes associated with corrosion at the metal interface [4,37–39]. The proposed methodology for corrosion inhibitor microencapsulation in CMC microspheres resulted in low values of moisture content; this is of utmost importance, since the stimulus-responsive mechanism involved in the release of the encapsulated material is triggered by contact with water molecules [4,37–39]. In summary, the MC % results were considered satisfactory, which validates the viability of the encapsulating technique used.

**Table 3.** Moisture content of CMC.BTA-MS obtained by different spray drying conditions.

| Condition Number | Moisture Content (%) |
|------------------|----------------------|
| 1                | 2.0 ± 0.23           |
| 2                | 2.3 ± 0.12           |
| 3                | 1.9 ± 0.32           |
| 4                | 2.0 ± 0.48           |
| 5                | 1.9 ± 0.02           |
| 6                | 1.8 ± 0.07           |

### 3.4. Yield

The product yield of the encapsulation process is a parameter that describes the amount of powder recovered in the collection vessel of the spray dryer. Encapsulation efficiency (EE%) and loading capacity (LC) depend on the amount of inhibitor in the particles. EE% is the amount of inhibitor successfully encapsulated in the polymeric matrix whereas LC (%) determines the percentage of microspheres that corresponds to the encapsulated material.

Product yield (PY%), encapsulation efficiency (EE%) and loading capacity (LC) for the different spray-dried CMC.BTA microspheres are displayed in Table 4.

**Table 4.** Effect of the different spray drying conditions on the product yield and loading capacity of the CMC.BTA-MS.

| Condition Number | Outlet Temperature (°C) | Product Yield (%) | Encapsulation Efficiency (%) * | Loading Capacity (g <sub>BTA</sub> /g <sub>microparticle</sub> ) * |
|------------------|-------------------------|-------------------|--------------------------------|--------------------------------------------------------------------|
| 1                | 86 ± 2                  | 63.4 ± 1.4        | 39.0                           | 15.6                                                               |
| 2                | 82 ± 2                  | 60.3 ± 1.2        | 35.9                           | 14.3                                                               |
| 3                | 82 ± 2                  | 45.2 ± 1.2        | 36.9                           | 14.8                                                               |
| 4                | 80 ± 2                  | 60.2 ± 1.2        | 34.4                           | 13.7                                                               |
| 5                | 106 ± 2                 | 43.5 ± 1.5        | 37.6                           | 15.0                                                               |
| 6                | 106 ± 2                 | 48.5 ± 1.5        | 36.1 ± 0.4                     | 14.4 ± 0.2                                                         |

\*—standard deviations obtained were very small and, therefore, do not significantly influence the values of EE% and LC%, with the exception of condition 6.

The inlet temperatures determine the volatilization (evaporation) rate of the solvent. In addition, inlet temperatures should be selected according to the boiling point of the solvent as well as the glass-transition temperature of the polymeric materials to be used. To ensure timely volatilization, inlet temperatures used in spray drying are generally higher than the boiling point of the solvent [15].

Product yields, presented in Table 4, show values between 43 and 63%. These results are in accordance with results previously reported in the literature for carboxymethyl cellulose microspheres and spray drying at a laboratory-scale, and therefore, are considered acceptable values [40–42]. Overall, low product yields may be a consequence of different factors, such as small volumes of liquid feed (50 mL), and the aspiration of smaller and lighter particles by the spray dryer's exhaustion system directly to the outlet filter, failing

to be separated in the cyclone and collected in the collection vessel [42–44]. Nevertheless, reports in the literature have shown that product yields may be influenced, among other spray drying parameters, by inlet air temperatures and compressed air-flow rates (spray flow rate) [14,45], two parameters studied in the present work, and thus, subject to deeper assessment.

According to the literature, high inlet temperatures increase the drying rate, leading to enhanced powder productivity and high yields [14]. However, an overall analysis of the obtained results suggests that an increase in inlet temperature had a detrimental effect on the product yield. An evaluation of the outlet temperatures for the different experimental conditions, may provide some insight on whether an increase in inlet temperatures negatively affects the process yield. Outlet temperature is a result of the heat and mass balance in the drying chamber [35] and, therefore, a consequence of gas inlet temperature, aspirator rate, pump performance (feed flow rate) and concentration of the feed solution [34,46]. Outlet temperature can also be described as the highest temperature to which a product may be heated [47] and is an indication of drying speed. In the work of Maa et al. [48] it was found that temperatures in different locations of the drying chamber were closer to the outlet temperatures than to the inlet temperatures, suggesting that the outlet temperature determined the droplet drying speed [14,48]. Moreover, Maa et al. determined in their work [48] that an increase in outlet temperature is directly proportional to the inlet temperature and spray flow rate which, in turn, corresponds to a higher drying rate, and thus leads to higher yields [14]. However, in the work of Su et al., for the spray drying of carboxymethyl cellulose, it was found that using high inlet temperatures, and consequently high outlet temperatures, could cause an accumulation of particles on the chamber wall, consequently leading to lower yields [35,48,49]. Another contributing factor may be the influence of the glass-transition temperature of CMC:PVA used (between 75 and 80 °C) [50]. Since the glass-transition temperature of the polymeric matrix is lower than the outlet temperature, the rubbery polymeric matrix may stick to the walls of the drying chamber, affecting the product yield [51].

In what concerns the influence of the spray flow rate (drying air rate) on the yields obtained, it is only noticeable for inlet temperatures of 180 and 190 °C. For 170 °C, the obtained yields are similar (considering the experimental error). Spray flow rate influences the rate of water evaporation, and thus the drying rate, of the droplets formed [14]. Increasing the spray flow rate leads to smaller drying times (faster drying), and consequently, to higher yields [49], which is in line with what was observed in the presented results (Table 4).

### 3.5. BTA Release Studies from Carboxymethyl Cellulose Microspheres

#### 3.5.1. Encapsulation Efficiency (EE%) and Loading Capacity (LC%)

The encapsulation efficiency (EE%) results, for the different experimental conditions, varied from 34% to 39%, and are shown in Table 4. Encapsulation efficiency is defined as the amount of corrosion inhibitor successfully encapsulated in regard to the initial amount before spray drying; similarly to the process yield, it depends on different factors, where spray drying parameters such as inlet temperature and spray flow rate—and consequently, outlet temperature—as well as carrier and encapsulated material properties (e.g glass-transition temperature) [49], are amongst the most relevant ones. Nevertheless, EE% values were not significantly influenced by the processing conditions. The loss of benzotriazole may have occurred in the drying step, where more volatile compounds can evaporate simultaneously with the solvent. Similar results regarding the use of spray drying technology as a microencapsulation process have been reported by Thenapakiam et al. [40] for carboxymethyl cellulose microparticles with different drug:polymer ratios, with encapsulation efficiencies in the range of 41 to 60%. Moreover, Tchabo et al. [52] encapsulated Mulberry leaf extracts in carboxymethyl cellulose and maltodextrin particles, achieving EE% values between 36 and 42%.

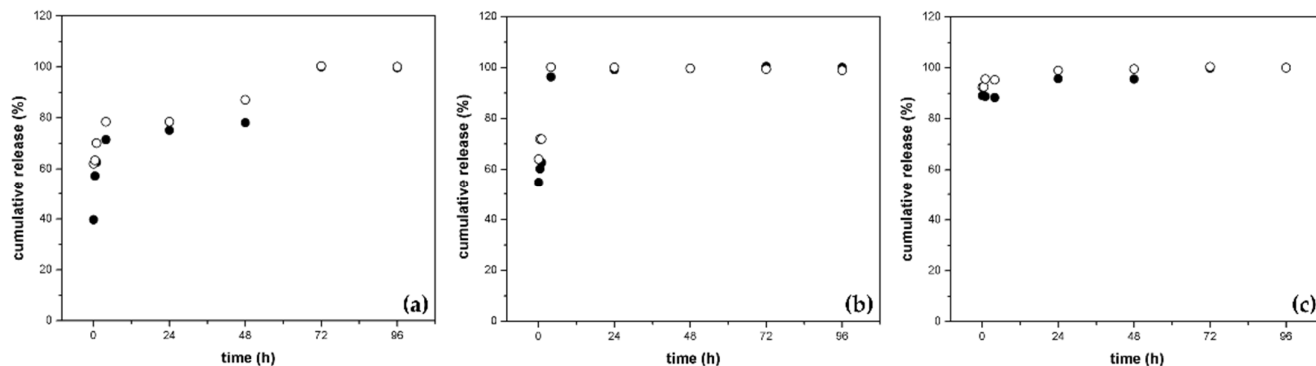
The loading capacity reflects the amount of inhibitor loaded (encapsulated) per unit weight of the particles, indicating the percentage mass of the particle that is due to the

inhibitor (in this case BTA). For particles prepared with a 440 L/h spray flow rate, it is possible to observe a slight decrease (from 16 to 15%) in the loading capacity of CMC-MS with increasing inlet temperature, contrary to the results obtained for higher spray flow rates, where no influence of temperature or spray flow rate is observed.

### 3.5.2. Release Studies

Release studies were performed in an aqueous medium, since water is present in most of the environments where coated metallic structures are exposed. It is worth mentioning that water contact with a metallic substrate will only occur if there is a failure in the protection barrier system (organic coating). Moreover, water is also involved in the most common mechanisms of metallic corrosion, i.e., corrosion in aqueous media. Typically, when exposed to service life conditions, a coated metallic structure will be subjected to different weather conditions, such as temperature gradients, electromagnetic radiation, water, salts and other contaminants, as well as mechanical actions (e.g., scratch induced chipping). Overall, this will contribute to coating degradation, creating pathways that will allow water,  $O_2$  and ions to reach the metal substrate and initiate the corrosion processes. Therefore, since water inlet is one of the first steps associated with onset of corrosion, the incorporation of materials in coatings that will respond to the presence of water and readily release corrosion inhibitors can be important to provide long-term protection when coatings start to fail. One example of such a material is CMC-Na microparticles. In this system, water molecules are absorbed by the hydrophilic biopolymeric network, and the encapsulated material swells, forming a gel that allows the release of the encapsulated material from the CMC-Na matrix [41].

The cumulative amount (%) of BTA released from CMC.BTA microspheres as a function of time is displayed in Figure 4.



**Figure 4.** BTA release behavior from CMC.BTA microspheres, obtained by spray drying at: (a) 170 °C; (b) 180 °C and 440 L/h; and (c) 190 °C. Spray flow rates 440 L/h (closed) and 600 L/h (open).

In general, all of the release profiles show similar behavior for all of the microparticles tested. (UV-Vis measurements of empty CMC-MS for every spray drying condition, were performed, and no absorbance was observed; therefore, CMC-MS does not interfere with BTA release data.) A high burst release of BTA was observed after 5 min of immersion with values ranging from 40 to 90% of the total loading content. Although this behavior can be associated with the hydrophilic nature of the biopolymeric matrix, which allows the permeation of water and consequent release of the encapsulated material, it is possible to observe an undoubtable influence of the spray drying parameters on the release profiles.

There is an accentuated increase in the amount of BTA released in the burst phase as the inlet temperatures increase. Moreover, an increase in the spray flow rate, for the same inlet temperature, leads to an increase of 22 and 9% in the burst release for 170 °C and 180 °C, respectively, and a smaller, less noticeable 3% increase for a 190 °C inlet temperature.

In what concerns the experiments conducted at 170 °C (conditions 1 and 2), after the initial burst release, there is a gradual and more controlled release of the remaining BTA up

to 72 h, where a plateau is reached, assumed as the total release of the encapsulated inhibitor. Similar behavior was observed for particles produced at 180 °C (conditions 3 and 4), although a pronounced increase in release after 1 h leads to a complete release by 4 h of immersion, instead of the 72 h previously identified. A drastically different release profile was obtained for conditions 5 and 6 (190 °C) where the burst release phase leads to an almost complete release (89–92%) of the encapsulated BTA in the first 5 min of immersion. Similar release profiles have been described in the literature. Aguiar et al. [41] reported the encapsulation of different natural antioxidants in sodium carboxymethyl cellulose, with releases of 50% of the encapsulated material in the first 10 min, as well as total releases at 45 min, 2 h and 4 h. The encapsulation of soybean extracts in sodium carboxymethyl cellulose by Sansone et al. [42] showed that the prepared microparticles were readily soluble in water, and released 80–100% of the encapsulated material in 15–30 min. Furthermore, Thenapakiam et al. [40] studied the encapsulation of piroxicam in CMC-Na, and observed a 50% release of the drug (at pH 7.4) from the polymeric matrix within 20 min.

Li et al. [53] reported the encapsulation of a poorly water-soluble drug, ibuprofen, in a gelatin matrix as a water-soluble polymer shell. Briefly, in a spray drying process of gelatin dissolved in ethanol–water mixtures, the evaporation of both ethanol and water first takes place, simultaneously, at the surface of the droplet. As the atomized liquid droplets contact the drying air, a concentration of solute at the surface occurs which leads to the formation of a layer (crust) of gelatin on the surface of droplets [46,53–55]. This layer will act as a semi-permeable membrane that allows the continuous evaporation of water, but should retain ethanol [54,55]. Due to the similar characteristics, it is possible to draw a parallel between the literature and our results, though these studies [53] have been performed for lower inlet temperatures. Nonetheless, in order to understand BTA's release behavior from the CMC microspheres, the glass-transition temperature of the polymeric wall material (CMC:PVA) should also be taken into consideration. The glass-transition temperature ( $T_g$ ) controls the diffusion of the encapsulated material (BTA) through the barrier formed by the wall material (CMC:PVA), which depends on whether the wall material retains its glassy state during spray drying [35]. Below the glass transition of CMC:PVA, the diffusion of BTA through the polymeric wall material would be limited, since the polymers are in their glassy state, however if spray drying occurs above the glass-transition temperature, the polymeric wall would be in a rubbery state, which would promote a faster diffusion of BTA. This will not only influence the product yield (as it was mentioned before) but suggests an influence on drug release due to the matrix-type nature of CMC-Na microspheres, where a small fraction of the encapsulated material remains exposed on the microparticles' surface [18,53].

For conditions 5 and 6, CMC.BTA microspheres were prepared at 190 °C, a temperature well above the glass-transition temperature reported in the literature for CMC:PVA mixtures (75–80 °C) [45,50], which means that, upon drying the microspheres, formation was characterized by a high rubbery state. Therefore, these conditions may lead to a faster diffusion of BTA towards the microspheres' surface. The result of this process can be a rapid formation of the microspheres with more BTA located near/at the surface of the polymeric microspheres, which might explain the higher extent of BTA release for short times.

Understanding the release process, from microparticles is of utmost importance to improve microparticulate formulations for controlled release purposes. A first approach to the assessment of release mechanisms is fitting experimental data to the Korsmeyer–Peppas equation [43]. However, since this equation can only be applied to the first 60% of release, due to the high release observed, it is not possible to fit the experimental data to this semi empirical equation [43]. On the other hand, the loading capacity allows us to assess whether the amount of BTA released is hindered due to its poor solubility in water or by another mechanism. According to Sigma-Aldrich's safety data sheet [56], Benzotriazole's solubility in water is 19 g/L. Considering that in the release studies, 50 mL of water were used, the maximum amount of BTA subject to solubilization in water would be 0.95 g/L. From Table 4, it is possible to verify that values of  $g(\text{BTA})/g(\text{microparticles})$  (loading capacity)

are considerably lower (approximately six times lower), and therefore, it is most likely that the release of BTA is governed by the swelling of the polymeric matrix.

In the present work, we observed a faster release for CMC.BTA particles produced at higher inlet temperatures (180 °C and 190 °C). This is most probably associated with a higher evaporation rate of the solvent, due to high inlet temperatures. Solvent evaporation is most likely very fast, hindering the immobilization of BTA within the polymeric matrix remaining mainly at the surface of the microparticles. Furthermore, one can infer that the higher releases observed for higher spray flow rates may also be associated with the concentration of BTA at the droplets surface, since a higher spray flow rate causes higher degree of water evaporation [14,18].

The proposed microreservoirs are designed to work as an on-demand release device for corrosion inhibitors, to be applied in the development of smart anticorrosive organic coatings. Inhibitor release from the CMC-Na biopolymeric matrix is based on a hydrogel-swelling-driven mechanism triggered by water molecules, which implies that the inhibitor will only be released from the microparticles when in contact with water; otherwise, the inhibitor-containing particles will be stable in the organic-coating formulation. Thus, the developed CMC.BTA microparticles can potentially be applied in protection systems where the presence of water initiates its degradation. For instance, the deterioration of protection systems based on organic coatings starts from the permeation of water through the pores, or micro-cracks, that are formed in the polymeric matrix, which can appear during exposure to the environment.

Given the aforementioned findings, it is believed that CMC-Na microparticles with release profiles that show an initial high release of BTA may be adequate for applications that require immediate protection of metal substrates that are known to be highly susceptible to corrosion processes, such as carbon steel. This burst release feature, combined with a gradual release of the remaining inhibitor, which in turn may prolong substrate protection, is achieved with microspheres prepared according to experimental condition 1 (170 °C and 440 L/h).

#### 4. Conclusions

The effects of spray drying parameters on the morphology, encapsulation efficiency, loading capacity and moisture content of microspheres were evaluated, and the release rate of BTA was determined in an aqueous solution. According to the discussed results, the best processing condition was obtained with an aspirator setting of 100%, an inlet temperature of 170 °C, a pump rate of 2.5 mL/min, and a drying gas flow rate of 440 L/h. This processing condition was selected based on its high product yield (63%), associated with a less pronounced burst release, after which a more gradual release profile of the encapsulated corrosion inhibitor is obtained.

The presented results provide relevant information on the influence of inlet temperature and spray flow rate on the loading and release of BTA in CMC-Na microspheres. This information is crucial to understand the implications of spray drying processing parameters on materials to be used in applications that rely on the amount of active species available (loading), as well as on their release behavior, to achieve their intended purposes. However, a fast release of BTA occurs, which limits the applicability of these micro reservoirs. Chemical modification by crosslinking might be useful to reduce CMC-MS permeability, and to provide better control on the release of BTA, in turn, leading to better performance in corrosion inhibiting applications.

Considering the growing interest around the application of agro-industrial cellulose residues for the development of new technologies, the obtained CMC microspheres address a novel eco-friendly microreservoir for corrosion inhibitor storage, reducing production costs and negative environmental impacts when compared to other commonly used materials. Moreover, although spray drying is not a conventional methodology for the encapsulation of corrosion inhibitors, this study supports the possibility of using this

technique as an advantageous method to obtain an on-demand corrosion inhibitor delivery system for incorporation in organic coatings.

Overall, the obtained results reveal the development of an environmentally friendly aqueous methodology based on the spray drying technique combined with a raw material with almost no ecological impact, CMC-Na, contributing to innovative material and corrosion-inhibitor reservoir preparation.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/app12041800/s1>, Figure S1: Size distribution histograms of BTA.CMC-MS at (a) 170 °C and 440 L/h, (b) 170 °C and 600 L/h, (c) 180 °C and 440 L/h, (d) 180 °C and 600 L/h, (e) 190 °C and 440 L/h, and (f) 190 °C and 600 L/h.

**Author Contributions:** F.C. carried out the experimental work; F.C. and I.S. were responsible for the developed methodology; F.C., I.S. and J.T. contributed to the conceptualization; C.E.B.M. validated the experiments; C.E.B.M., M.A.C.B. and J.T. supplied the resources necessary for the development of the experimental work; work and project administration were supervised by C.E.B.M., M.A.C.B., J.T. and M.G.S.F.; F.C. and I.S. contributed to data analysis and interpretation; original draft was prepared by F.C.; reviewing and editing of the manuscript was carried out by I.S., M.G.S.F., C.E.B.M. and J.T.; C.E.B.M., M.A.C.B. and J.T. were responsible for funding. All authors have read and agreed to the published version of the manuscript.

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