**Spray Drying Encapsulation of Geraniol Essential Oil using different wall materials**

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**Highlights**

- Arabic Gum is an efficiency polymeric material to encapsulated Geraniol.

- The system has up to 15 days stability in environmental conditions.

- This system has great potential for use in crop protection and pollinators' attraction.

**Introduction**

Geraniol (GRL) is an acyclic monoterpene alcohol (C10H18O) derived from essential oils plants and showed several uses, such as pharmo-therapeutics (antitumor), preservative (bactericide), odorizing (for food and cleaning products), attraction agent to pollinators insects and repellent of a large number of insects considered as pests in agriculture [1-4]. However, GRL does not draw the interest from agro-industry when it is used "*in natura*" due to its short activity time since it is easily volatilizing or degrades by its high sensitivity to light, temperature and humidity [4,5]. One strategy to preserve unstable materials is the encapsulation. In this system essential oil is surrounded by a mono or multilayer coating layers that are able to preserves or control the release into the environment [6]. As example, the micro or nano carrier systems can be produced from different polymeric matrices such as Maltodextrin (ML) and Arabic Gum (AG) as well as by different encapsulation techniques (spray drying, fluidized bed, coacervation, extrusion and molecular inclusion). The atomization technique, also known as "Spray Drying" demonstrated efficacy in the studies with essential oils, besides its low cost [7-9]. The spray-drying process combines fluid colloidal materials in an emulsion (hydrophobic substance and polymer matrix in solution or suspension) converting them to dried particulates by the action of heated air in a drying chamber. In this study ML and AG were used in different proportions to produce the polymeric wall in the encapsulation process of GRL using spray drying technique as an alternative to protect the GRL when exposed to field conditions. In this way, this study open perspectives for the use of encapsulated GRL in crop protection as well as attractive for pollinators.

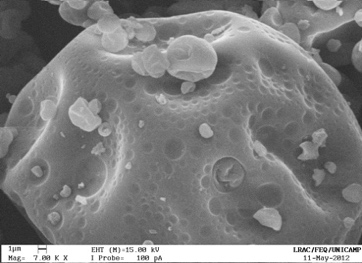
**Methods**

Three different formulations were prepared with GRL and polymeric materials wall. Each blend had 200 g as the final mass following these compositions (% w/w): A1 (30% ML, 10% GRL, 60% water); A2 (30% AG, 10% GRL, 60% water); A3 (15% ML, 15% AG, 60% water). Each sample was emulsified by ultraturrax (IKA T-18 ultra turrax emulsifier) at 17,000 rpm for 5 min (200 mL). Each emulsion had an aliquot diluted in deionized water at 1:1000 (v:v) at the 10, 20 and 30 minute intervals and zeta potential was analyzed in triplicate using Zetasizer (Nano-ZS 90 Malvern Instruments). The zeta potential demonstrates that the stability of the emulsion along the drying period in Spray Dryer process. Spray dryer was setup using air inlet temperature 95 °C ± 5 °C; compressed air pressure 5 bar; compressed air inlet flow 40 L/min; blower flow 3.9 m³/min; liquid flow rate 0.5 L/h. The dried material obtained in the atomization was collected from the Spray Dryer and storage to characterization studies.

*Capsules characterization -* Encapsulation efficiency: The encapsulation efficiency of GRL was determined by the quantification of GRL loaded and unloaded using gas chromatography (GC). Capsule morphology: size, shape, influence of the matrix in capsule parameters were determined by scanning electron microscopy (SEM). Oil stability/release profiles: each capsule preparation was kept in a stability chamber (30 °C and 65 % humidity). The samples were kept in the chamber along 15 days and in the periods of 1, 7 and 15 days the materials were submitted to moisture analysis (% - using thermogravimetry at 80 °C) and oil content inside and outside the capsule (by gas chromatography) and morphology. (by SEM).

**Results and discussion**

To prepare A1 samples we have been used only ML as material to form the wall. After mixing all components and emulsifying them by Turrax, the water and ML formed an unbalanced system. As consequence, the ML concentration was increased to 40% and the matrix continued with heterogeneous aspect. The same behavior was described by Reineccius [10] where maltodextrin when used as an emulsifier providing an unstable film formation. In this way, due these results, the sample A1 was not considered in this study. However, for samples A2 and A3 were stable by visual analysis and for this reason they were considered in the next steps. In this context, the zeta potential was measured with 30 minutes, and the samples A2 and A3 presented stable values (A2 = 38 ± 2 mV; A3= 36 ± 3 mV). In addition, we have been observed that the zeta potential was also stable in acid pH (pH ~ 4) [11]. The SEM analysis showed that both samples presented spherical shape (**Figure 1**). The stability results showed that for A2 and A3 at t1day, t7days and t15days a low decreasing in the internal volume of the capsules. This effect can be explained by the substitution of the geraniol present inside the capsule along the incubation time (15 days) in water in the stability chamber conditions (**Table 1**).



A3

A2

Figure 1. Morphology of the capsules obtained by SEM for samples A2 and A3.

Table 1. Results obtained for A2 and A3 samples:GRL assay (surface and inside capsules) and H2O assay during the stability studies. Both results behaviors have correlation analyzed by Person in Microsof Excel® software.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample** | **Time (days)** | **GRL Assay inside (% w/w)** | **GRL Assay surface (%w/w)** | **H2O assay (%w/w)** | **Person Correlation (H2O and GRL assay)** |
| **A2 - AG** | **t1** | 22.40 | > 1% | 5 | -0.80 |
| **t7** | 21.06 | > 1% | 12 | -0.80 |
| **t15** | 14.35 | > 1% | 18 | -0.80 |
| **A3 - ML + AG** | **t1** | 16.70 | > 1% | 11 | -0.91 |
| **t7** | 14.30 | > 1% | 14 | -0.91 |
| **t15** | 10.25 | > 1% | 21 | -0.91 |

Also, the release of GRL from the capsules as described in **Table 1** can be explained by the two mechanisms: i) release of GRL by diffusion and ii) the degradation of GRL in/out the capsule. Another point is that there was an inverse relation between the increasing in the water inside and the decreasing in GRL inside the capsules. In addition, it is observed a strong linear correlation between these two variables that was determined by the analysis of the Person coefficient. These results were probably observed due the porosity increasing in the capsules and also to the exposure of GRL to oxygen that converts Geraniol (C10H18O) to Geranial and consecutively Geranioic acid (C10H16O2).

**Conclusion**

The results showed that GRL and GA (as material wall) and its association with ML showed good results to produce capsules using Spray Drying technique. The characterization of both samples (A2 and A3) showed that the encapsulation efficiency remained in discrete decreasing in the first week (7 days) reaching approximately less than 50% of the total after 15 days. These results indicate that the encapsulation of Geraniol in both wall materials is able to preserve it for at least two weeks, therefore, a largest period comparing to GRL *in natura*. The results open perspectives for the use of GRL encapsulated in crop protection in field studies conditions.

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