Encapsulation of oil in Ca-alginate microcapsules by inverse gelation technique

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ABSTRACT SUMMARY

Usually, extruding drop wise alginate solution in jellifying calcium bath produces alginate gel beads. To produce oil single core capsules, an emulsion of calcium solution in oil is extruded drop wise in alginate bath leading to the formation of a membrane around the oil droplets (1).

This technology has been developed and optimize using different approaches to get capsules of different sizes and properties.

INTRODUCTION

Oil-core microcapsules produced by inverse gelation mechanism have some application in the food and non-food areas. Previously, the production of oil-core microcapsules by inverse gelation using an O/W emulsion was demonstrated (2). This technique consists in three steps: 1) formation of a primary O/W emulsion with oil and calcium chloride emulsion; 2) formation of a O/W/O secondary emulsion by dispersing primary O/W emulsion in oil and 3) mixing secondary O/W/O emulsion in an alginate solution. The process allows the production of well-defined shell-core microcapsules (~500 mm of diameter) with the thick membrane (~200 mm). This method is advantageous because it is environmentally safe, reproducible, and easily controlled. However, the oil used in the microcapsules production makes the process more expensive in the industrial scale.

The objective of this work is thus to propose a new method of microcapsules production by inverse gelation mechanism using a W/O emulsion. This method should be simpler and less expensive when compared with microcapsules production using an O/W emulsion.

EXPERIMENTAL METHODS

Sodium alginate powder, Saltialgine S 60 NS, was kindly donated by Cargill (France). Calcium chloride powder (CaCl₂. 2H₂O) (Panreac Quimica Sau, Spain), sunflower cooking oil (Associated Oil Packers, France) and PGPR 90 (Danisco, France) were used to prepare the W/O emulsion. All other chemicals of analytical grade were obtained from Sigma Aldrich (France).

For the calcium chloride solution, 240 g of CaCl₂.2H₂O were dissolved in 1 L of demineralized water. For the alginate solution, 10 g of alginate powder were dissolved in 1 L of demineralized water using a paddle stirrer.

Figure 1. Sketch of the experimental set-up.

For the preparation of a W/O emulsion, 100 mL of sunflower oil containing 0.01 g of PGPR 90 was stirred using a high shear mixer (Ultra-Turrax T25, IKA, Germany) at 13 500 rpm during 1 min. Thirty milliliters of calcium chloride solution (240 g/L) was then added slowly and a new shear mixing at 13 500 rpm for 3 min was performed (Figure 1A).

The W/O emulsion (5 mL) was added into 200 mL of alginate solution and stirred at 200 rpm for 1 min (Figure 1B). Then 0.01 % (v/v) of Tween 20 and 0.1 % (v/v) of ethanol (99%) were added to the solution and stirred at the same speed for 3 min at ambient temperature (20 ± 2 °C) (Figure 1C). After obtaining the wet microcapsules, filtrate and wash them using the demineralized water to remove...
excess alginate.

A microscope (Leica Microsystems, France) with a 40X objective was used to measure diameters and membrane thicknesses of the microcapsules.

RESULTS AND DISCUSSION

W/O emulsion containing calcium chloride is mixed with alginate solution. It was observed that if the release of Ca\(^{2+}\) from the W/O emulsion is very fast, small Ca-alginate fibers are formed instead of microcapsules. In the contrary, if Ca\(^{2+}\) release is very slow, a thin Ca-alginate membrane is formed around W/O emulsion droplets. Consequently, the formed microcapsules are fragile and can break easily during the rising and filtration steps.

To produce microcapsules with a well-defined shell-core structure, the W/O emulsion with a moderate Ca\(^{2+}\) released is necessary. In this methodology, the surfactant PGPR 90 was chosen to produce a W/O emulsions. Microcapsules produced with high concentrations of PGPR 90 (> 0.08 g of surfactant / 100 mL of emulsion) were easily broken during the filtration step. These observations suggest that the emulsions were very stables with a weak Ca\(^{2+}\) release, and consequently, both fine and fragile membranes were formed. For this reason, a low concentration of PGPR 90 was used (0.008 g of surfactant / 100 mL of emulsion) to allow a moderate released of calcium ions.

After the complete dispersion of the W/O emulsion into alginate solution, the calcium ions need to migrate from inside the emulsion to produce the Ca-alginate membrane. The best way to control the period of the calcium ions released is by a fine tuning of the destabilization of the W/O emulsion. To provoke destabilization and calcium ions release from the emulsion, destabilizer agents (Tween 20 / Ethanol) were added into the alginate bath. After the addition of the destabilizers, the calcium ions are released and the membrane is formed.

The methodology of microcapsules production can be divided into three steps:
1) **Formation of W/O emulsion** (Figure 1A): an emulsion with a moderate stability (~50 min) is produced because of the dispersion of calcium chloride solution into oil;
2) **Dispersion of the W/O emulsion into alginate solution** (Figure 1B): the droplets of W/O emulsion are dispersed into the alginate solution by the agitation of the alginate bath;
3) **Production of microcapsules** (Figure 1C): the Ca\(^{2+}\) release is induced with the destabilization of the W/O emulsion. Ca\(^{2+}\) ions will cross-link the alginate and form membranes around the W/O emulsion droplets. After 3 min of the curing time, microcapsules with an oil core and Ca-alginate membrane are formed (Figure 2).

![Figure 2. Ca-alginate microcapsules with oil core. Core: dark circle; membrane: white zone. Scale bar: 400 mm.](image)

Microcapsules with a mean diameter around 750 µm and 60 % of membrane (v/v) were produced (Table 1). The previous studies suggest that the membrane thickness and core size can be controlled by the concentration of calcium chloride presents in the W/O emulsion and the stirring rate of the alginate bath, respectively (Martins et al. 2014). Therefore, the expectation after the optimization of the technique is the size of microcapsules and its structure can be controlled.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Size (µm)</th>
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<tbody>
<tr>
<td>Microcapsules diameter</td>
<td>750 ± 130</td>
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<tr>
<td>Membrane thickness</td>
<td>230 ± 50</td>
</tr>
<tr>
<td>Core diameter</td>
<td>175 ± 95</td>
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</tbody>
</table>

CONCLUSION

A new process of microcapsules production using a W/O emulsion is proposed. These microcapsules could be easily produced at pilot scale and be applied in the cosmetics, pharmaceutics, agricultural and foods areas.

REFERENCES


2. Martins et al. (2014). Oil core microcapsules by alginate inverse gelation technique. J. Microencapsulation, 1-10 (online)