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Preparation of Ca-alginate beads containing high oil content: Influence of process variables on encapsulation efficiency and bead properties

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ABSTRACT

The encapsulation of model oil in Ca-alginate beads using high oil loading was studied. It was found that the alginate concentration, oil volume fraction and alginate type each have a significant influence on the encapsulation efficiency and on bead properties. The alginate-oil emulsion, comprising an oil loading up to 30 vol% and 25 g/L of high G alginate solution (equivalent to an oil-to-wall weight ratio of up to 15 g/g), was found to be stable and resulted in an encapsulation efficiency of 90% before drying. The oil-loaded, wet beads were spherical. The encapsulation efficiency was dependent on the degree of cross-linking at the surface of the extruded emulsion droplet as well as on the emulsion stability. The oil extraction profile of dried beads may be related to the structural properties of the beads, which are dependent on both the drying method and the oil loading. The overall encapsulation efficiency after freeze-drying and oven-drying were 90% and 79%, respectively, with an oil content of over 85 wt% for both types of dried beads. The freeze-dried beads were non-oily and free flowing, whereas the oven-dried beads were oily and sticky. The results of this work are compared to those in the literature, and the merits and the drawbacks associated with different methods are discussed.

1. Introduction

Encapsulation is a process of confining active compounds within a matrix in particulate form to achieve one or more desirable effects (Chan, Lee, Ravindra, & Poncelet, 2009). Oils are encapsulated for various reasons, such as for conversion of liquid to solid form to facilitate handling, transportation or incorporation into other components. Other reasons include taste/smell masking, protection from evaporation or oxidation, and controlled-release applications. Encapsulation of many different oils for nutrition, therapeutics, flavoring or for aromas has been reported in the past, with examples including fish oil, alpha-tocopherol, wheat germ oil, evening primrose oil, lemon oil, and citronella oil.

The choice of encapsulation material and process is governed by three main criteria: the application, economics and safety. At present, spray-drying is the most commonly used method to encapsulate oil, and the wall materials are usually carbohydrates, proteins and gums. The oil-to-wall weight ratios normally range from 0.1 to 1.0, although 0.2 to 0.5 are more common, and the oil content could reach up to 50% of the total weight of final product (Drusch, 2007; Drusch & Berg, 2008; Tan, Chan, & Heng, 2005, 2009). However, in some food, nutraceutical and cosmetic products, higher oil content may be required to reduce the product volume. Peniche, Howland, Corrillo, Zaldívar, and Argüelles-Monal (2004) have shown that it is possible to achieve high oil content (of about 65–70%) using a simple extrusion process, where the oil is encapsulated within Ca-alginate beads coated with chitosan. However, the scope of their study was not aimed to develop a product with a high oil content. Currently, the influence of process variables towards achieving this objective remains poorly understood.

The overall aim of this study was to encapsulate a model oil in Ca-alginate beads to produce dried beads containing a high oil content. Palm oil was chosen as a model oil because it is easily available. An alginate-oil emulsion was prepared and dropped into a gelling bath to produce oil loaded, Ca-alginate beads. The wet beads were then freeze-dried and oven-dried. The influence of process parameters, such as alginate type and concentration, oil volume fraction, emulsion stability and drying methods, on the encapsulation efficiency and bead properties was studied.

2. Materials and methods

2.1. Materials

Sodium alginate Manugel GHB, with a high guluronic acid content (M/G ratio = 0.59, denoted as high G), and sodium alginate Manugel DH, with a high mannuronic acid content (M/G

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ratio = 1.56, denoted as high M), were provided by ISP Technologies Inc., UK. The molecular weights of both types of alginates were about 97,000, and their viscosities ranged from 40 to 100 mPa s. Calcium chloride dihydrate, $CaCl_2{\cdot}2H_2O$ (Malinckrodt Bake, Mexico), was used as gelling ions, and palm oil (Lam Soon Edible Oils Co. Ltd., Malaysia) was used as the model oil.

2.2. Methods

2.2.1. Preparation of alginate and gelling solution

Sodium alginate powder was dispersed in distilled water to produce alginate solutions of desired concentrations (i.e., 5–45 g/L). The solutions were left standing for 24 h to disengage bubble before use. A calcium chloride dihydrate solution of 15 g/L was prepared by dissolving $CaCl_2{\cdot}2H_2O$ powder in distilled water.

2.2.2. Preparation of alginate-oil emulsion

One hundred milliliters of alginate solution and oil was mixed in a 200 mL beaker without baffles using an impeller at a speed of 300 rpm for 45 min to produce an alginate oil emulsion. The oil was gradually added to the alginate solution during mixing until the desired oil loading was obtained, which ranged from 10 to 60 vol% of oil to the total volume of emulsion. The impeller was fixed at a height of 0.5 cm below the surface of the mixture.

2.2.3. Determination of emulsion stability (ES)

Fifty milliliters of alginate-oil emulsion was left standing for 1 h to determine the extent of phase separation, if any. Emulsion stability (ES) was determined depending on the phase separation interface position, which was measured based on the volume of remaining emulsion, $V_{\text{emul.}}$, and on the initial emulsion volume, V_{initial}, as shown in Eq. (1) (Huang, Kakuda, & Cui, 2001):

$$\text{ES}\quad(\%) = \frac{V_{\text{emul.}}}{V_{\text{initial}}} \times 100\% \tag{1}$$

The oil droplets of emulsion immediately after preparation were viewed under a microscope, and their images were taken using an attached digital camera.

2.2.4. Encapsulation of oil

Fifty milliliters of alginate-oil emulsion was extruded through a 0.55 mm needle and was dripped into calcium chloride gelling solution to form oil-loaded, Ca-alginate beads. The tip of the needle was fixed at 15 cm above the surface of the gelling bath. The gelling solution was gently stirred with a magnetic stirrer to prevent the beads sticking together. The beads that formed then hardened for 30 min in the gelling bath.

2.2.5. Determination of encapsulation efficiency before drying (EE_{BD})

The oil-loaded, Ca-alginate beads were separated from the gelling solution using a sieve. The beads were rinsed with distilled water to remove excessive surface oil. The non-encapsulated oil before drying was determined by measuring the weight of free oil left on the surface of gelling solution as well as the surface on the wet beads. Filter paper was used to absorb the surface oil on the wet beads, and they were dried in an oven until a constant weight was achieved. The difference between the initial amount of oil used (W_1) and the non-encapsulated oil before drying (W_2) gives the amount of oil encapsulated (W_3), as shown in Eq. (2). The encapsulation efficiency before drying (EE_{BD}) was expressed as the percentage of oil encapsulated with respect to the initial amount of oil used, as shown in Eq. (3):

$$W_3 = W_1 - W_2 \tag{2}$$

$$\text{EE}_{\text{BD}}\quad(\%) = \frac{W_3}{W_1} \times 100\% \tag{3}$$

2.2.6. Drying of oil-loaded beads

The oil-loaded beads were dried using two drying methods. For freeze-drying, the beads were placed on drying trays and were freeze dried under vacuum pressure of 0.015 kPa at a condenser temperature of −55 °C for 24 h. For oven-drying, the beads were placed on drying trays and were dried in an oven at 70 °C until constant weight was achieved. The beads were placed in a container that was sealed immediately after drying for future use.

2.2.7. Determination of encapsulation efficiency after drying (EE_{AD}) and oil distribution profile

The encapsulation efficiency of the beads when subjected to freeze-drying and oven-drying was determined. The non-encapsulated oil, i.e., the oil that leaked from the beads due to drying, was determined by weighing the amount of free oil left on the drying trays as well as on the surface of the dried beads. The difference between the amount of oil encapsulated before drying (W_3) and the non-encapsulated oil after drying (W_4) gives the amount of oil encapsulated after drying (W_5), as shown in Eq. (4). The encapsulation efficiency after drying (EE_{AD}) was expressed as the percentage of oil encapsulated (W_5) with respect to the amount of oil encapsulated before drying (W_3), as shown in Eq. (5):

$$W_5 = W_3 - W_4 \tag{4}$$

$$\text{EE}_{\text{AD}}\quad(\%) = \frac{W_5}{W_3} \times 100\% \tag{5}$$

The oil distribution at the beads' surface was determined from the oil extraction profile. Hexane was added to a known amount of dried beads, followed by stirring for 15 min. The beads were sampled at suitable time intervals where they were filtered, air-dried for 30 min and weighed. The amount of extractable oil was calculated based on the difference between the weights of beads before and after extraction. It was expressed as the percentage of the extractable oil (W_6) with respect to the amount of oil encapsulated before drying (W_3), as shown in Eq. (6):

$$\text{Extractable}\quad\text{oil}\quad(\%) = \frac{W_6}{W_3} \times 100\% \tag{6}$$

2.2.8. Characterization of beads

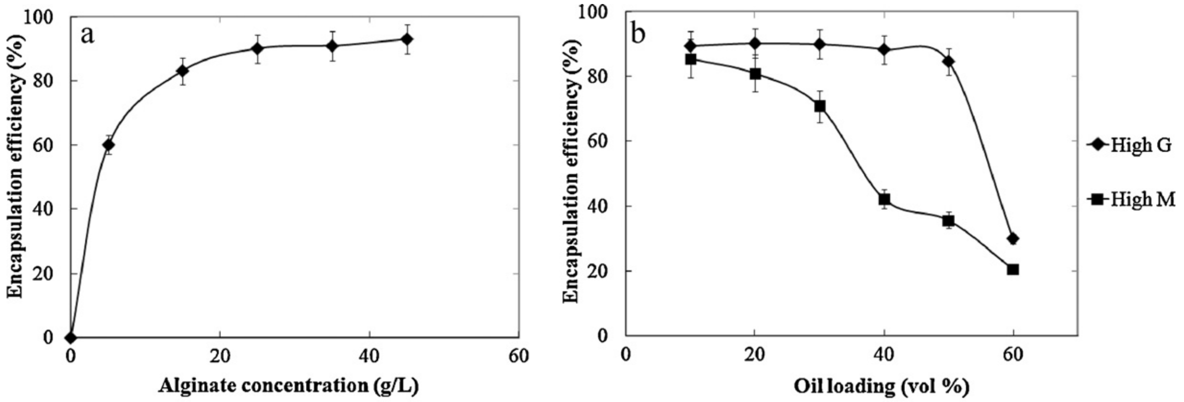
The size and the shape of the beads were determined using an image analyzer (Sigma ScanPro 5). A digital camera was used to capture the images of the wet and dry beads. Sphericity factor (SF) was used to indicate the roundness of the beads, as described by Chan et al. (2009), where the value zero indicates a perfect sphere and higher values indicate a greater degree of shape distortion. SF was calculated according to Eq. (7):

$$\text{SF} = \frac{D_{\max} - D_{\text{per}}}{D_{\max} + D_{\text{per}}} \tag{7}$$

where $D_{\max}$ is the maximum diameter passing through a bead centroid (mm) and D_{per} is the diameter perpendicular to $D_{\max}$ passing through the bead centroid (mm).

2.2.9. Statistical analysis

All samples were assayed in triplicate to determine the mean and the standard error. The bead size and shape were determined based on the measurement of 45 beads per sample.



Experimental conditions: oil loading = 30 vol %, alginate type = High G, nozzle diameter=0.55 mm. Error bars indicate standard errors.

Experimental conditions: alginate concentration = 25 g/L, nozzle diameter=0.55 mm. Error bars indicate standard errors.

Fig. 1. Encapsulation efficiency before drying. (a) Effect of alginate concentration; (b) effect of alginate type and oil loading.

3. Results

3.1. Encapsulation efficiency before drying (EE_{BD})

The effect of alginate concentration on the EE_{BD} of oil in Ca-alginate beads is shown in Fig. 1a. The EE_{BD} was determined immediately after the encapsulation process and before the drying process. In this experiment, the oil loading used was 30 vol% of the total volume of the alginate-oil emulsion. The EE_{BD}, expressed as the percentage of encapsulated oil relative to the total oil used, increased with increasing alginate concentration. The EE_{BD} was found to increase significantly (from 60% for the 5 g/L alginate solution to 90% for the 25 g/L solution). The EE_{BD} was found to level off and reach a maximum of 93% when the alginate concentration was increased to 45 g/L. The alginate concentration was fixed at 25 g/L in subsequent work because further increases in the concentration did not cause significant increases in the EE_{BD}.

The effects of alginate type and oil loading on the EE_{BD} are shown in Fig. 1b. The following two different types of alginate were used: high in guluronic acid (high G) and high in mannuronic acid (high M). The oil loading ranged from 10 to 60 vol%. In general, high G alginate gave a higher EE_{BD} for all oil loadings when compared to the high M alginate. The EE_{BD} using the high G alginate remained relatively constant (at about 85–90%) for oil loading up to 50 vol%, but it decreased drastically (to 30%) when oil loading was increased to 60 vol%. On the other hand, the EE_{BD} using the high M alginate showed a different trend, decreasing gradually from 86% to 70% for the oil loading from 10 to 30 vol%, respectively. Above the oil loading of 30%, the EE_{BD} decreased drastically; it was found to be approximately 20% for an oil loading of 60 vol%.

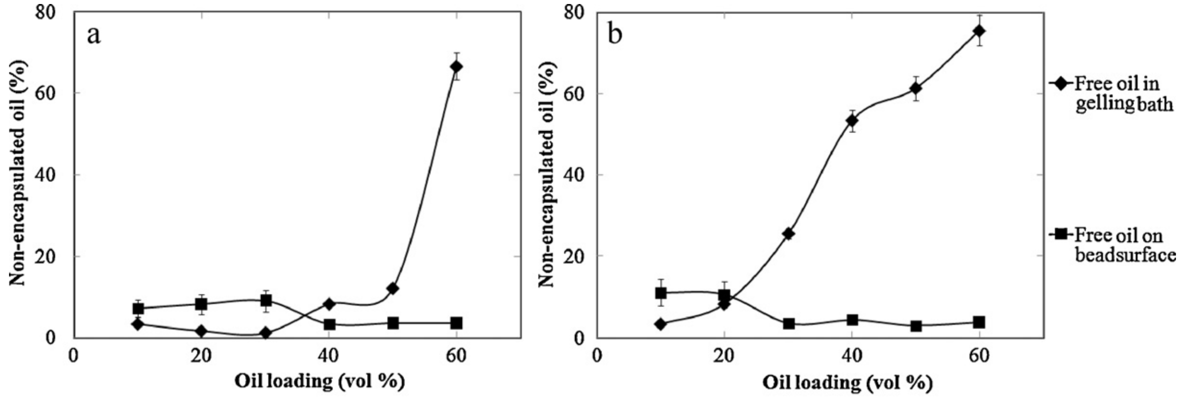
We also determined the fraction of non-encapsulated oil found in the gelation bath and on the surface of wet beads, and the results are presented in Fig. 2. Generally, the fraction of non-encapsulated oil found on the bead surface was in the range of 4–10% of total oil used. Interestingly, the surface oil fraction at lower oil loading was higher than that of higher oil loading. It is worth mentioning that the amount of surface oil found in all samples was about the same (i.e., 0.3–0.6 mL) despite the variation in oil loading. This is logical because the number of beads and the bead size were found to be relatively constant, and the amount of surface oil should be dependent on the total surface area of the beads. Therefore, the higher surface oil fraction obtained was a result of dividing the value with a lower oil volume. The data verifies that the non-encapsulated oil leaked into the gelation bath. The extent of leakage depended on the oil loading as well as on the type of alginate used.

Alginate is a natural polysaccharide derived from a marine plant, and its basic structure consists of linear unbranched polymers containing β-(1 → 4)-linked D-mannuronic acid (M) and α-(1 → 4)-linked L-guluronic acid (G) residues. In this study, the maximum encapsulation efficiency before drying that can be attained in Ca-alginate beads was over 90%, with alginate concentrations higher than 15 g/L and oil loadings up to 40 vol%. Lowering the alginate concentration below 15 g/L, or increasing the oil loading higher than 40 vol%, decreased the encapsulation efficiency. A logical explanation for both cases is that the encapsulation efficiency depends on the degree of cross-linking at the surface of the extruded emulsion droplet. If there was a lower concentration or volume fraction of alginate, once the emulsion droplet dropped into the gelling bath, there was insufficient cross-linking between the alginate and calcium ions at the droplet surface, which resulted in formation of loose Ca-alginate hydrogel wall barriers. These results are in good agreement with those of Chang and Dobashi (2003) who reported an encapsulation efficiency of about 90% at an oil loading of 20 vol%.

This explanation can be further supported when the results obtained using different alginate types (i.e., high G and high M alginates) are compared (Fig. 2b). Since the alginates have similar molecular weights, the physical properties of the emulsion, such as viscosity and density, can be assumed to be relatively constant when the same concentration of alginate is used. The difference between the alginates was in the gelling density because it is well accepted that most of the calcium cations cross-link to the guluronic sequences to form hydrogel networks. In other words, a higher gelling density can be achieved at the emulsion droplet surface with the high G alginate, thus yielding a higher encapsulation efficiency. Interestingly, the encapsulation efficiency before drying by using this method seems to reach a limit at about 90–93%, because the wet beads are always 'coated' by a layer of surface oil (at about 7–10% to the total oil used) irrespective of the process parameters. The reason might be due to the oil leakage from the bead surface before the alginate phase in the emulsion could form a continuous surface barrier.

3.2. Stability of alginate-oil emulsion

Prior to the encapsulation process, the alginate solution and oil were mixed and stirred using a mechanical stirrer (at 350 rpm for 45 min) to form an alginate-oil emulsion. It was found that a higher agitation speed (up to 500 rpm) and longer agitation duration (up to 90 min) had no influence on the emulsion stability (data not shown). In this experiment, the oil loading used was 30 vol% of the



Experimental conditions: alginate concentration = 25 g/L, nozzle diameter=0.55 mm. Error bars indicate standard errors.

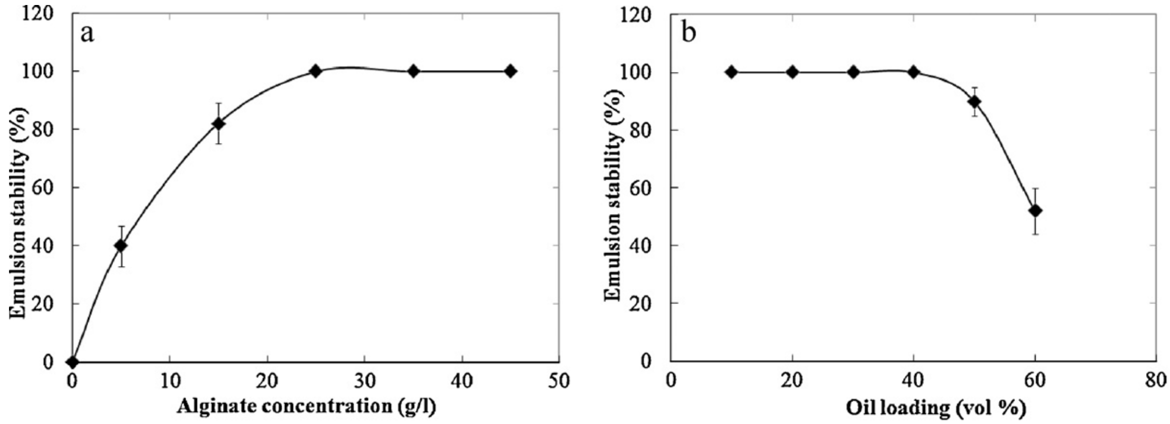
Fig. 2. Analysis of non-encapsulated oil. (a) Encapsulation using high G alginate; (b) encapsulation using high M alginate.

total volume of alginate-oil emulsion. The emulsion was left standing for 1 h to determine the extent of phase separation, if any. A duration of 1 h was used because the encapsulation process was complete within the time-frame. The alginate concentrations used ranged from 5 to 45 g/L. Higher alginate concentrations were not attempted because they were difficult to process due to their high viscosities. The effect of alginate concentration on the ES is shown in Fig. 3a. The ES was found to increase with higher alginate concentration (from 40% for the 5 g/L alginate solution to 82% for the 15 g/L solution). The emulsion was found to be stable, and no phase separation was observed when the alginate concentration was 25 g/L and higher. The effect of oil loading on the ES is shown in Fig. 3b. The emulsion was found to be stable for an oil loading up to 40 vol%. Further increasing the oil loading (i.e., >40 vol%) resulted in a sharp decrease in the ES, where 50 vol% of the oil separated out from the initial emulsion at oil loading of 60 vol%.

The alginate-oil emulsions, prepared from different alginate concentrations and oil loadings, were observed under a microscope to estimate the oil droplet size, and the microscopic images of the oil droplets are shown in Fig. 4. It was found that the oil droplet size decreased as alginate concentration increased (refer Fig. 4a). Based on visual estimation, oil droplet size decreased from 100–400 μm to 10–50 μm when the alginate solution increased from 5 g/L to 45 g/L. On the other hand, higher oil loading as expected increased the number density of oil droplet within the emulsion (Fig. 4b). For oil loading up to 50 vol%, the oil droplet sizes were relatively similar and were about 50–100 μm. However, large oil droplets (i.e., >500 μm) were observed when the oil loading was increased to 60 vol%.

The first stage of the oil encapsulation procedure normally includes preparation of an emulsion comprising an oil of interest and the encapsulation materials in aqueous form. It has been reported that emulsion stability has a significant influence on the encapsulation efficiency as well as on the powder or product qualities (Gharsallaoui, Roudaut, Chambin, Voilley, & Saurel, 2007; Klaypradit & Huang, 2008; Tan et al., 2005). According to Drusch (2007), for oil microencapsulation using a spray-drying method, the emulsion must be stable over a certain period of time prior to spray-drying, oil droplets should be rather small (below 2 μm) and viscosity should be low to prevent ballooning of the particles during the drying process. Some studies have found that a stable emulsion with minimum droplet size could increase the retention of encapsulated oil products through reduction of unencapsulated oil at the surface of particles (Minemoto, Hakamata, Adachi, & Matsuno, 2002; Soottitantawat, Yoshii, Furuta, Ohkawara, & Linko, 2003); therefore, one of the criteria for selection of encapsulation material is based on its emulsifying activity.

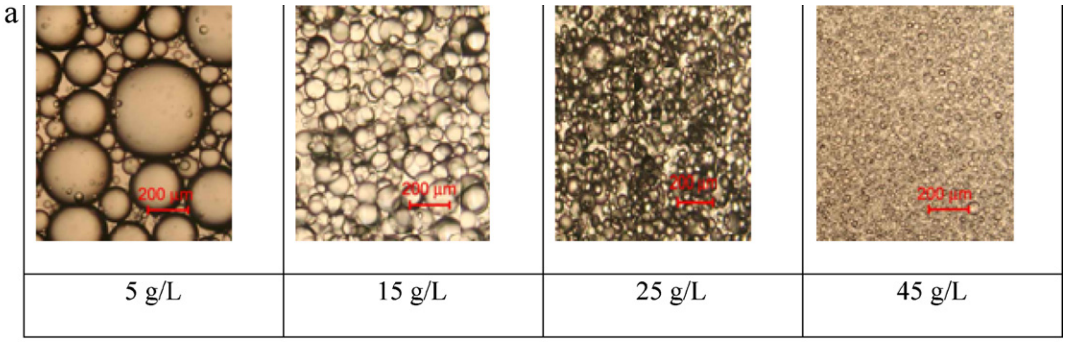
The most common initial sign of instability of oil-in-water emulsion is the formation of a distinctive bottom layer of aqueous serum and an upper layer of cream. This phase separation is commonly



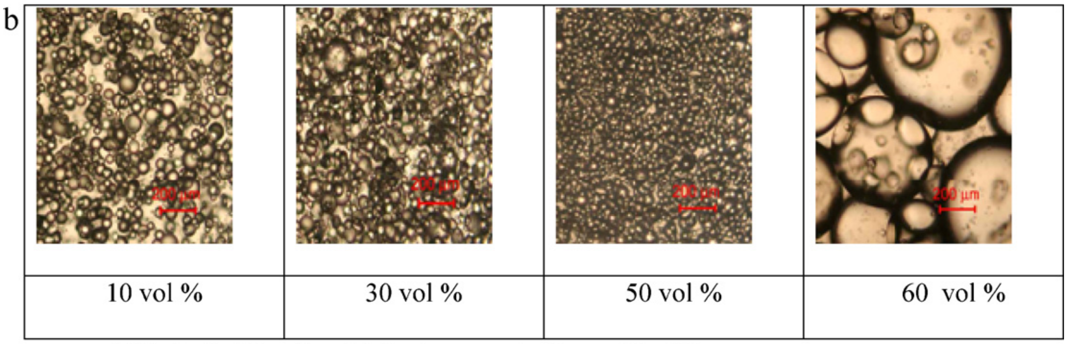
Expermental conditions: Oil loading = 30 vol %, alginate type = High G. Error bars indicate standard errors.

Expermental conditions: alginate concentration = 25 g/L, alginate type = High G. Error bars indicate standard errors.

Fig. 3. Stability of alginate-oil emulsion. (a) Effect of alginate concentration; (b) effect of oil loading.



Effect of alginate concentration (oil loading = 30 vol %)



Effect of oil loading (alginate concentration = 25 g/L)

Fig. 4. Microscopic images of oil droplets in alginate-oil emulsion.

referred to as creaming and may then be followed by coalescence of oil droplets within the cream (where an oil layer is formed at the top of the cream layer). In this work, the time taken to complete the encapsulation process for a batch was less than 60 min. Hence, the stability of alginate-oil emulsions was measured after they were left standing for 1 h.

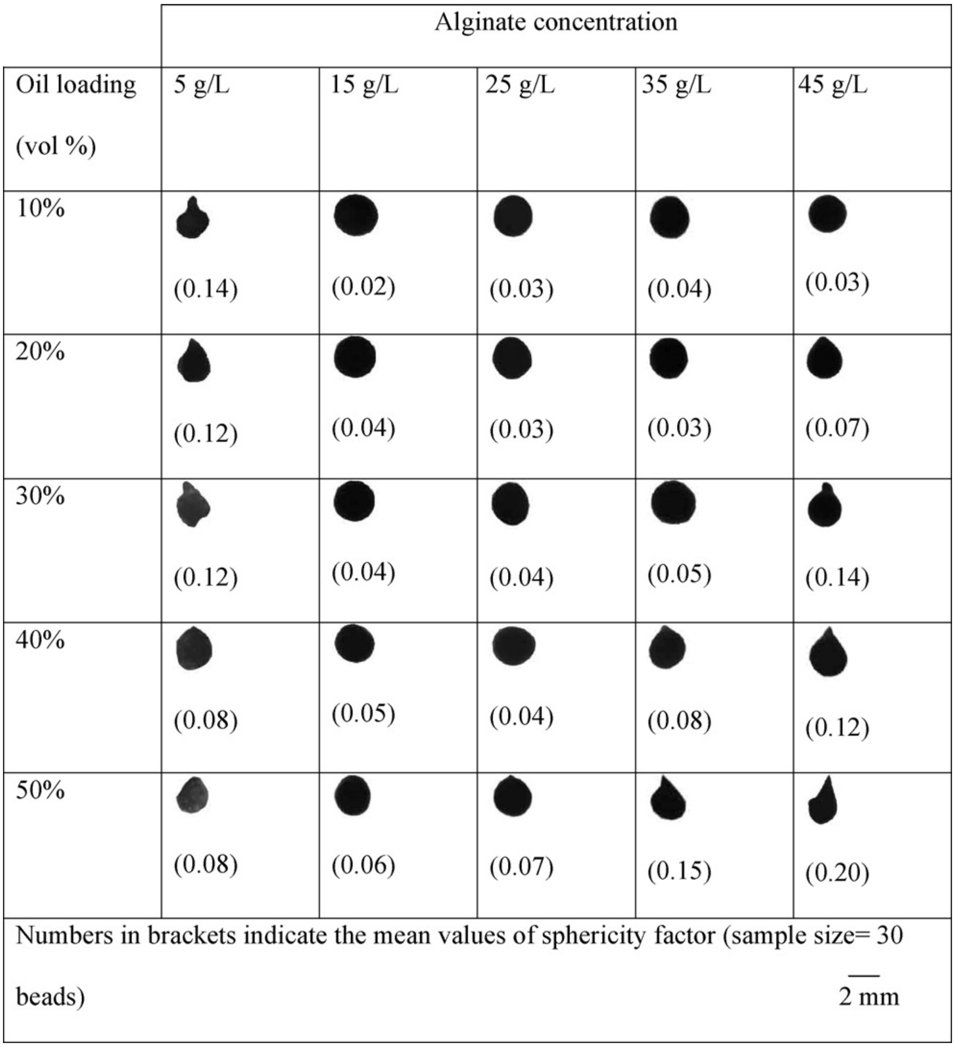
The results show that the alginate concentration and oil loading had an influence on the emulsion stability. Because alginate is a hydrophilic polysaccharide hydrocolloid, it is expected to have a low surface activity. However, increasing the alginate concentration resulted in smaller oil droplets as well as a more stable emulsion. This observation is in agreement with that of Huang et al. (2001), who reported that increasing the concentration of many hydrocolloid gums was found to improve the emulsion stability. This may be due to an increase in viscosity of the continuous phase surrounding the oil droplets restricting their movement and/or to the adsorption/precipitation of the gum at the oil-water interphase causing a reduction in interfacial tension.

In this work, we attempted to determine the influence of emulsion stability on the encapsulation efficiency of oil in Ca-alginate beads before drying. At alginate concentration of 5 and 15 g/L, the encapsulation efficiency was 60% and 83%, respectively. The poor encapsulation efficiency has been attributed to low surface gelling density, as mentioned earlier, but it could also be partly caused by an unstable emulsion and large oil droplet size. When the alginate concentration was increased to 25 g/L and higher, the emulsion was stable, as no phase separation was observed. In this case, the encapsulation efficiency was near its maximum, at about 90%, and further increases in alginate concentration (to 45 g/L) only resulted in a marginal increase in encapsulation efficiency to 93%. Also, when higher oil loadings (of 50 and 60 vol%) were used, emulsion stability was lower, which coincides with a decrease in encapsulation efficiency. In short, the stability of alginate-oil emulsion could have an effect on encapsulation efficiency apart from the surface gelling density because they consistently correspond to each other; however, the extent of the respective effects (i.e., emulsion stability or surface gelling density) cannot be quantitatively determined at this point and may require further work.

3.3. Size and shape of wet beads

In this work, the effects of alginate concentration and oil loading on the shape of the ca-alginate beads after oil encapsulation were determined. Fig. 5 shows the typical size and shape of the beads. In general, the size of the beads produced was about 2 mm in diameter, irrespective of the alginate concentration and oil loading. In terms of bead shape, a sphericity factor was used to quantitatively determine the bead sphericity, as described in Chan et al. (2009). A bead was considered spherical when its sphericity factor was <0.05. It can be clearly seen in Fig. 5 that the alginate concentration and oil loading had a significant influence on the bead shape. An alginate concentration of 5 g/L was found to give irregular bead shape for all oil loadings; however, the beads became spherical when the alginate concentration increased. The beads made from 15 and 25 g/L alginate solutions were spherical even at high oil loadings (50 vol%). Increasing the alginate concentration (i.e., 35 and 45 g/L) could result in production of beads with a tail, depending on the oil loading. At low oil loading (10 vol%), the beads produced were spherical for both alginate concentrations. For alginate solutions of higher concentration (i.e., 45 g/L), 'tailed' beads could be spotted at a lower oil loading (20 vol%) in comparison to 40 vol% for lower alginate concentrations (35 g/L). For both concentrations, the tail became more distinct at a higher oil loading.

By using the extrusion-dripping technique, a liquid pendant droplet grows at the capillary tip until the surface tension force no longer supports the weight of the droplet. At this instant, the liquid droplet detaches from the tip and falls into the gelling bath to form a bead. Tate's law (Tate, 1864), which approximates the balance between the gravitational force pulling the droplet down and the surface tension force holding the droplet pendant to the



Oil loading (vol %)	Alginate concentration 5 g/L	15 g/L	25 g/L	35 g/L	45 g/L
10%	(0.14)	(0.02)	(0.03)	(0.04)	(0.03)
20%	(0.12)	(0.04)	(0.03)	(0.03)	(0.07)
30%	(0.12)	(0.04)	(0.04)	(0.05)	(0.14)
40%	(0.08)	(0.05)	(0.04)	(0.08)	(0.12)
50%	(0.08)	(0.06)	(0.07)	(0.15)	(0.20)

Numbers in brackets indicate the mean values of sphericity factor (sample size= 30 beads)

Fig. 5. Size and shape of oil-loaded Ca-alginate beads.

tip at the instant of droplet detachment, can be used to predict the theoretical size of alginate beads formed. The accuracy of Tate's equation can be improved by taking into account the undetached liquid droplet volume and the shrinkage of beads during gelation, as recently proposed by Chan et al. (2009). If the alginate solution (25 g/L) were dropped into the gelling bath through a capillary diameter of 0.55 mm, the size of the wet beads estimated from the modified Tate's equation would be 2.4 mm in diameter, but the diameter of the oil-loaded wet beads produced in this study was about 2 mm. This effect was probably due to the decrease in surface tension of the alginate-oil emulsion. It is worth mentioning that the surface tension of the alginate solution (at 25 g/L) and palm oil was reported to be 69 mN/m (Chan et al., 2009) and 32 mN/m (Oh & Chong, 1992), respectively.

Recently, we have studied the shape of alginate beads prepared using the extrusion-dripping method (Chan et al., 2009). It was found that the minimum alginate concentration required to form spherical beads was 15 g/L, which corresponds to a viscosity of 130 mPa s. When the alginate liquid droplet hit and entered the gelling bath, there were competing forces between the viscous-surface tension forces and impact-drag forces to maintain the droplet shape. However, the viscosity of a 0.5 g/L alginate solution was insufficient to counteract the effect of impact and drag, thus resulting in bead deformation. Although the previous study was conducted without the presence of oil in the alginate solution, the same results were obtained in this study. Interestingly, the shape of the oil-loaded beads made using different alginate concentrations also resembled those in the previous work, with formation of spherical, pear- and tear-shaped beads. The optimum alginate concentrations to form spherical beads were found to be 15 and 25 g/L, since the beads remained spherical even at high oil loading (up to 50 vol%).

3.4. Oil distribution profile of dried beads

In this study, the extraction of oil from the dried Ca-alginate beads was performed using hexane as a solvent for 15 min. The purpose was to establish an oil distribution profile near the beads' surface. In this experiment, oil loadings of 20 and 30 vol% were used and the oil-loaded wet beads were dried using two different methods (i.e., freeze-drying and oven-drying). The results are shown in Fig. 6. In all cases, the extractable oils, expressed as the percentage of oil extracted to the total encapsulated oil, were found to follow a similar trend where they increased sharply at the beginning of extraction before leveling off. The time duration to level off and the fraction of oil extracted were found to be affected by both drying method and oil loading. Oven-dried beads took shorter times (i.e., 1–2 min, depending on the oil loading) to reach a plateau in comparison to freeze-dried beads, which took 2–4 min. In both cases, higher oil loading (at 30 vol%) resulted in a longer time to level off.

Table 1
Comparison of drying methods on encapsulation efficiency and bead properties.

Drying method	Oil loading (vol%)	Residual oil on drying tray (%)	Surface oil (%)	Encapsulation efficiency (%)	Bead diameter (mm)	Sphericity factor
Oven-dried	20	0.6	6.4[a]	93	1.50	0.041
	30	1.2	7.9[a]	90.8	1.64	0.039
Freeze-dried	20	0	N.A.	100	1.83	0.058
	30	0	N.A.	100	1.83	0.068

Experimental conditions: alginate concentration = 25 g/L, alginate type = high G, nozzle diameter = 0.55 mm.

[a] Based on oil extraction time of 2 min.

On the other hand, the fraction of extractable oil from oven-dried beads, which increased with higher oil loading, ranged from 9 to 16%. In comparison, the fraction of oil extracted from freeze-dried beads was significantly higher, from 58 to 69% for oil loading of 20–30 vol%, respectively.

The oil extraction profile can be related to the structural properties of beads, which are dependent on the drying method employed as well as on the oil loading. Freeze-dried alginate beads have a macroporous surface and internal structures (Chan et al., 2011; Smrdel, Bogataj, & Mrhar, 2008). Such characteristics are caused by the sublimation of water crystals from the alginate matrix, resulting in void spaces and minor structural shrinkage. As a result, the oil could be easily extracted from the open pores at the bead surface, which gave a sharp increase in the amount of oil extracted at the beginning of extraction. The amount of oil extracted seemed to level off after some time because the solvent had to penetrate deeper into the beads to extract the oil. Despite the resistance, the amount of oil extracted was still relatively higher than the oven-dried beads, indicating a porous internal structure of freeze-dried beads. On the other hand, oven-dried alginate beads, which are comparable to the air-dried or fluidized-bed-dried alginate beads, have a smooth surface and a dense interior (Smrdel et al., 2008). They are comparable because they are all dried by means of water evaporation, which causes the hydrogel matrix to shrink during drying. In this case, the shrinkage caused some oil to be squeezed out to the bead surface. The availability of the free surface oil explains the sharp increase in the amount of oil extracted from the beads at the beginning of extraction. Due to the dense interior of the beads, further extraction only caused a marginal increase in the extracted oil. On the other hand, the effect of oil loading on the oil extraction profile was the same for both drying methods, where higher oil loading resulted in a higher amount of oil extracted. This effect is expected because higher oil loading resulted in less alginate hydrogel networks, thus increasing the porosity of the beads.

3.5. Encapsulation efficiency after drying (EE_{AD})

The results of encapsulation efficiency (EE_{AD}) after drying are presented in Table 1. The EE_{AD}, expressed as the percentage of encapsulated oil relative to the total oil encapsulated before drying, was determined by adding up the amount of non-encapsulated oils, the residual oil on drying trays and the surface oil on the beads after the drying process. The amount of oil left on the drying trays was weighed immediately after drying. The surface oil was determined based on the amount of oil extracted in 2 min (refer Fig. 6), assuming a short duration of time was adequate in extracting the free oil from bead surface. We found that oven-drying caused the oil to leak from the oil-loaded wet beads during the drying process. As a result, the drying trays and the dried beads were oily and sticky after the drying process. The extent of oil leakage or the non-encapsulated oil was quantified. The residual oil was ranged from 0.6 to 1.2%, with respect to the total oil encapsulated, for oil loadings of 20–30 vol%, respectively. The surface oil, which also increased with higher oil loading, ranged from 6.4 to 7.9%.

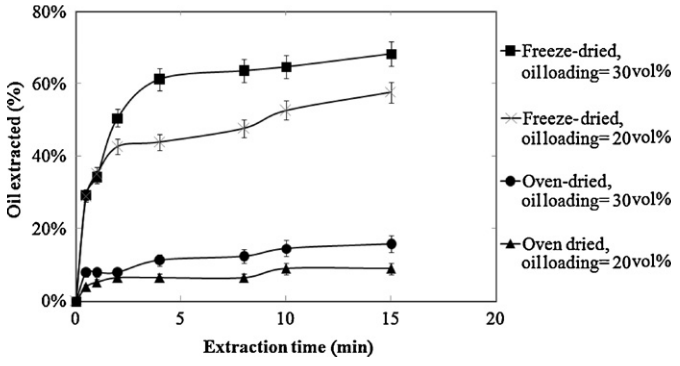


Fig. 6. Oil extraction profile of dried Ca-alginate beads.

In contrast, we could not detect any residual oil on the trays of freeze-dried beads. Therefore, we did not use the oil extraction profile (from Fig. 6) to estimate the surface oil of freeze-dried beads. Although the results show that a large portion of oil (i.e., 40–50% in 2 min) was extracted from the beads, the data were inappropriate to be used in this case because the beads' surface was found to be non-oily as felt by the fingers, unless a greater force was applied to squeeze the oil out from the inside of the beads. Also, the beads were found to be free flowing, a possible explanation is that the surface and internal pores of freeze-dried alginate beads act as small capillaries, allowing them to absorb and hold the oil like a reservoir. Based on this observation, we assumed there was negligible free oil on the beads' surface.

3.6. Dried bead properties

The results regarding the size and shape of the oil-loaded dried beads are shown in Table 1. The diameter of wet beads (i.e., before drying) was about 2 mm. Oven-drying caused a higher degree of bead shrinkage compared to freeze-drying. The oven-dried beads shrank by 18–25% when oil loading decreased from 30 to 20 vol%. In comparison, the freeze-dried beads shrank by 9% irrespective of the oil loading. In terms of the shape, the beads dried by both drying methods were generally spherical, with oven-dried beads slightly more spherical than that of the freeze-dried beads. The drying method also caused differences in bead appearance (figures not shown). The oven-dried beads appeared shiny because they were coated with a layer of surface oil and had a golden-yellowish color, whereas the freeze-dried beads were non-glossy and off-yellowish in color.

3.7. Comparison with previous works

There are many studies concerning the encapsulation of oils or hydrophobic compounds. To narrow down the scope of comparison, we have only reviewed the encapsulation studies using gel-beads system because they were closest to the scope of this study as well as the microencapsulation studies using spray-drying because of its popularity (Table 2). It has been reported that the first approach can use a higher oil loading ratio (i.e., 1.8–5.6 g/g) than can

Table 2
Comparison of previous work.

Reference	Core material and encapsulation method	Encapsulation materials	Oil-to-wall ratio (wt/wt)[a]	Drying mode	Overall process yield (%)	Oil content (wt%)[b]	Surface oil (%)	Particle mean size (μm)
This study	Palm oil encapsulated in Ca-alginate beads (extrusion-dripping)	Alginate (high G, $M_v = 9.3 \times 10^4$)	9	Oven-dried (evaporation)	84[c]	79	6.4	1500
			15		79[c]	88	7.9	1640
			9	Freeze-dried (sublimation)	90[c]	80	N.A.	1830
			15		90[c]	86	N.A.	1830
Peniche, Howland, Corrillo, Zaldívar, and Argüelles-Monal (2004)	Fish oil encapsulated in Ca-alginate beads (extrusion-dripping) and coated with chitosan	Alginate (high-M, $M_v = 7.2 \times 10^4$), chitosan	3.8	Dried at room temperature (evaporation)	92	65	N.A.	1400–2000
			5.6		89	70	N.A.	
Chang and Dobashi (2003)	Eucalyptus oil encapsulated in Ca-alginate beads (extrusion-dripping)	Alginate	9–11	N.A.	90–92%	N.A.	N.A.	N.A.
Chan, Lim, and Heng (2000)	Wheat germ oil encapsulated in Ca-alginate beads (emulsification-external gelation)	Alginate, starch	3.5	Fluidized air-dried (evaporation)	88	68	N.A.	84.2
Klaypradit and Huang (2008)	Fish oil encapsulated in chitosan gel-beads	Chitosan, maltodextrin	1.8	Freeze-drying (sublimation)	79–84	N.A.	N.A.	8–11
Tan et al. (2005)	Fish oil encapsulated using spray-drying	Modified food starch	1	Spray-drying (evaporation)	69	N.A.	11	19.5
			1.5		47.8	N.A.	43	18.9
Tan et al. (2009)	Fish oil encapsulated using spray-drying	Modified food starch/alginate	1.5	Spray-drying (evaporation)	40–77	55–78	45–22	18–20
Nunes and Mercadante (2007)	Lycopene dissolved in dichloromethane encapsulated using spray-drying	Gum arabic, sucrose	0.43	Spray-drying (evaporation)	51	N.A.	4	< 10
Fuchs et al. (2006)	Vegetable oil mixture encapsulated using spray-drying	Acacia gum, maltodextrin	0.05	Spray-drying (evaporation)	65	4.5	1.2	24–37
Kim and Morr (1996)	Orange oil encapsulated using spray-drying	Gum arabic, sodium caseinate, soy protein isolate, whey protein isolates	0.3	Spray-drying (evaporation)	N.A.	21–26	0.001–0.003	33–41
Drusch and Berg (2008)	Fish oil encapsulated using spray-drying	n-Octenylsuccinate-derivatised starch and glucose syrup	0.3	Spray-drying (evaporation)	N.A.	~30	1–4	30–50
			0.5		N.A.	~50	6–14	

[a] Weight ratio of oil with respect to dry weight of encapsulation materials used.

[b] % weight of oil to total weight of dry product.

[c] Amount of oil encapsulated in dried beads with respect to original amount of oil.

the latter (typically 0.1–0.5 g/g). It has been found that using high oil loading in the spray-drying process not only decreased process yield, it also increased the surface oil significantly (Drusch & Berg, 2008; Tan et al., 2005, 2009). These effects are undesirable from process economics and product quality viewpoints. Through this study we demonstrated that it is possible to increase the oil loading to as high as 15 g/g and still obtain process yield in the range between 80 and 90%. In comparison, the yield obtained in a spray-drying process is generally between 50 and 70%. Because high oil loading can be used, highly concentrated oil beads or powders containing 65–88 wt% of oil can be produced. The oil concentration is about 2–3 times higher than that produced by spray-drying.

Although spray-drying is a rather inexpensive method to encapsulate oil, the large amount of wall material used and low yield during processing should be taken into account when considering the process economics. On the other hand, the alginate or gel beads encapsulation method involves additional processing steps, which may not be desirable from an industrial point of view because the encapsulation and drying processes have to be performed separately in batch process. Furthermore, the scale-up potential of gel-bead production is still lower than that of the spray-drying process.

However, oil encapsulation using the gel-bead system still has its distinct advantages. For example, its high process yield could be an advantage for encapsulating expensive oil. Also, the process could preserve volatile or easily oxidized compounds because the encapsulation process is normally carried out at room temperature without the use of air. The subsequent drying process can then be customized to avoid product loss or degradation. Other advantages of the process include the possibility of producing highly concentrated oil powders or beads or of controlling the release of oil because Ca-alginate hydrogel is a well known material for controlled-delivery applications. The wet Ca-alginate beads can also be easily coated with biopolymers, such as chitosan, alginate and pectin, under gentle conditions to create single or multiple shells. These flexibilities open up many opportunities for the development of new products.

4. Conclusion

Encapsulation of model oil in Ca-alginate beads using high oil loading has been studied. The alginate-oil emulsion, comprising oil loading up to 30 vol% (equivalent to an oil-to-wall weight ratio up to 15 g/g) and 25 g/L of high G alginate solution, was found to be stable and resulted in an encapsulation efficiency of 90% before drying. The oil-loaded, wet beads were spherical. The overall encapsulation efficiency after freeze-drying and oven-drying were 90% and 79%, respectively, with an oil content of over 85 wt% for both types of dried beads. The freeze-dried beads were non-oily and free flowing, whereas the oven-dried beads were oily and sticky.

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