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Release Kinetics of Encapsulated Herbal Antioxidants during Gelation Process

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Abstract: Dripping-gelation method was used for encapsulation of aqueous herbal extract. This objective of this study was to determine the release kinetics of the antioxidants during the gelation process. The process variables studied were particle size, alginate M/G ratio, concentration, gelling cation concentration and extract strength. Results showed that under all studied variables, a sharp release of the encapsulated antioxidant was observed during the initial gelation period (i.e., in the first 20 min). This amounted to about 80% of the total antioxidants. After this time, the antioxidant release was significantly reduced. In general, the amount of antioxidant that could be retained within the beads after prolonged gelation time was about 10-20%. In conclusion, by using the encapsulation system, prolonged gelation time resulted in about 10-20% encapsulation efficiency.

Key words: Release kinetics, encapsulation, herbal extract, antioxidants, gelation process

INTRODUCTION

Encapsulation could be defined as a process of confining active compounds within a matrix or membrane in particulate form to achieve one or more desirable effects (Chan *et al*., 2009a). Encapsulation of most plant-derived antioxidant compounds such as lycopene, olive leaf extract, Amaranthus betacyanin extracts, β-carotene, d-Limonene and Procyanidins were achieved by using spray-drying method. Generally, the common excipient materials used alongside with this method are limited to maltodextrins, gum Arabic and gelatin (Shu *et al*., 2006; Cai and Corke, 2000; Desobry *et al*., 1997; Rodríguez-Huezo *et al*., 2004; Soottitantawat *et al*., 2003; Zhang *et al*., 2007). Despite the popularity, spray-drying may trigger degradation of active compounds (Shu *et al*., 2006; Cai and Corke, 2000; Desobry *et al*., 1997; Rodríguez-Huezo *et al*., 2004; Soottitantawat *et al*., 2003; Zhang *et al*., 2007; Kosaraju *et al*., 2006). The susceptibility of these compounds to high operating temperature during spray-drying is the major reason of degradation (Cai and Corke, 2000; Lee and Chen, 2002; Saguy *et al*., 1978). Therefore, a mild encapsulation process is needed to encapsulate these heat-sensitive compounds.

Alginates, which are derived from seaweeds, have been extensively used for encapsulation. This is because the encapsulation process that involves the material is simple, mild and non-toxic (Chan *et al*., 2009b). The process does not require complicated instrumentation and it can be performed at ambient temperature and pressure. Moreover, it does not use toxic material nor it produces harmful by-products. The easiest way to encapsulate active compounds within alginate matrix is by using the dripping-gelation method. In this method, alginate liquid droplets containing active compounds are extruded from an orifice and are allowed to fall into a gelling bath under gravity (Chan *et al*., 2009b). The droplets surface will solidify almost instantly when in contact with the gelling bath and the droplets will fully gelled by prolonging the gelation time. This method has been widely used to encapsulate many heat sensitive active ingredients such as living cells, enzymes, drugs and plant extracts (Kosaraju *et al*., 2006; Peppas *et al*., 2000; Deladino *et al*., 2008; Idris and Suzana, 2006; Kailasapathy, 2002; Kulkarni *et al*., 2000; Lin and Metters, 2006; Poncelet *et al*., 1993; Martinesen *et al*., 1989).

The antioxidant compounds of herbal extracts, such as phenolic compounds represented by (-)-epigallocatechin gallate (EGCG); gallic acid, ascorbic acid, naringenin and etc., have small molecular weights of 176-458 and they are mainly water soluble. Since, alginate hydrogel matrix is semi-permeable, the encapsulated antioxidants within the matrix could diffuse to the gelling bath during the gelation process. Consequently, the encapsulation efficiency will be reduced and this will compromise the feasibility of using this method. The absence of knowledge on the antioxidants release during the gelling process has led to the motivation to conduct this study. It is thought that this knowledge will be useful to determine the feasibility of the method or to design process strategy to control the antioxidant release. The

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main objective of this study was to determine the release kinetics of the antioxidants during the gelation process. The process variables studied were particle size, alginate M/G ratio, concentration, gelling cation concentration and extract strength.

MATERIALS AND METHODS

Materials: Sodium alginates of high guluronic acid content (guluronic acid 63%, mannuronic acid 37%) (Manugel GHB, UK), denoted as high-G and high mannuronic content (mannuronic acid 61%, guloronic acid 39%) (Manugel DH, UK), denoted as high-M were obtained from ISP Technologies Inc., UK. Meanwhile, P. sarmentosum aqueous extracts were prepared by Furley, Malaysia.

Effect of process conditions on the release kinetics: Figure 1 shows the experimental setup of dripping-gelation method. In brief, the alginate solution containing aqueous extracts was prepared and filled into a syringe. The solution was allowed to drip into gelation bath containing calcium cations under gravity. The process variables studied is shown in Table 1.

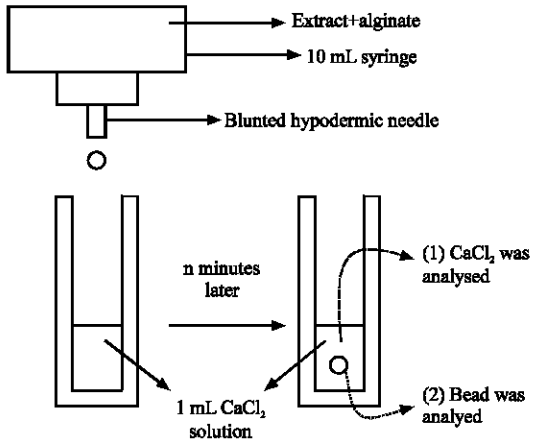

Fig. 1: Experimental setup for dripping-gelation method

Table 1: Process variables of this study

No	Algin-ate type	Algin-ate concentration % (w/v)	Bead diameter (mm)	Extract strength*	$CaCl_2$, % (w/v)
1	High-M	2	2.2	1x	1.5
2		2			
	High-G	3	2.2	1x	1.5
		4			
3	High-G	2	2.2	1x	1.5
			3.5		
4				0.50x	
	High-G	2	2.2	0.75x	1.5
				1x	
5					1.5
	High-G	2	2.2	1x	7.5
					15

*1x designates original strength of *P. sarmentosum* aqueous extract

The *P. sarmentosum* herbal extract was diluted with deionised distilled water to prepare extract of lower strength. The size of the beads was varied by using capillary of different diameter. The herbal antioxidant contents within the beads and diffused into the gelation bath were quantified at different time intervals to determine the release kinetics of antioxidant during the encapsulation process.

Quantification of encapsulated antioxidants: Based on existing method, an improved DPPH method for quantification encapsulated herbal antioxidant was used (Yim *et al*., 2009). In brief, contents of encapsulated antioxidant were determined by first disintegrating the gelled matrix by mechanical crushing and followed by dilution with appropriate amount of distilled water. Eighty microliter of the sample was added into 3 mL of reagent solution containing 2,2-Diphenyl-1-picryl-hydrazyl (DPPH) (Sigma, USA) and ethanol (Fluka, USA). The mixture was then allowed to react for 40 min and its absorbance was measured at a wavelength of 515 nm by using a spectrophotometer (Thermo Electron Corporation, USA). The antioxidants contents were calculated based on Ascorbic Acid Equivalent (AAE) by referring to a developed calibration diagram.

RESULTS AND DISCUSSION

Release kinetics of antioxidants: Figure 2 shows the effect of the process variables on the release kinetics of herbal antioxidants during gelation. In this study, the antioxidants contents encapsulated within the hydrogel matrix and released to the gelation bath were quantified. In all cases, a sharp release of the encapsulated antioxidant was observed during the initial gelation period (i.e., in the first 20 min). This amounted to about 80% of the total antioxidants. After this time, the antioxidant release was significantly reduced. In general, the amount of antioxidant that could be retained within the beads after prolonged gelation time was about 10-20%. Varying the process variables did not obviously increase the encapsulation efficiency although, some marginal improvements could be observed in some cases.

The rate of release of antioxidant from the beads could be explained by the concentration gradient and the different stages in the bead formation process. During the initial gelling period, the rapid release of antioxidant was due to the large concentration gradient between the internal bead and the external medium. In addition, the thin gel-layer that was instantly formed at the drop surface at this stage could not create an effective mass transfer barrier to slowdown the release. The gel network

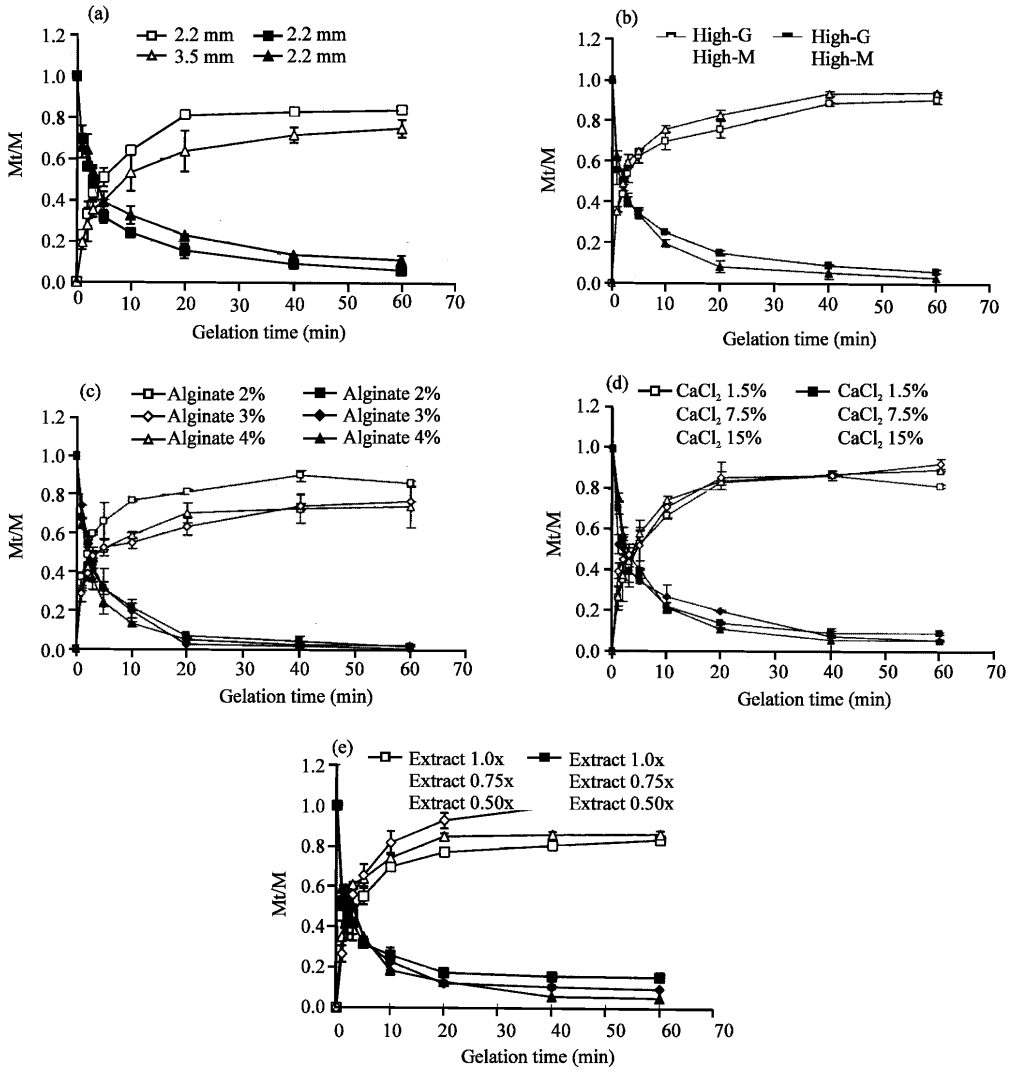

Fig. 2: Effect of (a) bead size, (b) alginate type, (c) alginate concentration, (d) CaCl2 concentration, (e) extract loading or strength on the release kinetics of herbal antioxidants during gelation (Opened and closed symbols represent the antioxidant contents in the gelation bath and within the bead, respectively)

could also be loose and may have large molecular cut-off. When the gelling period was prolonged, the rate of release decreased because the concentration gradient has become smaller. At the same time, the resistance to mass transfer has increased due to the formation and consolidation of gel networks throughout the beads.

In order to retard the release of antioxidant during the initial gelation stage, it was thought that the mass transfer resistance of the beads could be increased by manipulating process variables such as increasing the alginate and cation concentration. This should create higher and faster degree of cross-linking between the alginate polymeric networks and cations. However, the changes in the bead properties were not able to slowdown the release kinetics. This shows that the release kinetics was primarily driven by the concentration gradient. One way to solve this problem is by pre-loading the antioxidant into the gelation bath in order to reduce the concentration gradient between bead and gelation bath. As demonstrated by Moses *et al.* (2000), this strategy improved the encapsulation efficiency by reducing the release of the active compounds during gelation. However, the main disadvantage of this method is the hold-up of active compounds in the gelation bath. This method may not be feasible if it involves large volume of gelation bath or expensive active compounds. Another way to increase the encapsulation efficiency is through absorption with blank calcium alginate bead, as reported

in our recent work (Yim *et al*., 2009). This technique is particularly suitable for aqueous extract which has low molecular weight.

Shorter gelation time would be the only most effective process condition to preserve most of the herbal antioxidants within the encapsulated matrix. In this case, the gelation time has to be less than 5 min to yield encapsulation efficiency of 50% and above. This is possible if the beads can be harvested immediately, provided the beads have adequate strength for handling.

CONCLUSION

In conclusion, by using the encapsulation system, about 80% of the antioxidant encapsulated within ca-alginate beads was released during the initial gelation period. Prolonged gelation time resulted in about 10-20% encapsulation efficiency. The release kinetics was primarily driven by the concentration gradient. An ideal encapsulation system should offers attributes such as high encapsulation efficiency and technically simple. Low encapsulation efficiency may lead to wastage of active compounds or usage of more encapsulating materials, thus increase the operating cost. Moreover, the final encapsulated product may contain little amount of active compounds and this may affect the product effectiveness. Therefore, appropriate measures have to be taken to increase the encapsulation efficiency of this system.

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