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FULL PAPER

Effect of stirring to produce ferric saccharide capsules with alginate coating

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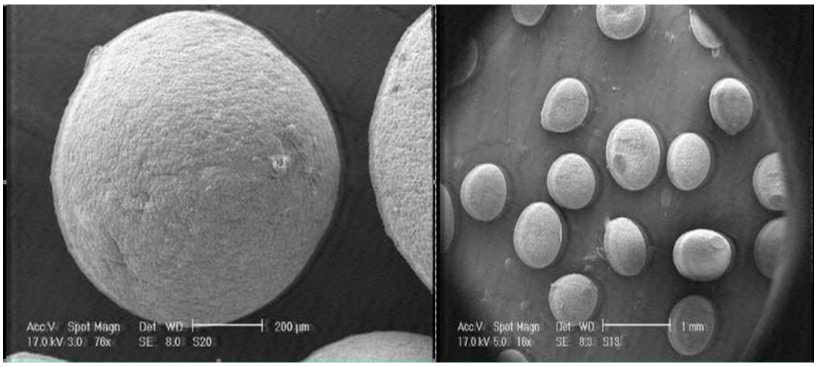
ABSTRACT: The present study focused on the effect of stirring to produce ferric saccharide capsules with alginate coating applying the coacervation method, enabling us to obtain the best capsules for fortification of hydrated and dehydrated food products. At first, three methods including, stirrer, ultra-sonic, and sonic bath were compared to find out the best way of stirring. The results showed that the turning provided by the stirrer method resulted in capsulation with spherical morphology and uniform distribution of surface. Other factors such as the alginate and calcium salt concentration were investigated, as well. After studying the various conditions, it was suggested that the best capsules were formed in alginate 3% at 500 rpm with the concentration of calcium chloride salt of 1M. The capsules produced by this method had a high efficiency and were more stable in hydrated and dehydrated food ingredients network for a long time.

KEYWORDS: Microcapsules, Coacervation, Ferric saccharide, Alginate, Ultra-sonic.

GRAPHICAL ABSTRACT:



1. Introduction

One of the reasons of iron deficiency in third world countries is less iron fortification of food ingredients. Iron encapsulation is one approach of fortification, protecting iron against the instability which results in a better processing (improvement in solubility, dispersion, and allegiance), increase of iron life by preventing from decomposition reaction (oxidation), control, stability, timely releasing, safe, and proper handling, covering and protection against odor or taste and destructive materials, as well [1-5, 35].

Capsules consist of two parts of core and coating in which core contains active compound and coating plays a protective rule for core. The proper selection of core, coating and method in encapsulation can lead to elimination of many requirements and cost reduction [6-8]. Therefore, ferric saccharide iron was chosen due to its high bioavailability and high absorbance power (absorbency) which is in the second group

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of iron compounds and is less soluble in water but soluble in acidic conditions, with higher absorbance power and the less apparent problems than the first group. On the other hand, ferric saccharide as a chelating agent binds to the iron cation, Fe (II) or Fe (III) and keeps it from precipitating due to a basic pH or to any other compound, which traps and precipitates iron, so improve iron absorption [9-13].

Calcium alginate is a natural fiber extracted from the food algae with high nutritional value is water-insoluble with adhesive property which at room temperature and neutral pH forms. This fiber has an even and clear layer around the core to protect iron against its surrounding environment. morever release it purposefully in the gastrointestinal tract resulting in the increase of absorbance power and reduction of the organoleptic problems in food ingredients, more over due to its insoluble property in aqueous environment can be used in hydrated and dehydrated food fortification [14-17].

The method of coacervation was applied to produce the ferric saccharide capsules with alginate coating. Water-soluble alginate salt such as sodium carrying carboxylic groups which is able to create complex with metallic polyvalent ions.

When a water-soluble iron salt comes in contact with a water-soluble alginate salt, cross- linking of carboxylic groups of alginate will take place by reaction with the iron cations, such as Fe^{+2} or Fe^{3+}.

When a core comprising iron alginate comes in contact with an aqueous solution of calcium salt, a capsule (formed by the core covered with an outer layer comprising calcium alginate) will form by the reaction of the alginate salt with the calcium cations. The outer layer would not soluble in water or in weak acids, avoiding the contact of iron with the environment while increasing the mechanical strength of capsules [15, 19, 34, 36].

In the coacervation method, it is possible to achieve micro and nano capsules by setting the header (iron-alginate solution is removed from it). Micro-Nano capsules are used in the enrichment of hydrate and dehydrate foods. For instance, the presence of nano-capsules in the enrichment of milk products is essential, because the size of the capsules should be equal to the size of the fat molecules in the milk. Until the homogenizer process, there is no change in the uniform phase of milk and milk products. In addition to size, spherical morphology and uniform size distribution in capsules are important for enrichment of materials. Because, the capsules with spherical morphology and uniform distribution will have a significant effective on creating homogeneous and uniform tissue in the enriched foods. Whereas, the contact between the iron-alginate core and aqueous solution of calcium affects the size, morphology, and surface distribution of capsules. Therefore, in this study providing contact in three methods of stirrer, ultra-sonic, and bath sonic was investigated.

Materials and methods

Sodium alginate salt with an average viscosity (Cas.no. 9005. 38.3) was purchased from Sigma Aldrich (Germany) and calcium chloride ($CaCl_2$) with average

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molecular mass of 147.02 (Cas .no -2380-Merck, Germany). Ferric saccharide iron with an average molecular mass of 45200Da (Cas.no .8047-67-4, Shanghai Boyle Chemical Company, China). All other chemicals used in this research study were agent grade. Ultra-pure water from Mili-Q water system was used to prepare the aqueous solutions.

For Preparation of micro/nano capsules, Alginate 1.5% is added to 0.798g Ferric saccharide iron (coating to core ratio:70/30) at the high rotation of stirrer to form uniform solution of alginate iron, then this alginate solution is added to the solution of calcium chloride salt(as small as the nozzle head, small capsules will be created from micro to nano) under three conditions of stirrer , ultra-sonic and sonic bath [18, 19].

The solution of alginate –iron was added drop wise to 300 Ml of calcium chloride salt 1M at 500 rpm. Upon adding the iron-alginate solution, calcium ion replacement to sodium took place consequently, capsules formed in calcium alginate coating.

After capsulation, they were filtered three times under vacuum condition and were washed three times with water which was distilled twice till all the existing free ions on the capsules were washed away finally they were dried.

Alginate- iron solution was added drop wise into the beaker which includes 300 Ml of 1M cacl$_2$ and a sonic probe is located inside it. In this case stirring was provided with sonic, after capsulation they are filtered under vacuum condition and were washed with water which was distilled twice, afterwards they were collected and were dried.

The alginate-iron solution was added to calcium salt in the sonic bath. This solution was added drop wise and slowly to the beaker which contained 300Ml of CaCl$_2$ 1M and was located inside the sonic bath to form capsules then they were washed and dried.

The morphological characteristics of the micro-particles were examined by scanning electron microscope (JSM-5900Lv, JEol, Japan). The micro-particles were sputtered using gold and maintained at room temperature to complete dryness before the observation. The particle size distribution was detected using laser diffraction (nano-ZS90, Malvern Instrument, UK; BT-2002 laser particle size Analyzer, Dandong Better Size Instruments LTD, China). The zeta analyzer (Nano-ZS90, Malvern Instrument; UK) with ultrapure water as solvent (PH=7, 25 ^{O}C).

The loading efficiency (LE) value was calculated using the Equation 1.

$$LE\ (\%) = \frac{\text{Total amount of Fe} - \text{free Fe}}{\text{Total amount of Fe}} \quad \text{(Equation 1)}$$

When capsules were being washed at centrifuge, every times the existing water on the capsules was threw away and replaced with a new water ,by measuring the iron exists in washing water on the capsules using spectrophotometer, the free iron can be calculated. The ability of the capsules to avoid the release of its payload during the storage was tested in different conditions, close to those that can be found in different media to be supplemented with the capsules. The capsules were storage at room

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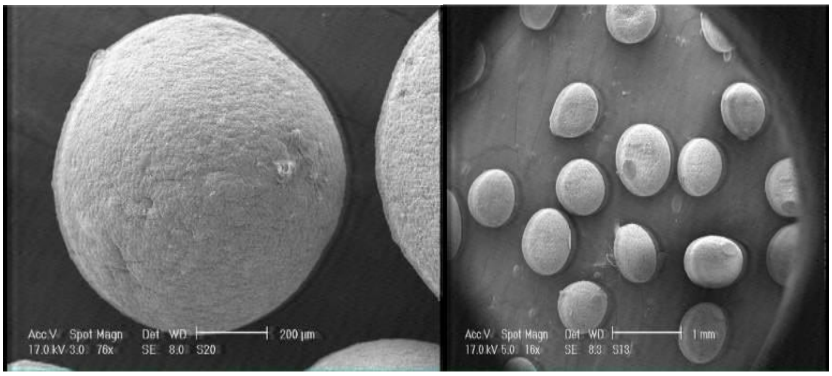
temperature, in aqueous solution and solid capsules. The two different conditions regarding the water content were chosen to simulate the two extreme environments that the capsule are most likely to face: liquid food stuffs or food stuffs with a high content of water, and dry food stuffs or food stuffs with a low content of water. By weighing about 100 mg of capsules and adding 15 ml of distilled water.

Each sample was kept sealed at room temperature for 0, 0.5, and 1 month. After 0, 0.5, and 1 month, 15ml of the distilled water was added to the "solid capsules" samples. All the samples analyzed were then filtered to remove the solid, and the released iron was quantified in the supernatant by spectrophotometer.

Result and discussion

Effect of Stirring by Stirrer, Ultra-sonic, and Sonic Bath-Stirrer

Upon adding the solution of alginate-iron to calcium salt solution which was turning uniformly on stirrer, ionic exchange took place and this uniform turning caused to form more fine capsules (400 µm), with spherical morphology and uniform distribution of surface. The SEM results are presented in Figure 1.



Figu. 1. Spherical morphology and uniform distribution of prepared capsules by the bath-stirrer.

Ultra-Sonic

Since the contact between iron salt-alginate solution and $CaCl_2$ salt under ultra-sonic condition, is violent with pulse, creates rapid movement and contact and this factor resulting in non- uniform distribution of surface and change in capsules spherical morphology (average size of 450 µm (Figure 2).

The solution of calcium salt moves slowly in the sonic bath and this slow stirring leads to form capsules with wider and larger average size (average size of 500 µm, the SEM result of sonic bath is presented in Figure 3.

Determination of the average particles size in three situations is presented in Table 1 and Figure 4.

In every three methods, efficiency was high and almost constant (Table1). But by comparing the morphology (Figure 1, 2, and 3) and particles size distribution (Fig. 4), it

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was seen that mixing by stirrer produced capsules with more spherical morphology, uniform distribution of surface, and partly smaller than the other two methods. Ronald *et al.* (1988), Dong *et al.* (2007), Yuri Pessoal Lemos *et al.* (2017), and Alavitalab *et al.* (2010) also used the stirrer for turning in coacervation method to obtain better results [21-24].

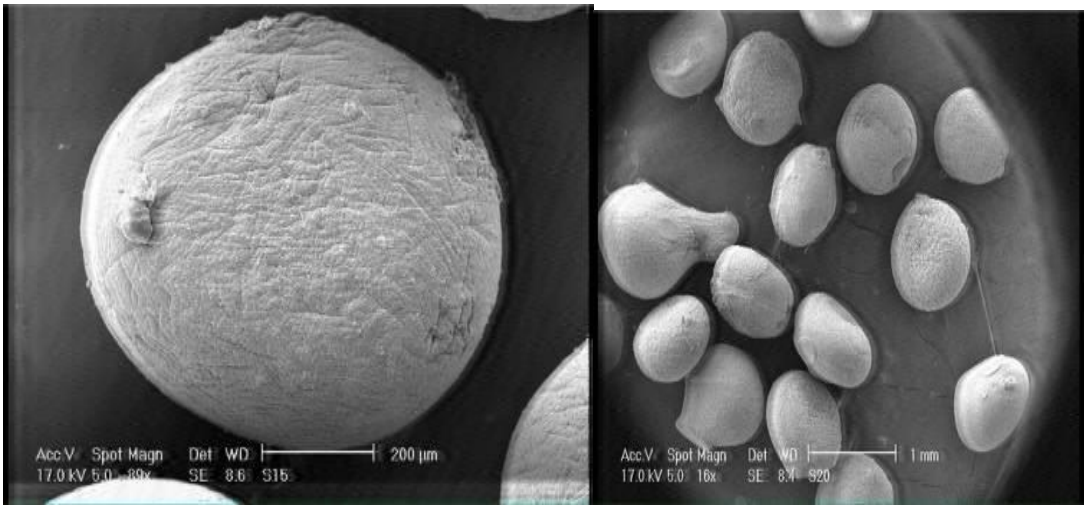

Fig. 2. Spherical morphology and uniform distribution of prepared capsules by ultra-sonic condition.

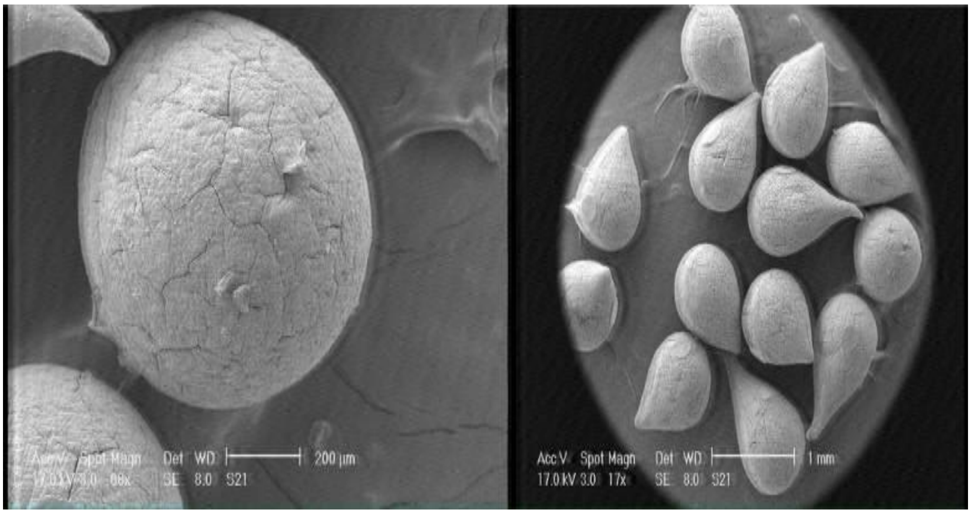

Fig.3. Spherical morphology and uniform distribution of prepared capsules by sonic bath.

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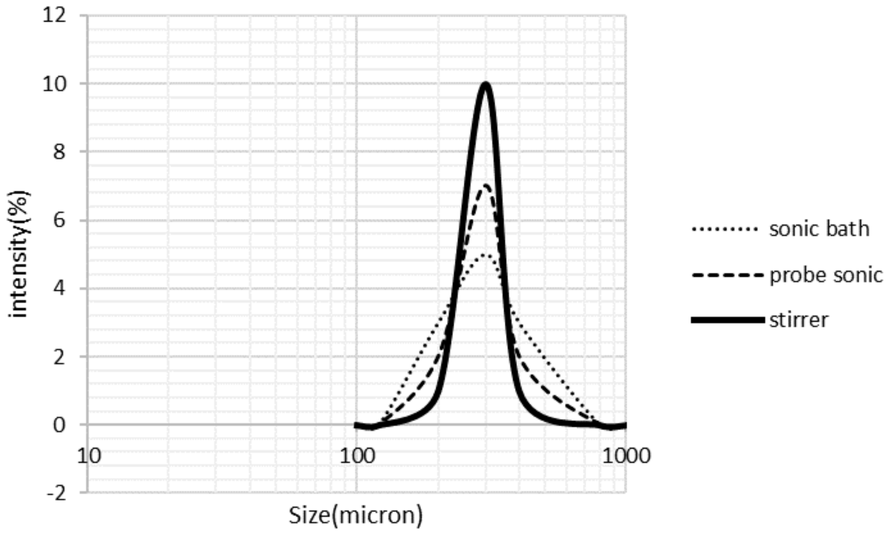

Fig.4. Effect of the agitation on the Particle size distribution of micro capsules.

Table1. Effect of the agitation in various situations on the Particles size distribution of micro capsules

Sample	Mean Diameter(Micron)	PDI	Zeta potential (mv)
Stirrer	400	0.2	47.6
Ultra sonic	480	0.28	46.2
Bath sonic	520	0.31	46

Effect of different concentration core/wall ratio

By increasing the core/wall ratio, the morphology of micro capsules changed from spherical to irregular and the mean particle size gradually increased and the particle size distribution became wider (Figure 5 and 6). Similar conclusions also archived by Annan *et al.* (2007), Yili *et al.* (2008), J. Dong *et al.* (2007), A Kanellopoulos *et al.* (2017), and Alavitalab et al. (2010) [15, 16, 22, 25].

So, in accordance with the results of the SEM (Figure 5) and the particle size distribution of micro capsules (Figure 6), it can be concluded that the capsules that were obtained in by core/wall=1/4 are better.

-Effect of the different concentration of $CaCl_2$ on the formation and stability of micro capsules

As the results showed, increasing the concentration of $CaCl_2$ produced better capsules. The test of particles size distribution was performed at two various conditions of alginate (Table 2).

As shown in Table 2, as the $CaCl_2$ Concentration increases, the strength (Zeta potential) of the capsules increases, the best result achieved at the Alg 3% $CaCl_2$ 1M, Speed rotation(500 rpm) Fe(0.798 gr). The release of iron and calcium from the capsules was used as an indicator of the capsule stability. The release of iron and calcium are demonstrated in Figure 7.

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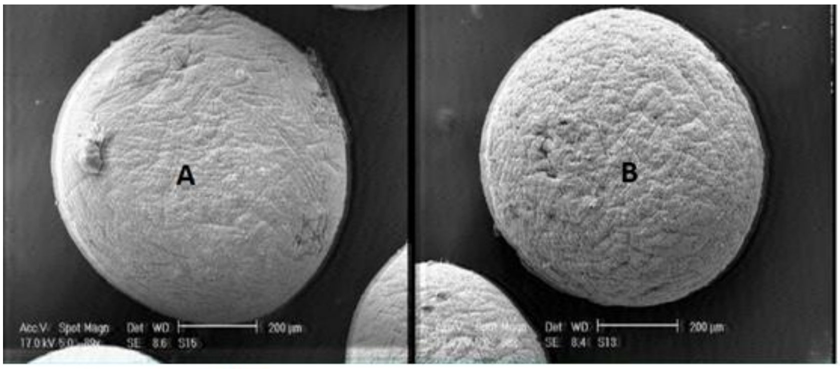

A: core/wall=1/2 **B: core/wall=1/4**

Fig.5. Effect of the increase core/wall ratio on the morphology of micro capsules. ($CaCl_2$ 1M and stirring speed of 500 rpm).

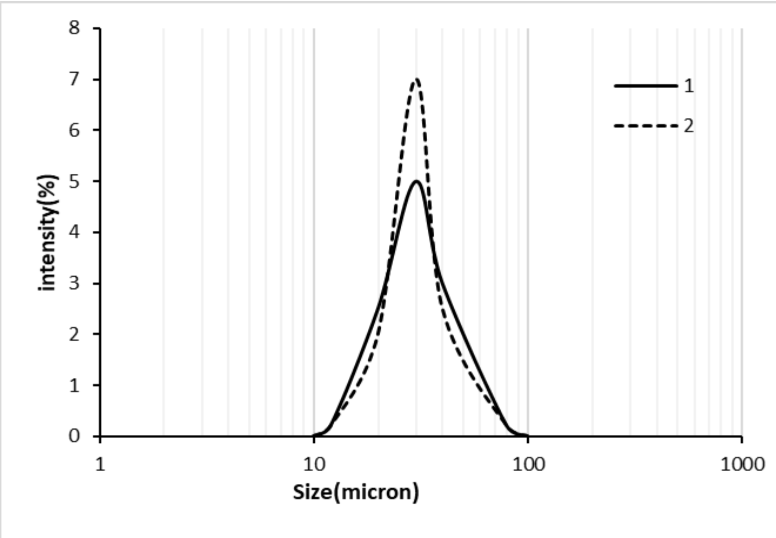

Fig. 6. Effect of the increasing core/wall ratio on the particle size distribution of micro-capsules (1- Alg 1/5%, Fe: 0.798 gr, 2- Alg 3%, Fe: 0.798gr, $CaCl_2$ 1 M & stirring speed of 500 rpm).

Table 2. Effect of the different concentration of $cacl_2$ and Alginate on the particle size distribution of micro capsules (Fe: 0.798 gr and stirring speed=500 rpm).

Sample	$CaCl_2$ (m)	Mean particle size (micron)	PDI	Zeta potential (mv)
Alg 1.5% Fe 0.798 gr	0.05	412.1	0.499	12.5
Alg 1.5% Fe 0.798 gr	1	410	0.450	22.5
Alg 3% Fe 0.798 gr	0.05	405.2	0.393	27.1
Alg 3% Fe 0.798 gr	1	400	0.34	34

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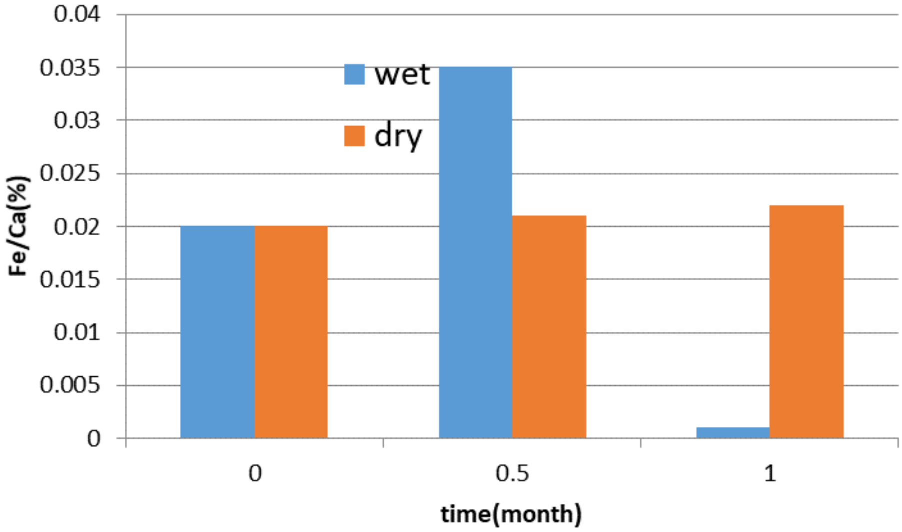

Fig. 7. Iron and calcium Release in different conditions of storage.

The less iron released, the better the ability of the capsules to keep the payload with in the capsules, and to protect the environment from being degraded by the iron, and the iron from being captured by the environment. By comparing the release rate in different conditions it can be seen how the presence of water affect the stability of the capsules as, having more water in contact with the capsules increase the release rate.

The fraction of calcium released into the environment is larger than that of iron, showing that the ability of the capsules to keep the metal inside is much better for the iron than for the calcium. The release of calcium indicates that most probably the capsules get worn out with time, but as calcium is more accessible than iron, calcium is first released into the environment.

The studies of the other researches revealed that in microencapsulation, the presence of outer layer act as a coating protect the core from interaction with the environment and the more aqueous environment , the faster is releasing of capsules than the dry conditions .Since, so far more capsulations was performed in dry conditions. Similar conclusions were also archived by Roya Bagheri *et al.* and Hoda Alipour Mazandrani *et al.* [32-33]

But in the present study, the presence of alginate coating due to it is insoluble property in aqueous environment , protect the core for a long time and it is storage changes is not much different in dry or wet conditions. The resulted capsules by this method had a high efficiency and were more stable in hydrated and dehydrated food ingredients network for a long time.

Conclusion

In the present study, the capsules contains ferric saccharate core produced with high absorbance power with alginate coating which has a high nutritional value and is insoluble in water. Therefore these capsules can extend the enrichment range of food ingredients and can be used in hydrated and dehydrated food fortification, since they are stable for a long period of time in the food matrix. They are also able to release the soluble iron component when they enter the gastrointestinal tract. The results showed that the best contact for producing the capsules with spherical morphology and uniform surface distribution in three methods of stirrer, ultra-sonic, and sonic bath at the coacervation method was provided using stirrer. Thus, the other significant factors in this method such as the effect of alginate concentration, iron calcium chloride salt were studied and it was observed that the stable capsules with spherical morphology and uniform surface can be produced at concentration of alginate 3% and calcium salt 1M at 500 rpm.

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