Microencapsulation of spices with Methylcellulose/alginate/methylcellulose and the components stability during storage

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Microencapsulation of spices with Methylcellulose/alginate/methylcellulose and the components stability during storage

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Abstract: Composite core material (2-Phenethyl alcohol/Cinnamaldehyde/β-ionone) microcapsules were prepared by spray drying using amphiphilic methylcellulose (MC) as the emulsifier and interior wall material, alginate (ALG)/methylcellulose (MC) as the composite external wall materials to embed core materials and improve the stability of core materials. The release of core material of the microcapsules and composition changes of core material during storage and the protective effect of microencapsulation on core materials was also analyzed.

1. Introduction
Microencapsulation is a micro-packaging technique for storing trace amounts of core material (solid, liquid, or gas) in polymer films [1]. Microencapsulation of the active substances can control the oxidation reaction, cover the smell and color, provide sustained and controlled release, increase shelf life, etc. [2,3]. Microencapsulation has been widely used in the fields of medicine, pharmacy, biotechnology, food, and agriculture due to its wide application prospects [4].

The common embedding techniques in microencapsulation are spray drying, emulsification, extrusion, complex aggregation, fluidized bed, freeze-drying, electrospinning, etc. [5,6]. In a variety of microencapsulation methods, spray drying is economical and flexible. With its low cost and simple operation has been considered to be widely used. The core material is about 50-80°C during spray drying, which makes spray-drying a good choice for drying temperature-sensitive material [7]. Encapsulation efficiency of microcapsules has much to do with wall materials. The emulsifying ability of wall material is of crucial importance. Methylcellulose is an amphiphilic polymer emulsifier. It could be used as both an emulsifier and the wall material. We found methylcellulose (MC) can increase the microencapsulation efficiency of tea tree oil in our previous paper [8].

2-Phenylethyl alcohol, cinnamaldehyde and β-ionone are spice materials which are prone to volatilize and oxidize [9]. The main aims of this study were to prepare composite core material (2-phenylethyl alcohol/cinnamaldehyde/β-ionone) microcapsules by spray drying using amphiphilic methylcellulose (MC) as the emulsifier and the interior wall material, alginate (ALG)/methylcellulose (MC) as composite external wall materials and improve the stability of core materials. The release and composition changes of core material of microcapsules during storage will also be investigated to analyze the protective effect of microencapsulation on core materials.
2. Experimental

2.1. Materials
2-Phenethyl alcohol (100 mL, 99.0%, GC), cinnamaldehyde (100 g, 95.0%, GC), β-ionone (100 mL, 97.0%, GC), MC (400 mPa.s) and sodium alginate (ALG, 200±20 mPa.s) were purchased from Aladdin Industrial Corporation (Shanghai, China). Anhydrous ethanol was purchased from Guangzhou Reagent Company (China). All the materials were used as received.

2.2 Preparation of composite core material (2-Phenethyl alcohol/Cinnamaldehyde/β-ionone) microcapsules
1.0 g of MC was dissolved in 50 mL deionized water. Composite core material (1.5 mL of 2-Phenethyl alcohol, cinnamaldehyde and β-ionone, respectively) was well mixed and dropped into MC solution. Then, 3.0 g of ALG dissolved in 180 mL deionized water was dropped into above composite core material/MC emulsion. Finally, 1.0 g of MC dissolved in 50 mL deionized water was dropped into above composite core material/MC/ALG emulsion. The emulsion was stirred at 10,000 rpm all the time. The composite core material/MC/ALG/MC emulsion was dried by a spray-drier (YC-015, Shanghai Yacheng Instrument Co. Ltd.) to obtain the microcapsules.

2.3 Characterization of composite core material microcapsules
The structure of composite core material microcapsules, microcapsules without any core material and composite core material microcapsules were characterized by a FTIR Spectrometer to investigate the embedding of microcapsules. Appropriate amount of microcapsules and KBr crystals were grinded and tableted. When test the composite core material, 2-Phenethyl alcohol/cinnamaldehyde/β-ionone was smeared on the pressed KBr crystals tablet. The test was performed in the scan range of 4000-400 cm⁻¹ by a Tensor 27 FTIR spectrometer.

2.4 In vitro release studies
In order to observe the release properties of the composite core material microcapsules, in accordance with the pre-set time interval, x g composite core material microcapsules stored in sealed bags were put into 25 mL anhydrous ethanol. After sonication for 1 h, the filtrate was used to analyze the content of microcapsules by GC. The 2-phenethyl alcohol, cinnamaldehyde and β-ionone content of microcapsules were calculated according to the equation (1), (2) and (3), respectively.

\[
\begin{align*}
W & = 2.5 \times \frac{y + 0.7971}{0.2689} \times \frac{10}{x} \quad (1); \quad y = 2.5 \times \frac{y + 0.9333}{0.2750} \times \frac{10}{x} \quad (2); \quad y = 2.5 \times \frac{y + 0.9219}{0.2954} \times \frac{10}{x} \quad (3)
\end{align*}
\]

Where, W was the core material content; y was the peak area; x was microcapsule mass.

2.5 The composition changes studies
Compare the composition changes of core material before and after microencapsulation to further investigate the protection of microencapsulation on core materials. Composite core material and composite core material microcapsules were put into the same conditions (sealed plastic bag) for storage. At specific time interval, put 0.1 g sample out into 25 mL anhydrous ethanol. After sonication for 1 h, the filtrate was used to analyze the composition changes of samples by GC-MS.

3. Results and Discussions

3.1 Characterization of composite core material microcapsules
The structure of composite core material microcapsules, microcapsules without any core material and core materials were characterized by FTIR. The infrared spectrum was shown in Fig. 1. Fig. 1 (a), (b), (c), (d) and (e) corresponded with the composite core material microcapsules, microcapsules without any core material, β-ionone, cinnamaldehyde and 2-phenylethanol, respectively. The C=O of β-ionone
and cinnamaldehyde had a stretching vibration peak around 1730 cm\(^{-1}\) in Fig. 1 (c) and (d). C-H of cinnamaldehyde had a stretching vibration peak at 2750 cm\(^{-1}\) in Fig. 1 (d), it was an important characteristic that distinguished aldehydes and ketones [10]. In Fig. 1 (c), there was a C=O stretching vibration peak at 1680 cm\(^{-1}\). In Fig. 1 (d) and (e), there was a C-O stretching vibration peak on benzene ring at 3010 cm\(^{-1}\). In Fig. 1 (e), there were two C-O bending vibration peaks on benzene ring of 2-phenylethanol at 745 cm\(^{-1}\) and 699 cm\(^{-1}\). The characteristic absorption peaks shown in above curves can be matched with the chemical structure of all materials during microencapsulation. It means microencapsulation of the core material achieved a well entrapment.

![Figure 1 FT-IR spectra of microcapsules and core materials](image)

**Figure 1** FT-IR spectra of microcapsules and core materials (a. composite core material microcapsules; b. microcapsules without any core material; c. β-ionone; d. cinnamaldehyde; e. 2-phenylethanol)

### 3.2 In vitro release studies

Fig. 2 expressed the core material release of the microcapsules with different pre-set time interval. According to Fig. 2, Fig. 2 (a), (b) and (c) represented the release of 2-phenylethanol, cinnamaldehyde and β-ionone in the composite core material microcapsules, respectively. The content of 2-phenylethanol in the newly prepared composite core microcapsules was 0.65%. The release of 2-phenylethanol was fast during the first 3 days, it was because a part of 2-phenylethanol remained on the surface of the microcapsules during spray drying. In the next 12 days, it was due to the capsule-wall of the microcapsules played a protective role on the inner core material, thus the release of 2-phenylethanol was slower. After 15 days of storage, the capsule wall of the microcapsules was affected by the environment and resulted in the core material of microcapsules released faster. The content of cinnamaldehyde in the newly prepared composite core microcapsules was only 0.49% in Fig. 2 (b). That was due to MC has a less emulsifying effect on cinnamaldehyde. At the same time, the low total embedding content resulted in the slow release rate during storage. The content of β-ionone in the newly prepared composite core microcapsules was 1.97% in Fig. 2 (c). At the first 6 days, the release of β-ionone was very fast, it was due to a part of β-ionone remained on the surface of the microcapsules during spray drying. In the next 24 days, its release speed slowed down. That was due to the increased mass transfer resistance that β-ionone needed to release from inside of microcapsules [11].
3.3 The composition changes Studies

Core materials are easily affected by the environment (oxygen, temperature, humidity, etc.) and have oxidation or cyclization to influence its quality [12]. The composition changes of core material (2-phenethyl alcohol, cinnamaldehyde and β-ionone) before and after microencapsulation were compared. The fresh core material (2-phenethyl alcohol/cinnamaldehyde/β-ionone) along with the composite core material microcapsules was analyzed by GC-MS. Fig. 3 showed the total ion chromatogram of core material at different time (A. 0 d; B. 7 d) and composite core material microcapsules at different time (C. 7 d; D. 15 d). After the core material was placed for 7 days, some new materials appeared. However, after the microcapsules were respectively placed for 7 days and 15 days, there only appeared traces of these above impurities. Until they stored for 15 days, a larger amount of the above impurities appeared in the composite core material microcapsules.
Table 1 was a summary of the component changes of core material and the composite core material microcapsules. The core material contained little or no impurities at first, there were some composite changes after 7 days of storage at room temperature. 2-Phenylacetaldehyde, 1-phenethyl alcohol, cinnamic acid, 2-indanol, isomethyl ionone, 4-hydroxy-β-ionone, dihydrogen kiwi lactone, 4-oxo-β-ionone and other substances appeared. Fig. 4 showed the results of the component analysis (exclude the main components) identified by total ion chromatogram. Core material placed alone in the environment was prone to deteriorate. 2-Phenylacetaldehyde, 1-Phenethyl alcohol were come from 2-phenyl ethanol. Cinnamic acid and 2-indanol were come from cinnamaldehyde. Isomethyl ionone, 4-hydroxy-β-ionone, dihydrogen kiwi lactone, 4-oxo-β-ionone were come from β-ionone. Their reaction and principle were shown in Fig. 5. In Table 1, the metamorphic rate of core material was significantly slow down after microencapsulation due to wall material of microcapsules can block the direct and adverse impact of environment to extend the shelf life of the core material.

| Table 1 Composition changes of core material and composite core material microcapsules |
|---------------------------------|-----------------|-----------------|
| **Series** | **Retention time** | **Compound name** | **Area percentage** |
| Fresh core material | 10.013 | 2-phenyl ethanol | 18.93 |
| | 13.833 | cinnamaldehyde | 5.55 |
| | 18.576 | β-ionone | 75.76 |
| New substances of core material after 7 days | 7.900 | 2-phenylacetaldehyde | 1.01 |
| | 8.293 | 1-phenethyl alcohol | 1.99 |
| | 14.704 | 2-indanol | 0.63 |
| | 16.529 | cinnamic acid | 0.36 |
| | 16.551 | isomethyl ionone | 1.01 |
| | 19.442 | dihydrogen kiwi lactone | 0.59 |
| | 21.303 | 4-hydroxy-β-ionone | 0.12 |
| | 22.08 | 4-oxo-β-ionone | 5.48 |
| Composite microcapsules 7 days later | 10.065 | 2-phenyl ethanol | 21.29 |
| | 13.792 | cinnamaldehyde | 13.62 |
| | 16.792 | cinnamic acid | 1.15 |
| | 18.517 | β-ionone | 64.52 |
| New substances of composite | 7.900 | 2-phenylacetaldehyde | 0.55 |
| | 8.293 | 1-phenethyl alcohol | 1.41 |
|                | Microcapsules after 15 Days |
|----------------|-----------------------------|
| 2-indanol      | 14.704                      |
| Cinnamic acid  | 16.529                      |
| Ectopic ionone | 16.551                      |
| Dihydrogen kiwi lactone | 19.442       |
| 4-Hydroxy-β-ionone | 21.303       |
| 4-Oxo-β-ionone | 22.08           |

Figure 5 Reaction mechanisms of 2-phenylethyl alcohol, cinnamaldehyde and β-ionone

4. Conclusions
Composite core material (2-Phenethyl alcohol/Cinnamaldehyde/β-ionone) microcapsules were prepared through spray-drying, using amphiphilic methylcellulose (MC) as the emulsifier and the interior wall material, alginate (ALG)/methylcellulose (MC) as the composite external wall materials. In the composite core material microcapsules, the content of 2-phenethyl alcohol, cinnamaldehyde and β-ionone was 0.65%, 0.49% and 1.97%, respectively. The release of single core material was not affected by other core materials. The release of core material was fast in the early days and slowed down in late period due to the barrier effect of capsule-wall of microcapsules during storage. Core material of microcapsules was vulnerable to deteriorate because of the moisture, temperature, oxygen and other adverse environmental factors. Microencapsulation not only has the effect on controlling core release slow, but also the capsule-wall of microcapsules can obstruct the direct and adverse influence of environment and extend the shelf life of core materials.

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