Preparation Technics and Properties Research of Peppermint Essential Oil Microcapsules

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Abstract: Peppermint essential oil is widely used in food industry, but it is easy to be oxidized. In order to improve its oxidation stability, the peppermint essential oil microcapsule was prepared by single factor experiment and response surface optimization experiment in the paper. The effect of core wall ratio, pH value of complex coagulation and agitation speed on the embedding rate of peppermint essential oil microcapsules was studied respectively. The optimum experimental conditions were obtained as follows: core wall ratio, 1.9:1; pH value of complex condensation, 4.0; and the optimal agitation speed, 400r/min. The maximum embedding rate of peppermint essential oil microcapsules was 89.67%. POV value showed that the oxidative stability of peppermint essential oil microcapsules was significantly higher than peppermint essential oil.

1. Introduction

Microencapsulation technology is the use of natural or synthetic polymer compounds to form a film, the core material is embedded in a closed microcapsule to avoid or reduce the impact of external environment on the core material [1]. Peppermint essential oil is unstable and easy to oxidize, so it is often made into microcapsules [2]. The methods of preparing microcapsules are interfacial polymerization, in situ polymerization, orifice method, spray drying, molecular packing and multiple emulsion method [3]. These manufacturing methods have the disadvantages of complex operation, long time consuming, high temperature material loss, low output and difficult to control, etc. Due to its good controlled release and heat resistance characteristics of the method of complex condensation was used in this paper as a method to prepare microcapsules of peppermint essential oil, so as to improve the embedding rate and oxidation stability of peppermint essential oil microcapsules.

2. Experiment

2.1Experimental Reagent

The information of the experimental drugs used in the experiment is shown in table 1.

TABLE 1. Experimental drugs

Name	Content（%）	Manufacturer
Chitosan	≥98%	Qingdao Jifa New Materials Co., Ltd.
Arabia Gum	≥99%	Wuhan Geeyeschem Chemical Co., Ltd.
Peppermint Essential Oil	≥99%	Jishui Shengyuan Fragrance Factory
Transglutaminase	≥99%	Xi'an LAVIA Biotechnology Co., Ltd.
Acetic Acid	≥90%	Xi'an LAVIA Biotechnology Co., Ltd.
Sodium Hydroxide	≥99%	Henan Yusheng Chemical Co., Ltd.

2.2 Experimental Instruments and Equipment

The experimental instruments and equipment used in the experiment are shown in table 2.

TABLE 2. Experimental instruments and equipment

Name of Instrument	Model	Manufacturer
Electronic Balance	BSA124S	Shanghai Youyi Instrument Co., Ltd.
Temperature Control Magnetic Stirrer	85-2	Jiangsu Jinyi Instrument Technology Co., Ltd.
Ultrasonic Cleaner	KQ-250E	Kunshan Ultrasonic Instruments Co., Ltd.
Biomicroscope	PH50-3A43L-PL	Jiangxi Phoenix Optical Technology Co., Ltd
PH Meter	SG78	Mettler Toledo Instruments Co., Ltd.
Freezer	FCD-178XHT	Qingdao Haier Special Electric Freezer Co., Ltd.

2.3 Preparation of Microcapsules

Refer to the method of Xia Huiting et al[4]. Prepare Arabia gum solution and chitosan solution in advance, and reserve it for use. Take a certain amount of arabic gum solution and add a certain proportion of peppermint essential oil to mix evenly, emulsify at 10000r / min for 3min at high speed and chitosan solution is also emulsified at the same speed for the same time. Drop by drop, the chitosan solution is added, stir with a temperature controlled magnetic stirrer at 400r / min for 10min, acetic acid with a mass fraction of 10% was added to adjust the pH to the appropriate value, complex coacervation 30min. The water bath cooled the system to 10℃ for 15min. Transglutaminase was added and cured at 10℃ for 1h. Add 10% NaOH solution to adjust pH value to 6 and continue curing at room temperature for 12h. Wash and filter with distilled water for 3 times to obtain wet microcapsules.

2.4 Single Factor Experiment

2.4.1 Selection of Agitation Speed

Other technological conditions and external parameters were fixed, and the agitation speeds of the complex condensation were changed to be 300r/min, 350r/min, 400r/min, 450r/min, and 500r/min, respectively, the morphology of condensate was observed by biomicroscope and the optimum agitation speed was determined by screening.

2.4.2 Selection of Complex Coagulation PH Value

On the basis of selecting the optimal agitation speed, other process conditions and external parameters were fixed, and the pH values of complex condensation were changed to 3.0, 3.5, 4.0, 4.5 and 5.0, respectively, the morphology of condensate was observed by biomicroscope and the optimal pH value of complex condensate was determined by screening.

2.4.3 Selection of Core Wall Ratio

On the basis of selecting the optimal agitation speed and the optimal pH value of complex condensation, other technological conditions and external parameters were fixed and the core wall ratio of complex condensation was changed to be 1:1, 1:2, 1:3, 2:1 and 3:1, the morphology of condensate was observed by biomicroscope and the optimum core wall ratio was determined by screening.

2.4.4 Calculation of Embedding Rate

Refer to the method of Chen Lin et al[5].

$$\text{Embedding rate} = \left(1 - \frac{\text{Surface oil content of microcapsules}}{\text{Total oil content of microcapsules}}\right) \times 100\%$$

2.5 Response Surface Experiment

In order to obtain the best preparation technology, on the basis of single factor experiment, the response surface experiment was used to optimize the experimental design, with agitation speed, complex condensation pH value and core wall ratio as the influencing factors, and embedding rate as the determination index. The level of experimental factors on the response surface is shown in table 3.

TABLE 3. Horizontal table of factors affecting response surface

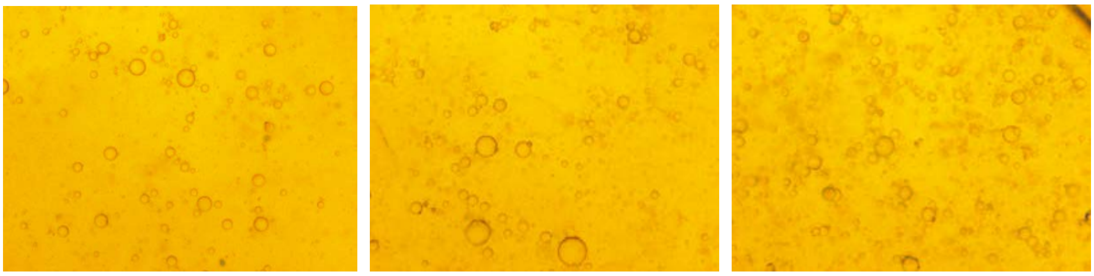
Level	Factor		
	A Agitation Speed (r/min)	B PH Value of Complex Condensation	C Core Wall Ratio
1	350	3.5	1:1
0	400	4.0	2:1
-1	450	4.5	3:1

3. Results and Discussion

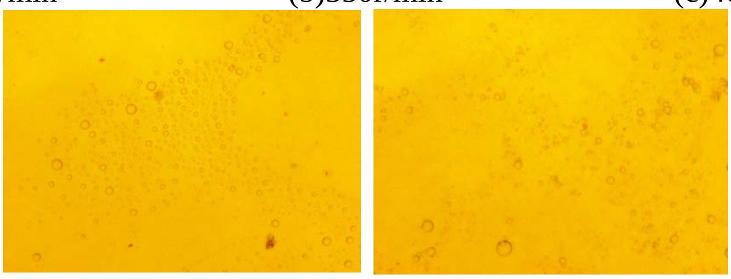
3.1 Single-factor Experiment

3.1.1 Agitation Speed

The influence of agitation speed on the morphology of microcapsules prepared by complex condensation method is shown in Fig.1. The effect of agitation speed on the embedding rate of microcapsules is shown in Fig.2.



(a)300r/min (b)350r/min (c)400r/min



(d)450r/min (e)500r/min

Figure 1. Effect of agitation speed on microcapsule morphology (60 times)

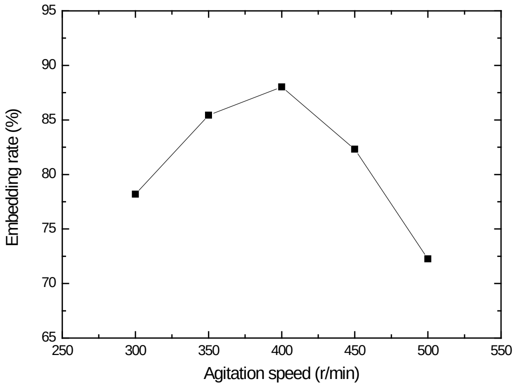


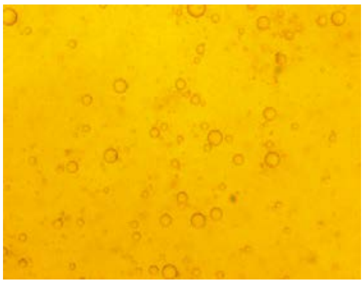
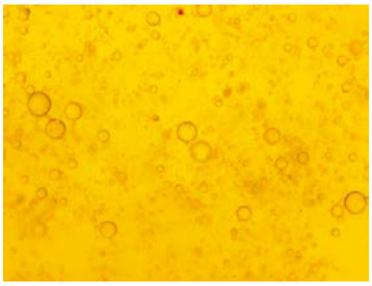
Figure 2. Effect of agitation speed on microencapsulation rate

As can be seen from figure 1, the number of microcapsules first increased and then decreased with the increase of agitation speed. When the agitation speed was 400r/min, the microcapsules observed under the microscope had good shape and uniform dispersion, and the embedding effect was the best, with the increase of agitation speed, the microcapsules formed gradually decrease in size, smaller in oil content and easier to aggregate. The best agitation speed is 400r / min based on the shape, particle size and embedding rate.

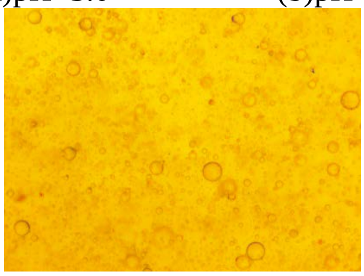
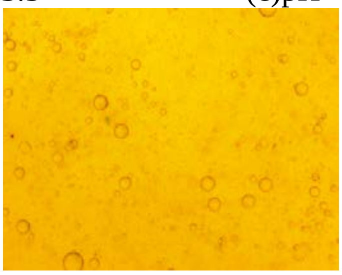
It can be seen from Figure 2 that with the increase of agitation speed, the embedding rate of microcapsules increases first and then decreases. When the agitation speed is 400r / min, the maximum embedding rate is taken.

3.1.2 The PH of the Complex Condensation

The influence of complex condensation pH value on the morphology of microcapsules prepared by complex condensation is shown in Fig.3. The effect of complex condensation pH value on the embedding rate of microcapsules is shown in Fig.4.

(a)pH=3.0 (b)pH=3.5 (c)pH=4.0

(d)pH=4.5 (e)pH=5.0

Figure 3. Influence of pH value of complex condensation on microcapsule morphology (60 times)

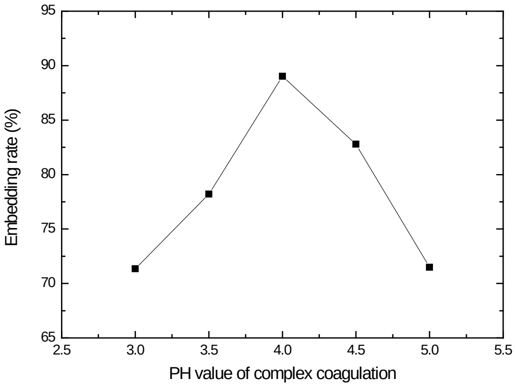


Figure 4. Effect of different pH value of complex coagulation on the embedding rate of microcapsules

It can be seen from figure 3 that either too high or too low pH value will reduce the embedding rate of microcapsules, while when the pH value is too low, the solubility of chitosan is large and the reaction of the two wall materials is insufficient, and the embedding rate is low. When the pH is too high, it is close to the isoelectric point, which limits the reaction between chitosan and Arabic gum, so the embedding rate is reduced.

It can be seen from Figure 4 that the embedding rate of the microcapsules increases first and then decreases with the increase of the complex condensation pH value. When the pH value of complex condensation was 4.0, the maximum embedding rate is taken.

3.1.3 Core Wall Ratio

The influence of core wall ratio on the morphology of microcapsules prepared by complex condensation is shown in Fig.5. The effect of core wall ratio on microcapsule embedding rate is shown in Fig.6.

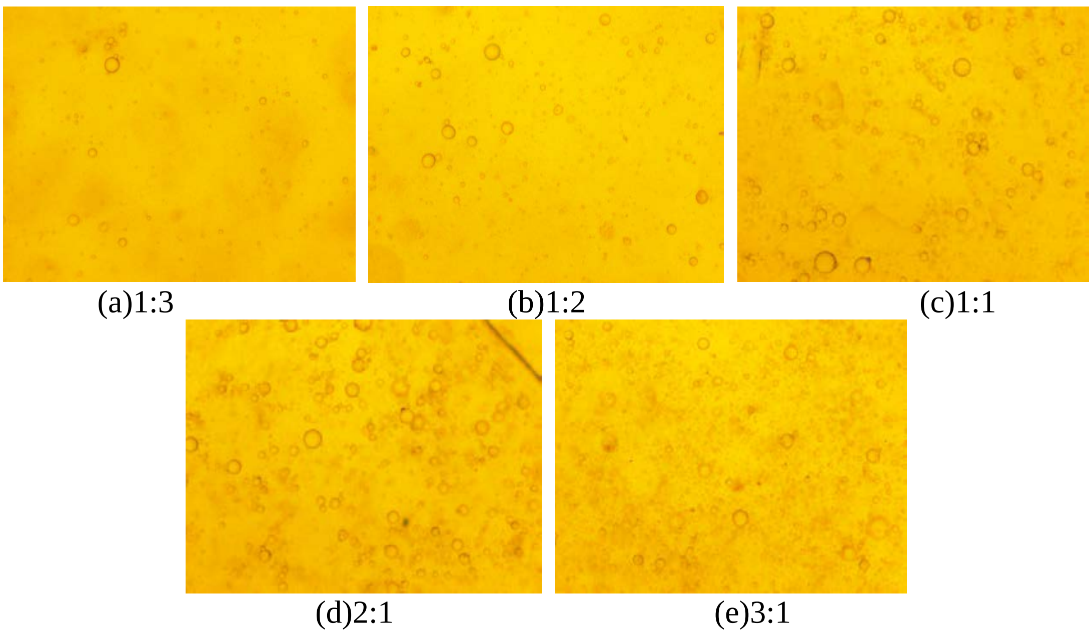


Figure 5. Influence of core wall ratio on microcapsule morphology (60 times)

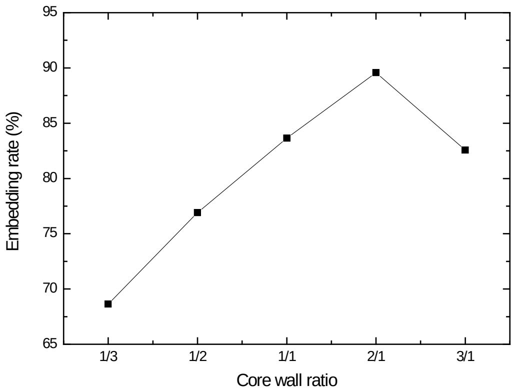


Figure 6. Effect of core wall ratio on microcapsule embedding rate

As can be seen from figure 5, the shape of microcapsules was less affected by the ratio of different core walls, and the embedding of microcapsules first increased and then decreased with the decrease of wall material concentration, when the ratio of 2:1 core wall under a microscope to the good and the amount of microcapsule morphology, with the increase of concentration of core material oil content increased, the core material of wall surface complex condensate decreases, the observed microcapsules form fuzzy and there are many unformed microcapsules, microcapsules in reducing the number of the microcapsule embedding rate gradually decreased.

It can be seen from Figure 6 that the embedding rate of microcapsules increases first and then decreases with the increase of core wall ratio, when the core wall ratio is 2:1, the maximum embedding rate is taken.

3.2 Response Surface Experiment

3.2.1 Analysis of Response Surface Experiment Results

The response surface experimental design scheme and experimental results are shown in table 4.

TABLE 4. Experimental design and results of response surface

Test Number	A-Agitation Speed	B-PH Value of Complex Condensation	C-Core Wall Ratio	Y-Embedding Rate/%
1	0	0	0	89.76
2	1	0	-1	79.54
3	0	0	0	90.81
4	0	1	1	74.62
5	-1	-1	0	81.25
6	-1	0	1	79.39
7	1	0	1	80.01
8	1	1	0	79.85
9	0	-1	1	75.41
10	0	1	-1	77.84
11	0	0	0	89.94
12	0	0	0	89.97
13	0	-1	-1	78.25
14	-1	1	0	81.62
15	-1	0	-1	80.27
16	0	0	0	90.98
17	1	-1	0	79.63

3.2.2 Response Surface Analysis of Variance Results

TABLE 5. Variance analysis of response surface regression model

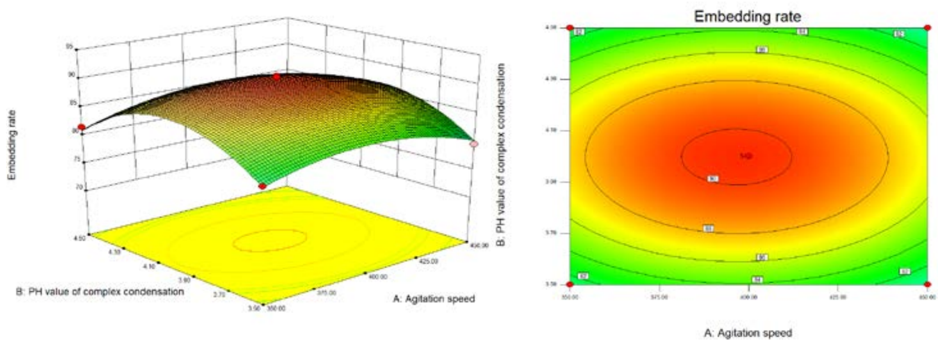
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob>F
Model	496.52	9	55.17	55.26	<0.0001
A- Agitation Speed	1.53	1	1.53	1.53	0.2554
B- PH Value of Complex Condensation	0.047	1	0.074	0.047	0.8353
C- Core Wall Ratio	5.23	1	5.23	5.24	0.0559
AB	5.625-003	1	5.625-003	5.635-003	0.9423
AC	0.46	1	0.46	0.46	0.5210
BC	0.036	1	0.036	0.036	0.8546
A2	43.55	1	43.55	43.62	0.0003
B2	177.27	1	177.27	177.57	<0.0001
C2	222.75	1	222.75	223.14	<0.0001
Residual	6.99	7	1.00		
Lack of Fit	5.74	3	1.91	6.11	0.0565
Pure Error	1.25	4	0.31		
Cor Total	503.51	16			
P<0.0001 R2=0.9861 R2adj=0.9683					

Design expert v8.0.6 software was used to analyze the experimental data by quadratic response surface regression analysis, and the regression equation between the embedding efficiency of peppermint essential oil microcapsules and each dependent variable was obtained:

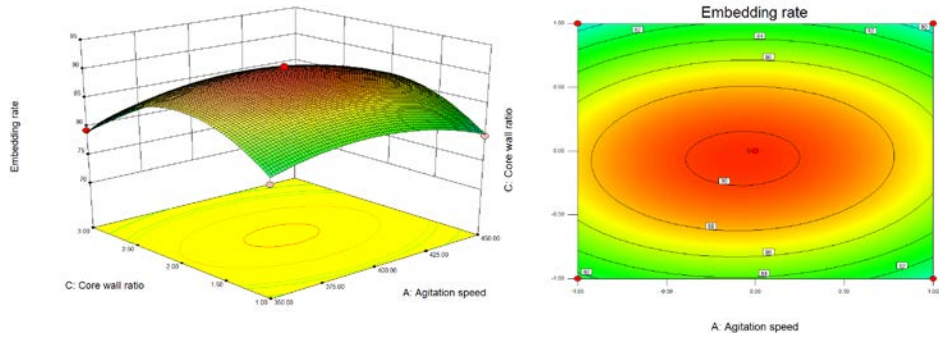
Y/%=+90.29-0.44A-0.076B-0.81C-0.038AB+0.34AC-0.095BC-3.22A2-6.49B2-7.27C2

It can be seen from table 5 that P < 0.0001 of the model indicates that the quadratic equation model is very significant. The complex correlation coefficient was R2=0.9861, and the corrected correlation coefficient was R2adj=0.9683, indicating the high fitting degree of the regression model, the actual value is close to the predicted value with high accuracy and credibility, and the regression equation is representative. From the variance analysis results of the regression equation, it can be concluded that the unfitting term of the equation is P=0.0565>0.05, which is not significant, indicating that the equation has good experimental fitting and small error. Therefore, the model is suitable for the optimization of the process parameters of peppermint essential oil microcapsules.

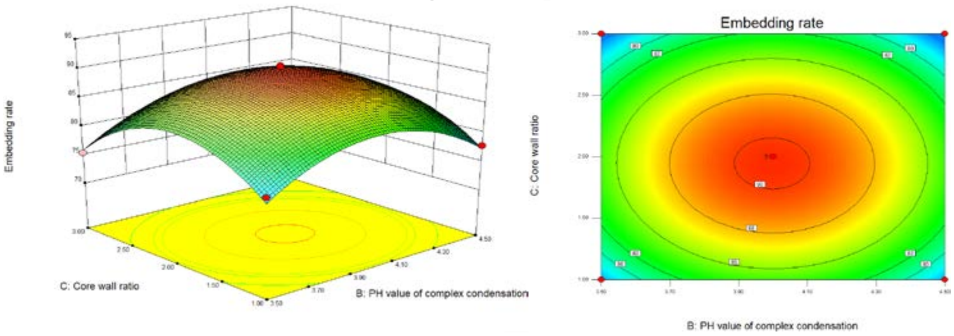
3.2.3 Response Surface and Contour Analysis



(a) Interaction between agitation speed and pH value of complex coagulation



(b) Interaction between agitation speed and core wall ratio



(c) Interaction between pH value and core wall ratio of complex coagulation

Figure 7. Influence of interaction of various factors on embedding rate

It can be seen from Fig 7(a), the interaction between A (agitation speed) and B (pH value of complex coacervation) is not significant. It can be seen from Fig 7(b), the interaction between A (agitation speed) and C (core wall ratio) is significant, showing that the 3D curve is steep. It can be seen from Fig 7(c) that the interaction between B (pH value of complex coacervation) and C (core wall ratio) is significant, and the contour map is the flattest, indicating that the interaction between these two factors is the largest, with the increase of core to wall ratio, embedding first increases and then decreases, when the core to wall ratio is about 2:1, the maximum value is taken. According to the results of response surface regression model, the best predicted values are: core wall ratio 1.94:1, complex coagulation pH value of 4.00, agitation speed 396.45r/min, and the embedding rate is 90.33%.

Under the condition of core to wall ratio of 1.9:1, complex coagulation pH value of 4.00 and agitation speed of 400r / min, the maximum embedding rate was 89.67% after repeated experiments and considering the influence of external conditions.

3.3 Performance Analysis of Peppermint Essential Oil Microcapsules

3.3.1 Microstructure of Microcapsules

Scanning electron microscope was used to observe the external structure of the microcapsule of peppermint essential oil prepared by the complex coacervation method. It can be seen from Fig.8 that the microcapsule is irregular in shape, and the surface of the microcapsule is rough and wrinkled, which may be due to the water gasification during the drying process, resulting in the excessive expansion of the microcapsule, and the shrinkage during the cooling process, resulting in the formation of wrinkles on the surface. In the figure, the microcapsule did not break, indicating that the composite wall material of chitosan and Arabic gum realized the embedding of peppermint essential oil, the composite wall material played a protective role in peppermint essential oil, and improved the stability of peppermint essential oil.

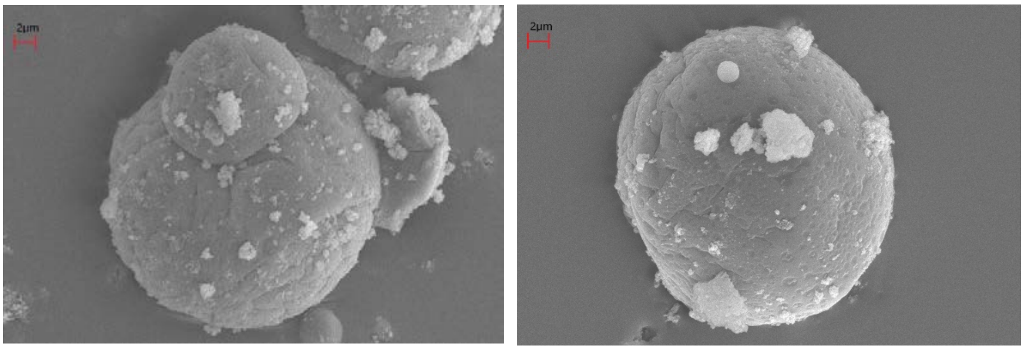


Figure 8. Electron scanning microscope of peppermint essential oil microcapsule

3.3.2 Particle Size Distribution of Microcapsules

The particle size of microcapsule is measured by laser particle size analyzer, and the particle size distribution of microcapsule is shown in Fig.9.

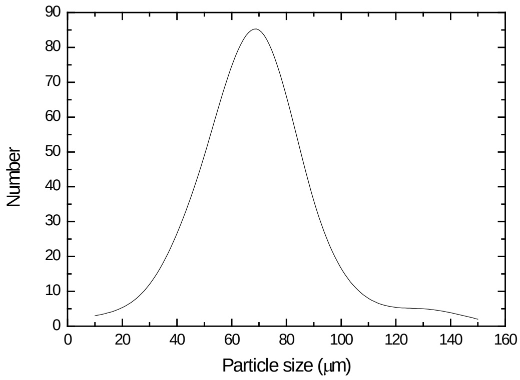


Figure 9. Particle size distribution of peppermint essential oil microcapsules

As shown in Figure 9, in the statistical samples, the particle size range of microcapsules is 0-150 μ m, and the average particle size is 69.3 μm. the normal distribution of the particle size of microcapsules is relatively concentrated, indicating that the particle size is uniform.

3.3.3 Oxidative Stability of Peppermint Essential Oil Microcapsules

Refer to the method of Zhou Xue et al[6], POV value is measured by titration. Fig.10 is a comparison of POV value growth of peppermint essential oil and peppermint essential oil microcapsules under the same external conditions in accelerated storage experiment.

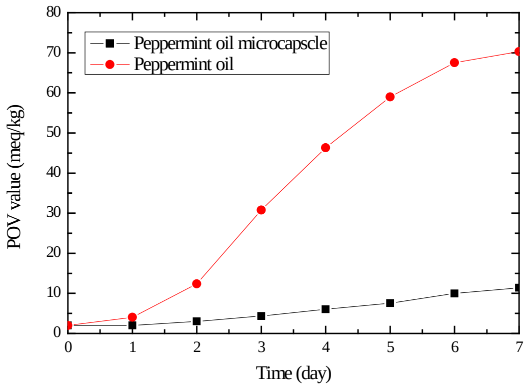


Figure 10. POV value trend of peppermint essential oil and peppermint essential oil microcapsule accelerated storage experiment

It can be seen from Figure 10 that the POV value of peppermint essential oil microcapsule is significantly different from that of peppermint oil under accelerated storage conditions. The POV value of peppermint essential oil increased rapidly from the second day, and reached 70.29meq/kg after 7 days storage. POV increased with the increase of hydroperoxides produced by oil oxidation, after microencapsulation, the POV value of peppermint essential oil increased slowly with time, which was much lower than that of peppermint essential oil. The results showed that the microcapsule composite wall material had a good embedding effect on the core material peppermint essential oil and hindered the influence of external conditions on peppermint essential oil, which indicated that peppermint essential oil microcapsule had a good antioxidant effect.

4. Conclusion

Peppermint essential oil microcapsules were prepared with chitosan and gum arabic as wall materials by complex condensation method. On the basis of single factor test, response surface method was used to optimize the preparation process, the optimal process parameters were core wall ratio of 1.94:1, complex coacervation pH value 4.00, agitation speed of 396.45r/min, and the embedding rate was 90.33%. Under the condition of 1.9:1 core to wall ratio, 4.00 complex coagulation pH value and 400 r/min agitation speed, the maximum embedding rate was 89.67% after repeated experiments and considering the influence of external conditions. Through the study of oxidation stability, it is concluded that the microencapsulation of peppermint essential oil can effectively delay the oxidation of peppermint essential oil and make it have good oxidation stability.

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