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Research Article

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Preparation of chlorothalonil microcapsules by interfacial polymerization

Kefeng Xiao, Zhihui Hao* and Leilei Wang

Agricultural Bio-pharmaceutical Laboratory, Institute of Chemistry and Pharmacy, Qingdao Agricultural University, Qingdao, China

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ABSTRACT

Chlorothalonil, a kind of antiseptic used widely, has special control effect on plant disease caused by fungus of fruits. Its existing dose forms have many disadvantages including active ingredients exposing in wind, rain and sunshine, easy decomposition and volatilization. In order to solve above-mentioned problems, the best way is to microencapsulate chlorothalonil. In the study, chlorothalonil microcapsules were prepared by interfacial polymerization with toluene-2,4-diisocyanate and hexamethylenetetramine as wall materials. By large number of pre-experiments, the optimal shear speed, shear time, stirring speed, stirring time and suitable solvents used in preparation process of chlorothalonil microcapsules were determined. By orthogonal experiments, the optimal ratio of wall materials, solvent and dispersant were determined with encapsulation efficiency measured by ultraviolet spectrophotometry as indicator. The particle size distribution of chlorothalonil microcapsules prepared was even, and the encapsulation efficiency is up to 94.65%.

Keywords: chlorothalonil; microcapsule; interfacial polymerization; encapsulation efficiency.

INTRODUCTION

Chlorothalonil is a kind of antiseptic used widely and has special control effect on plant disease caused by fungus of fruits. Chlorothalonil plays an irreplaceable role in agriculture. Its dose forms include smoke suppressant, granules, 75% wettable powders, suspensions and so on [1-5]. However, active ingredients in these existing dose form were exposed in wind, rain and sunshine, which lead to many disadvantages including easy decomposition, easy volatilization, short bactericidal persistence and non-environment-friendly [6, 7]. In order to improve insecticidal effect, the traditional approach is to increase the concentration of the active ingredients, which increases the cost of production and increased the toxicity of pesticides to a dangerous level. This approach brings great harm to the production and people's life [8]. With the continuous improvement of people's environmental awareness, it's urgent to develop new dose form so as to solve above-mentioned problems.

Currently, microcapsule technology has been utilized widely in the field of food, pesticide, medicine and chemical. Especially, its applications in pesticide have been paid more and more attention by researchers [9, 10]. Compared with other pesticides formulations, microcapsule formulation have many advantages such as long bactericidal persistence [11], high utilization, decreasing decomposition and volatilization, and reduce toxicity and phytotoxicity [12, 13]. If chlorothalonil was microencapsulated, above-mentioned issued would be addressed. Therefore, it is of importance to prepare chlorothalonil microcapsules. In literatures, there are few reports about the preparation of chlorothalonil microcapsules [14-16]. In this study, interfacial polymerization was used to prepare chlorothalonil microcapsules with toluene-2,4-diisocyanate and hexamethylenetetramine as wall materials. And the optimal process and formulation were determined by orthogonal experiments.

EXPERIMENTAL SECTION

Reagents and Instruments

Chlorothalonil (96.2%) were provided by Qingdao Haohan Agricultural Science and Technology Co., Ltd. Toluene-2,4-diisocyanate (TDI), chloroform, hexamethylenetetramine and poly(vinyl alcohol) were purchased from Tianjin BASF Chemical Co., Ltd and used as received. Acetone (99.5%) and xylene (99.0%) were purchased from Laiyang Kant Chemical Co., Ltd.

JRJ-300-I shear emulsifying mixer (Shanghai model and specimens factory) was used to shear mixture liquid. BT-9300H laser particle size distribution analyzer (Dandong Baxter Instrument Co., Ltd.) was used to measure the size of microcapsules prepared. Electric mixer (3000 rev/min, 40W, Jiangsu Jincheng Guosheng Experimental Instrument Factory) was used to stir. TV-190 UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) was utilized to measure encapsulation efficiency of microcapsules. 95-2 ultrasonic disintegrator (Shanghai Fun Limited) was used to break microcapsules so as to extract them.

Determination of optimal experimental conditions

In the process of preparation of chlorothalonil microcapsules, factors of affecting particle size and encapsulation efficiency include shear speed, shear time, stirring speed, stirring time, the material and amount of solvent, and ratio of raw materials. Most of them were determined by a series of pre-experiments. The results were that optimal shear speed was 2500r/s, optimal shear time was 16min, optimal stirring speed was 1500r/s, and optimal stirring time was 30min. The most important factor, ratio of raw materials, was determined by following orthogonal experiments.

Preparation process of chlorothalonil microcapsules

Firstly, quantitative chlorothalonil was dissolved in certain amount of chloroform and xylene, and then add certain amount of TDI. Secondly, put quantitative poly(vinyl alcohol) into a beaker and add certain amount of water in. And then the water is heated to boiling with constant stirring until complete dissolution of poly(vinyl alcohol). Thirdly, after being cooled to room temperature, poly(vinyl alcohol) solution was mixed with the solution prepared in the first step. And then the mixture was sheared by shear emulsifying mixer at the speed of 2500r/s for 16 minutes. Its particle size was measured by laser particle size distribution analyzer. Fourthly, after being sheared, the mixture was put into four-neck flask and was stirred by electric mixer while adding hexamethylenetetramine in. Finally, chlorothalonil microcapsules formed.

The methods of characterization

Encapsulation efficiency of chlorothalonil microcapsules was measured by UV-Vis spectrophotometer. Quantitative chlorothalonil was dissolved in acetone so as to form solution with suitable concentration. With acetone as blank reference, the solution was scanned by UV-Vis spectrophotometer at the range of 190-400nm. There was an absorption peak at 326nm in the scanning curve. It didn't affect absorption peak to add chloroform and xylene to the solution under test. Therefore, the standard curve was drawn at the position of 326nm.

Firstly, standard chlorothalonil acetone solutions were prepared. Secondly, standard curve was drawn by measuring absorbance values in different concentrations. Thirdly, measured absorbance value of the solution under test was used to find corresponding concentration from the standard curve. Finally, Encapsulation efficiency of chlorothalonil microcapsules was calculated according to these parameters.

Drawing of standard curve.

0.104g chlorothalonil was dissolved in acetone and more acetone was added to the solution till the volume of the solution became 100mL. The mother liquid was gotten with concentration as 1000ppm. Take 10ml mother liquid to 100ml volumetric flask and add acetone to 100mL so that 100ppm standard solution was gotten. Get different amount of standard solution and add acetone to 10mL. Their concentrations and absorbance measured were shown in Table 1.

Table 1. Concentrations and absorbance of different solution

Standard solution (ml)	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10
Concentration(μg/ml)	20	30	40	50	60	70	80	90	100
Absorbance	0.145	0.227	0.300	0.381	0.451	0.534	0.609	0.680	0.709

With concentration as X-axis and absorbance as Y-axis, the standard curve was drawn as Figure 1. Absorbance A and concentration C meet the linear relationship A=0.0076C-0.0046. Relevance meet the equation R^2= 0.9998.

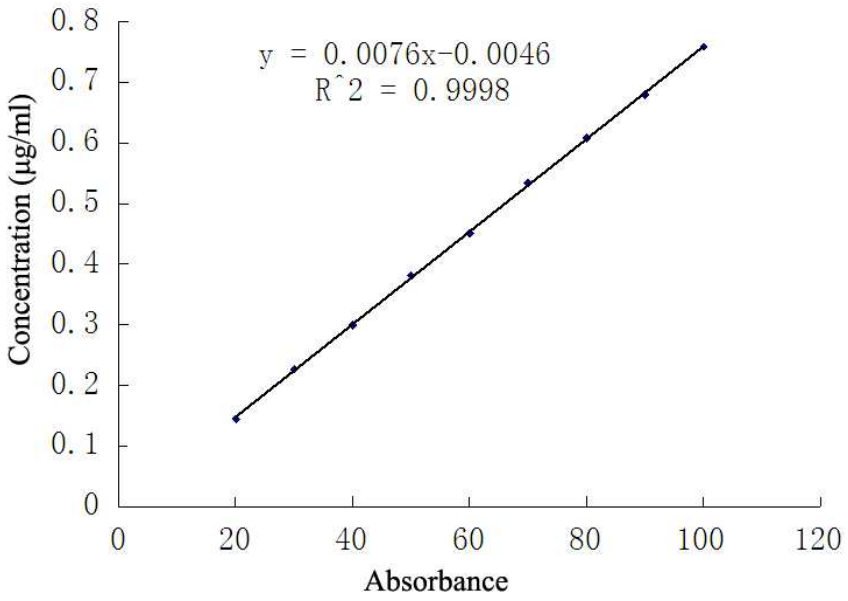

Figure 1. The standard curve of chlorothalonil solution

Measurement method of encapsulation efficiency of chlorothalonil microcapsules.

Firstly, stir the sample so as to mix completely. And then remove some of the samples using a pipette to a beaker. The weight of the sample in beaker was a(g). Secondly, these samples were filtered with suction by circulating water vacuum pump, and then let it dry naturally. Thirdly, dried samples and filter paper were added to 20ml acetone to be extracted with ultrasonic wave for 20min. And then the solution was separate from the microcapsules and filter paper. After that, 15ml acetone was added to this remainer to extract with ultrasonic wave for 10min. And then the solution was separate from the samples again. Repeat above-mentioned procedure one time and combine the extracts. Fourthly, above-mentioned solution was filtered by membrane and was diluted to 100ml by acetone. With acetone as blank reference, absorbance was measured by UV-Vis spectrophotometer at 326nm. And the concentration of the solution, b (μg⁄ml), was obtained from standard curve. That is, there was 100b (μg) chlorothalonil in a (g) samples. Assumed that the mass of total samples was M(g) and the mass of hexaflumuron added was N(g). Then the encapsulation efficiency of hexaflumuron can be calculated by Equation (1).

$$\text{Encapsulation efficiency} = \frac{100 \times b \times M \times 10^{-6}}{a \times N} \times 100\% \quad (1)$$

Orthogonal experiment design for optimization of raw materials ratio

In order to determine the optimal raw materials ratio, the amount of chlorothalonil is 1.0g in all test formulations. Wall materials, solvent and dispersant were selected as three factors of orthogonal experiment and they have three levels respectively. Wall materials are TDI and hexamethylenetetramine. Solvent used in this series of experiments were made up of chloroform and xylene. And poly(vinyl alcohol) acted as dispersant. The factors and levels of orthogonal experiment were shown in Table 2.

Table 2. Factors and levels of orthogonal experiment

Levels	Factor A TDI+ hexamethylenetetramine（g）	Factor B chloroform + xylene（ml）	Factor C poly(vinyl alcohol)（g）
1	0.2+0.4	22.5+9	0.7
2	0.3+0.3	23+10	1.0
3	0.4+0.2	24+10	1.3

RESULTS AND DISCUSSION

The encapsulation efficiency of chlorothalonil microcapsules was selected as indicator. The results of orthogonal experiments were shown in Table 3. As can be seen from Table 3, the optimal ratio of raw materials was $A_2B_1C_2$, that is, the amount of TDI was 0.3g, the amount of hexamethylenetetramine was 0.3g, the amount of chloroform and xylene were 22.5mL and 9mL respectively, and the amount of poly(vinyl alcohol) was 1.0g. According to the effect of different factors on the process of preparation of chlorothalonil microcapsules, the sequence of the three factors was determined, wall material> dispersant>solvent. Although the effect of error range was weaker than that three

factors, its value 21.12 was higher than normal, which meant that there was innegligible interaction among these factors, or some important factors, such as reaction temperature and storage time, were missed. These factors should be studied in the future.

Table 3. Results of orthogonal experiments

No.	A TDI+ hexame-thylenetetramine	B Chloroform + xylene	C Poly(vinyl alcohol)	D Error	Encapsulation efficiency（%）
1	1	1	1	1	36.2
2	1	2	2	2	54.5
3	1	3	3	3	41.03
4	2	1	2	3	94.65
5	2	2	3	1	83.55
6	2	3	1	2	76.13
7	3	1	3	2	56.44
8	3	2	1	3	67
9	3	3	2	1	61.81
K_1	131.73	187.29	179.33	181.56	
K_2	254.33	205.05	210.96	187.07	
K_3	182.25	178.97	181.02	202.68	
k_1	43.91	62.43	59.78	60.52	
k_2	84.78	68.35	70.32	62.36	
k_3	61.75	59.66	60.34	67.56	
R	122.6	26.08	31.63	21.12	

After shearing and after polymerization, particle sizes of chlorothalonil microcapsules prepared were measured by laser particle size distribution analyzer. These results were shown in Table 4.

Table 4. Particle sizes of chlorothalonil microcapsules and wall thickness

No	1	2	3	4	5	6	7	8	9
Particle size after shearing	28.7	19.98	18.53	6.37	18.25	14.55	16.24	17.47	15.14
Particle size after polymerization	34.59	34.99	20	13.35	19.53	17.21	18.9	25.61	19.33
Wall thickness	6	15	1.5	7	1.2	3	3	8	4

(Note: the units of all of the data in Table 4 are μm)

As can be seen from Table 4, the result of interfacial polymerization was comparatively excellent. The particle size distribution of chlorothalonil microcapsules was uneven and was sensitive to the change of wall material, solvent and dispersant. In terms of a single experiment, particle size distribution was stable before polymerization and after polymerization, which indicated that the result of shearing emulsification was excellent and the preparation process was reliable.

A drop of chlorothalonil microcapsules suspension prepared in optimal conditions was dropped on glass slide. And then it was observed by 40x microscope and the image was shown in Figure 2. It can be seen that most of chlorothalonil microcapsules were spherical and there wasn't agglomeration among these microcapsules. These phenomenons indicated that in the optimal conditions, chlorothalonil microcapsules prepared have good shape and even particle size distribution.

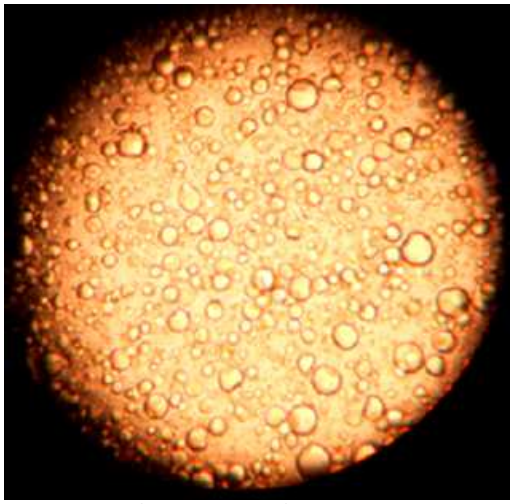

Figure 2. 40x magnification image of chlorothalonil microcapsules

CONCLUSION

The optimal process conditions were determined by pre-experiment. And the optimal formula of preparing chlorothalonil microcapsules was determined by orthogonal experiments. In the optimal formula, TDI and hexamethylenetetramine acted as wall materials and both of their amounts were 0.3g. Chloroform and xylene served as solvents and their amount were 9mL and 22.5mL respectively. As dispersant, poly(vinyl alcohol) was 1.0g. And the active ingredient, chlorothalonil, was 1.0g. In the optimal conditions and optimal formula, chlorothalonil microcapsules with excellent stability and uniform particle size distribution can be prepared by interfacial polymerization. The encapsulation efficiency of chlorothalonil microcapsules can be up to 94.65%. This study provided a new formula and optimal process for industrial production of chlorothalonil microcapsules, which will be conducive for chlorothalonil to play a more important role in agriculture.

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