Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2013, 5(5):319-323

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Preparation of chlorpyrifos 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

---

ABSTRACT

Chlorpyrifos microcapsules were prepared by interfacial polymerization, with toluene-2,4- diisocyanate and hexamethylenetetramine as wall material, and poly(vinyl alcohol) as dispersant. Optimal emulsification shear rate, shear time and interfacial polymerization stirring speed and interfacial polymerization time were determined by pre-experiment. Optimal ratio of raw materials for preparation of chlorpyrifos microcapsules was obtained by experiments. The chlorpyrifos microcapsules prepared were characterized by UV spectrophotometer and laser particle size distribution analyzer. The optimum mount of raw materials are that chlorpyrifos is 1.0g, toluene-2,4-diisocyanate is 0.3g, hexamethylenetetramine is 0.7g and poly(vinyl alcohol) is 1.0g. The optimal operating conditions are that interfacial polymerization stirring speed is 500r/min and interfacial polymerization time is 40 minutes. In above-mentioned conditions, mean particle size of chlorpyrifos microcapsules prepared is 0.89μm, and encapsulation efficiency can reach 92.98%.

Keywords: chlorpyrifos; hexamethylenetetramine; interfacial polymerization; microcapsule;

INTRODUCTION

Chlorpyrifos, a kind of insecticide and acaricide with a broad-spectrum activity, control various soil pests and pests on leafy crops by contact, stomach poisoning and fumigation. It can also control mosquito larvae and adults as well as ectoparasites cattle of sheep. However, strong photolysis of chlorpyrifos results in a shorter persistence on plant leaves [1, 2]. Currently, the main formulation of chlorpyrifos are 48% EC and 40% EC [3] which consume a large mount of organic solvent. These formulations result in environment pollution and waste of resources. These disadvantages have hampered greatly the application of chlorpyrifos[4-6]. Microcapsulating chlorpyrifos can reduce the decomposition of chlorpyrifos caused by light, air, water and microbial and reduce the volatilization, loss and possibility of reacting with other substances [7]. Moreover, it can prolong persistence, widen spraying intervals, and decrease the frequency of spraying. Besides, it can enhance the stability of chlorpyrifos.

According to wall formation mechanism and the conditions of microcapsule formation, the methods used in microcapsule preparation are classified into three categories: physical, chemical and physic-chemical methods [8-10]. Nowadays, chemical method which includes interfacial polymerization and situ polymerization are utilized widely in microcapsule preparation. While interfacial polymerization is used more widely than situ polymerization[11]. Polymerization is simple and react quickly at room temperature[12]. Polymerization usually relates to two reactants, which can be dissolved respectively in the oil phase and water phase[13, 14]. Although preparation of chlorpyrifos microcapsules by interfacial polymerization were reported in literatures [15, 16], the reactants in the polymerization reaction were different and the encapsulation efficiency of these reports were not satisfying. This study attempted to prepare chlorpyrifos microcapsules by interfacial polymerization with toluene-2,4- diisocyanate and hexamethylenetetramine as reactants.

EXPERIMENTAL SECTION

Reagents and Instruments

Chlorpyrifos (96.9%), toluene-2,4-diisocyanate (TDI), hexamethylenetetramine and poly(vinyl alcohol) were purchased from Tianjin BASF Chemical Co., Ltd and used as received. Hexane were purchased from Tianjin Guangcheng Chemical Reagent Co., Ltd.

Mixed liquid was sheared by JrJ-300-I shear emulsifying mixer (Shanghai model and specimens factory). Stirring was conducted by electric mixer (3000 rev/min, 40W, Jiangsu Jincheng Guosheng Experimental Instrument Factory). Encapsulation efficiency was measured by TV-190 UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.). When being extracted, microcapsules were broken by 95-2 ultrasonic disintegrator (Shanghai Fun Limited). The size of microcapsule was measured by BT-9300H laser particle size distribution analyzer (Dandong Baxter Instrument Co., Ltd.).

Preparation method of chlorpyrifos microcapsules

Put certain amount of poly(vinyl alcohol) and distilled water into beaker, and dissolve that by heating and mix fully so as to form solution in aqueous phase. Then mix fully chlorpyrifos, emulsifiers and benzene so as to form solution in oil phase. And then both solution in aqueous phase and solution in oil phase were added to a 250mL beaker. The mixture was stirred by shear emulsifying mixer in high speed for a period of time at room temperature. And then the mixture was transferred to a 250mL boiling flask-3-neck and continues to be stirred. At the same time, hexamethylenetetramine was added to the mixture slowly. With continual stirring and adding hexamethylenetetramine, chlorpyrifos microcapsules were formed.

Determination of optimal experimental conditions

By pre-experiments, optimal emulsifying shear speed was determined as 3000r/s, and shear time was 8 minutes. Stirring speed of electric mixer was 500r/s and stirring time was 40 minutes.

Optimization method of raw materials ratio

In experiments, the amount of chlorpyrifos was 1.0g and was constant, while the amounts of TDI and hexamethylenetetramine were variable. According to the literature of DX Jiang et al[17], the ratio of core materials and wall materials should be 30:7 to 50:7. Therefore, select 0.5g, 1.0g and 1.2g as the total amount of wall materials. On the basis of this, different values were selected for TDI and hexamethylenetetramine. There are six experiments being conducted and the amount of wall materials in each experiment are shown in Table 1.

Table 1. The amount of wall materials in each experiment

No.	TDI(g)	hexamethylenetetramine (g)
1	0.3	0.2
2	0.2	0.3
3	0.7	0.3
4	0.5	0.5
5	0.3	0.7
6	0.7	0.5

The methods of characterization

Encapsulation efficiency indicates the mass ratio of the amount of chlorpyrifos in microcapsules and actual added amount. In this study, encapsulation efficiency of chlorpyrifos microcapsules was measured by UV-Vis spectrophotometer. Firstly, draw the standard curve of chlorpyrifos. And then according to the absorbance of chlorpyrifos in microcapsules prepared, obtain the amount of chlorpyrifos in microcapsules by contrast corresponding standard curve. Finally, calculate encapsulation efficiency of chlorpyrifos microcapsules according to the data obtained in experiment.

Drawing of standard curve. Certain amount of chlorpyrifos was dissolved in Hexane to form solution with certain concentration. With hexane as a blank reference, scan the solution using a UV-Vis spectrophotometer in the range of 190 ~ 400nm. It can be seen from scanning curve that there are three absorption peaks at 200nm, 229nm and 292nm respectively. Because the impact of solvent is great at 200nm and solution with low concentration is requested at 229nm leading to bigger error, standard curve was draw at 292nm.

Weigh chlorpyrifos 0.10g. Then dissolve it in hexane and add hexane making the volume be 100ml. The solution prepared act as standard mother liquor. Get standard mother liquor 0.5ml, 1.0ml, 1.5ml, 2.5ml, 3.0ml respectively and dilute to 50ml with hexane. Their corresponding concentration are 10mg/L, 20mg/L, 30mg/L, 50mg/L and 60mg/L respectively. With hexane as a blank reference, their absorbances at 292nm were measured to be 0.170,

0.315, 0.474, 0.782 and 0.936 respectively. With concentration as X-axis and absorbance as Y-axis, the standard curve was drawn as Figure 1.

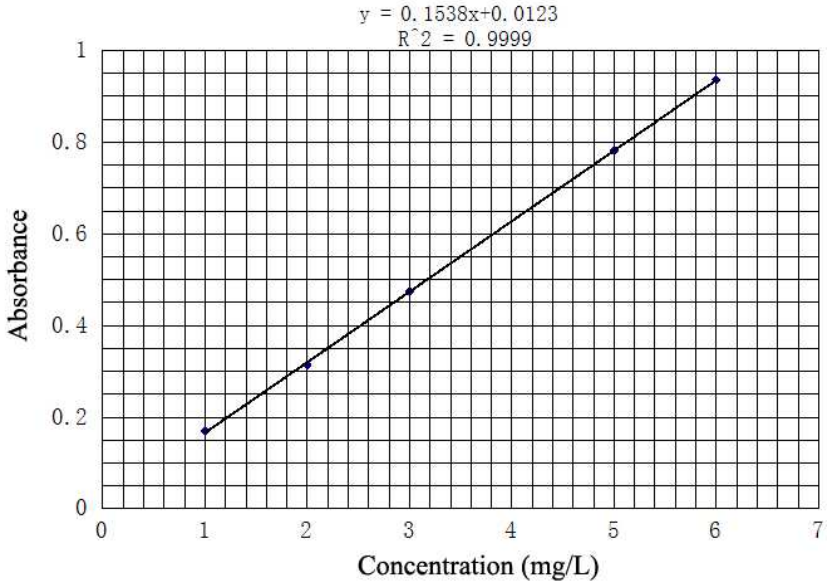

Figure 1. The standard curve of chlorpyrifos

Absorbance A and concentration C meet the linear relationship A = 0.1538C + 0.123. Relevance meet R^2= 0.9999.

Ultrasonic extraction of microcapsules. Weigh certain amount of chlorpyrifos microcapsules suspension and filter it with vacuum. Then wash 3times with deionized water and discard filtrate, let chlorpyrifos microcapsules and filter paper dry naturally together. Put dried chlorpyrifos microcapsules and filter paper into beaker, add 20mL hexane, extract 10min with ultrasonic wave and then pour the solution out. Repeat previous step 2 times and the three extracts were combined to be extracted 10min with ultrasonic wave. The final extracts was filtered by filtration membrane, and volume to 100mL and shake to be even.

Measurement of encapsulation efficiency. With hexane in quartz cuvette as blank reference, the absorbance of extracts obtained from previous step was measured by UV-Vis spectrophotometer at 292nm. The absorbance measured was A. It can be obtained by standard curve that the content of chlorpyrifos in 100mL extracts was C mg/L. Consequently, encapsulation efficiency of chlorpyrifos can be calculated by Eq. (1).

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

where *C* is the content of chlorpyrifos in 100mL extracts (mg/L), *M* is the total weight of chlorpyrifos microcapsules suspension (g), *a* is the sample volume for crushing treatment (g), *N* is actual added amount of chlorpyrifos (g).

Testing methods of stability

Storage experiment in high temperature. Weigh 10g chlorpyrifos microcapsules suspension prepared in optimal experimental conditions, put them into clean tubes, seal the tubes by plastic wrap, and then make the tubes stay in incubator at 60 ºC. After 14 days, take the tube out and observe whether there is precipitation so as to determine the stability of that.

Storage experiment in low temperature. Weigh 10g chlorpyrifos microcapsules suspension prepared in optimal experimental conditions, inject them into clean injection vials, cover so as to seal, and then put the injection vials in incubator at 0 ºC. After 14 days, take the tube out and observe whether there is precipitation so as to determine the stability of microcapsules suspension.

RESULTS AND DISCUSSION

Determination of the optimal ratio of raw materials.

When the proportion of wall materials is high, microcapsule wall will be thick, which isn't conducive to the release

of drug efficacy. While the proportion of wall materials is low, encapsulation efficiency of core materials will be low. Therefore, the balance between fast acting and persistent of effective ingredient can be obtained by adjusting the proportion of core materials and wall materials. The effect of different amount of core material and wall materials on the microcapsule size and encapsulation efficiency was shown in Table 2.

Table 2. The effect of different amount of core material and wall materials on the microcapsule size and encapsulation efficiency

No.	1	2	3	4	5	6
Amount of chlorpyrifos (g)	1	1	1	1	1	1
Total amount of wall material (g)	0.5	0.5	1	1	1	1.2
TDI (g)	0.3	0.2	0.7	0.5	0.3	0.7
Hexamethylenetetramine (g)	0.2	0.3	0.3	0.5	0.7	0.5
Particle size (mm)	0.9	2.26	0.99	3.42	0.89	1.06
Encapsulation efficiency (%)	59.1	78.34	86.3	92.68	92.98	34.39

As can be seen from Table 2, when the proportion of wall materials was changed in experiments, the difference of particle size and encapsulation efficiency was significant. When the amount of TDI was 0.3g and the amount of hexamethylenetetramine was 0.7g, the encapsulation efficiency reached up to 92.98% which is an excellent result. In the same conditions, minimum particle size was obtained, being 0.89mm. Consequently, when other conditions were same, the optimal ratio of chlorpyrifos, TDI and hexamethylenetetramine was 10:3:7.

Determination of dispersant amount.

Poly(vinyl alcohol) was selected to be dispersant. The effect of different amount of poly(vinyl alcohol) on microcapsule size and encapsulation efficiency was shown in Table 3. Table 3 indicates that when the amount of poly(vinyl alcohol) was 0.5g or 2.0g, the particle size was relatively large and the encapsulation efficiency was relatively low. When the amount of poly(vinyl alcohol) was 1.0g, the particle size was the smallest and the encapsulation efficiency was the highest among these results. Therefore, the optimal amount of poly(vinyl alcohol) was 1.0g.

Table 3. The effect of different amount of poly(vinyl alcohol) on microcapsule size and encapsulation efficiency

No.	1	2	3
Poly(vinyl alcohol) (g)	0.5	1.0	2.0
Particle size when shearing (mm)	6.54	0.92	8.23
Particle size after Polymerization (mm)	7.48	1.06	9.66
Encapsulation efficiency (%)	80.24	92.15	78.99

a. before being stored in high temperature **b. After being stored in high temperature**

Figure 2. The states of sample of test in high temperature

The results of stability test.

The results of storage in high temperature. The states of sample both before being stored and after being stored in high temperature were shown in Figure 2. It can be observed that after the microcapsule suspension being stored in high temperature, there was no solid precipitation. Mobility and homogeneity of the chlorpyrifos microcapsule suspension still be good and there was no significant change on particle size after being shaken. It can be concluded

that the chlorpyrifos microcapsules prepared have excellent stability in high temperature.

a. Before being stored in low temperature **b. After being stored in low temperature**

Figure 3. The states of sample of test in low temperature

The results of storage in low temperature. The states of sample both before being stored and after being stored in low temperature were shown in Figure 3. As can be seen from Figure 3, after the microcapsule suspension being stored in low temperature, the color of this suspension hasn't changed, and there was no visible solid precipitation. Microcapsules distributed evenly in suspension and there was no agglomeration or freezing. Particle size didn't change. All these indicate that chlorpyrifos microcapsules prepared can be stored in low temperature and have good stability in low temperature.

CONCLUSION

With toluene-2,4- diisocyanate and hexamethylenetetramine as wall material and poly(vinyl alcohol) as dispersant, chlorpyrifos microcapsules prepared by interfacial polymerization have high encapsulation efficiency and excellent stability. By a series of experiments, the optimal ratio of raw materials was determined, which provides a new formulation for industrial production of chlorpyrifos microcapsules. Chlorpyrifos microcapsules prepared enhance the stability of chlorpyrifos and is conducive to ecology and t environment.

Acknowledgement
This work was financially supported by the National Key Technology R&D Program for the 12th Five-Year Plan. (No. 2011BAD44B01).

REFERENCES

[1] SM Wang; ZL Wang; YB Zhang, et al., *Food Chem.*, **2013**, 138(2-3), 2016-2025.
[2] SM Morcillo; JL Yela; Y Capowiez, et al., *Ecotoxicology.*, **2013**, 22(4), 597-607.
[3] FG Uzun; Y Kalender, *Food Chem Toxicol.*, **2013**, 55, 549-556.
[4] P Vijayalakshmi; M Usha, *J Chem Pharm Res.*, **2012**, 4(5), 2532-2539.
[5] PK Pankaj; P Kumar; RC Nigam, et al., *J Chem Pharm Res.*, **2012**, 4(8), 3934-3938.
[6] AP Mishra; P Gupta, *J Chem Pharm Res.*, **2011**, 3(2), 150-161.
[7] L Zhu; ZH Wang; ST Zhang, et al., *J Pesti Sci.*, **2010**, 35(3), 339-343.
[8] PC Hui; WY Wang; CW Kan, et al., *Int J Biol Macromol.*, **2013**, 55, 32-38.
[9] Z Chen; GY Fang, *Renew Sust Energy Rev.*, **2011**, 15(9), 4624-4632.
[10] Q Zhang; P-p Zhang; Q-z Jiao, *Chem Res Chin Univ.*, **2006**, 22(3), 379-382.
[11] SF Lu; JW Xing; ZH Zhang, et al., *J Appl Polym Sci.*, **2011**, 121(6), 3377-3383.
[12] DY Li; ZC Guan; WH Zhang, et al., *ACS Appl Mater Interfaces.*, **2010**, 2(10), 2711-2714.
[13] W Raja; P Rathaur; P Ramteke, et al., *J Chem Pharm Res.*, **2012**, 4(2), 1340-1348.
[14] PK Pankaj; P Kumar; RC Nigam, et al., *J Chem Pharm Res.*, **2012**, 4(8), 3939-3943.
[15] J Zdybel; J Karamon; T Cencek, *Bull Veteri Inst Pul.*, **2011**, 55(3), 411-416.
[16] V Stejskal; R Aulicky; S Pekar, *Pest Manag Sci.*, **2009**, 65(1), 93-98.
[17] D JIang; H Xu; X Yang, *Trans Chin Soc Agri Eng.*, **2008**, 24(2), 205-208.