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Research Article

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Optimization of encapsulation conditions of chlorpyrifos microcapsules

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ABSTRACT

With UF-resin as wall material, chlorpyrifos microcapsules was prepared by in-situ polymerization. The effect factors on the particle size and encapsulation efficiency of microcapsules were investigated and optimized. The result showed when the mass concentration of the emulsifier Tween-20 was 6%, the size of chlorpyrifos microcapsules were suitable. The amount of UF-resin has slight effect on the encapsulation rate. However, the effects of acidification and curing time on encapsulation ratio were quite notable，and the optimal acidification and curing time were 75 min and 90 min respectively. Chlorpyrifos microcapsules prepared under the optimum condition were spherical and smooth with the particle size of 10 μm, entrapment efficiency of chlorpyrifos microcapsules were above 95%.

Keywords: Chlorpyrifos; UF-resin; in-situ polymerization; microcapsule

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INTRODUCTION

At present, Chlorpyrifos, as one of the largest amount of insecticide in the world, widely used to control agricultural and health pest for good control effect. However, the drawback of chlorpyrifos is obvious, mainly because of its high toxicity, unpleasant smell, and strong photolysis that results in a shorter persistence on plant leaves [1, 2]. Currently, the main formulation of chlorpyrifos is EC which consume a large amount of organic solvent and pollute the environment [3]. Therefore, microcapsulating chlorpyrifos can solve the problems of shielding odor, reduce toxicity and stable efficacy, moreover, it has the control release properties which can reduce liquid erosion, prolong persistence, and decrease the frequency of spraying.

The development of controlled release pesticide formulation is an important concern derived from the immediate release of the active ingredient of the commercial formulations. Unlike the classical formulations, microcapsule as a kind of controlled release formulation make a gradual release of the pesticides, which permits a lower concentration of the active ingredients in the environment, at the same time, it is high to maintain biological efficacy[4-6]. The methods used in microcapsule preparation are classified into three categories: physical, chemical and physic-chemical methods [7-9].Chemical method includes interfacial polymerization and situ polymerization and used widely in microcapsule preparation. Because of its abundant raw materials, sophisticated technology, high encapsulation efficiency, good stability, resistant to water penetration ability, good morphology characteristics, situ polymerization method is one of the most promising methods for pesticide microencapsulation [10]. In situ polymerization process，urea formaldehyde resin as wall material is the most economic, because the cost is far lower than the interfacial polymerization technology, manufacturing of pesticide microcapsule has great market potential, and there were some literatures of preparation microcapsules by situ polymerization with urea formaldehyde resin as encapsulant [11-14]. This study attempted to prepare chlorpyrifos microcapsules by situ polymerization with chlorpyrifos as capsule core, urea formaldehyde resin as encapsulant material，and investigated the effect of different factors on the properties of microcapsules.

EXPERIMENTAL SECTION

Experimental materials

Chlorpyrifos were provided by Jiangsu Jinghong Chemical Co., Ltd, And the active ingredient content of the pesticide in the commercial product was 96.6%. Urea(≥ 96%) and formaldehyde solution(40%) were provided by Tianjin North Tianyi Chemical Reagent Factory. Benzene; xylene, carboxymethyl cellulose, sodium dodecyl benzene sulfonate Tween- 20, and Sodium Dodecyl Sulfate were analytical grade, and purchased from Tianjin city, BASF Chemical Co., Ltd.. Chloroform was analytical grade and purchased from Beijing Chemical Works.

Experimental instruments

JrJ-300-I shear emulsifying mixer (Shanghai model and specimens factory), electric mixer (3000 rev/min, 40W, Jiangsu Jincheng Guosheng Experimental Instrument Factory), 95-2 ultrasonic disintegrator (Shanghai Fun Ltd.) BT-9300H laser particle size distribution analyzer (Dandong Baxter Instrument Co., Ltd.), GC-14B liquid chromatograph (SHIMADZU Japan).

Preparation method of chlorpyrifos microcapsules

(1) 15g urea, 30g 37-40% formaldehyde solution (molar ratio =l:2) and 15g of distilled water were added into a three- neck- flask with thermometer and a stirring device, with sodium hydroxide to adjust the pH of 9, rising to 65 ~ 70 ℃, reacted under stirring of 100 $r \cdot min^{-1}$ for 1 hour, then the mass fraction of 25% urea formaldehyde resin prepolymer (UF) was obtained aqueous solution.

(2) The chlorpyrifos was dissolved in the solvent at room temperature, stirred uniformly, and then added UF aqueous solution, a certain amount of emulsifier and dispersant, with a homogenizer at 1500 r/ min^{-1} for 20 min, stable O / W emulsion was formed. The stirring speed reduced to 800 r/ min^{-1}, the solution sample was adjusted to pH 2.0 by Hydrochloric acid. At the same time, chlorpyrifos containing microcapsules with formaldehyde resin prepolymer walls were formed by situ polymerization reaction at the phase interface of emulsion globules. Then the stirring speed was gradually reduced to 200 r/min^{-1}, heated to 80-85℃ progressively for solidifing microcapsules walls. Finally, Stopping the reaction by adjusting the pH value to 7.

The methods of characterization

Measurement of encapsulation efficiency

Weigh certain amount of chlorpyrifos microcapsules into beaker, add benzene extracted chlorpyrifos with ultrasonic wave and then pour the solution out, extracted with ultrasonic wave for three times. The final extracts were filtered by filtration membrane, and volume to 100mL and shake to be even. Microcapsules of encapsulation efficiency was measured by HPLC method with Amethyst C18-H column (4. 6 mm×250 mm), and the mobile phase was the mixture of methanol-water (90 :10), and the flow rate was 1.0 $mL \cdot min^{-1}$. With the detection wavelength of 289 nm. Injection volume: 20 μL [15]. Encapsulation efficiency of chlorpyrifos can be calculated by Eq. (1).

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

where C is the content of chlorpyrifos in 100mL extracts (mg/L), M is the total weight of chlorpyrifos microcapsules (g), a is the sample volume for crushing treatment (g), N is actual added amount of chlorpyrifos (g) [16].

Measurment of the particle size of microcapsules

The particle size of microcapsules was determined by BT-9300H laser particle size distribution analyzer and get median diameter D_{50} to represent of particle size distribution.

RESULTS AND DISCUSSION

Effects of type and amount of emulsifier on chlorpyrifos microcapsules

The emulsification degree of chlorpyrifos pesticide has an important influence on appearance of microcapsule. In this study, twelve sodium alkyl sulfate, sodium dodecyl benzenesulfonate, Tween-20, sodium carboxymethyl cellulose were used as the emulsifier, their influences on the microcapsule properties were showed in Table 1.

As can be seen from Table 1, the different type of emulsifier have different effect on the microcapsule properties, when using the Tween -20 as the emulsifier, the microcapsules were spherical and the system had moderate viscosity that can keep good suspension of microcapsules. Therefore, the Tween-20 was selected as the emulsifier to further study. Fig 1 showed the effect of amount of Twain -20 on the diameter of chlorpyrifos microcapsules. The curve of Fig. 1 indicates when the mass concentration of Tween-20 was 6%, the minimum size of chlorpyrifos

microcapsules were obtained.

Table 1 the effect of different type of emulsifier on the microcapsule properties

NO.	emulsifier	microcapsule properties
1	twelve sodium alkyl sulfate	precipitate of UF particles, smell of Chlorpyrifos
2	sodium dodecyl benzenesulfonate	precipitate of UF particles
3	Tween-20	Moderate viscosity, spherical of microscope particles
4	sodium carboxymethyl cellulose	caking and adhesion

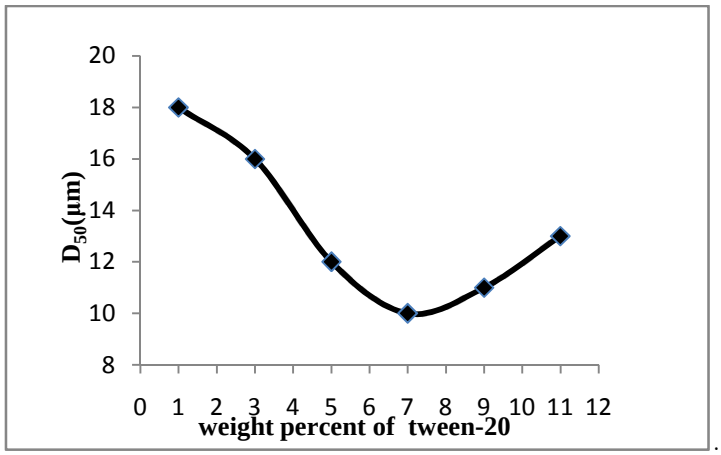

Fig.1 the effect of amount of Twain -20 on the diameter of chlorpyrifos microcapsule

Determination of the optimal ratio of capsule core and wall

The amount of capsule core and wall has great influence on the forming of microcapsule, especially, the release properties and encapsulation efficiency of microcapsule. The encapsulation efficiency was study through the selection of different proportions of urea formaldehyde resin prepolymer and capsule core. The effect of different amount of core material and wall materials on the encapsulation efficiency was shown in fig. 2.

The results of fig. 2 shows that the effect of different rate of capsule core and wall on the encapsulation was not obvious. The performance of different amounts of capsule core and wall mainly influenced the wall thickness, the particle size and distribution of microcapsule, but the encapsulation efficiency was little effected.

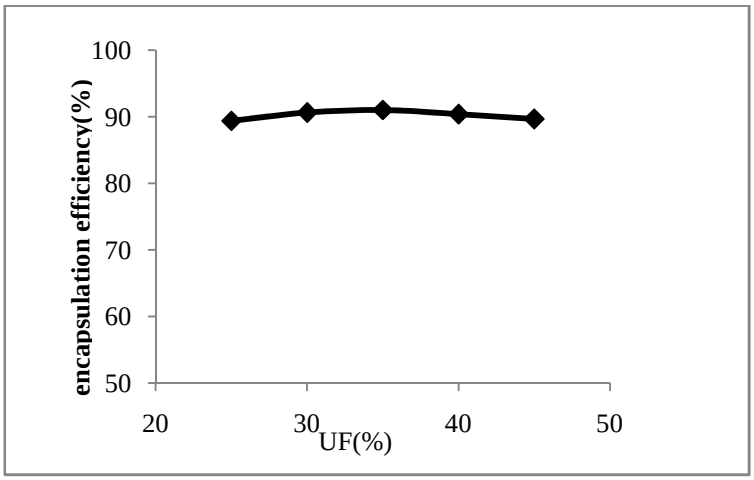

Fig.2 The effect of different amount of core material and wall materials on the encapsulation efficiency

Effect of acidification time on the encapsulation efficiency of the microcapsules

Condensation reaction of urea formaldehyde resin prepolymer was catalyzed by acid in situ polymerization. Therefore, the effects of different acid regulating speed on the encapsulation efficiency were investigated, the results shown in Fig. 3.

The curve of fig.3 indicates that different acidification time has certain influence on the encapsulation efficiency, the

acid regulating speed was not too fast, otherwise it would caused faster reaction rate, rapid deposition, which result in the microcapsule incomplete and low encapsulation efficiency. As can be seen from the curve of fig.3, when acidification time was 75 min and 90 min, the encapsulation efficiency were above 95%.

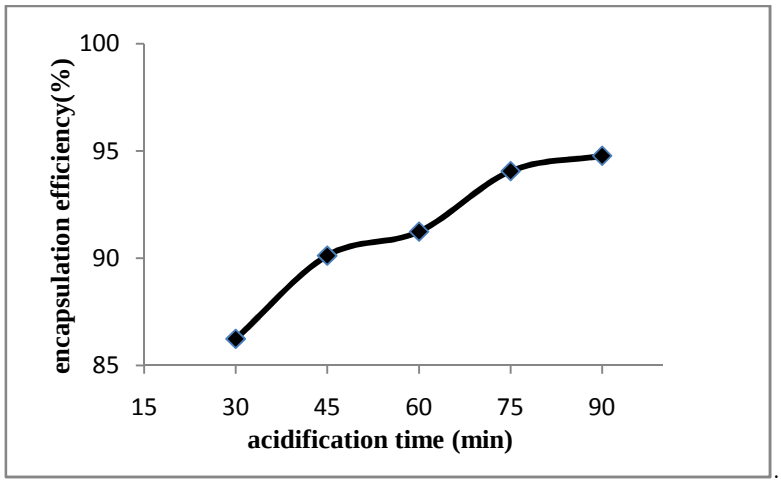

Fig.3The effects of different acidification time on the encapsulation efficiency

Effect of curing time on the encapsulation ratio of the microcapsules

Curing time of microencapsulation has influence on the encapsulation efficiency, mainly impacts on the microcapsule strength. In this study, the effect of different curing time on encapsulation rate was investigated and the result were given in fig. 3. With prolonging the curing time, the encapsulation rate gradually increased. When curing time exceeded 90 min, microcapsule wall formed firmness structure, and the microcapsule has high encapsulation efficiency.

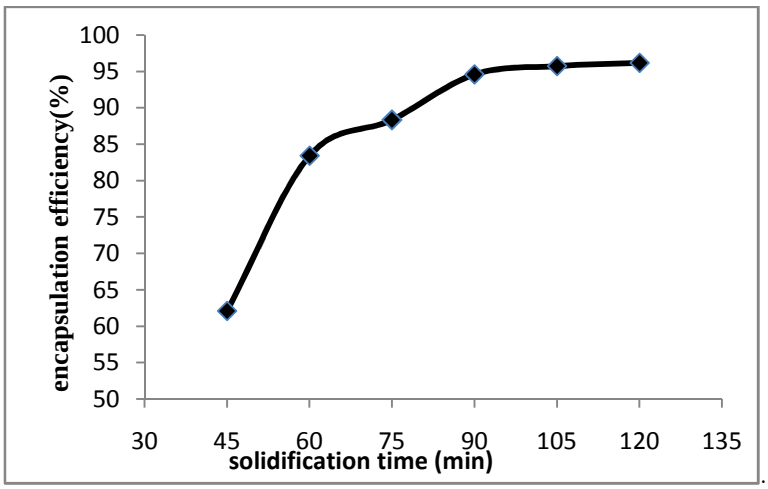

Fig. 3 Effect of curing time on the encapsulation ratio of the microcapsules

CONCLUSION

Microcapsules encapsulation efficiency directly influences on the physical and chemical properties of pesticide microcapsule. In the microcapsule preparation process, the amounts of capsule core and wall, emulsifier, reaction conditions has different effects on the microcapsule particle size and encapsulation efficiency. In order to improve the encapsulation efficiency and stability of suspension, various influencing factors must be comprehensive considered. Chlorpyrifos microcapsule was prepared with urea and formaldehyde as microcapsule walls by using the in-situ polymerization. With the encapsulation efficiency and particle size as evaluated indexes, the emulsifier, the amounts of capsule core and wall, acid regulating speed and solidification time were optimized ,which provided some guidance for chlorpyrifos microcapsules preparation.

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