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Preparation of acetamiprid-loaded polymeric microcapsules: Influence of preparation parameter in emulsion system on microcapsule characteristics

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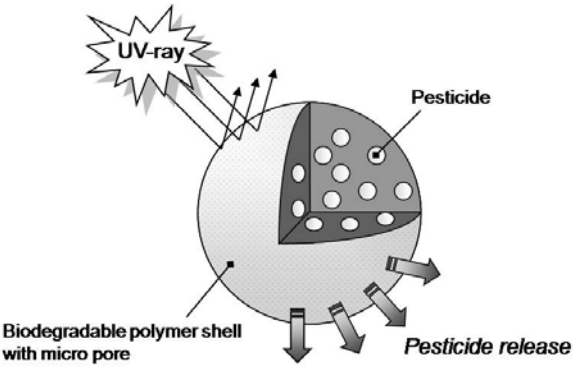
Summary

Microencapsulation of pesticides is a promising technique for avoiding high initial doses and multiple applications of the chemicals to agricultural land which cause environmental pollution. It is because the formulation is possible to improve the stability of the chemicals against environmental degradation and control the release rate. In the present study, polymeric microcapsules prepared by the solvent evaporation method via water-in-oil-in-water (W/O/W) emulsion were used as immobilization supports of acetamiprid, a water-soluble pesticide. The pesticide was loaded in the microcapsules by impregnating the polymeric supports with acetamiprid dissolved in an organic solvent. Increased volume ratio (ϕ) of inner aqueous phase to oil phase in the emulsion system contributed to more pores in the microcapsules and increase in the content of acetamiprid in the polymeric supports. Release rate of acetamiprid from the microcapsules could be controlled by changing ϕ.

Introduction

Pesticides are important chemicals for the stabilization of agricultural production, improvement of the quality of the products and saving in labor [1]. Because of their high volatility and low stability against environmental degradation, the pesticides were generally applied to agricultural land by spraying at high concentration or repeatedly-spraying to obtain the optimum insecticidal effect. The application of the pesticides to the land has been considered to cause global environmental pollution and produce harmful effects on ecological systems [2-4]. Microencapsulation of the pesticides has been demonstrated to be a promising technique for resolving such issues [5]. This is because the formulation is possible to prevent degradation of the encapsulated pesticides by ultraviolet ray and control the release rate of the chemicals (Scheme 1) [6-8], resulting in reduced spraying at high concentrations or repeated spraying.



Scheme 1. Conceptual illustration of microcapsules containing pesticide.

Acetamiprid, (E)-N^1-[(6-chloro-3-pyridyl)methyl]-N^2-cyano-N^1-methylacetamidine, is a novel pesticide developed by Nippon Soda Co., Ltd., to control various noxious insects in agriculture (Figure 1) [9]. The pesticide is soluble in water and certain organic solvents such as ethanol (solubility: approximately 300 mg per 100 ml phosphate buffer solution (pH 7.0) and 2 g per 100 ml ethanol), and has a strong osmosis and an excellent systemic activity against insect pests such as aphids and the diamondback moth, which have resistance to other pesticides [10]. Although studies regarding immobilization supports of the pesticide are essential for environmental conservation and its further widespread utilization, there are very few studies concerning the supports except for our report [8,11].

In the previous study, we prepared acetamiprid-loaded microcapsules with biodegradable polymeric shell by the solvent evaporation method via an oil-in-oil (O/O) emulsion method [8]. The methodology resulted in the low content of acetamiprid in the microcapsules. From the view point of subsequent practical application, achievement of further increased content of acetamiprid in the microcapsules is desired.

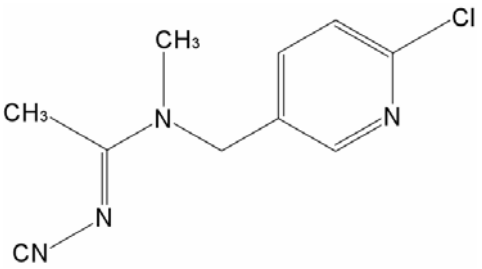


Figure 1. Structure of acetamprid.

In this study, we developed a novel technique for the preparation of the polymeric microcapsules enclosing acetamiprid. Acetamiprid was loaded into the microcapsules by impregnating the polymeric supports with acetamiprid dissolved in an organic solvent to increase the content of acetamiprid in the microcapsules compared to our previous method. Biodegradable polymers such as polylactide (PLA) [12,13] and

poly(ε-caprolacton) (PCL) [14] was used as microcapsule shell materials. Acetamiprid-free microcapsules were prepared by the solvent evaporation method via water-in-oil-in-water (W/O/W) emulsion. We investigated the influence of microcapsule preparation parameter in the emulsion system on microcapsule characteristics such as inner structure and acetamiprid release property.

Experimental

Materials

Acetamiprid was kindly donated by Nippon Soda (Tokyo, Japan). D, L-polylactide (PLA) (Mw; 140000) and poly(ε-caprolactone) (PCL) (Mw; 10000) were obtained from Wako Pure Chemicals (Osaka, Japan) and Daicel Chemical Industries (Osaka, Japan), respectively.

Preparation of microcapsules

Pesticide-free microcapsules were prepared by utilizing the solvent evaporation method via a W/O/W emulsion. An aqueous solution containing 0.5wt% gelatin (inner aqueous phase) was dispersed in 50 ml of a dichloromethane solution with 5% (w/v) dissolved PLA (Mw=140,000), 5% (w/v) PCL (Mw=10,000) and 0.14wt% sorbitan monooleate (oil phase) under agitation using a homogenizer (6000 rpm, Polytron PT10-35, Kinematica Inc.) for 10 minutes for formation of the W/O emulsion. The emulsion was dispersed in 200 ml of an aqueous solution containing 0.5wt% gelatin (outer aqueous phase) under agitation using a mechanical stirrer (150 rpm) for formation of the W/O/W emulsion. The agitation was continued in a nitrogen atmosphere at 25°C for an hour. The solvent was then eliminated with agitation (150 rpm) under reduced pressure (700 hPa, 35°C, 3 hours). After the solvent evaporation, papain was added to the outer aqueous phase to degrade the gelatin. The resultant microcapsules were filtered, washed with distilled water and dried under vacuum. The volume ratio (ϕ) of the inner aqueous phase to the oil phase was varied from 0.2 to 0.5. The procedure for preparation of microcapsules is shown in Scheme 2.

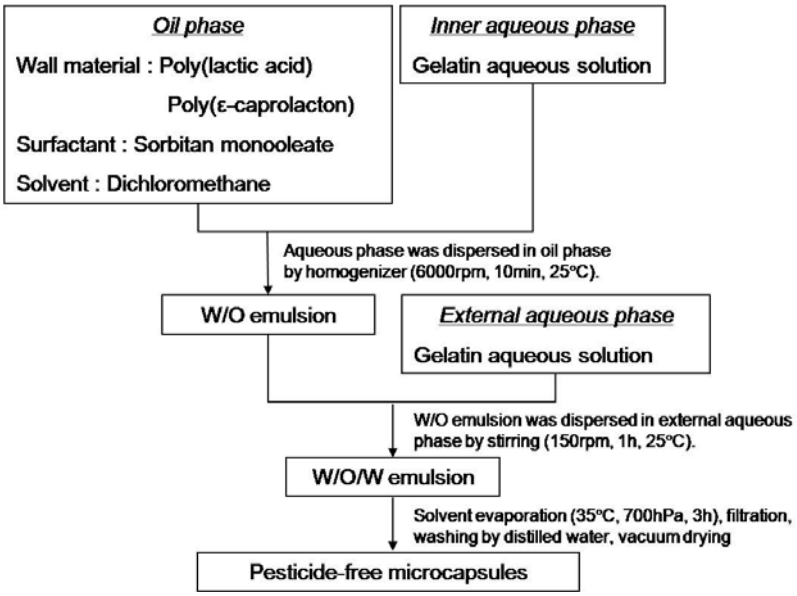
Loading of acetamiprid into microcapsules

One g of the pesticide-free microcapsules were added to 30 ml ethanol solution with 5% (w/v) dissolved acetamiprid and then shaken at 200 rpm for 1 or 3 day(s) to load the pesticide into the polymer supports. Resultant microcapsules were filtered, washed with distilled water and dried under vacuum. We confirmed that the washing process with water scarcely caused decrease in the content (less than 0.1%).

Determination of acetamiprid enclosed in microcapsules

The procedure for measurement of the amount of acetamiprid loaded in the microcapsules was similar to that reported previously [8]. Briefly, 100 mg of the microcapsules suspended in acetonitrile (20 ml) was sonicated for 30 min. The solution was filtered and diluted 1:4 with acetonitrile. The acetamiprid concentration in the solution was determined using a high-performance liquid chromatography

system (SC-8020, Tosoh, Tokyo, Japan) with a reversed phase column (TSKgel ODS-80Ts column, 4.6 × 250 mm, Tosoh). The elution (acetonitrile/acetate-acetic buffer = 1/1 (v/v)) was spectrophotometrically monitored at 245 nm and 0.5 ml/min. Based on the concentration, we calculated the content of acetamiprid in the microcapsules.



Scheme 2. Preparation scheme of pesticide-free microcapsules.

Release of acetamiprid

One hundred mg of the microcapsules containing acetamiprid was put into 500 ml of distilled water containing 0.02 wt% polyoxyethylene sorbitan monooleate in a vial [8], which was then shaken in a water bath kept at 30 ºC. The surfactant was used to prevent the aggregation of microcapsules in the release medium. Four ml of the solution was pipetted out at predetermined intervals. The concentrations of acetamiprid in the samples were spectrophotometrically determined at 245 nm.

Observation by scanning electron microscopy

The morphology of the microcapsules was observed by means of scanning electron microscopy (SEM, Topcon model SM-300; Topcon Co., Ltd). The samples were coated with gold at approximately 300-Å thickness using an ion coater (IB-2; Eiko Engineering Co., Ltd.) and examined by SEM.

Diameters of microcapsules

The mean diameters of the pesticide-free microcapsules were measured by a particle size analyzer (LA-920, HORIBA, Ltd.)

Specific surface areas of microcapsules

The specific surface area of prepared microcapsules was determined by automatic surface area analyzer (Micromeritics FlowSorb III 2310, Shimadzu Co, Tokyo, Japan).

Results and discussion

Preparation of microcapsules

In our previous study, we prepared acetamiprid-loaded polymeric microcapsules by the solvent evaporation method via an O/O emulsion [8]. Acetamiprid was dissolved in the inner oil phase with dissolved synthetic polymers before formation of the O/O emulsion in the previous study. This methodology caused the leakage of the pesticide from the inner oil phase to the outer oil phase and a low content of acetamiprid in the resultant microcapsules (less than 5%). In the present study, we first attempted to increase the content of the acetamiprid by impregnating the pesticide-free microcapsules with acetamiprid dissolved in an organic solution.
Diameters of the pesticide-free microcapsules prepared at ϕ of 0.2, 0.25 and 0.5 were 617 ± 259 μm, 771 ± 223 μm, 700 ± 207 μm, respectively (Figure 2). Figure 3 (a) shows the surface morphology of microcapsules prepared at ϕ = 0.5. Pores and indentations were observed in the surface. The surface morphologies of the microcapsules prepared at ϕ = 0.2 and 0.25 were similar to that of the microcapsules at ϕ = 0.5 (data not shown). Figure 3 (b)-(d) show the inner structures of the microcapsules. The images indicate that increased ϕ resulted in more pores in the microcapsules. An examination using a surface area analyzer shows that increased ϕ contributed to an increase in specific surface area (Figure 4). This examination exemplifies our finding that increased ϕ resulted in more pores, i.e., well-developed porous structure in the microcapsules.

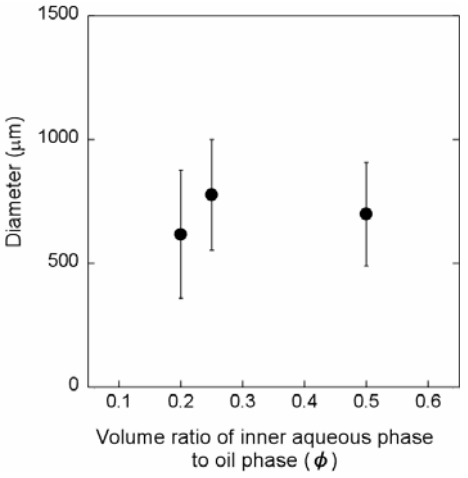


Figure 2. Diameters of pesticide-free microcapsules prepared at ϕ = 0.2, 0.25 and 0.5.

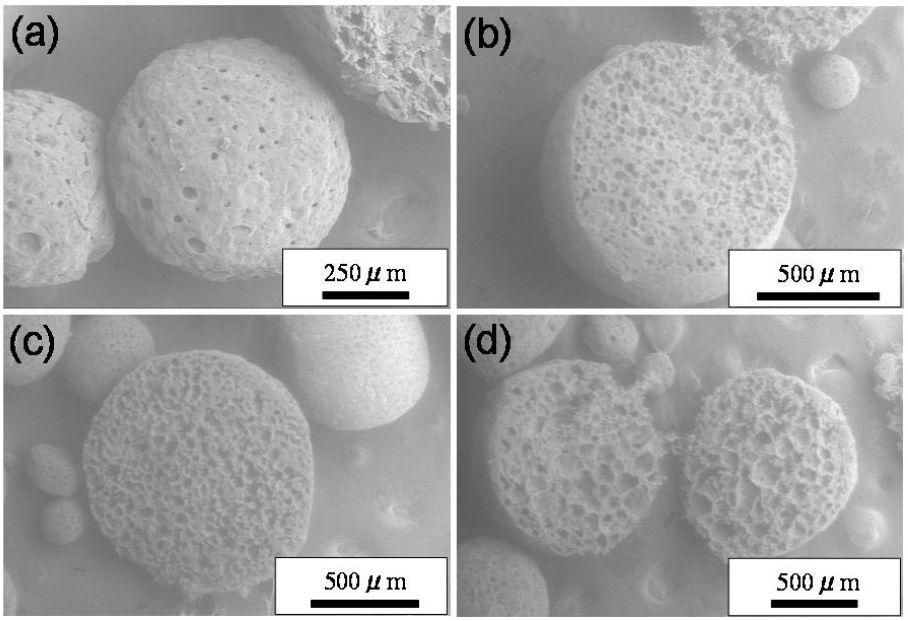


Figure 3. (a) The surface morphology of microcapsules (ϕ = 0.5). (b-d) Cross-sections of the microcapsules prepared at ϕ = 0.2 (b), 0.25 (c) and 0.5 (d).

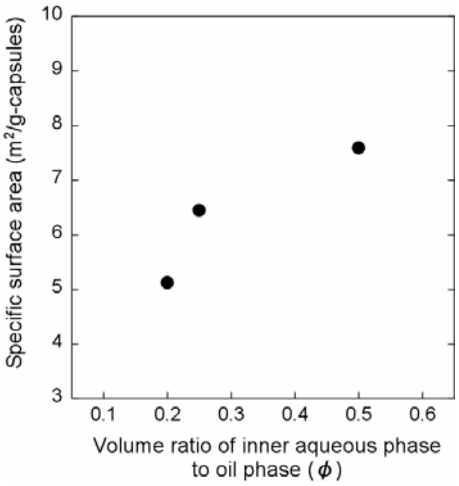


Figure 4. Specific surface area of the microcapsules as a function of ϕ.

Figure 5 shows the influences of ϕ and incubation time of microcapsules in an ethanol solution with the dissolved pesticide on the content of acetamiprid in the microcapsules. Theoretical contents at ϕ = 0.2, 0.25 and 0.5 were 10.5%, 13.2% and 26.5%, respectively. The values were calculated based on a hypothesis that the ethanol

solution only penetrated the pore space in the microcapsules derived from inner aqueous phase. Much difference between incubation time of 1 and 3 day(s) on the content was not observed, indicating that incubation time of 1 day is sufficient to load the pesticide into the microcapsules. The contents of the acetamiprid at ϕ of 0.2, 0.25 and 0.5 at the incubation time of 1 day were 9.8, 10.2 and 11.0%, respectively. Thus, the impregnation of microcapsules with acetamiprid dissolved in an organic solvent was the efficient technique to increase the content compared to our previous method. The increased content of the acetamiprid with increasing ϕ, i.e., specific surface area of the microcapsules indicates that crystalline acetamiprid was immobilized to the surfaces of pores.

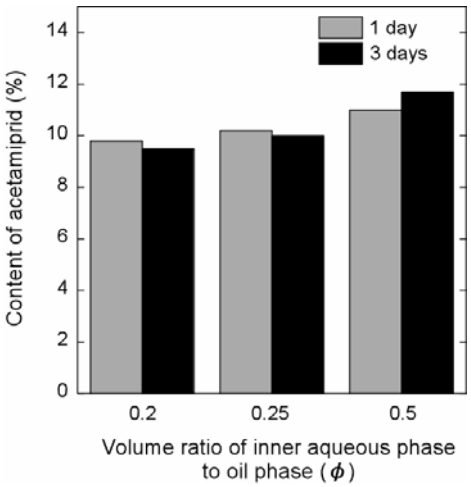


Figure 5. Contents of acetamiprid in microcapsules as a function of ϕ and incubation time in an ethanol solution containing pesticide. Theoretical contents at ϕ = 0.2, 0.25 and 0.5 were 10.5%, 13.2% and 26.5%, respectively.

Release of acetamiprid

To obtain basic experimental knowledge essential for preparing the acetamiprid-loaded microcapsules for practical application, we investigated the effect of ϕ on the release property using microcapsules incubated in an ethanol solution with the dissolved pesticide for 3 days. Releasable amount of acetamiprid loaded in microcapsules tended to increase with increasing ϕ, i.e., specific surface area of the polymeric supports (Figure 6). We subsequently determined permeability coefficient (k_p) of acetamiprid in microcapsules to investigate the effect of ϕ on the acetamiprid release property in more detail. The coefficient was calculated from the release profiles within an hour using the following equation defined under the assumption that the microcapsule shell is plate, which is based on the fact that thickness of the shell is much smaller than the diameters of microcapsules [15].

$$\ln((C_\infty - C) / (C_\infty - C_o) = - 6\, k_p\, t / \alpha\, d_p \qquad \textbf{(1)}$$

where t is the time, α is the content of acetamiprid in the microcapsules, d_p is the mean diameter of the microcapsules, C_o is the acetamiprid concentration in the release

medium at $t = 0$, C is the concentration in the medium at $t = t$ and C_∞ is the concentration in the medium at $t = \infty$. Figure 7 shows the permeability coefficients as a function of ϕ. This figure apparently demonstrates that an increased ϕ resulted in an increased permeability coefficient. The finding is interpreted as a consequence of the enhanced diffusion of the pesticide in the polymer supports with development of porous structure inside the microcapsules. Thus, the release rate and releasable amount of the acetamiprid from the microcapsules could be controlled by changing ϕ.

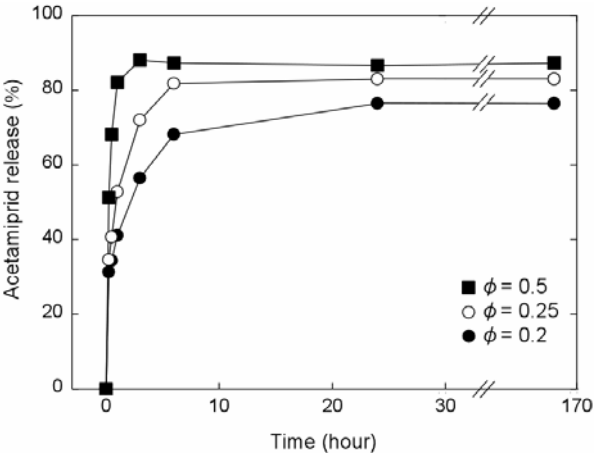


Figure 6. Release profiles of acetamiprid from the microcapsules.

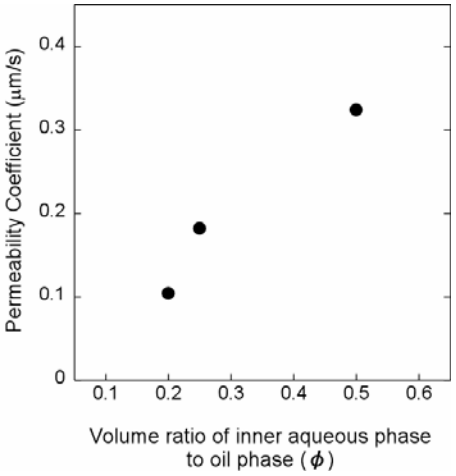


Figure 7. Permeability coefficients of acetamiprid loaded in the microcapsules.

Conclusion

In the present study, we loaded acetamiprid, a water-soluble pesticide, into polymeric microcapsules by impregnating the pesticide-free polymeric supports with acetamiprid dissolved in an ethanol solution. The acetamiprid-free microcapsules were prepared

using the W/O/W emulsion solvent evaporation method. Increased volume ratio (ϕ) of inner aqueous phase to oil phase resulted in more pores in the microcapsules and increase in the content of acetamiprid in the polymeric supports. Release rate of acetamiprid from microcapsules could be controlled by changing ϕ.

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