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Preparation, Characterization, and Bioactivity Evaluation of Lambda-Cyhalothrin Microcapsules for Slow-Controlled Release System

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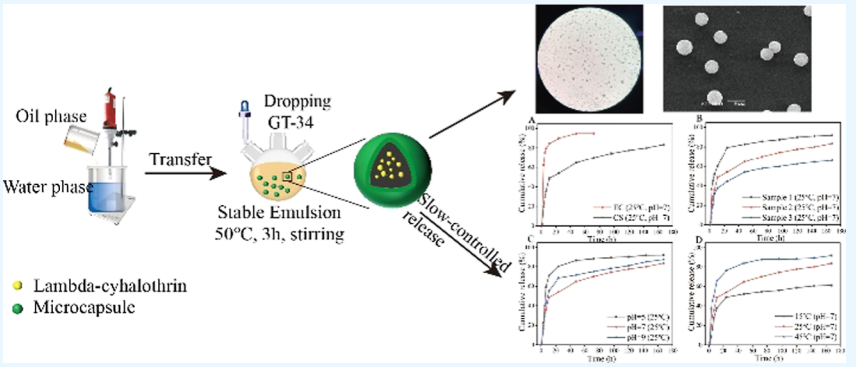

ABSTRACT: The utilization of interfacial polymerization in the preparation of microcapsules with a slow-controlled release has been shown to effectively improve pesticide efficacy and reduce environmental pollution. In this study, polyurea microcapsules loaded with lambda-cyhalothrin were prepared by an interfacial polymerization method using modified isocyanate (MDI) as the wall material and GT-34 as the initiator. The microcapsules were fully characterized by optical microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis, etc., and release behaviors were investigated. The results indicated that the microcapsules had a smooth surface and uniform distribution, the average particle size of the microcapsules was 1.97 μm, and the encapsulation efficiency of lambda-cyhalothrin microcapsules could reach 91.48%. Compared with other commercial formulations, the microcapsules exhibited an excellent sustained release property (>7 days) in a 50% acetonitrile aqueous solution (v/v). Subsequently, in vitro release studies showed that the lambda-cyhalothrin microcapsules could consistently control the release of the core materials at different pH, temperature, and MDI addition amount conditions. The release of lambda-cyhalothrin microcapsules was in accordance with the first-order model release, which was mainly by the Fickian diffusion mechanism. Furthermore, the biological activity on *Myzus persicae* showed that the microcapsules' persistence period was above 21 days, which was longer than that for the emulsifiable concentrate formulation.

1. INTRODUCTION

Planted crops are an important part of the agricultural industry.[1] Insect pests drastically reduce crop yields through direct and transmitted diseases. It is estimated that pests can reduce crop yields by about 30−40%.[2] Pesticides play an important role in pest and disease control as an important raw material for agricultural production.[3] Therefore, the use of pesticides is essential to protect crops and promote sustainable agriculture.[4] More than 80% of pesticides are lost through biodegradation, chemical degradation, photolysis, and evaporation, as reported by Liu et al.[5] However, the long-term widespread and inefficient use of pesticides to control pests has led to increasing resistance to pests and diseases, causing serious harm to the environment and human health.[6] With the increasing awareness of environmental protection, the use of formulations with slow and controlled release properties for control appears necessary and is one strategy to overcome or delay the development of resistance.

Slow-controlled-release formulations of pesticides are known as storage systems and have great potential in the field of pesticides. The advantages are a more effective treatment, reduced side effects, prolonged efficacy, and improved safety and reliability.[7,8] Among them, microencapsulation is a common method used to achieve a slow and controlled release

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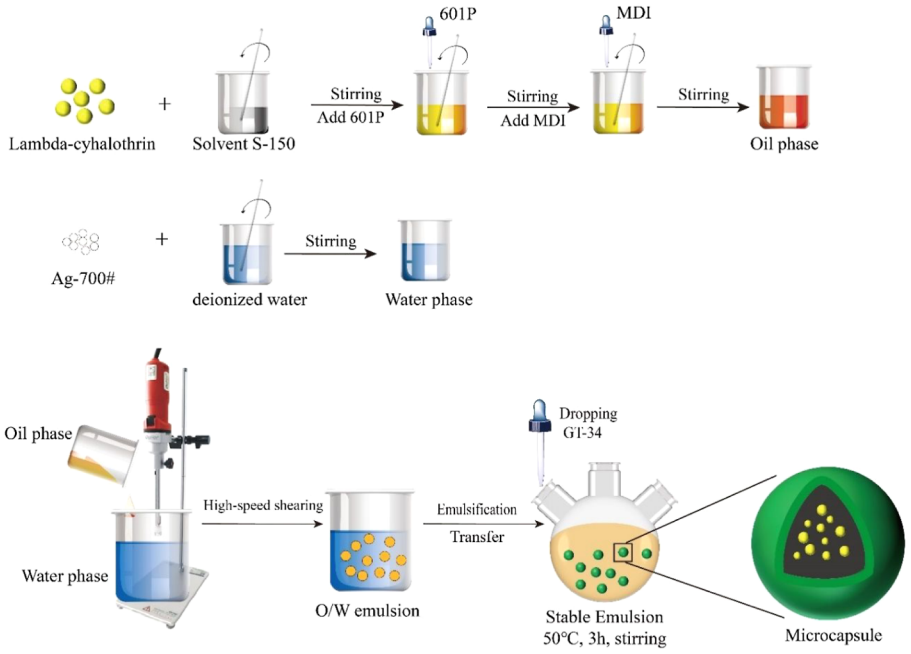

Figure 1. Schematic diagram for preparing microcapsules by interfacial polymerization.

performance for many kinds of pesticides. Microencapsulation as a controlled release technology refers to the use of natural, seminatural, or synthetic polymeric materials to encapsulate pesticide-active ingredients to form microcapsules with semipermeable or sealed capsule membranes by chemical, physical, or physicochemical methods.[9] Microcapsules have been widely used in many fields, such as food,[10] cosmetics,[11] materials,[12] and pesticides.[13] In pesticides, microencapsulated shells isolate the original drug from the external environment, which not only masks the odor but also avoids the degradation of sensitive pesticides and improves the utilization of pesticides. It also reduces skin irritation and toxicity of some pesticides to users and delays the development of resistance to the target. There are various methods for the preparation of microcapsules, including in situ polymerization,[14] interfacial polymerization,[15,16] emulsion polymerization,[17] double-emulsion method,[18] and solvent evaporation.[19]

Interfacial polymerization is one of the most commonly used methods to produce pesticide microcapsules; it has the unique advantages of high encapsulation rate, good thermal stability, and good slow release and has become the mainstream method for microcapsule preparation in the field of pesticide preparation.[20,21] Interfacial polymerization mainly uses polyisocyanate to react with polyol or polyamine to form polyurethane or polyurea. Among them, polyurea refers to a compound with a repeated urea-based structure (−NH−CO−NH−) in its molecular structure, which is a common wall material for preparing microcapsules by interfacial polymerization and is widely studied as one of the packaging materials for controlled release applications. It has the advantages of stability, good film formation, and good release characteristics.

Lambda-cyhalothrin is an efficient, broad-spectrum, and fast-acting pyrethroid insecticide,[22] which affects insects when they ingest or touch the insecticide, and is widely used in agriculture and other fields in China.[23,24] However, the main formulations of lambda-cyhalothrin in Chinese agriculture chemical registrations are emulsifiable concentrate (EC), microemulsion (ME), and emulsion in water, while microencapsulated formulations are fewer. Conventional formulations usually experience a rapid decrease in effect after the early burst release of active ingredients, which has induced serious concerns about the ecological environment. The interfacial polymerization method for the preparation of polyurea microcapsules as drug carriers not only reduces environmental pollution but also has been extensively investigated as a drug carrier for sustained and controlled release. To date, the construction of lambda-cyhalothrin-loaded polyurea microcapsules has not received significant effort, nor has the optimization of the process conditions. This work provides some technical support for the study of the preparation of lambda-cyhalothrin polyurea microcapsules by interfacial polymerization.

In this work, we prepared lambda-cyhalothrin polyurea microcapsules by interfacial polymerization under optimized preparation conditions using modified isocyanate (MDI) as the precursor and GT-34 as the curing agent. Lambda-cyhalothrin microcapsules with controlled encapsulation efficiency (EE) and particle size were obtained by changing the MDI addition amount, emulsion addition amount, and dispersant addition amount. A comprehensive characterization of lambda-cyhalothrin microcapsules was performed to investigate the slow and controlled release performance of the microencapsulated formulations, and release kinetic modeling was performed to investigate the release mechanism. In addition, bioactivity studies were carried out.

2. RESULTS AND DISCUSSION

2.1. Preparation of Lambda-Cyhalothrin-Loaded Microcapsules. The lambda-cyhalothrin microcapsules were prepared in two steps. First, the oil phase was poured into a water phase, and the two phases were mixed and sheared at a high speed of 10,000 rpm to form a uniform O/W emulsion. Second, GT-34 was dropped into the emulsion as the initiator. The −NCO group of MDI and the -NH2 group of GT-34 react at the stable O/W interface to produce a polyurea shell. The preparation procedure and the reaction mechanism of lambda-cyhalothrin are illustrated in Figures 1 and 2.

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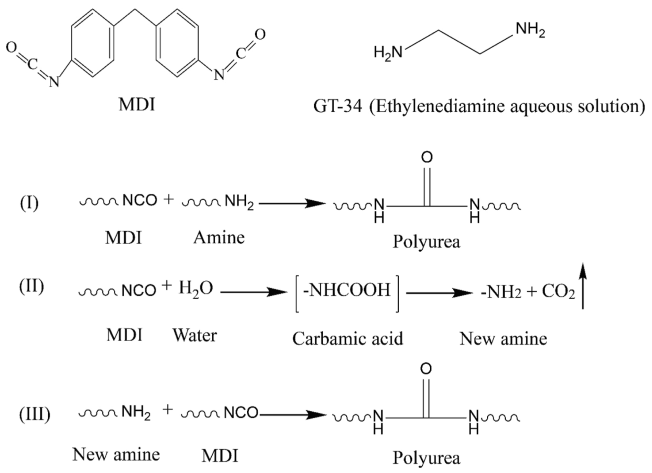

Figure 2. Mechanism of microcapsule preparation by interfacial polymerization.

The preparation of lambda-cyhalothrin microcapsules was influenced by several factors, including the MDI addition amount, the 601P addition amount, and the AG-700# addition amount. To optimize the microcapsule preparation process, the EE and particle size distribution of lambda-cyhalothrin microcapsules were investigated.

2.1.1. Effect of Each Composition Content on Microencapsulation. The effects of the amounts of MDI, 601P, and AG-700# on the particle size and EE of microcapsules are given in Table 1. As shown in Table 1, the particle size (D50) became bigger from 1.58 to 6.84 μm, and the EE increased slightly from 89.73 to 91.82% when the content of MDI increased from 1 to 6 g. It could be attributed to the fact that increasing the amount of MDI addition amount increased the thickness of the capsule shell and increased the particle size. It was shown in samples 2, 4, and 5 that with the increasing amount of 601P, the D50 decreased from 2.52 to 1.88 μm. When the amount of 601P was 3 g, the EE was only 83.24%. It could be concluded that the increased amount of emulsifier in a certain range resulted in enhanced emulsification of the oil phase, which resulted in smaller particle sizes of the oil droplets distributed in the emulsion. Samples 2, 6, and 7 showed that the particle size D50 decreased from 2.40 to 1.97 μm and the EE increased from 84.83 to 91.48% when AG-700# was increased from 1 to 3 g. It was mainly because the addition of the right amount of dispersant made the microcapsules have a certain repulsive force between them and were not easy to agglomerate.

As shown in Table 1, for samples 2, 3, and 4, the EE of the microcapsules was more than 90%. However, sample 2 was better dispersed and had the smallest particle size. Finally, MDI 3 g, 601P 2 g, and AG-700# 3 g were selected to prepare the lambda-cyhalothrin microcapsule suspension (sample 2), which was characterized for physicochemical properties.

2.2. Morphological Characterization. The microcapsules had a good appearance, morphology, and dispersibility, which were beneficial to improve the adhesion and penetration of pesticides to the target crop and increase their activity.[25,26] The optical microscopy (OM) and scanning electron microscopy (SEM) images of the microcapsules containing lambda-cyhalothrin are presented in Figure 3. The OM images showed

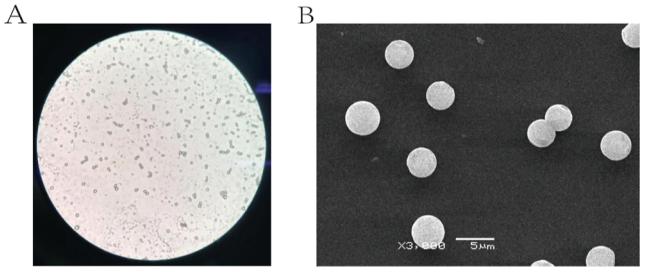

Figure 3. Appearance and morphology image of lambda-cyhalothrin microcapsules. (A) OM image of microcapsule sample 2, (B) SEM image of microcapsule sample 2.

that the microcapsules were uniformly dispersed without aggregation (Figure 3A). The SEM images revealed that the microcapsule particles were spherical, compact, and had a smooth outer surface, and there was no ruptured phenomenon (Figure 3B).

2.3. Particle Size Analysis. The smaller particle size not only easily adheres to the target crop but also increases the contact area with the target crop, thus achieving a better control effect.[27] The particle size distributions of the microcapsules are given in Figure 4. The particle size curve of lambda-cyhalothrin microcapsules showed a normal distribution with a particle span of 2.31, indicating a relatively concentrated particle size distribution. The average particle size of the microcapsules was 1.97 μm, and the particle size distribution range was between 0.78 and 5.53 μm.

2.4. FTIR Spectral Analysis. Figure 5 shows the FTIR spectra of the technical lambda-cyhalothrin, blank microcapsules, and lambda-cyhalothrin microcapsules. As shown in curve a, the absorption peaks at 3070, 1728, 1587, and 1130 cm^{-1} were attributed to the characteristic stretching vibration peaks of $-CH_3$, C=O, aromatic ring, and C−F, respectively, in technical lambda-cyhalothrin.[23,28] In curve b, the absorption peak at 2277 cm^{-1} was the stretching vibration of C=O in the polyurea formed by MDI and GT-34, indicating the successful formation of polyurea; similar results were reported before.[29] In curve c, the characteristic absorption peaks of technical lambda-

Table 1. Effects of Different Component Amounts on EE and Particle Size Distribution of Microcapsules (Mean ± SD, n = 3)

				size distribution(μm)			
samples	MDI (g)	601P (g)	AG-700# (g)	D10	D50	D90	EE (%)
1	1	2	3	0.53 ± 0.02	1.58 ± 0.04	4.88 ± 0.03	89.73 ± 0.62
2	3	2	3	0.78 ± 0.05	1.97 ± 0.02	5.53 ± 0.03	91.48 ± 0.51
3	6	2	3	2.42 ± 0.08	6.84 ± 0.05	9.40 ± 0.11	91.82 ± 0.84
4	3	1	3	0.80 ± 0.03	2.52 ± 0.04	5.97 ± 0.08	90.67 ± 0.33
5	3	3	3	0.76 ± 0.07	1.88 ± 0.04	4.62 ± 0.06	83.24 ± 1.02
6	3	2	2	0.78 ± 0.03	2.09 ± 0.02	5.34 ± 0.08	86.60 ± 0.57
7	3	2	1	0.81 ± 0.09	2.40 ± 0.09	12.01 ± 0.12	84.83 ± 0.86

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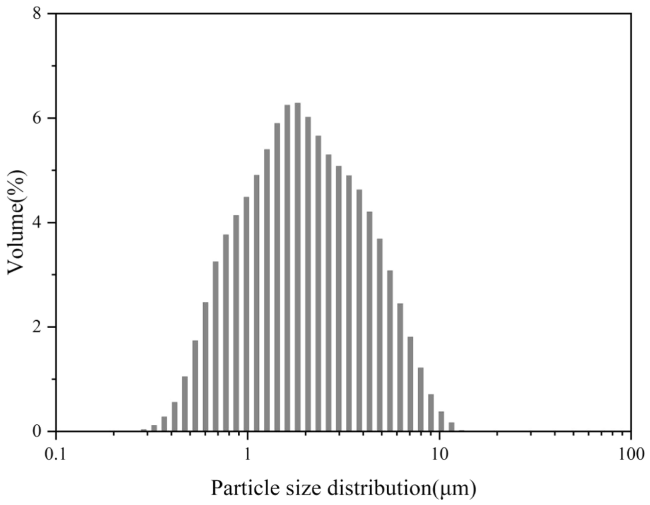

Figure 4. Particle size distribution of microcapsule sample 2.

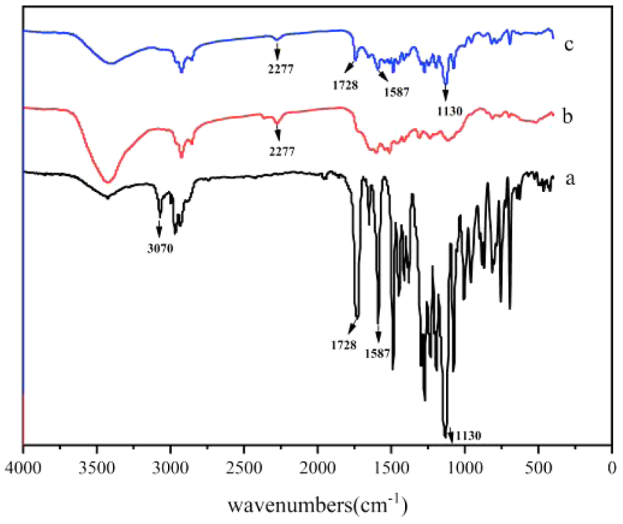

Figure 5. FTIR spectra of (a) technical lambda-cyhalothrin, (b) blank microcapsules, and (c) microcapsules sample 2.

cyhalothrin at 1728, 1587, and 1130 cm^{-1} can be found, and the characteristic absorption peak of polyurea was at 2277 cm^{-1}, which confirmed the formation of polyurea microcapsules and the successful loading of lambda-cyhalothrin.

2.5. Thermal Stability of Microcapsules. Thermogravimetric analysis (TGA) has frequently been used to study the decomposition pattern and thermal stability of chemicals and materials.[30] In this work, TGA was performed for the technical lambda-cyhalothrin, lambda-cyhalothrin microcapsules, and blank microcapsules, as shown in Figure 6. In curve c, the obtained blank microcapsules underwent two main mass loss phases in the investigated region, i.e., 100−500 °C. This was mainly due to the decomposition and incomplete decomposition of polyurea wall materials. It was shown in curve a that the weight loss between 200 and 300 °C may be due to the volatilization and decomposition of lambda-cyhalothrin. The platform appeared at around 300 °C, indicating the complete decomposition of lambda-cyhalothrin.[28] It is worth noting that the mass loss of lambda-cyhalothrin microcapsules had two main stages. The first mass loss, at 100−300 °C, originates from the decomposition of the shell material and volatilization of the core material. The second mass loss, at ranges over 300 °C, was

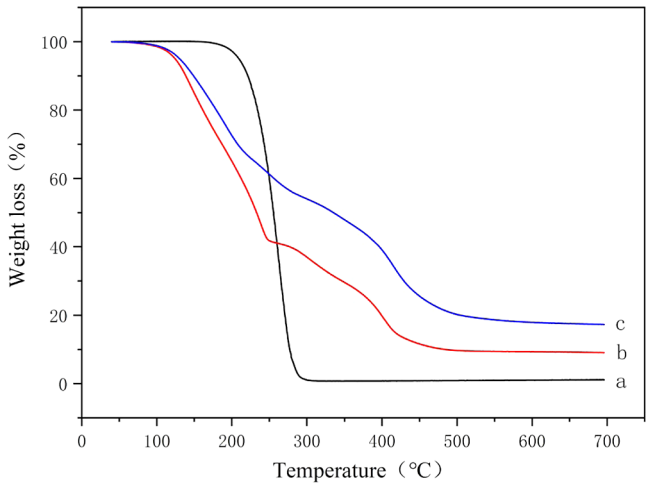

Figure 6. TGA curves of (a) technical lambda-cyhalothrin, (b) microcapsules sample 2, and (c) blank microcapsules.

caused by the decomposition of the residues remaining from the first phase. Compared with blank microcapsules, the weight loss of the lambda-cyhalothrin microcapsules was significantly increased, so this two-stage mass loss provides clear evidence of core material encapsulation.

2.6. Release of Microcapsules. Figure 7 shows comparative images of the appearance and morphology of lambda-

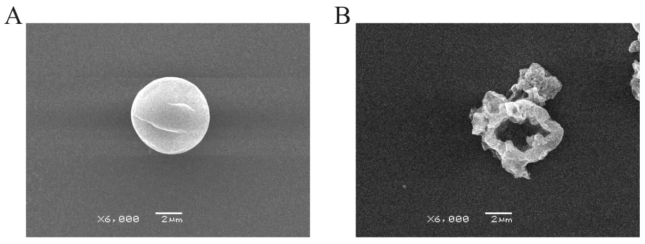

Figure 7. SEM images of microcapsule sample 2 before and after release. (A) Before release. (B) After release.

cyhalothrin microcapsules before and after release. Figure 7A shows the SEM image of the original microcapsule sample. Figure 7B shows the SEM image of lambda-cyhalothrin microcapsules after 312 h of release in the release medium. In this case, the microcapsules' spherical shells collapsed and released the active ingredient, leaving only the capsule shell material. From this, it is initially believed that the microcapsule was released through the mechanism of osmotic diffusion through the capsule membrane. The process was that the release medium wet the capsule, then the capsule core material dissolved in the slow-release medium, and finally it was gradually released due to the concentration difference between the inside and outside of the capsule wall.[31] This indicated that the microcapsules prepared by this method and the material had good release performance.

2.7. Slow-Controlled Release Performance. Sustained-release from microcapsules and commercial formulations were compared. As shown in Figure 8A, the release behaviors of the prepared lambda-cyhalothrin microcapsules and commercial lambda-cyhalothrin EC were investigated at 25 °C, pH = 7. In the case of the lambda-cyhalothrin EC, an initial rapid release was observed within 3 h (i.e., 62.19%), with complete release occurring by 48 h. In contrast, lambda-cyhalothrin was released

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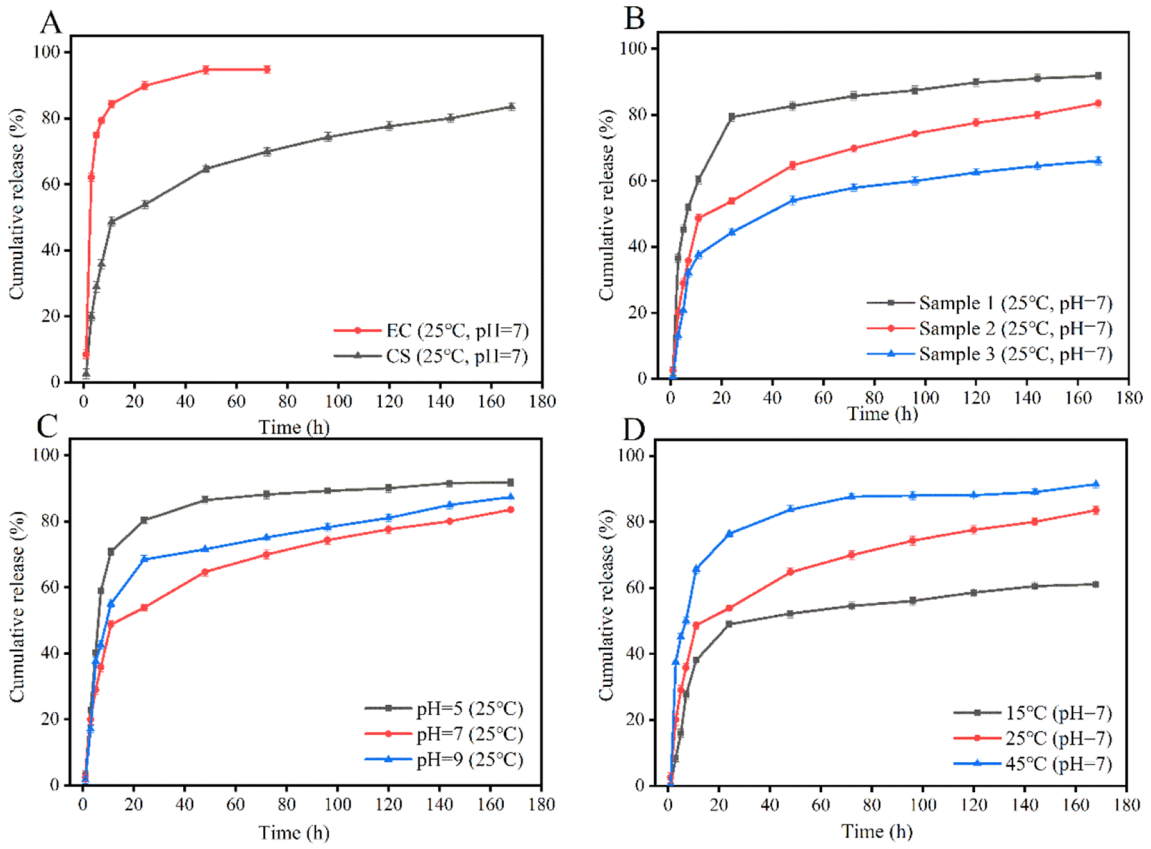

Figure 8. Release behavior of lambda-cyhalothrin microcapsules. (A) Release behaviors of microcapsules with different formulations (microcapsules sample 2 and EC). (B) Release behaviors of microcapsules with different MDI addition amounts (samples 1, 2, and 3). (C) Release curves of microcapsules sample 2 at different pH. (D) Release curve of microcapsules sample 2 at different temperatures.

more slowly from the microcapsules, with a release of 20.07% being reached at 3 h, followed by a slow and sustained release to a cumulative release of 83.53% after 168 h and continuing to be released. These results indicate that under the same conditions, the lambda-cyhalothrin microcapsules exhibited a longer sustained-release profile than the commercial lambda-cyhalothrin EC, which showed that the lambda-cyhalothrin microcapsules have good slow-release performance. Indeed, previous reports have consistently shown that polyurea microcapsules prepared from MDI exhibited a long slow-release performance, thus confirming the potential of such systems.[32,33]

The release behavior of microcapsule samples (samples 1, 2, and 3) prepared with different MDI addition amounts was studied under the same conditions (25 °C, pH = 7), as shown in Figure 8B. The results of the release within the first 24 h showed that there was a quick release of microcapsules sample 1, with a cumulative release of about 79.36%; the release of microcapsules samples 2 and 3 was relatively slow, with a cumulative release of 53.90 and 44.38%. After 168 h, the cumulative release increased due to the increase of the active ingredient content in the release medium; with samples 1, 2, and 3, the cumulative release reached up to 91.23, 83.53, and 66.30%, respectively. During the preparation of microcapsules, the increased amount of wall material made the capsule walls thicker, which made the complete release of active ingredients from microcapsules more difficult, and the cumulative release was small, which had been similarly reported before.[34] Adjusting the MDI addition amount therefore enables the preparation of microcapsules with an ideal release rate.

The release behaviors of lambda-cyhalothrin from microcapsules under different pH values (5, 7, and 9) are shown in Figure 8C. It was noticed that in the initial release, the three release curves were relatively similar. Subsequently, after 168 h, the cumulative release reached up to 91.32, 83.53, and 87.37% at pH = 5, 7, and 9, respectively. When the other conditions were the same, in release media with a pH = 5, because the reactive free primary amine groups of the polyurea shell wall generated soluble salt under acidic conditions, a high degree of lambda-cyhalothrin was released in the core.[35] Because the hydrolysis of polyurea under alkaline conditions was also faster than in neutral media, the cumulative release rate of lambda-cyhalothrin at pH = 9 was slightly higher than at pH = 7, which was consistent with previous results.[36]

To investigate the release performance of lambda-cyhalothrin at different temperatures, Figure 8D shows the lambda-cyhalothrin cumulative release in buffer solutions from lambda-cyhalothrin microcapsules at 15, 25, and 45 °C. After the lambda-cyhalothrin microcapsules were incubated with the release medium at 15, 25, and 45 °C for 168 h, the cumulative amount of lambda-cyhalothrin released reached 61.13, 83.53, and 91.47%, respectively. The release rate of microcapsules increased with the increase in temperature, which was consistent with previous results.[9] This also demonstrated the potential application of lambda-cyhalothrin microcapsules in different temperature environments.

2.8. Release Kinetics of Microcapsules. The mathematical model fitting of the sustained release system of pesticides provides a theoretical basis for microcapsule design. To understand the release mechanism of lambda-cyhalothrin, the

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Table 2. Mathematical Model Fitting of the Release Curve of Lambda-Cyhalothrin Microcapsules and Lambda-Cyhalothrin EC in the Release Medium[a]

	zero-order		first-order		Higuchi model		Ritger−Peppas model	
	equation	R^2	equation	R^2	equation	R^2	equation	R^2
CS	$Q_t = 0.349t + 34.571$	0.709	$Q_t = 74.352(1 - e^{-0.079t})$	0.925	$Q_t = 5.531t^{1/2} + 18.735$	0.866	$Q_t = 16.584t^{0.352}$	0.879
EC	$Q_t = 0.576t + 64.062$	0.189	$Q_t = 92.555(1 - e^{-0.294t})$	0.924	$Q_t = 6.952t^{1/2} + 49.248$	0.364	$Q_t = 17.024t^{0.946}$	0.797
sample 1	$Q_t = 0.347t + 46.458$	0.546	$Q_t = 87.607(1 - e^{-0.127t})$	0.967	$Q_t = 5.537t^{1/2} + 31.361$	0.720	$Q_t = 20.107t^{0.410}$	0.859
sample 2	$Q_t = 0.349t + 34.571$	0.709	$Q_t = 74.352(1 - e^{-0.079t})$	0.925	$Q_t = 5.531t^{1/2} + 18.735$	0.866	$Q_t = 16.584t^{0.352}$	0.879
sample 3	$Q_t = 0.321t + 23.479$	0.690	$Q_t = 60.792(1 - e^{-0.080t})$	0.965	$Q_t = 4.870t^{1/2} + 11.137$	0.853	$Q_t = 13.976t^{0.318}$	0.909
pH = 5	$Q_t = 0.354t + 47.869$	0.477	$Q_t = 89.238(1 - e^{-0.126t})$	0.979	$Q_t = 5.687t^{1/2} + 32.182$	0.661	$Q_t = 10.254t^{0.383}$	0.939
pH = 7	$Q_t = 0.349t + 34.571$	0.709	$Q_t = 74.352(1 - e^{-0.079t})$	0.925	$Q_t = 5.531t^{1/2} + 18.735$	0.866	$Q_t = 16.584t^{0.352}$	0.879
pH = 9	$Q_t = 0.384t + 35.978$	0.616	$Q_t = 79.301(1 - e^{-0.103t})$	0.966	$Q_t = 5.902t^{1/2} + 20.340$	0.786	$Q_t = 16.951t^{0.401}$	0.810
15 °C	$Q_t = 0.289t + 23.759$	0.571	$Q_t = 57.640(1 - e^{-0.082t})$	0.975	$Q_t = 4.552t^{1/2} + 11.586$	0.759	$Q_t = 14.034t^{0.306}$	0.835
25 °C	$Q_t = 0.349t + 34.571$	0.709	$Q_t = 74.352(1 - e^{-0.079t})$	0.925	$Q_t = 5.531t^{1/2} + 18.73$	0.866	$Q_t = 16.584t^{0.352}$	0.879
45 °C	$Q_t = 0.357t + 45.449$	0.511	$Q_t = 86.925(1 - e^{-0.134t})$	0.962	$Q_t = 5.670t^{1/2} + 30.186$	0.697	$Q_t = 13.934t^{0.270}$	0.823

[a]The Ritger−Pappas model was fitted to 60−70% of the respective release due to model constraints.

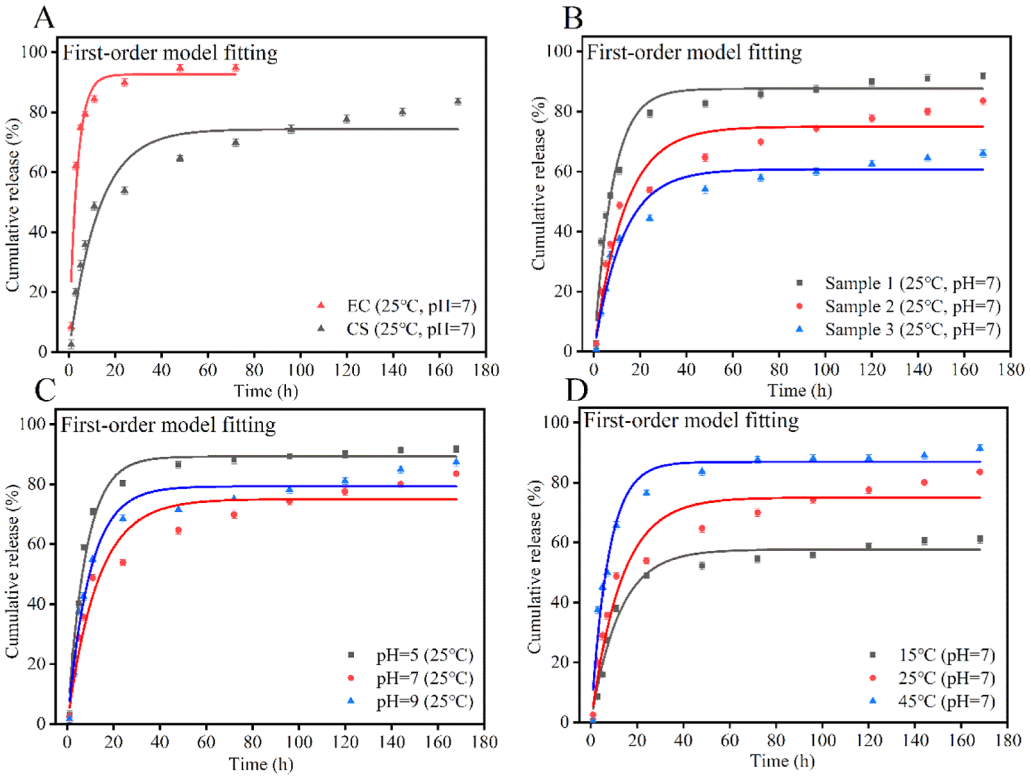

Figure 9. Results of the first-order model fitting of the lambda-cyhalothrin release curves (A) different formulations (microcapsules sample 2 and EC), (B) different MDI addition amounts (samples 1, 2, and 3), (C) different pH, and (D) different temperatures.

Table 3. Results of the Indoor Duration of Lambda-Cyhalothrin Microcapsules against *M. persicae* (Mean ± SD, $n = 3$)

samples	effective component (mg/L)	1d mortality (%)	7d mortality (%)	14d mortality (%)	21d mortality (%)
lambda-cyhalothrin microcapsules	25	76.75 ± 1.07	86.54 ± 0.50	87.57 ± 0.22	84.05 ± 0.20
	50	80.88 ± 0.90	92.32 ± 0.39	89.76 ± 1.07	85.55 ± 0.51
	100	85.94 ± 0.44	95.89 ± 0.65	94.52 ± 0.14	90.17 ± 1.05
lambda-cyhalothrin EC	25	82.67 ± 0.56	85.02 ± 0.23	70.88 ± 0.84	47.12 ± 1.01
	50	85.58 ± 0.76	90.14 ± 0.51	75.02 ± 0.22	52.88 ± 0.63
	100	90.75 ± 0.64	94.96 ± 0.83	80.05 ± 1.02	54.02 ± 0.24
water		2.34 ± 0.40	−3.78 ± 0.35	−7.65 ± 0.33	−6.67 ± 0.47

release results were simulated by the zero-order model, first-order model, Higuchi model, and Ritger-Peppas model. The obtained fitting parameters are shown in Table 2. Among these models, the release of lambda-cyhalothrin from the microcapsules and EC was more suited to the first-order models because the correlation coefficient R^2 was higher ($R^2 > 0.92$),

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which inferred that the release of lambda-cyhalothrin in the microcapsule and EC belonged to Fickian diffusion. In addition, the release of lambda-cyhalothrin from the microcapsules under the various MDI addition amounts, pH values, and temperature conditions examined herein also fit the first-order model; simple diffusion appeared to dominate, with an exponentially decreasing release rate over time. The first-order model fit figure of lambda-cyhalothrin release is shown in Figure 9.

2.9. Insecticidal Biological Assays. To verify the feasibility of developing lambda-cyhalothrin microcapsules as a new pesticide formulation, trials were conducted using the residual spray method to control *Myzus persicae* on cabbage leaves. As shown in Table 3, the biological prevention and cure effects of lambda-cyhalothrin microcapsules and lambda-cyhalothrin EC were compared through indoor biological experiments. The data showed that 1 day after the drug application, the prevention and cure effect of lambda-cyhalothrin microcapsules was slightly lower than that of commercial formulations, which was mainly caused by the sudden release of emulsion. And 7−21 days after the drug application, the prevention and cure effect of lambda-cyhalothrin microcapsules was higher than that of commercial formulations, among which the prevention and cure effect of 50 mg/L lambda-cyhalothrin microcapsules reached 85.55% at 21 days after the drug application, while lambda-cyhalothrin EC was only 52.88%. These results confirm the superior control effect exhibited by the lambda-cyhalothrin microcapsules compared with the lambda-cyhalothrin EC at the same dosage. It showed that microcapsules can prolong the persistent period of insecticides and reduce the number of drugs, which provides a new direction for market development of pesticides.[21,37]

3. CONCLUSIONS

In this study, lambda-cyhalothrin microcapsules were prepared by means of an interfacial polymerization approach, wherein MDI was used as the wall material and GT-34 was employed as the initiator. Several parameters that affected particle size and EE were optimized, and the optimal preparation process for lambda-cyhalothrin microcapsules was as follows: the MDI addition amount was 3 g, the 601P addition amount was 2 g, and the AG-700# addition amount was 3 g. The surfaces of the prepared microcapsules were found to be smooth, and they exhibited an average particle size of 1.97 μm and an EE of 91.48%. FTIR and TGA showed that the core material was successfully encapsulated in polyurea. Compared with other commercial formulations, lambda-cyhalothrin microcapsules effectively prolonged the release time of lambda-cyhalothrin, and the microcapsules exhibited an excellent sustained release property (above 7 days) in a 50% acetonitrile aqueous solution (v/v). Subsequently, in vitro release studies showed that the lambda-cyhalothrin microcapsules could consistently exhibit controlled release of the active drug under different pH and temperature conditions, thereby indicating their potential for future applications in different soil environments. The release of lambda-cyhalothrin microcapsules was in accordance with the first-order model release, which was mainly by the Fickian diffusion mechanism. Furthermore, the bioactivity tests showed that the microcapsules were more prevention- and cure-effective and had longer persistent periods (>21 days) against *M. persicae* compared to lambda-cyhalothrin EC. Therefore, the microcapsules prepared in this paper were important for improving pesticide utilization rate, reducing pesticide application time, and reducing environmental and human health hazards. At present, we are further studying to improve the stability and safety of lambda-cyhalothrin microcapsule preparation to obtain microcapsules suitable for field application.

4. MATERIALS AND METHODS

4.1. Materials. Lambda-cyhalothrin at a purity of 97.5% was provided by Zhejiang Tianyi Agrochemical Co., Ltd. (Zhejiang, China). Solvent S-150 was purchased from Zhejiang Yulong Chemical Co., Ltd. (Zhejiang, China). MDI was purchased from Wanhua Chemical Group (Yantai, China). The emulsifier tristyrylphenol polyoxyethylene ether phosphoric esters (601P) was purchased from Nanjing Deyi Chemical Co., Ltd. (Nanjing, China). The modified polyacrylate copolymer dispersant (Ag-700#) was provided by Nanjing Jierun Technology Co., Ltd. (Nanjing, China). Ethylenediamine aqueous solution (GT-34) was provided by Nanjing Gutian Chemical Co., Ltd. (Nanjing, China). The methanol and acetonitrile used for HPLC were purchased from Fisher Chemical (Shanghai, China).

4.2. Preparation of Lambda-Cyhalothrin Microcapsules. The lambda-cyhalothrin microcapsules were prepared by interfacial polymerization using lambda-cyhalothrin as the core material and MDI as the wall material. First, Ag-700# was dissolved in deionized water to form a water phase. 6.67 g of lambda-cyhalothrin (97.5%), 601P, and MDI were dissolved in the solvent to form an oil phase. The oil phase was poured into the water phase at a uniform speed and dispersed into a uniform O/W emulsion through high shear. Then the emulsion was transferred to a three-neck flask and mechanically stirred at a stirring speed of 300 rpm. At the same time, GT-34 was dissolved in deionized water and added to the emulsion at a uniform speed. The interfacial polymerization was carried out at 50 °C for 3 h. After the reaction, the polymer shell was completely cured and 6.5% lambda-cyhalothrin microcapsules were obtained.

4.3. Characterization. *4.3.1. Morphological Characterization.* (1) OM. The dispersion state of the microcapsules was examined by OM. The obtained microcapsule dispersions were appropriately diluted with distilled water, applied on microscope slides (2.5 × 7.5 cm), and covered with cover glass.

(2) SEM. The surface morphology and structure of microcapsules were studied by SEM (JSM-6360LV, Jelltd, Japan). The microcapsule suspension was diluted properly, then evenly coated on a thin layer of aluminum foil, and dried at room temperature. A layer of gold powder was plated on the sample by the ion sputtering coating method to make the sample.

4.3.2. Particle Size Analysis. The particle sizes and distribution of the microcapsules were evaluated at room temperature by using a laser particle size analyzer (Better-Size2600, Dandong Baxter Instrument Co., Ltd.). The D10, D50, and D90 values of the microcapsules were also determined; these values represent the corresponding particle sizes when the cumulative particle size distribution reaches 10%, 50%, and 90%, respectively, and they are used to evaluate the size distribution range of the microcapsules. It should be noted here that the D50 value is commonly used to represent the average size of a microcapsule sample. Each sample was measured in triplicate.

4.3.3. Measurements of Encapsulation Efficiency (EE %). An amount of lambda-cyhalothrin was dissolved in methanol solution, and the volume was adjusted to 25 mL as a standard solution. An amount of the microcapsule suspension was weighed and placed into a 25 mL volumetric flask; an appropriate amount of methanol was added, and the suspension was then ultrasonically disrupted for 2 h and subsequently

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diluted to 25 mL with methanol solution to determine the total content of lambda-cyhalothrin in the microcapsule suspension (DL) %. An amount of the sample was tested and mixed with 10 mL of methanol. It was added to a 20 mL centrifuge tube and centrifuged at 8000 rpm for 5 min. A certain amount of supernatant was aspirated into a 25 mL volumetric flask, diluted with methanol, and shaken well to determine the content of lambda-cyhalothrin outside of the microcapsules (X)%. It was filtered with a 0.22 μm organic phase microporous membrane and put into an HPLC injection vial, and the free lambda-cyhalothrin content was determined by HPLC (Agilent 1260, USA). The HPLC separation of lambda-cyhalothrin was carried out on a Diamonsil-C18 column (4.6 × 250 mm, 5 μm) with an isocratic elution of methanol-acid water (80/20, v/v) as the mobile phase. 5 μL of the solution was injected into the HPLC system and separated at 25 °C using a constant flow rate of 1.0 mL/min at a detection wavelength of 230 nm. The encapsulation efficiency (EE %)[38] of lambda-cyhalothrin was calculated according to the following eq 3

$$\mathrm{DL}\ (\%) = \frac{0.975 \times A_a \times m_b}{m_a \times A_b} \times 100 \tag{1}$$

$$\mathrm{X}(\%) = \frac{\mathrm{DL}\ \% \times m_a \times A_c}{m_c \times A_a} \times 100 \tag{2}$$

$$\mathrm{EE}\ (\%) = \frac{\mathrm{DL} - \mathrm{X}}{\mathrm{DL}} \times 100 \tag{3}$$

where A_a is the peak area of lambda-cyhalothrin in the disrupted microcapsule suspension, A_b is the peak area of lambda-cyhalothrin in the standard solution, A_c is the peak area of lambda-cyhalothrin in the extraction solution, m_a is the mass of the disrupted microcapsule suspension, m_b is the mass of lambda-cyhalothrin in the standard solution, and m_c is the mass of the lambda-cyhalothrin microcapsule suspension for extraction. X % was the content of lambda-cyhalothrin outside of the microcapsule, and DL % was the drug-loading content of the microcapsule.

4.3.4. Fourier Transform Infrared Spectroscopy. The samples were prepared as potassium bromide pellets, and a blank potassium bromide pellet was used as the background, which was scanned on an FTIR spectrometer (Thermo-Nicolette Nexus 410 FTIR, Nibco colliers instrument company) with a wavelength range from 4000 to 450 cm^{-1}.

4.3.5. Thermogravimetric Analysis. A comprehensive thermal analyzer (TGA-103, Beijing JinYang Wanda Technology Co., Ltd.) was used to study the thermal stability properties of the microcapsules. The measurement conditions were as follows: temperature increase from 10 to 800 °C at a rate of 10 °C/min and a nitrogen flow rate of 50 mL/min.

4.4. Release Kinetics of Lambda-Cyhalothrin Microcapsules. The lambda-cyhalothrin microcapsule release kinetics study was performed using the dialysis bag method. The purchased dialysis bags (cutoff molecular weight: 8000−14,000) were cut into small sections of about 5 cm for pretreatment. An accurately weighed sample (6.5% lambda-cyhalothrin microcapsule suspension) of 1.0 g was placed in the dialysis bag, which was immersed in a conical flask containing 50 mL of 50% acetonitrile aqueous solution (v/v) and placed in a 25 ± 2 °C double-shaking incubator at 100 rpm for release tests. An equal amount (1 mL) of media outside the dialysis bag was collected at different time intervals and supplemented with 1 mL of 50% acetonitrile aqueous solution, maintaining the volume of the release medium at 50 mL at all times. The sampled solution was passed through an organic phase microporous filter membrane with a pore size of 0.22 μm. The content of lambda-cyhalothrin in the filtrate was determined by HPLC. The cumulative amount of lambda-cyhalothrin released was the value for lambda-cyhalothrin from the measurement results.

The cumulative release of lambda-cyhalothrin was calculated by the following eq 4

$$m_{t-\mathrm{act}} = \left(C_t + \frac{v}{V} \sum_{0}^{t-1} C_t \right) \times V \tag{4}$$

Here, C_t represents the concentration of lambda-cyhalothrin in the time t release medium, $m_{t\text{-act}}$ represents the cumulative release of lambda-cyhalothrin at time t, v represents the volume of the release medium taken out each time (1 mL in this experiment), and V represents the total volume of the release medium (50 mL in this experiment).

The cumulative release curves of the microcapsules were fitted with the following mathematical models:

(1) Zero order release model[39]

$$Q_t = Q_0 + k_0 t \tag{5}$$

where Q_t is the release amount of active ingredient at time t, Q_0 is the amount of active ingredient in the release medium, and k_0 is the release constant.

(2) First-order release model[40]

$$\ln Q_t = \ln Q_0 + kt \tag{6}$$

where Q_t is the release amount of active ingredient at time t, Q_0 is the initial amount of active ingredient in the microcapsule sample, and k is the release constant.

(3) Higuchi release model[41]

$$Q_t - Q_0 = k_H t^{0.5} \tag{7}$$

where Q_t is the release amount of active ingredient at time t, Q_0 is the amount of active ingredient in the release medium, and k_H is the release constant.

(4) Ritger−Peppas model[42]

$$\frac{M_t}{M_\infty} = kt^n \tag{8}$$

where M_t is the release amount of active components per unit time t, M_∞ is the total amount of active components in the microcapsule, k is the release constant, n is the diffusion index, and t is the release time.

4.5. Insecticidal Biological Assays. *M. persicae* was introduced from the cabbage greenhouse at the base of Shenyang Sinochem Pesticide and Chemical R&D Co., Ltd. *M. persicae* was transferred into pots for multigeneration propagation in the laboratory, and *M. persicae* of the same size was selected for the experiment. Cabbage seedlings were cultured in the greenhouse, and the prepared liquid medicine was sprayed evenly on the front and back of the leaves with an airbrush manual sprayer when the cabbage seedlings grew to 2−3 leaves. The treated samples were cultured under the plant growth regulating lamp in the observation room. On the 1, 7, 14, and 21 d after application, more than 50 artificially raised healthy *M. persicae* populations were inoculated on the leaves, and the water and fertilizer management were normal. After inoculation with aphids, the base number was investigated, the number of residual insects was investigated 48 h later, and the mortality rate

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was for lambda-cyhalothrin. This process was repeated 3 times for each group.

The effective component concentrations of 6.5% lambda-cyhalothrin microcapsules were 25.0, 50.0, and 100.0 mg/L and those for the control drug 2.5% lambda-cyhalothrin EC were 25.0, 50.0, and 100.0 mg/L. Clear water treatment was set as a blank control. Lambda-cyhalothrin of mortality was calculated according to eq 9

$$\text{mortality}\ (\%) = \frac{\text{population base} - \text{residual insects number}}{\text{population base}} \times 100 \quad (9)$$

4.6. Statistical Analysis. All data in this paper were processed by SPSS 22.0 software, and the mean value and standard deviation of each data set were calculated.

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Notes

The authors declare no competing financial interest.

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