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Distribution of Emamectin Benzoate Granules in Maize Plants by Broadcasting into Maize Leaf Whorls

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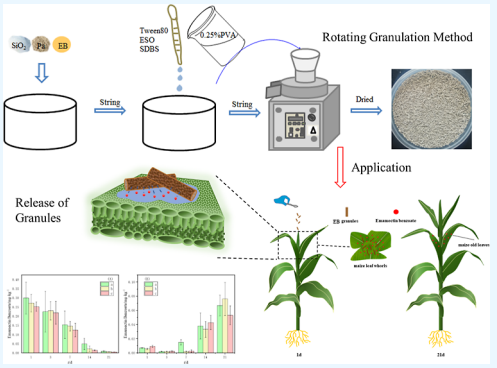
ABSTRACT: Good control effects on fall armyworm (FAW) can be obtained by broadcasting emamectin benzoate (EB) granules into maize leaf whorls. However, the distribution of EB in maize plants is not clear. In this study, EB granules were prepared by the rotating granulation method, and the granules were characterized using a Fourier transform infrared spectrometer. The behavior of EB granules in water was observed using a microscope, and in vitro release of EB from granules was also studied. A method for the determination of EB in maize plants, old leaves, grains, and cobs was established by using ultra-performance liquid chromatography-tandem mass spectrometry. The results showed that EB was loaded in granules successfully, and the granules disintegrated slowly in water, so the release of granules could be regulated using various water contents. The prepared EB granules were qualified and stable. The field experiment showed that the concentration of EB in maize leaf whorls could be maintained above 0.23 mg·kg^{-1} within 3 days after broadcasting EB granules. This ensured that FAW could be killed in a short time. Then, EB gradually transferred to the old leaves. After 21 days of application, the content of EB in the old leaves was 0.07 mg·kg^{-1}, which has long-time control effects on FAW. The control effects of the three doses of granules against *Spodoptera frugiperda* were higher than 78% after 14 days of application. At the tested dosage, no phytotoxicity to crops was observed. At harvest, neither the maize grain nor the cobs had EB content. New controlled formulations to *S. frugiperda* were developed and will be suitable for application in mountainous areas where the lack of water resources is a factor.



1. INTRODUCTION

The fall armyworm [*Spodoptera frugiperda* (J.E. Smith) (FAW)] (Lepidoptera: nocturnal) is one of the most important pests of maize in the world. It has a serious effect on the yield and quality of maize.[1−3] The larvae like to drill into the whorls and cobs of maize plants and feed on young leaves, filaments, and grains.[4] According to previous research, an effective method for controlling FAW was by broadcasting insecticidal granules into maize leaf whorls. It can not only improve pesticide utilization efficiency significantly, but it can also reduce pesticide drift and minimize environmental risks.[5] By adding bait to the insecticidal granules, one can induce the engulfing of larvae hiding in the flesh of the leaf and killing them.[6,7] Bacillus and other biological insecticides are also used to control FAW.[8]

Pesticide slow-release formulations can be prepared by the application of polymer materials that help the pesticide reach the specified location consistently and stably at a specific time to ensure its control effects on harmful organisms. Its release behavior can be affected by light, temperature, pH, and other factors.[9,12] Compared to polymer materials, inorganic fillers are widely used in the preparation of slow-release formulations. In addition, the performance of granules can be affected by the filler. Attapulgite, kaolin, diatomite, and other inorganic minerals have a large specific surface area, strong adsorption, and good adhesion and have become important carriers in the pesticide industry.[5,10−13] With the development of nanocomposites, the release process can be controlled by the addition of nano-carriers, which can significantly increase pesticide coverage and effectively reduce rainwater erosion.[14] In addition, nanoscale photothermal materials have been used to achieve physical contact with killing pests, effectively reducing the use of chemical pesticides.[15] Silica particles have a large specific surface area and strong adsorption capacity for polar substances.[16] Pesticides can be embedded with silica and sprayed on the surface or absorbed by the roots of plants and transported to other parts.[17,18]

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Emamectin benzoate (EB) is a new, highly effective semi-synthetic antibiotic insecticide with both stomach and contact toxicity.[19] It can reduce cell viability, induce a significant increase in cell apoptosis, and cause the formation of single-strand and double-strand DNA breaks.[5] Previous studies show that it has a strong toxic effect on Sf-9 cells, and the 72 h mortality rate on FAW is 100%.[20] In addition, it also has a strong sublethal effect, which can significantly affect the life cycle of the offspring of FAW.[21] At present, new formulations of EB, such as gels, nanoparticles, nanogel suspensions, and nanocapsules, have been developed[9,22−24] Good control efficacy against FAW can be obtained. However, the materials used in these preparations are usually expensive, and the preparation process is tedious and time-consuming.[22,24,25] Therefore, it is difficult to conduct large-scale production in a factory setting and promote their application in the field. Additionally, it is necessary to ascertain the distribution of pesticides in maize plants before application in order to ensure food safety in field production.[26,27]

In this study, EB granules were prepared by the rotating granulation method, and the granules were characterized using a Fourier transform infrared (FTIR) spectrometer. The disintegration process of the granules in water and in vitro release were studied. A method for determining the content of EB in maize leaf whorls, old leaves, grains, and cobs was established using ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). The product was qualified and stable. Good results were obtained in field control of FAW. The distribution of EB in maize plants after broadcasting into maize leaf whorls was clarified. The preparation of the granules was simple and safe. Their large-scale industrial production and wild application would be easy. This study will be helpful in efforts to control FAW in water-deficient mountainous areas.

2. RESULTS AND DISCUSSION

2.1. Preparation of Controlled-Release EB Granules. As shown in Table 1, four kinds of carriers were involved, including kaolin, diatomite, attapulgite, and maize starch. Tween-80, silica, polyvinyl alcohol (PVA), SDBG, and epoxidized soybean oil (ESO) were used as inert ingredients to prepare EB granules via the extrusion granulation method. Among them, due to the easy absorption of kaolin moisture, the EB particles prepared with kaolin as the filler were extremely unstable, which was not conducive to storage and transportation. Using diatomite as the carrier formula required about 1.5 times more water solution of PVA than that of attapulgite under the same conditions. Because EB slightly dissolves in water, the EB granules used methanol−water as the release medium, and the granules with corn powder as the carrier were dissolved in methanol−water and could not be released for testing. Finally, attapulgite was selected to prepare the granules, as shown in Figure 1. The length of the granules ranged from 3 to 6 mm. In addition, the characteristics of the granules were evaluated; the water content was less than 2.67%. The bulk density was 0.53−0.81 g·mL^{-1} and the tab density was 0.63−0.86 g·mL^{-1}; drop rates were less than 1%. The prepared EB granules were qualified and stable. Their performance is presented in Table 6.

Table 1. Granule Control Index

item		index
EB, %		±0.17 ± 0.01
water, %		≤2.67 ± 0.03
bulk density, g·mL^{-1}		0.53−0.81
tap density, g·mL^{-1}		0.63−0.86
pH		5.0−8.0
length, mm		3−6
	small	0.9−1.0
diameter, mm	middle	1.3−1.4
	big	1.7−1.8
drop rates, %		≤1.0
thermal storage stability		qualified

Figure 1. Images of EB granules.

2.2. FTIR Analysis of EB Granules. FTIR spectra of attapulgite, EB, and EB granules are shown in Figure 2. Strong absorption can be found around 3400 and 2965 cm^{-1} in EB due to the stretching vibration of O−H and saturated C−H.[9] The peak at 1596 cm^{-1} was due to the characteristic skeletal vibration of the benzene ring and those at 1458 and 1376 cm^{-1} were from the asymmetry bending vibration and symmetry bending vibration of C−H.

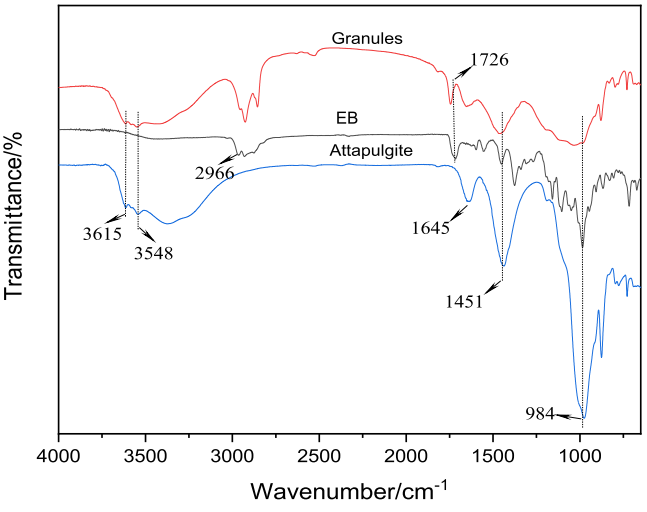

Figure 2. FTIR spectra of EB granules.

For attapulgite, the absorption peak at 3000−3600 cm^{-1} can be attributed to the stretch vibration of −OH groups. The bands at 3615 and 3548 cm^{-1} were assigned to hydroxyl groups and stretching vibration and bending vibration of coordination water and adsorbed water in the channels of the attapulgite crystals.[28−30] The absorption at 3389 cm^{-1} was due to the stretching vibration of O−H that connected with Mg

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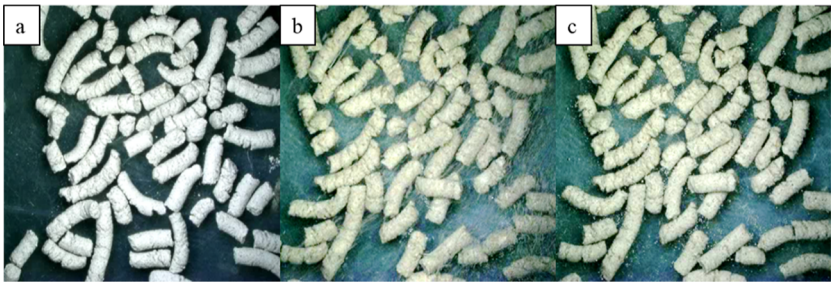

Figure 3. Images of the disintegration process of EB granules. (a−c) Images at 0, 5, and 55 s after water was added.

and Al, located between the tetrahedral and octahedral structures inside attapulgite. The peak at 1645 cm^{-1} corresponded to the bending vibration of zeolite water, while the strong absorption at 987 cm^{-1} was due to the stretching vibration of the quartz Si−O−Si bond.[28]

As can be observed from the above figure, there were characteristic absorption peaks of EB in the granules, for example, at 2965, 1726, and 1596 cm^{-1}, indicating that EB was loaded into the granules.

2.3. Behavior of EB Granules in Water. Based on the special application conditions, that is, that granules were broadcast into maize leaf, disintegration should be slowed in order to maintain a continuous active compound release from the granules. In this study, the disintegration process of granules in water was studied using a super depth-of-field 3D microscope in order to better understand the disintegration of granules in water. Figure 3 presents the images of different time points in the recording process. The results suggested that the granules bubbled and collapsed into crumbs just after water was added. The disintegration was rapid and violent in the initial time frame, that is, the 5 s image. Obviously, the process then slowed down, almost ceasing to collapse and bubble after a certain period of time. This may be attributed to abundant internal channels and the strong water absorption capacity of attapulgite; when water was added, attapulgite absorbed it very quickly.[31] However, the preparation of granules used a PVA aqueous solution (0.25%) as a binder, and the granules disintegrated more slowly due to the effects of that binding. Only a small amount of attapulgite disintegrated from the granules after absorbing water.

2.4. In Vitro Release. Figure 4 shows that the release rate of the EB particulate is controlled by the moisture content of the environment. EB particles exhibited good stability in the environment with low moisture content, and only about 2% of EB was released into the environment after 32 h. The cumulative release of EB progressively increased with the constant increase in the moisture content in the environment. This may be attributed to abundant internal channels and hydrophilic groups, which can rapidly absorb water in the environment.[31] Cracks developed in attapulgite due to axial and radial shrinkage during evaporation.[32] Moreover, the increase in water content will also accelerate the disintegration of attapulgite. The release rate of EB particles at the primary stage is rather rapid and retards gradually afterward, which is consistent with the disintegration results of particles in water observed using a super depth-of-field 3D microscope.

The Korsmeyer−Peppas and Higuchi's model have often been used to describe the law and control mechanism of drug release in polymers.[10,33,34] In order to understand the release properties of acitretin salt particles, the Korsmeyer−Peppas

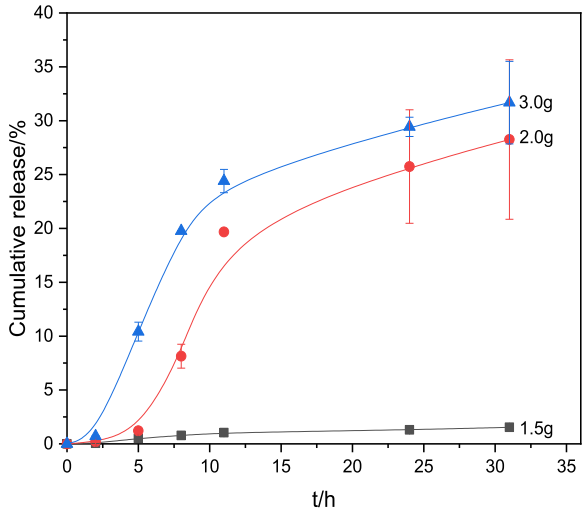

Figure 4. Cumulative release of EB granules in a methanol−water solution with different additive amounts: 1.5, 2.0, and 3.0 g.

model (eq 1) and Higuchi's model (eq 2) were used to fit the release data of EB.

$$M_t/M_0 = kt^n \quad (1)$$

$$M_t/M_0 = kt^{1/2} \quad (2)$$

where M_t/M_0 is the drug release rate at time t, k is a constant, and n is the diffusion index. The fitting results are summarized in Table 2. A comparison of the R^2 between the Higuchi and Korsmeyer−Peppas models revealed that the Korsmeyer−Peppas model is more suitable with respect to the release of EB from EB granules. The diffusion coefficient n is the basis for analyzing the drug release mechanism. In this study, EB particles can be regarded as a cylindrical drug release system. When the n values were less than 0.45, it indicates that their release process follows Fickian diffusion. When the n values were between 0.45 and 0.89, the release process was defined as non-Fickian diffusion. When the n values were greater than 0.89, it belongs to case II transport, swelling, diffusion, and erosion release mechanism may coexist for the controlled release process of the active ingredient. The fitting results show that the diffusion index n of the release of methylcobalamin salt from the particles is between 0.55 and 0.86, which is a non-Fickian diffusion, that is, diffusion and dissolution coexist.

2.5. Determination of EB in Maize Plants. As shown in Figure 5, the retention time of EB was 10 to 11 min in this method. As shown in Table 3, at concentrations of 0.005, 0.01, 0.05, 0.1, and 0.5 $mg{\cdot}L^{-1}$, the standard solution of EB dissolved in methanol showed a good linear range, and the correlation was greater than 0.999.

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Table 2. Fitting Results of EB Release Data

	Korsmeyer−Peppas			Higuchi	
amount of methanol−water/g	k	N	R^2	k	R^2
1.5	0.20 ± 0.06	0.60 ± 0.10	0.948	0.27 ± 0.02	0.935
2	1.61 ± 1.08	0.86 ± 0.21	0.899	4.63 ± 0.61	0.803
3	5.09 ± 1.95	0.55 ± 0.13	0.907	5.95 ± 0.45	0.903

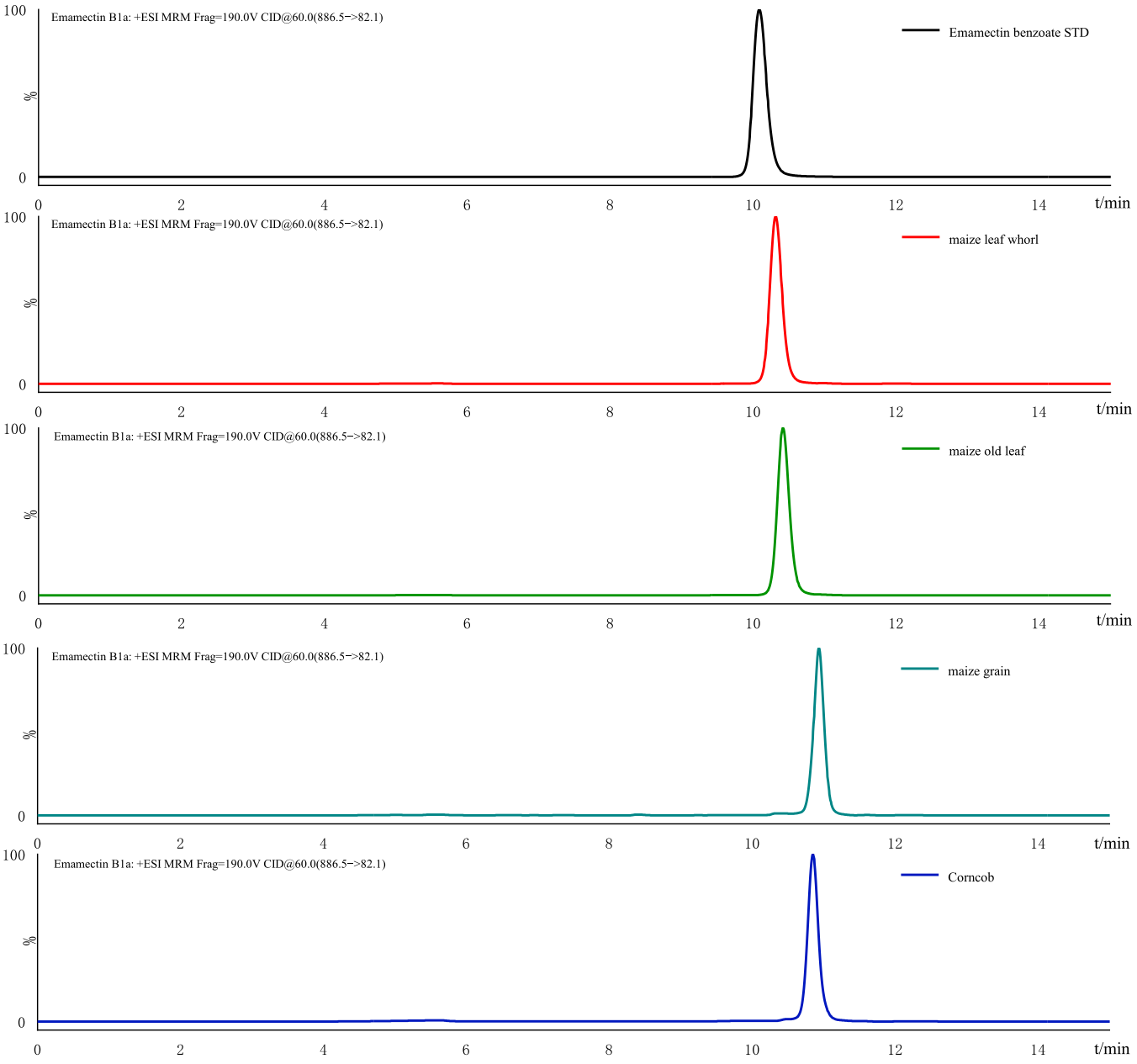

Figure 5. Typical chromatogram of EB in different matrices.

Table 3. Linear Relationship and Regression Equation between the Standard Working Solution of Tretinoin and Matrix Matching Standard Solution

sample	solvent	regression equation	R^2	LOQ (mg·kg^{-1})	matrix effects (%)
emamectin	acetonitrile	$y = 590276.53x - 4318.60$	0.9993		
benzoate	maize leaf whorl matrix matching solution	$y = 496965.19x - 1556.21$	0.9994	1.23×10^{-3}	−15.80
	maize old leaf matrix matching solution	$y = 484225.52x - 188.79$	0.9997	1.38×10^{-3}	−17.97
	maize grain matrix matching solution	$y = 440518.14x + 4959.51$	0.9999	1.97×10^{-3}	−25.37
	corn cob matrix matching solution	$y = 500436.53x + 4708.44$	1	1.20×10^{-3}	−15.22

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Table 4. Test Results of Recoveries

matrix	level/(mg·kg^{-1})	recycling rate/%					average recovery/%	RSD/%
		1	2	3	4	5		
maize leaves whorls	0.005	89.16	82.57	91.18	84.74	86.12	86.75	4.0
	0.05	87.34	91.60	82.22	83.04	84.97	85.83	4.4
	0.5	86.24	92.36	78.54	85.70	89.41	86.44	6.0
maize old leaves	0.005	88.73	83.19	96.88	94.16	95.64	91.71	6.2
	0.05	96.49	94.62	86.32	104.50	93.15	95.02	6.9
	0.5	87.92	93.77	100.24	90.02	106.87	95.76	8.1
maize grains	0.005	92.97	89.85	85.45	100.71	95.66	92.93	2.8
	0.05	94.61	94.66	94.80	97.27	102.81	96.83	1.6
	0.5	100.51	99.71	92.60	95.33	99.18	97.47	1.6
corncobs	0.005	84.80	101.85	85.80	82.27	90.66	89.08	8.7
	0.05	86.57	92.80	76.13	85.74	83.50	84.95	7.1
	0.5	99.82	102.49	88.93	94.03	93.66	95.79	5.6

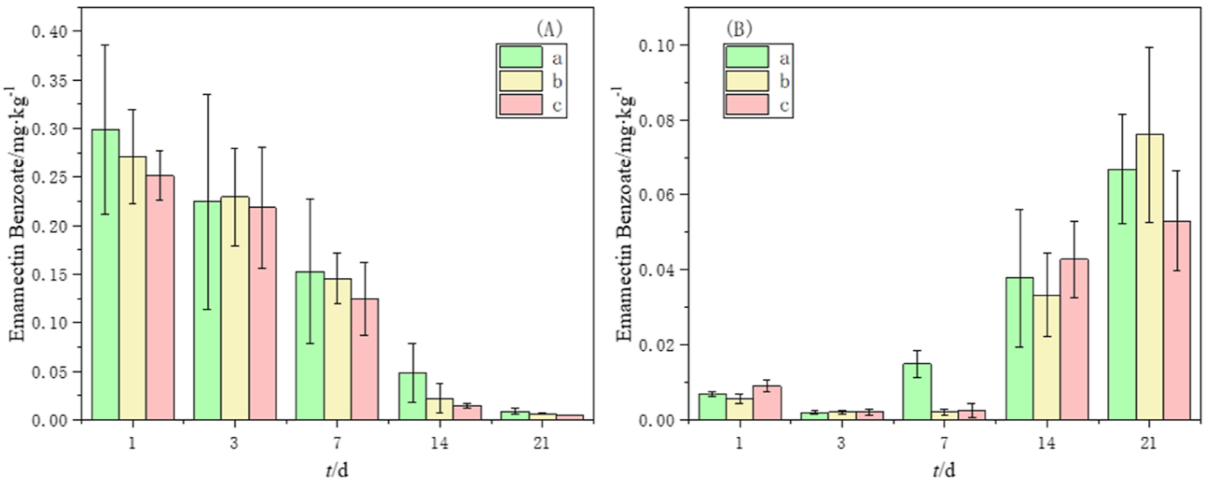

Figure 6. Concentration of EB in maize leaves. (A) Concentrations of EB in the maize leaf whorls. (B) Concentrations of EB in maize old leaves, where a, b, and c represent the size of EB granules, i.e., large, medium, and small.

Because corn samples are rich in sugars, lipid, pigments, and other components, they can significantly affect the sensitivity and accuracy of this method. Therefore, the evaluation of matrix effects is an important part of the validation of the quantitative LC−MS/MS method.[35] Primary secondary amine (PSA), graphitized carbon black (GCB), and octadecyl (C_{18}) are commonly used purification agent combinations in processing of plant samples. The combination can effectively remove sugars, lipids, pigments, vitamins, and minerals from the sample and weaken the matrix effect.[36,37] In addition, research showed that the use of $MgSO_4$ and NaCl at 4:1 can effectively remove the water and salts in the sample and significantly improve the recovery rate.[38]

Therefore, PSA, GCB, C_{18}, $MgSO_4$, and NaCl were used as pretreatment purification agents for corn samples in this study. The results showed that despite the use of cleaning agents, there were some endogenous compounds in the matrix. The four matrixes showed matrix weakening effects (−25.37% < ME < −15.22%). Therefore, in order to obtain more accurate results, the matrix matching calibration curve was used to eliminate the matrix effect. Fortunately, all calibration curves that were in a fortified blank of maize leaf whorls, old leaves, grains, and corncobs samples showed adequate linearity in the related concentration ranges (0.005, 0.01, 0.05, 0.1, and 0.5 mg·L^{-1}). The correlation coefficients were all greater than 0.999. At the concentrations of 0.005, 0.05, and 0.5 mg·L^{-1}, the average recoveries of tretinoin in the four matrices were 86−98%, and relative standard deviation (RSD) was 2.8−8.7% (Table 4). The results of recovery and precision were satisfactory. The limits of quantification (LOQs) were smaller than the maximum residue limit established by the European Union.

2.6. Distribution of EB in Maize Plants. In this study, the distribution behaviors of EB granules with different particle sizes in maize plants were studied. As shown in Figure 6, the concentration of EB in maize leaf whorls decreased gradually from 1 to 21 days. On the contrary, the concentration in maize old leaves increased gradually. Combined with the weather conditions during the test (Table 1), rainfall may be the main factor affecting the distribution of EB in maize plants. Due to showers following application, the water content in maize leaf whorls increased significantly, and EB was rapidly released from the granules by dissolution and diffusion. The concentration of EB in maize leaf whorls could be maintained above 0.23 mg·kg^{-1} within 3 days after broadcasting EB granules, ensuring that FAW could be killed in a short time. Interestingly, within 24 h after application, the content of EB in maize leaf whorls increased with granule size. Generally, EB particles with a small particle size may release faster in the environment. On the one hand, at the same dosage, EB particles with a small grain size cover a wider area on the surface of maize leaves, which is conducive to the absorption of

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Table 5. Control Effects of Granules against *S. frugiperda*

granules	treatment	initial population	1 d decline rate of insect (%)	1 d average control effect (%)	3 d decline rate of insect (%)	3 d average control effect (%)	7 d decline rate of insect (%)	7 d average control effect (%)	14 d decline rate of insect (%)	14 d average control effect (%)
0.2 %EB granules (GR)	200 g	33.00	93.31	94.14 ± 5.43	96.93	95.85 ± 4.61	97.36	98.24 ± 2.71	83.36	78.08 ± 3.24
	300 g	35.75	98.18	96.48 ± 4.88	98.75	98.59 ± 2.18	85.94	91.17 ± 6.59	82.31	84.14 ± 5.34
	500 g	40.00	95.73	95.02 ± 3.06	93.44	92.13 ± 9.18	97.22	93.59 ± 9.91	82.12	89.39 ± 8.63
blank control	water	41.50	11.73		28.54		−32.91		−66.87	

water in the environment by particles. On the other hand, EB particles with a large particle size extend the drug release paths. However, due to rainfall, EB released by particles will soon be lost to the environment. In addition, particles with a large particle size may be stronger against erosion by rainfall. Then, the concentration of EB in corncob leaves decreased gradually. This is because it is easy for EB exposed to the environment to be degraded by light, microorganisms, and other factors. Zhou et al.[39] reported a half-life of EB of 1.0−1.3 days in tea. However, about 0.15 mg·kg^{-1} of EB was still detectable in maize leaves 7 days after the granules were broadcasted into maize leaf whorls. This indicated that EB in the particles was slowly released into the environment during this period. Only trace amounts of EB were found in maize old leaves due to less rainfall in 7 days. After 7 days, affected by the rainfall, the concentration of EB in the old leaves increased gradually. On the 21st day after application, the concentration levels of EB in old leaves were around 0.07 mg·L^{-1}. This could increase the contact of EB to larvae during production, preventing FAW from transferring from drooping leaves to other maize plants at night.[28] This would be essential to extending the validity period in field management. It is worth mentioning that during the harvest of maize (35 days after the granules were broadcasted into maize leaf whorls), the EB content was not detected in the grains and cobs of maize. It was safe to broadcast EB granules into the maize leaf whorls directly. However, there were no obvious differences in the distribution patterns of the pesticide between different size treatments, showing that the particle size did not affect the distribution of EB granules in maize plants.

2.7. Control Effects of Granules against *S. frugiperda*. Studies have shown that the effect of EB on FAW is much higher than that of other insecticides. The LC50 lethal effect of EB 5 SG on FAW third instar larvae for 24 h was 0.103 mg·L^{-1} and that of LD95 was 0.552 mg·L^{-1}.[18,40] After 12.5 g.a.i.·ha^{-1} of EB was sprayed in the field, the decline rate of FAW was 94.54% within 3 days, but the control effect was only maintained for 7 days. After 7 days, the number of FAW larvae on the maize plants increased gradually. At 14 days, the number of larvae on maize plants increased from 0.1 to 1.03 larvae per plant, and the decline rate was only 43.72%.[41,42] As shown in Table 5, after the treatment with EB granules, the decline rate of insects was as high as 85.94−100.00%. The 1 d, 3 d, and 7 d, average control effects reached 91.17−100.00%; the decline rate of insects reached 82.12−83.36% in 14 days after granules' application; the average control effect reached 78.08−89.39%. In the present study, the granules were prepared by the granulation method, and the dosages were 3, 4.5, and 7.5 kg·ha^{-1} (5.1, 7.65, and 12.75 g.a.i.·ha^{-1}), respectively. The application of the granulation method had a higher utilization rate of pesticides, as can be seen from the results. Essentially, the EB granules that were prepared had a greater speed and efficacy. In addition, the control effects were able to last for a long time.

3. CONCLUSIONS

In the present study, attapulgite was used as a carrier to prepare EB granules. Using the rotating granulation method, the loading content of the prepared EB granules was 0.17%, and they were stable and qualified. The granules disintegrated slowly in water, and the release of granules could be regulated by varying the water contents. By broadcasting the EB granules into maize leaf whorls, EB was slowly released into maize plants. The concentrations of EB in young leaves were around 0.15 mg·L^{-1} on the seventh day. This was conducive to reducing the degradation rate of EB. In addition, EB can be absorbed by maize leaves and transferred from whorl leaves to old leaves. The concentration of EB in old leaves increased as time passed. This was beneficial to controlling the migration of FAW to other maize plants. EB content was not detected in fresh corn, which indicated that it was safe and reliable to broadcast insecticidal granules into the whorl of maize plants. The results showed that the EB granules have a good control effect on FAW. By broadcasting EB granules into maize leaf whorls, the dosage of EB could be reduced, as can the environmental risk of pesticides. Further studies should be conducted to determine the specific distribution of EB in maize leaves, stems, and grains. In addition, it is also worth considering whether it could influence the natural enemies of these insects in contact with the whorl leaves. Still, this study provided a new strategy for FAW control, especially for those regions where water resources were limited.

4. MATERIALS AND METHODS

4.1. Materials. EB (73.5%) was obtained from Guizhou Daoyuan Biotechnology Co., Ltd. (Guizhou, China). Sodium dodecyl benzene sulfonate, used as a wetting agent, was purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Tween-80, attapulgite, silica, PVA, and ESO were purchased from Shandong Yousuo Chemical Technology Co., Ltd. (Shandong, China). Acetonitrile and methanol alcohol (HPLC grade) were obtained from Anhui Tedia High Purity Solvents Co. Ltd. (Anhui, China). Ammonia was obtained from Chongqing Chuandong Chemical Co. Ltd. (Chongqing, China). Acetic acid glacial was obtained from Tianjin Guangfu Technology Development Co., Ltd. (Tianjin, China). Ammonium acetate was issued by Chengdu Kelong Chemical Reagent Factory (Chengdu, China). Sodium chloride (NaCl) and magnesium sulfate ($MgSO_4$) were obtained from Sinopharm Chemical Reagent

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Table 6. Pesticide Formulations

number	1	2	3	4	proportion %
1	EB	EB	EB	EB	0.2
2	Tween-80	Tween-80	Tween-80	Tween-80	2
3	silica	silica	silica	silica	4
4	PVA	PVA	PVA	PVA	12
5	SDBG	SDBG	SDBG	SDBG	4
6	ESO	ESO	ESO	ESO	10
7	kaolin	diatomite	attapulgite	maize starch	complement 100

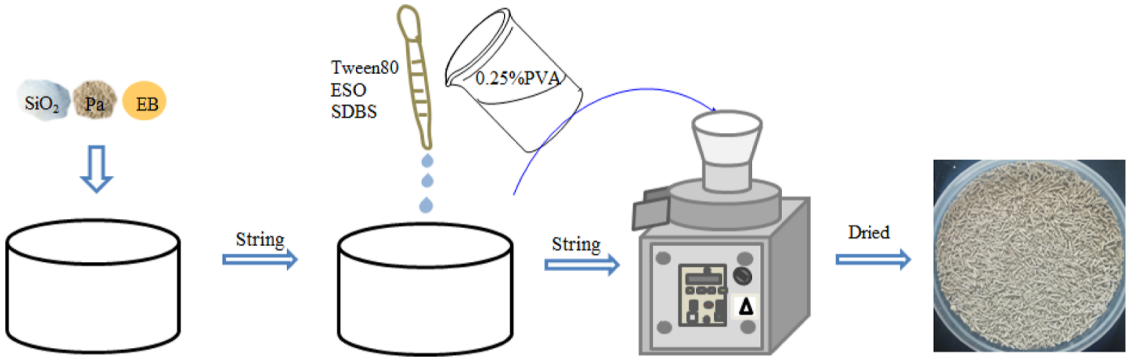

Figure 7. Preparation of EB granules (EB = emamectin benzoate, ESO = epoxidized soybean oil, SDBS = sodium dodecyl benzene sulfonate, and PVA = polyvinyl alcohol).

Co., Ltd. (Shanghai, China). PSA, GCB, and C_{18} were purchased from Agela Technologies (Tianjin, China). UPLC-MS/MS was performed using an Agilent 1290 Infinity II Ultra-performance Liquid Chromatograph and Agilent 6470 Triple Quadrupole Mass Spectrometer (Agilent, America). Deionized water was used in all the experiments, and all experimental samples were prepared to be ready-to-use. All of the above chemicals were used as required.

4.2. Methods. *4.2.1. Preparation of EB Granules.* As shown in Table 6, EB, fillers, and silica were mixed together to form a homogeneous powder. Specially, silica was used to adsorb EB, and then, sodium dodecyl benzene sulfonate was added as a wetting agent. Then, emulsifiers and solvents were added and stirred evenly. Then, a PVA aqueous solution (0.25%) was added as a binder and was stirred to mix well. Finally, a granulator was used to obtain EB granules, as shown in Figure 7. The resulting granules were dried at 45 °C. The lengths of the granules were in the range of 3−6 mm. The products were stored in a dry place and kept away from light.

4.2.2. Determination of EB Content. 0.500 g of EB granules was placed into a 50 mL volumetric flask, and approximately 30 mL of methanol was added. This was then disintegrated into the granules for 2 h with ultrasound, diluted to 50 mL with methanol, and filtered using a 0.22 μm filter. The content of EB in the filtrate was determined using an Agilent 1260 high-performance liquid chromatograph (USA) equipped with a diode array detector set at 245 nm. The mobile phase was a methanol−acetonitrile−ammonia (ammonia/water = 1:300) = 42:42:16 mixture at a flow rate of 1.5 mL·min^{-1}. The measurement was performed in triplicate.

4.2.3. Determination of the Bulk Density and Tap Density of EB Granules. About 90% of the cylinder volume of granules was slid smoothly and slowly into a measuring cylinder of known mass with a plug. Then, the surface of the sample was gently smoothed without shaking the measuring cylinder, the volume of granules was measured, recorded as V_1 (accurate to 2 mL), and then, the mass of the granules was weighed, recorded as W (accurate to 0.1 g). The measuring cylinder was covered with a plug and it was carefully installed on the measuring cylinder holder of a SHDM-2 pesticide bulk density tester. Then, the instrument was lifted 25 mm while it was automatically rotated about 10°, and then it was dropped onto the rubber base pad freely. It was then lifted and dropped every 2 s, repeated 50 times. Afterward, the cylinder lock on the holder was opened, the cylinder taken out, the plug removed, and the volume of the granules at this moment measured, recorded as V_2 (accurate to 2 mL). The calculation formulas for the bulk density and tap density of the granules were as follows (eqs 3 and 4), and the results are shown in Table 3.

$$\text{Bulk density (g/mL)} = \frac{W}{V_1} \tag{3}$$

$$\text{tap density (g/mL)} = \frac{W}{V_2} \tag{4}$$

4.2.4. Determination of the Attrition Resistance of Granules. Approximately 60 g of granules (ensuring that the amount was not less than 50 g after sieving) was turned 5 times at 180° to mix well and then transferred to a 125 μm test sieve and shaken for 3 min. 50.0 g of the screened granules was accurately weighed, recorded as W_1, and put into a glass bottle, the mouth of the bottle was sealed, and it was placed horizontally on the rotating shaft before rotating it at 4500 r at 100 rpm. At the end of the rotation, the samples were transferred from the glass bottle to a 125 μm test sieve carefully, the sieve was covered, and it was vibrated for 3 min. After the vibration, the sample was transferred from the sieve to a watch glass, and the mass of the sample on the watch glass was weighed, denoted as W_2. The attrition resistance of the granules was calculated according to the following formula (eq 5).

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$$\text{Attrition resistance}\ (\%) = \frac{W_2}{W_1} \times 100\% \quad (5)$$

4.2.5. FTIR Analysis of EB Granules. Appropriate amounts of EB granules were ground to powder. EB and attapulgite were prepared and measured using an FTIR spectrometer (Thermo Fisher, IS 20, USA) equipped with an attenuated total reflectance accessory within the range of 4000−650 cm^{-1}, with a resolution of 4 cm^{-1}.

4.2.6. Super Depth-of-Field 3D Microscope Analysis. About 0.5 g of EB granules was placed in a plastic Petri dish that was, in turn, placed on the stage of a super depth-of-field 3D microscope. The stage was adjusted so that the plastic Petri dish faced the objective lens, and then the focus was adjusted to make the image appear clear. Then, the record icon was clicked and an appropriate amount of deionized water was poured into the plastic Petri dish to record the disintegration process of the EB granules.

4.2.7. In Vitro Release. 1.00 g of granules was placed in a plastic Petri dish with a paper filter at the bottom, and the particles were paved flat. Three groups were prepared. The methanol/water (methanol/water = 30:70) solution was used as the release medium, the contents of the release medium were set as 1.5, 2.0, and 3.0 g, dropped evenly on the filter paper above, and sealed with a film, as shown in Figure 8. At intervals, the granules were transferred to another Petri dish with a filter paper, after which the same amount of release medium was added, and the above steps were repeated. Then, methanol−water was added to fill up to 5 g to wash the Petri dish after the particles were transferred and ultrasonicated to make the EB homogeneously distributed. Then, the solutions were filtered and analyzed by HPLC. Additionally, the amounts of EB released at intervals were calculated, and experiments were run in duplicate.

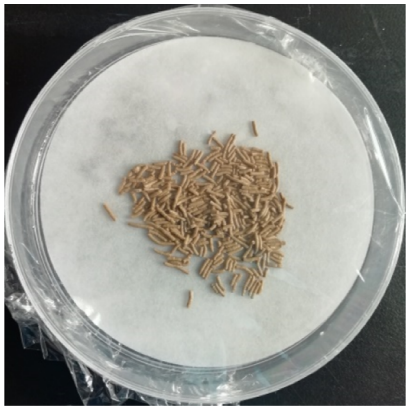

Figure 8. Release in different water content conditions.

4.2.8. Distribution of EB in Maize Plants. The field experiment was conducted in July 2021 in Huaxi, Guiyang, China (26°30′8″N, 106°39′15″E, Guizhou Province), according to the NY/T 788-2004 Guideline on Pesticide Residue Trials issued by the Ministry of Agriculture, China. The maize variety tested was glutinous corn, and the soil was yellow. Plots with no application history of EB were selected to be used during the trial period to make sure that there was no residue of EB in blank fresh corn leaf samples. The weather condition during the period of experiment is shown in Table 7.

Table 7. Weather Condition during the Period of the Experiment

trial date	application interval/d	temperature/°C	weather	rainfall/mm
Jul 28, 2021	0	20−29	shower	6.10
Jul 29, 2021	1	22−31	cloudy	0
Jul 30, 2021	2	21−30	clear	0
Jul 31, 2021	3	20−31	cloudy	0
Aug 1, 2021	4	20−31	cloudy	0
Aug 2, 2021	5	21−33	clear	0
Aug 3, 2021	6	21−32	clear	0
Aug 4, 2021	7	21−32	clear	0
Aug 5, 2021	8	21−32	cloudy	0
Aug 6, 2021	9	22−32	cloudy	0
Aug 7, 2021	10	22−32	overcast	0
Aug 8, 2021	11	23−32	cloudy	0
Aug 9, 2021	12	22−27	shower	5.08
Aug 10, 2021	13	21−29	shower	4.96
Aug 11, 2021	14	21−28	rain	16.51
Aug 12, 2021	15	21−30	cloudy	0
Aug 13, 2021	16	20−26	shower	6.60
Aug 14, 2021	17	20−24	overcast	0
Aug 15, 2021	18	18−22	shower	2.79
Aug 16, 2021	19	20−27	cloudy	0
Aug 17, 2021	20	20−27	overcast	0
Aug 18, 2021	21	21−27	overcast	0

The prepared EB granules were broadcast into maize leaf whorls at a dosage of 300 g a.i.·ha^{-1} to study the distribution behaviors of EB in maize plants. The experimental treatment for EB consisted of three replicate plots and a control plot as well as a 1 m buffer area set to separate each plot. Maize leaf whorls and old leaf samples were collected from at least five random sampling points at intervals of 1, 3, 5, 7, 14, and 21 days after the application of EB granules (Figure 9). All of the maize samples were stored at −20 °C before analysis.

About 10 g of the samples was weighed and added into a 50 mL centrifuge tube. Subsequently, 5 mL of deionized water and 10 mL of 1% acetic acid acetonitrile were added into the centrifuge tube and vortex oscillated for 10 min. Then, they were left standing for 30 min at room temperature, after which 1 g of NaCl and 4 g of $MgSO_4$ were added, they were vortex oscillated for 10 min, and then they were centrifuged at 6000 rpm for 5 min. Finally, 1.5 mL of the supernatant was placed in a 2 mL centrifuge tube, which contained 60 mg of PSA, 40 mg of GCB, and 20 mg of C_{18}. This was vortex oscillated for 10 min and then centrifuged at 6000 rpm for 2 min to obtain the sample solution to be tested.

100 mg·L^{-1} of an EB standard solution was configured. The solution was gradient diluted into a series of standard working solutions with concentrations of 5, 1, 0.5, 0.1, 0.05, 0.01, and 0.005 mg·L^{-1}. The corresponding series of standard blank matrix working fluid was obtained by adding a blank matrix extract into the standard working solutions. The working standard prepared solution and matrix-matching standard solution were stored in a refrigerator at 4 °C.

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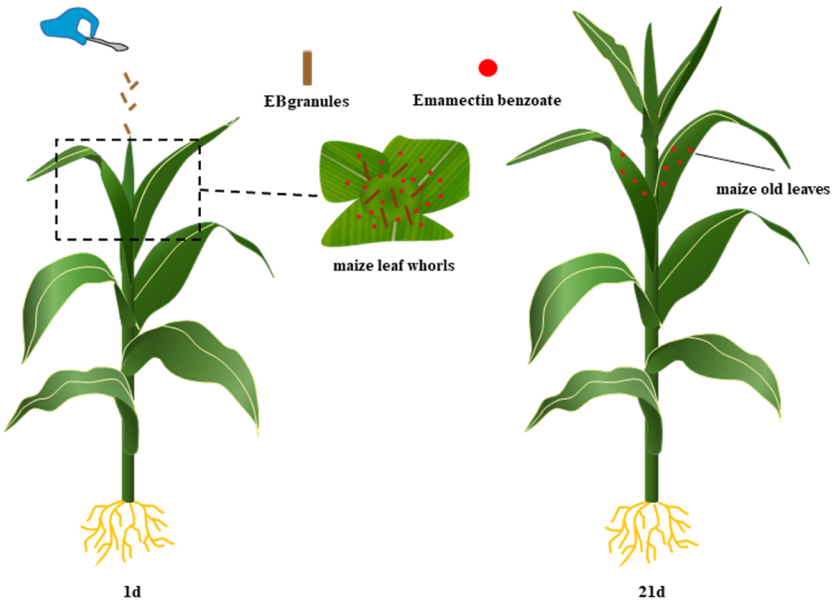

Figure 9. Distribution of EB in maize plants.

HPLC was performed on a CORTECS C18 column (100 mm × 2.1 mm, 2.7 μm) at 30 °C with a sample size of 1 μL. The mobile phase was an ammonium acetate (10 mmol)−acetonitrile mixture at a flow rate 0.5 mL·min^{-1} (Table 8).

Table 8. Gradient Elution Mobile Phase and Flow Rate

total time/min	flow rate/mL·min^{-1}	ammonium acetate water/%	acetonitrile/%
0	0.5	40	60
2	0.5	40	60
4	0.5	5	95
9	0.5	5	95
12	0.5	40	60

Using ESI ion source, the ionization mode selected positive ion scanning and multi-reaction monitoring mode. The capillary voltage parameter was 5500 V. The ion source temperature TEM was 600 °C, Cur was 20 psi, GS1 was 50 psi, and GS2 was 50 psi. The precursor ion of EB B1a was 886.4, and the product ions were 82.1 and 158. The charge mass ratio was 158, the pause time was 0.1 s, and the collision energy levels were 40 and 60 EV, respectively.

4.2.9. Control Effect of EB Granules against S. frugiperda. This field experiment was conducted in Kaiyang, Guizhou, China, in July 2021. The maize variety Qiannuo 938 was planted on June 8, 2021 at the field experimental base of the Guizhou Institute of plant protection in a plot sized 6 m × 5 m. The plots were under the same water and fertilizer management. Additionally, the plots with a serious occurrence of FAW were chosen as the test plots, and the maize plants were in the seedling stage of growth. In this study, three treatments (200 g/667 m^2, 300 g/667 m^2, and 500 g/667 m^2) and one blank control were involved, each plot was 30 m^2, and the study was repeated four times. The insect population density was investigated before the application of EB granules. The general survey method was applied to investigate and record the number of larvae in each plot. After 1 d, 3 d, 5 d, 7 d, and 14 d, the number of live larvae was recorded. The control efficacy was calculated using the decline rate (eq 6) and control efficacy (eq 7)

$$K\ (\%) = \frac{N_b - N_a}{N_b} \times 100 \tag{6}$$

where K is the decline rate, N_b is the live larvae before treatment, and N_a is the live larvae after treatment.

$$E\ (\%) = \frac{K - Kc}{1 - Kc} \times 100 \tag{7}$$

where E is the control efficacy, K is the decline rate of the blank control, and Kc is the decline rate of the treatment.

4.3. Data Processing. Statistical analysis was performed using software Origin Lab 2019b to process and map the release data of EB granules in different release medium contents.

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Author Contributions

Y.L. and H.Z. contributed equally to this work. Y.L. and H.Z. performed the conceptualization, methodology, validation, and writing of the original draft. G.L. and M.C. carried out the investigation and formal analysis. X.C. and L.Q. executed the supervision and investigation. C.C. and Z.C. accomplished the formal analysis. X.W. and F.Z. conducted the conceptualization, supervision, project administration, funding acquisition, and writing—review editing.

Notes

The authors declare no competing financial interest.

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