Caustion Analysis and Improvement Strategy for Reduced Pendimethalin Herbicidal Activity in the Field after Encapsulation in Polyurea

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ABSTRACT: To reduce the amount of organic solvents in pendimethalin emulsifiable concentrate (EC), small-size microcapsules (S-MCs) and large-size microcapsules (L-MCs) were prepared with polyurea as a wall material. Petri-dish bioassays were carried out to investigate the bioactivity of formulations and the influence of both organic matter and moisture. The relationships between degradation and the biological activity of three pendimethalin formulations in the soil were investigated, and field experiments were executed to verify the laboratory results. The laboratory tests showed the following: (1) the bioactivity of EC and S-MCs was similar and greater than that of L-MCs; (2) organic matter could reduce the bioactivity of MCs and EC, and the impact of organic matter on L-MCs was greater; (3) increased soil moisture content had no significant effect on the bioactivity of EC but slightly reduced that of the MCs; and (4) the L-MCs showed significantly more prolonged residual and effective persistence in the soil than did EC and S-MCs. However, the field experiments indicated that the herbicidal efficacies of L-MCs at the early and late stages were both lower than those of EC. Comprehensive analysis of the results indicated that the main reason that the herbicidal efficacy of L-MCs was lower than that of EC in the field was that L-MCs missed the optimal herbicidal periods due to the slow-release characteristics of L-MCs. The S-MCs had both similar release rates and herbicidal efficacy in the field as EC. Therefore, to develop a good pesticide formulation, the occurrence and damage characteristic of pests must be considered.

INTRODUCTION

Encapsulation technology has been widely used in the field of agrochemicals, as encapsulation can reduce the volatilization and degradation of the active ingredient to prolong its persistence.1–4 To date, more than 150 kinds of pesticide microcapsules (MCs) have been registered in China, including insecticides, fungicides, herbicides, and plant growth regulators. The advancements of pesticide MCs in China also stem from the limitations of using organic solvents in pesticide emulsifiable concentrate (EC), which was officially issued in the Limit of Harmful Solvents of Emulsifiable Concentrate Pesticides.5 Petroleum derivatives, such as benzene, toluene, xylene, and N,N-dimethyformamide, are widely used as solvents for the production of EC. However, these solvents are not biodegradable and can be hazardous to the environment.6 The development of water-based formulations is one of the most significant developments for EC. Among the extensive developments, capsule suspension is a promising orientation that accommodates the encapsulated pesticide in water.7–9 Pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzamidine; Scheme S1 in the Supporting Information) is a dinitroaniline primarily preemergent herbicide; pendimethalin is one of the top herbicides and can control various annual grasses and certain broadleaf weeds in a variety of crops. At present, the dominant formulation for pendimethalin is still an EC. Thus, the development of water-based formulations for pendimethalin is helpful to reduce the consumption of organic solvents and pollution to the environment.10 However, pendimethalin preparations of emulsion oil in water and suspension concentrates can easily lead to technical material crystal Ostwald ripening, which can cause formulation instability. Therefore, microencapsulation is an alternative formulation for pendimethalin in terms of environmental considerations.

Mogul et al. suggested that the efficacy of a controlled release system is the most important indicator when evaluating pesticide products.1 The development of water-based formulations for pendimethalin can increase or reduce pesticide biological activity.11–15 Studies have reported that the conventional EC of alachlor shows quicker bioavailability16,17 but shorter residual activity than encapsulated alachlor.18,19 Furthermore, Hatzinikolaou et al.20 indicated that the bioactivity of pendimethalin EC in the
soil was greater than that of pendimethalin MCs, but the
authors did not reveal the reasons for this result. Unfortunately,
none of the above studies indicated the type of capsule wall
material used. Wall material is a key factor that influences the
release characteristics and mechanical strength of MCs.21,22
When the wall material differs, the biological activity of the
pesticide MCs will especially vary.23,24 Therefore, the kinds of
wall materials used should be specified in research involving the
biological activity of pesticide MCs. In addition, a decrease in
MC particle size can lead to increases in the total surface area of
MCs, thus accelerating the release of the encapsulated
ingredient(s). In addition, the impact of pesticide particle size
on efficacy has generated concern among researchers.25−27
Therefore, this study examined the effect of particle size on the
efficacy of pendimethalin MCs.

At present, interfacial polymerization is the most commonly
used method in the preparation of pesticide MCs.28,29 In the
present study, small-size microcapsules (S-MCs) and large-size
microcapsules (L-MCs) fabricated with polyurea wall material
were obtained using an interfacial polymerization method
(Scheme S2 in the Supporting Information). A series of
laboratory tests and field experiments were carried out to reveal
the cause of the pendimethalin herbicidal activity reduction
after encapsulation in polyurea and to explore the method of
improving the herbicidal activity.

■ RESULTS AND DISCUSSION

Microcapsule Characterization. Figure 1a,d,g illustrates
the dispersed states of pendimethalin EC, S-MCs, and L-MCs
in water. Particles of the three samples exhibited favorable
dispersibility, and the size distributions were unimodal (Figure
1c). The $D_{10}$, $D_{50}$, and $D_{90}$ of the L-MCs were 2.63, 10.35, and
23.12 μm, respectively; those of the S-MCs were 0.98, 1.32, and
1.73 μm, respectively; and those of the EC were 0.38, 0.45, and
0.50 μm, respectively.

After the pendimethalin EC dilution was air-dried, rod- or
sheetlike crystals emerged with the volatilization of water and
the solvent (Figure 1b). The $D_{10}$, $D_{50}$, and $D_{90}$ of the L-MCs were 2.63, 10.35, and
23.12 μm, respectively; those of the S-MCs were 0.98, 1.32, and
1.73 μm, respectively; and those of the EC were 0.38, 0.45, and
0.50 μm, respectively.

After the pendimethalin EC dilution was air-dried, rod- or
sheetlike crystals emerged with the volatilization of water and
the solvent (Figure 1b). The crystals undoubtedly were the
technical material of pendimethalin. It was clear that all of
the pendimethalin maintained a bare state. However, MCs
exhibited rather different stabilities even after being air-dried.
As depicted in Figure 1e,h, the MCs appeared to be stable.
spheres, which was further confirmed by SEM. It was apparent from the SEM images that the membrane of the MCs was nonporous and that the surface was relatively smooth with several dents (Figure 1f,i). However, the subsidence of S-MCs was more severe. Regarding the MCs containing pendimethalin, the vast majority of active ingredient was encapsulated in the polymeric shell. We were interested in to what extent the technical material of pendimethalin was encapsulated, although no apparent crystals were observed. Therefore, the contents of free pendimethalin in the L-MC and S-MC suspensions were measured, which were 2.30 and 2.99%, and they increased to 2.84 and 3.3%, respectively, after storage at 54 °C for 14 days. This indicates that pendimethalin cannot easily be released when the MCs are suspended in water, as the solubility of pendimethalin in water is only 0.33 mg/L at 20 °C.

The results showed that the biological activity of pendimethalin MCs mainly depends on the active ingredient released from the capsule core. Thus, it was necessary to investigate the release characteristics of the MCs. The results are shown in Figure 2. The release characteristics of the three samples were largely different. After the EC sample was added to the release medium, pendimethalin quickly became evenly distributed, whereas the MCs showed clearly sustained release characteristics. After 2 h, the release volume of the S-MCs reached 90%, and the slow-release phase then began. After 5 h, the release volume of the S-MCs reached 100%. The release of L-MCs was significantly slower than that of S-MCs, and the release time of L-MCs was longer than that of S-MCs by approximately 5 h.

Moreover, MCs have significant advantages considering the financial and environmental costs, as they contain 10% solvent, whereas the EC contains 60% solvent. Therefore, the wide application of MCs can substantially lessen the consumption of organic solvents.

**Pure Inhibitory Activity of Pendimethalin MCs and EC against the Root Growth of Sorghum.** The results of the inhibition of MCs and EC to sorghum root growth are shown in Figure 3. The inhibition of EC and S-MCs was similar and greater than that of L-MCs at the same concentration. When the concentration increased from 0.25 to 4 mg kg⁻¹, the EC group inhibition rate ranged from 59.26 to 86.46%, that of the S-MC group ranged from 53.64 to 85.33%, and that of the L-MC group ranged from 30.49 to 81.87%. This phenomenon could mostly be due to the active ingredient release mechanism. When the EC was applied into sand, the pendimethalin was completely exposed (as shown in Figure 1b). However, the polyurea wall of the MCs was very stable and never broke during application (as shown in Figure 1e,h). Therefore, the pendimethalin must gradually be released by slow osmosis. More biologically available pendimethalin was initially present where EC had been applied, compared with MCs. In addition, the inhibition of S-MCs was higher than that of L-MCs. This may have been because the larger surface area of the S-MCs was conducive to the release of pendimethalin. This result demonstrated that microencapsulation can reduce pendimethalin bioactivity, and adjusting the particle size can regulate the biological activity of pendimethalin MCs.

**Influence of Soil Conditions on the Biological Activity.** The biological activity of preemergence herbicides largely depends on dynamic field conditions, such as rainfall intensity, organic matter (OM), and soil moisture content. Therefore, it is crucial to clarify the influence of soil conditions on the biological activity of preemergence herbicides.

**Effect of Organic Matter (OM) on the Inhibitory Activity of Pendimethalin MCs and EC against the Root Growth of Sorghum.** As depicted in Figure 4, the inhibition of pendimethalin EC and MCs gradually decreased with increasing amounts of OM. More importantly, the decreased levels of pendimethalin L-MCs were more significant than when using the S-MC and EC treatments. When the content of OM increased from 0 to 8%, the inhibition rate of the L-MC group decreased by 42.7%, that of the S-MC group decreased by 21.38%, and that of the EC group decreased by only 10.58%. There are two possible reasons for this result. First, the pores in the surface of peat, which is the main component of OM, can adsorb the pendimethalin, thus reducing contact between the seed and pendimethalin. In the treatment of L-MCs, the insufficient biologically active pendimethalin becomes scarcer after being absorbed by OM. Second, the presence of OM promoted root growth. In the treatment without herbicides, the sorghum root length increased gradually with increased OM content (Figure 4A), as OM can both provide nutrients and loosen the growth matrix.
Effect of Absolute Moisture Content (AMC) on the Inhibitory Activity of Pendimethalin MCs and EC against the Root Growth of Sorghum.

As shown in Figure 5A, the AMC had a slight influence on root length with the treatment of pendimethalin EC or MCs, although no significant differences were observed. However, AMC had a relatively larger influence on the bioactivity of L-MCs and S-MCs. Pendimethalin in the EC-treated group was uniformly dispersed and exposed in the sand, and the roots were then completely exposed to pendimethalin. Therefore, AMC only showed a slight influence on the root growth of sorghum after treatment with EC, as the dose of the dissociative active ingredient did not vary with the variation of AMC. However, when pendimethalin was encapsulated into the polyurea wall material, it did not show bioactivity unless the active ingredient was released from the MCs. Nevertheless, it was difficult for pendimethalin to be released when the MCs were suspended in water (the effect of the particle range of MCs on the release of pendimethalin was not obvious), which is due to the low water solubility of pendimethalin. This conclusion was confirmed by the results of free pendimethalin in the MC formulations (Microcapsule Characterization). Thus, the increase in moisture is unfavorable for the release of pendimethalin from MCs. As shown in Figure 5B, the fluctuating inhibition rate was more apparent because the root length of sorghum decreased in the control group containing higher amounts of AMC (may have been due to the anaerobic respiration of the root system). Nevertheless, when the AMC in the sand reached 15%, the system was saturated. As the AMC continued to increase, the root length and inhibition rate in the various treatment groups remained unchanged.

Relationship between the Residues and Biological Activity of Pendimethalin MCs and EC. As has been reported, it was difficult for pendimethalin to volatilize and...
concentration of pendimethalin in the 20 g of soil sample was 1000 μg kg⁻¹. Twenty days after treatment, 413.73 μg kg⁻¹ of pendimethalin remained in the EC-treated soil; 505.74 and 833.74 μg kg⁻¹ of pendimethalin remained in the S-MC- and L-MC-treated soils, respectively. The degradation rates of pendimethalin from the EC and S-MCs were similar and faster than that of L-MCs at the same concentration. One hundred days after treatment, the residual of the EC group decreased to 6.97 μg kg⁻¹, whereas those of the S-MC and L-MC groups were approximately 56.57 and 260.35 μg kg⁻¹, respectively.

A cubic polynomial fit well with the L-MC (y = 911.37 − 4.5644x − 0.0112x² − 8.1013 × 10⁻⁵x³, R = 0.9962) dissipation points, whereas an exponential function was a more appropriate fit for the EC (y = 923.12 e⁻⁰⁻⁰⁴⁵⁴₄x, R = 0.9930, with a half-life of 14.76 days) dissipation points. Thus, the EC degradation curve essentially conformed to a first-order kinetics model, whereas the L-MC curves did not fit a first-order model. Chen et al.36 and Zhang et al.24 showed that when pesticides are incorporated into EC, they rapidly dissipate and fit with a first-order kinetics equation; after the pesticide was encapsulated, the degradation curve did not fit a first-order kinetics equation. This result is consistent with ours. Unlike previous findings, an exponential function was a more appropriate fit for the S-MC (y = 28.77 + 864.33 e⁻⁰⁻⁰³₄₆₉x, R = 0.9983) dissipation points. This result may still depend on the rapid release of S-MCs.

To demonstrate the bioactivity of residual pendimethalin, the soil samples treated with S-MCs, L-MCs, or EC were tested for the inhibition of sorghum root growth at different time intervals (Figure 6B). Within the first day, the inhibition rate gap between EC and L-MCs was 19% in the soil, whereas this gap was approximately 14% in the sand (Pure Inhibitory Activity of Pendimethalin MCs and EC against the Root Growth of Sorghum). These results indicate that the bioactivity of MCs was lower in the soil. The inhibition rates of the EC and S-MCs were similar. Within the first 20 days, the inhibition of both types of MCs was lower than that of the EC. However, the inhibition rate of the EC treatment sharply decreased, whereas that of the MCs gradually decreased. After 40 days, the inhibition of both kinds of MCs was higher than that of the EC. After 100 days, the inhibition rate of the EC group decreased to 0%, whereas that of the S-MCs was approximately 8% and that of the L-MCs was approximately 26%.

**Field Experiments.** The efficacies of pendimethalin EC and MCs in controlling different kinds of weeds were investigated in field experiments, and the results are shown in Figure 7. Three weeks after treatment, when the herbicide dose was the same, the numbers of Gramineae, Cyperaceae, and Portulacaceae of EC- and S-MC-treated plots were less than those of the L-MC-treated plots. Six and ten weeks after treatment, the tendency of grass numbers and total plant control efficacy in all herbicide treatments were similar compared with those at 3 weeks. Ten weeks after treatment, the total fresh weight control efficacy against Gramineae, Cyperaceae, and Portulacaceae of the EC and S-MC 1500 g a.i. ha⁻¹ groups was approximately 75% of that of the control, and the total fresh weight control efficacies of other treatments were approximately 45–60%. It is worth noting that the control efficacy of the L-MCs was lower than that of the EC in the early and late stages of the field experiment. These results are not in accordance with those of the laboratory tests.

The same experiment was repeated in Tai’an, China, in 2016 (Figure S2 in the Supporting Information). The results were similar to those shown in Figure 7.

Efficacy must be considered in the development of pesticide preparations. The following two reasons were responsible for the lower herbicidal activity of L-MCs compared with that of EC in the early stage of the field experiment:

First, the reduced biological activity was due to the hardened polyurea capsule wall blocking the release of pendimethalin. This conclusion was confirmed by microscopy and biological activity tests.
Second, the influence of the OM and water on the soil played a role. In farmland, OM consists of residual weeds, crop straw, and decaying farmyard manure. OM is an important component in the soil and can provide nutrients and improve the porosity of the soil. Moreover, the OM content also influences the adsorption of herbicides in the soil; thus, its herbicidal activity is significantly influenced. Soni et al.\textsuperscript{32} indicated that the presence of OM in the soil can reduce the bioactivity of pendimethalin EC. Our research found that the reduced bioactivity of pendimethalin MCs by OM was more apparent, when compared with EC, and that the impact of L-MCs was greater than that of the other two formulations. Interestingly, the influence of OM on different herbicides was different. Vasilakoglou et al.\textsuperscript{16} found that OM could significantly reduce the bioactivity of alachlor MCs more than that of alachlor EC, but the influence of OM on acetochlor

Figure 7. Efficacies of pendimethalin EC and MCs in controlling different kinds of weeds in field experiments. Data with different lowercase letters are significantly different at the $p < 0.05$ level by Tukey's multiple-range test. Error bars represent the standard errors of the means of four replicates.

Figure 8. Schemes explaining the efficacy differences caused by seed depth between pendimethalin MCs and EC in the field.
MCs and acetochlor EC was not significantly different. This may have been related to both the adsorption ability of OM to the compound and the mobility of the compound in the soil. Furthermore, irrigation before or after spraying preemergence herbicides is a typical farm operation. Therefore, investigation of the influence of soil humidity on herbicide bioactivity has great practical significance. The results showed that the soil humidity has little effect on the biological activity of pendimethalin MCs and EC.

The persistence experiment in the laboratory showed that (i) microencapsulation by polyurea can reduce the degradation of pendimethalin in the soil, particularly for L-MCs, and that (ii) as time progresses, pendimethalin in the microcapsules can be released to exert its biological activity. Nevertheless, at the late stages of the field experiments, the efficacies of L-MCs in controlling weeds were still lower than that of the EC.

Our results contradict those reported by Hatzinikolaou et al. who found that the field persistence of pendimethalin MCs was slightly longer than that for EC. However, this conclusion does not represent the actual field effect because the field persistence of the herbicide was studied with the Petri-dish bioassays that were carried out after the soil herbicide treatment was taken back to the laboratory.

To explain the opposite results between the laboratory and field experiments, the biological characteristics of control objects should be analyzed. Yang et al. and Yuan et al. showed that microencapsulated insecticides were significantly more stable against degradation in the soil and had much greater efficiencies against white grubs than the conventional formulation, as microencapsulation increased the chance of exposure of insects to insecticides. However, we should note that the control targets of preemergence herbicides are newly germinated seed. Figure 8 can be used to understand the reason for the efficacy differences caused by seed depth between pendimethalin MCs and EC in the field. The germination of seeds is closely related to the depth of the seed. The appropriate soil layer is beneficial to the seed to germinate, whereas the deeper soil layers are adverse to seed germination. In the field experiment, the number of weeds in the control area gradually decreased, which indicated that no or very few new weeds grew. In addition, preemergence herbicides cannot kill weeds that have penetrated the soil surface.

As such, extending the period of preemergence herbicides is not needed. Therefore, it is very important to control weeds at early stages for preemergence herbicides. In other words, the herbicidal efficacy of L-MCs was lower than that of EC because the slow-release characteristics caused L-MCs to miss the critical period of seed germination.

There are three strategies for improving the weeding efficacy of pendimethalin MCs. First, we can regulate the construction of polyurea. For example, previous studies have shown that assembling photosensitive, acidic groups, alkali-sensitive groups, or temperature-sensitive groups onto the capsule wall material can regulate the release of the core. Second, we can choose other special microcapsule membranes that will rupture as a chemical response to an applied stimulus, e.g., water and temperature. Third, we can adjust the biological activity of pesticide microcapsules by changing the size of the microcapsules. This study adopted the third method to improve the bioactivity of pendimethalin MCs. The results showed that when the particle size range was 0.1–2 μm, the herbicidal activity of pendimethalin MCs in the laboratory and field was analogous to that of EC.

This study revealed the reasons for the poor weed control effect of pendimethalin MCs and the increased herbicidal activity of pendimethalin MCs with the polyurea wall material by reducing the particle size. Importantly, the development of pesticide formulations must account for the biological characteristics of the control object. Our results can simultaneously provide a reference for the microencapsulation of pesticide compounds. In addition, whether the impact of particle size on bioactivity is suitable for other pesticides or microcapsule wall materials needs further study.

**CONCLUSIONS**

In the present study, to reduce the use of organic solvents in pendimethalin formulations, pendimethalin MCs with polyurea as the wall material were prepared using interfacial polymerization. The laboratory tests obtained the following results: (i) the influence of OM on the bioactivity of MCs was greater than that of EC; (ii) the effects of soil moisture on the efficacy were minor, but excessive moisture was unfavorable for the release of pendimethalin from MCs; (iii) although L-MCs were more stable in the soil and exhibited biological activity, the slow-release properties of L-MCs caused pendimethalin to miss the critical period of weed germination; and (iv) the bioactivity and field efficiency of S-MCs and EC were similar and greater than those of L-MCs. These results show that in the development of the MC formulations of preemergence herbicides, developers should pay attention to the quick release of the capsule core. In summary, it is necessary to consider the occurrence and damage rules of pests during the development of pesticide formulations.

**MATERIALS AND METHODS**

**Chemicals.** The technical material (purity = 97%) of pendimethalin was kindly provided by Shandong Huayang Technology Co., Ltd. (Shandong, China). The chemical 4,4'-methylene diphenyl disocyanate (MDI) was purchased from Wanhua Chemical Group Co. (Shandong, China). The hydrophilic monomer 1,6-hexanediame (HDA) was purchased from Sinopharm Chemical Reagent Beijing Co. (Beijing, China). Calcium dodecylbenzene sulfonate (emulsifier 500#, CAS No. 26264-06-2) and polyoxyethylene styrylphenyl ether (emulsifier 600#, CAS No. 99734-09-5) were purchased from Jiangsu Zhongshan Chemical Co., Ltd. (Jiangsu, China). Poly(vinyl alcohol) (PVA), polyoxyethylene castor oil (EL-40), xylene, acetone, hexane, methanol, xanthan gum, and ethanediol were all purchased from Aladdin Reagent Co. (Shanghai, China). Distilled water was used throughout the study.

**Preparation of Formulations.** Microencapsulation procedure. Polyurea L-MCs were obtained using an interfacial polymerization method. In the first step, 30.93 g of pendimethalin, 10.00 g of xylene, and 2.5 g of MDI were weighed and mixed, which constituted the organic phase. Then, an O/W emulsion was prepared by pouring the organic phase into 60 g of aqueous solution containing 1.5% EL-40 and 0.1% PVA as a stabilizer. After homogenizing the mixture at 8000 rpm for 2 min at room temperature, the oil in water emulsion was then transferred to a three-neck flask and stirred at 300 rpm. Next, 5.5 g of HDA solution (10%, w/w) was added in dropwise increments. The reaction was carried out at 60 °C for 3 h at a stirring rate of 300 rpm. The preparation process of S-MCs was the same as that for L-MCs except for increasing the dosage of EL-40 from 1.5 to 5.5%.
The microcapsule slurry was centrifuged at 1 × 10⁴ rpm. The microcapsule suspension formulation was prepared by resuspending the sedimented material in an aqueous solution containing 4 g of emulsifier 500° and 6 g of emulsifier 600°. The final volume of the solution was brought to 100 mL with water. The concentration of pendimethalin in this microencapsulated formulation was 300 g L⁻¹.

Preparation of pendimethalin EC. The conventional formulation was prepared by mixing 30.93 g of pendimethalin technical material, 4 g of emulsifier 500°, and 6 g of emulsifier 600°. The final volume of the solution was brought 100 mL with xylene.

Characterization. The particle size and size distribution of the MCs were measured with a laser particle size analyzer (LS-POL 6; Omec Instruments Co., Ltd., Guangdong, China). The surface morphology of the MCs was observed using scanning electron microscopy (SEM) (Hitachi SU8010, Tokyo, Japan). Photomicrographs were obtained using a BX51 microscope (Olympus Corporation, Tokyo, Japan).

The free active ingredients of both MC preparations and the preparation samples after 14 days at 54 °C were tested according to previous methods, with modifications. The release properties of the three pendimethalin preparations were examined according to previous methods, with modifications. The standard procedures used are described in the Supporting Information.

Bioactivity of Pendimethalin EC and MCs. Petri-dish bioassays were carried out based on the method of Hatzinikolaou et al. to compare the root growth of Sorghum bicolor (L.) Moench in sand after treatment with pendimethalin EC, S-MCs, or L-MCs. Pendimethalin EC, S-MCs, and L-MCs were dissolved in deionized water and added to their respective sand samples. Then, the mixtures were thoroughly mixed by shaking to achieve the concentrations of 0.25, 0.5, 1, 2, and 4 mg a.i. kg⁻¹ of air-dried sand and an absolute water content of 13.5%. Untreated sand received the same amount of water but was otherwise handled in an identical way as the herbicide-treated sand. Each treatment was repeated three times. Then, the glass containers were sealed and placed in a growth chamber at 25 ± 2 °C. The mixture (87 g) was removed from each glass container every 20 days for the bioassay. The bioassay procedure was performed in a similar way as described in the section titled “Bioactivity of Pendimethalin EC and MCs”. Simultaneously, 20 g of the samples was removed from each glass container, and the amount of pendimethalin in the soil samples was then detected using an HPLC system. Extraction and clean-up of pendimethalin from the soil were carried out according to previously described protocols.

Soil samples (20 g) was weighed and transferred to a 50 mL centrifuge tube that contained 25 mL of acetone–hexane solution (1:4, v/v). The pendimethalin in the soil sample was extracted in accordance with an ultrasonic method for 1 h and then shaken for 30 min by a table concentrator (100 rpm, 25 °C). After centrifugation, the supernatant was filtered through filter paper in a round-bottom flask. Again, 25 mL of acetone–hexane solution was added to centrifuge tubes, and the same procedure was repeated. The supernatants obtained from the two extractions were combined. The combined supernatant (25 mL) was removed and transferred to a round-bottom flask and evaporated at 45 ± 2 °C using a rotary evaporator. After removing the solvent by reduced pressure distillation, the residue in the round-bottom flask was dissolved in 2 mL of acetonitrile (HPLC grade) and then filtered through a 0.22 μm millipore filter (polycaprolactam, Tianjin Jinteng Experimental Equipment Co., Ltd., Tianjin, China) for HPLC analysis. The conditions used for HPLC detection were performed in a similar manner as that described in the Supporting Information.

FIELD EXPERIMENTS

Field experiments were conducted during the growing season in 2015 at the corn farm of Shandong Agricultural University, China (117°10′12″E, 36°10′47″N). The same experiment was repeated in 2016. The soil type was a silty clay loam consisting of 4% clay, 40% silt, 56% sand, and 1.45% OM and had a pH of 6.69. The daily rainfall and mean temperature data recorded
near the experimental area are shown in Figure 9. A randomized complete block design was used for the experiment with four replicates per treatment. The plot size was 2.0 m × 7.0 m, and all plots were separated from the others by a 1 m wide buffer zone. Corn (Zhengdan 958) was sown in 80 cm rows at 62 500 seeds/ha on June 20, 2015. The herbicides used were pendimethalin EC, S-MCs, and L-MCs. Detailed designs about herbicide applications are shown in Table 1. An untreated control was also included. All herbicides were applied after corn sowing using a backpack sprayer (AGROLEX HD400, Singapore) with flat-fan nozzles delivering 450 L/ha dilutions. The experimental area was irrigated with water immediately after herbicide applications. In addition, all experimental plots were irrigated three times until harvest. To determine the efficacy of the herbicide, weed species and weed quantity were assessed at 3, 6, and 10 weeks after herbicide applications for all plots using four 50 cm × 50 cm quadrants placed randomly in the plots. In addition, the aboveground biomass of 1 m² of each plot was collected and weighed in accordance with the same protocol in the previous survey.

The weed species assessed included those of the Gramineae (Cynodon dactylon L. Pers., Eleusine indica L. Gaertn., Digitaria sanguinalis L. Scop., Setaria viridis L. Beauv., and Polypogon fugax Nees ex Steud.), Cyperaceae (Cyperus diffusus L., and Cyperus rotundus L.), and Portulacaceae (Portulaca oleracea L.).

**Statistical Analyses.** Data from the release characteristics of microcapsules, the determination of laboratory bioactivity, degradation tests, and field experiments were statistically analyzed using SPSS software (version 16.0) and were displayed as the means and SEs by Tukey’s multiple-range test ($p = 0.05$). All figures were obtained using Sigmaplot 13 software.

| Herbicides                  | Application Rate (g a.i. ha$^{-1}$) |
|-----------------------------|-------------------------------------|
| pendimethalin L-MCs         | 1000                                |
| pendimethalin L-MCs         | 1500                                |
| pendimethalin S-MCs         | 1000                                |
| pendimethalin S-MCs         | 1500                                |
| pendimethalin EC            | 1000                                |
| pendimethalin EC            | 1500                                |
| Control                     |                                     |

![Figure 9. Daily rainfall and mean temperature during the experiment in 2015.](image)

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01651.

Method of detecting free active ingredients of MC preparation and the determination of release properties of three pendimethalin preparations; average recoveries and standard error of pendimethalin S-MCs, L-MCs, and EC in soil (Table S1); rainfall and temperature of the field experiment period in 2016 (Figure S1); results of the field experiment repeated in 2016 (Figure S2); chemical structure of pendimethalin and the formation of polyurea, respectively (Schemes S1 and S2) (PDF)

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**Notes**

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