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Tank-Mix Adjuvants Enhance Pesticide Efficacy by Improving Physicochemical Properties and Spraying Characteristics for Application to Cotton with Unmanned Aerial Vehicles

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Cite This: *ACS Omega* 2024, 9, 31011−31025

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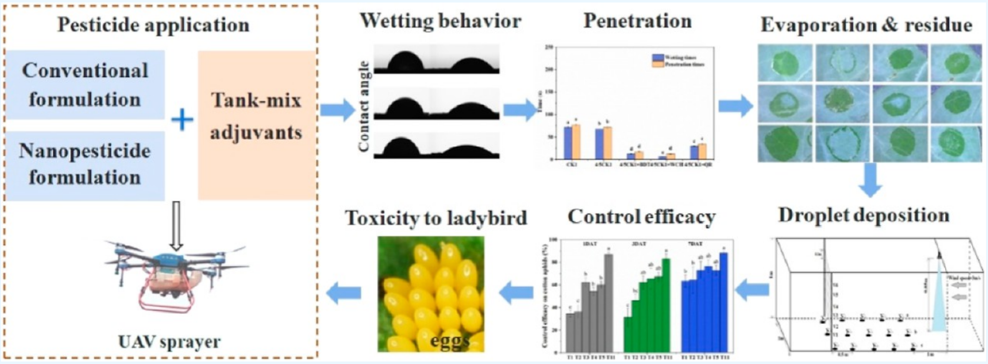

ABSTRACT: Tank-mix adjuvants have been used to reduce spray drift and facilitate the efficacy of pesticides applied with unmanned aerial vehicles (UAVs). However, the effects of specific adjuvants on pesticide characteristics and the mechanism of action remain unclear. Herein, we analyzed the effects of three different types of tank-mix adjuvants (plant oil; mineral oil; and mixture of alcohol and ester) on the surface tension (ST), contact angle, wetting, permeation, evaporation, spray performance, and aphid-control effects of two types of pesticides. The mineral oil adjuvant Weichi (WCH) was highly effective in reducing the pesticide solution ST, improving the wetting and penetration ability, increasing droplet size, and promoting droplet deposition. The mixed alcohol and ester adjuvant Quanrun (QR) showed excellent wetting and antievaporation properties and promoted droplet deposition. A plant oil adjuvant (Beidatong) moderately improved wetting and penetration ability and reduced droplet drift. Field tests showed that the control efficiencies (CEs) of two pesticides were increased after the addition of adjuvants, even with 20% reductions in pesticide application. When the UAV was operated at 1.5 m, the CEs of two pesticides were increased from 65.39 and 66.63% to 73.11−76.52% and 77.91−88.31%, respectively. When operated at 2.5 m, the CEs were increased from 51.24 and 68.60% to 65.06−75.70% and 77.57−92.59%, respectively. Especially, the CEs of pesticides with WCH and QR increased obviously. Importantly, neither WCH nor QR inhibited hatching of the critical insect natural enemy ladybird beetle at concentrations used in the field. This study provides a framework for assessment of tank-mix adjuvants in aerial sprays and directly demonstrates the value of specific adjuvants in improving pesticide bioavailability and minimizing associated environmental pollution.

1. INTRODUCTION

Pesticide application is an important method of minimizing crop yield losses and ensuring plant quality. However, the application process (spraying) may lead to pesticide droplet evaporation, drifting, and/or splashing, which decrease binding to leaves and pollute the surrounding environment. In addition to causing soil and water contamination, pesticide overuse also has adverse impacts on nontarget organisms, such as honeybees and insect natural enemies.[1−4] Methods of increasing pesticide efficacy and minimizing their release to the environment have therefore been focuses of increasing research attention.[5]

Recently, the use of tank-mix adjuvants in pesticide spray mixtures has been identified as an effective strategy to improve pesticide effectiveness and minimize environmental risks.[2,5] He et al.[6] found that the addition of surfactants into fungicides can improve droplet wettability on plant leaf surfaces by reducing

Received: May 6, 2024
Revised: June 14, 2024
Accepted: June 17, 2024
Published: July 2, 2024

https://doi.org/10.1021/acsomega.4c04301

surface tension (ST), diminishing the contact angle (CA), and inhibiting evaporation of the pesticide diluent. Green-peel orange essential oil, a common tank-mix adjuvant, improves pesticide absorption and translocation within rice plants.[7] Adding this plant oil adjuvant to a defoliant increases the droplet coverage rate and retention in cotton leaves.[8] Furthermore, other types of tank-mix adjuvants such as surfactants, organosilicon, mineral oils, and plant essential oil are also commonly used in the process of management of crop diseases and pests.[7,9] Thus, prior results have indicated that different types and concentrations of spray additives have varying effects on pesticides; overall, appropriate adjuvant use can increase pesticide deposition on plant leaves and increase efficiency.

Cotton is a critical cash crop and industrial raw material that supports the national economy and individual farmers' livelihoods. However, cotton plants are vulnerable to attack by various pests, diseases, and weeds during all growth stages. At present, chemical pesticide application remains the primary method of pest control in cotton. However, manual pesticide spraying is time-consuming and labor-intensive. Rising labor costs in East Asia have increased the need for simplified methods of cotton plant cultivation and highlighted the value of upgrading and utilizing machinery for plant protection.[10] Although some ground-based machine sprayers (including self-propelled sprayers) have high efficiency, they lack the flexibility needed to treat entire fields. Unmanned aerial vehicles (UAVs) have attracted a great deal of research attention as potential solutions to these challenges. UAVs have several key advantages: low operating costs, high efficiency, low water consumption, and a lack of constraints based on field topography.[11] Thus, UAVs have gradually become the preferred method for pesticide application to cotton and other crops.[12−14] Previous studies have assessed the influence of UAV type, spraying volume, working height, velocity, and other parameters on pesticide droplet deposition, drift, and pest control efficiency (CE) in cotton fields.[15−17] For example, the standard UAV operating height above the cotton canopy is 1−3 m; this long distance has been shown to cause pesticide droplet evaporation and drifting into nontarget areas.[18] It is therefore necessary to research methods of improving the effective utilization rates of UAV-applied pesticides and of minimizing the associated environmental risks.

Pesticide application is a complex process that includes steps such as atomization, deposition, adhesion, spreading, osmosis, absorption, and translocation. Each step can be optimized to improve pesticide efficiency. Research into the use of tank-mix adjuvants in UAV-applied pesticides has previously focused on the effects of adjuvants on droplet deposition and pesticide efficiency.[19] However, there have been few studies related to improving pesticide bioavailability and minimizing environmental risks and still fewer comprehensive evaluations of the effects and mechanisms of tank-mix adjuvants on pesticides in the context of UAV-based spraying. To address this gap in knowledge, we here investigated the effects of three types of commonly used tank-mix adjuvants (plant oil; mineral oil; and mixture of alcohol and ester) in agriculture on the physicochemical properties and application effects of two pesticides sprayed by UAVs in cotton fields. We systematically explored the effects and mechanisms of these tank-mix adjuvants on the physicochemical properties, wetting, permeation, evaporation, deposition, spraying performance, and CE of pesticide solutions. Finally, we addressed adjuvant safety in an important insect natural enemy, ladybird beetle. This study provides both a framework for assessing the effects of adjuvants on pesticide characteristics and suggestions for optimal adjuvants to be used in UAV-based pesticide spraying of cotton fields.

2. MATERIAL AND METHODS

2.1. Chemicals and Reagents. The nanopesticide acetamiprid·lambda-cyhalothrin (3.5%) was obtained from Nanjing Scienx Modern Agriculture Co., Ltd. (Jiangsu, China). The conventional pesticides acetamiprid emulsifiable concentrate (EC) (5%) and lambda-cyhalothrin emulsion in water (EW) (2.5%) were purchased from Tianjin Shipule Pesticide Technology Co., Ltd. (Tianjin, China) and Henan Luba Pesticide Technology Co., Ltd. (Henan, China), respectively. Three types of tank-mix adjuvants, plant oil adjuvant (Beidatong, BDT), mineral oil adjuvant (Weichi, WCH), and mixture of alcohol and ester adjuvant (Quanrun, QR), which are common used adjuvants in plant protection in China,[20,21] were selected for the experiments. BDT (Hebei Mingshun Agricultural Co., Ltd., Hebei, China) is a formulation of 85% methylated plant oil and 15% surfactant. WCH (TotalEnergies Fluid Co., Paris, France) is composed of 95% mineral and plant-derived alkanes, biobased alcohol esters, and fatty alcohols, with 5% surfactants. QR [Zhonghe Tiancheng Agricultural Development (Wuhan) Co., Ltd. (Wuhan, China)] is 85% fatty alcohols, alkyl polyoxyethylene esters, and hydroxy esters, with 15% surfactants.

2.2. Particle Size Measurements. Samples of 3.5% acetamiprid·lambda-cyhalothrin and equivalent concentrations of the constituent conventional pesticides (40 μg/mL acetamiprid EC and 30 μg/mL lambda-cyhalothrin EW) were prepared. These samples were diluted 6.5-fold in deionized water. The average particle sizes of the preparations were then measured with the Zetasizer Nano ZS90 dynamic light scattering instrument (Malvern Instruments Co., Ltd., Malvern, England). Three replicate solutions were prepared and measured for each formulation.

2.3. Pesticide Preparation. The base conventional pesticide formulation without tank-mix adjuvants (CK1) comprised 5% acetamiprid EC and 2.5% lambda-cyhalothrin EW. The base nanopesticide formulation (CK2) contained 3.5% acetamiprid·lambda-cyhalothrin. Each base formulation was used to generate four other treatments: one containing four-fifths the original pesticide concentration (4/5CK) and three adjuvant mixtures, each containing four-fifths the original pesticide concentration and one adjuvant (4/5CK + BDT, 4/5CK + WCH, and 4/5CK + QR). This yielded a total of 10 treatment groups (Table 1). To generate each formulation, the pesticides and adjuvants were added to water and mixed thoroughly with a glass stirring rod.

2.4. Physicochemical Properties of Pesticide Formulations. *2.4.1. Static ST and Dynamic ST Measurements.* The static ST (SST) of each solution described in Section 2.3 was measured with a K100 ST meter (KRUSS, Co., Hamburg, Germany) using the Wilhelmy plate method.[7] There were three biological replicates per treatment group. The dynamic ST (DST) of each solution was measured with a BP 50 tension meter (KRUSS, Co., Hamburg, Germany), which uses the maximum bubble pressure method. The time scale was 15−5000 ms and the diameter of the capillary tube was 0.898 mm. Measurements were taken at 25 °C under 40−50% humidity.

Table 1. Composition and Dosage of Spray Dilutions

pesticide	full dosage (g/ha)[a]	reduced dosage (g/ha)
acetamiprid	600	480
lambda-cyhalothrin	900	720
acetamiprid·lambda-cyhalothrin	1500	1200
adjuvant	recommended concentration (v/v)[a]	abbreviation
Beidatong	1.5%	BDT
Weichi	3%	WCH
Quanrun	0.05%	QR

[a] The dosage of pesticides and tank-mix adjuvants was the recommended dosage.

There were three technical replicate measurements of each sample.

2.4.2. CA Measurements. Seedlings of the cotton variety "CCRI 79" were selected for this study. The plant height and leaf area index were 10.3 ± 0.2 cm and 0.13, respectively. To measure the CA, flat cotton cotyledons were fixed on glass slides (76 × 26 mm) with double-sided adhesive tape. For each treatment, a 4 μL droplet was generated and placed on the adaxial and abaxial leaf surface. CA was then measured at 25 °C with a DSA 100 droplet shape analyzer (KRUSS, Co., Hamburg, Germany). The droplets were recorded at 0.05 frames per second (fps) for 6 min. CA values were measured from the photographs. There were three biological replicates per solution.

2.4.3. Wetting and Penetration Time Measurements. The wetting and penetration times of each treatment were measured on standard canvas sheets of 35 mm in diameter (Shanghai Nuocai Trading Co., Ltd., Shanghai, China) as previously described.[22] Briefly, 50 mL of pesticide solution was added to a 50 mL beaker. The canvas sheet was placed above the beaker and brought into contact with the liquid surface. The canvas fell into the beaker when the sheet was completely wetted; the wetting time was recorded as the amount of time from initial contact to the preliminary fall. The penetration time was recorded as the amount of time from initial contact to having fully sunk to the bottom of the beaker.

2.4.4. Wetting Area Measurements. Fresh, flat cotton leaves were collected, cut into 20 × 20 mm strips, and fixed to glass slides with double-sided adhesive. Half of the slides had the abaxial surface exposed and the other half exposed the adaxial surface. Droplets (5 μL) of each pesticide solution were placed on the exposed surfaces and visually assessed for expansion. When the droplet no longer expanded, the wetted leaves were visualized and photographed with a ZEISS Smartzoom 5 ultradepth-of-field microscope (Carl ZEISS, Oberkochen, Germany) at 25 °C with 60% humidity. The wetting area (WA) was then quantified with ImageJ software (National Institutes of Health, Bethesda, MD, USA). There were four biological replicates per treatment group with four droplets per replicate.

2.4.5. Leaf Surface Characterization. Leaf surface nanostructures were characterized with the SU3500 scanning electron microscope (SEM) (Hitachi, Tokyo, Japan).[2] Vacuum freeze-dried leaves were fixed on the sample table with conductive tape and sprayed with gold for 100 s using an ion sputtering apparatus prior to observation. The accelerating voltage, working distance, and emission current were 5.0 kV, 8.3 mm, and 130 μA, respectively.

2.4.6. Evaporation Characteristic Measurements. For each pesticide formulation, evaporation characteristics were assessed with a DSA100 droplet shape analyzer (KRUSS, Co., Hamburg, Germany). Each sample was pumped into the instrument with a microsyringe to form 5 μL droplets in a box maintained at 25 °C with 50% humidity. Changes in droplet volume were recorded over 1 min and fitted to the evaporation equation using a linear regression model.[23] The evaporation inhibition equation is fitted according to the volume change of droplets within 1 min, and the slope of the equation represents the volume change rate of the droplets. Therefore, the larger the absolute value of the slope, the faster the volume reduction rate, the worse the antievaporation performance and the easier it is to evaporate. The evaporation inhibition rate also shows the antievaporation performance of the droplets directly. The evaporation performance of the liquid was then expressed as the evaporation inhibition rate (R), as shown in eq 1

$$R(\%) = (V_0 - V_i)/V_0 \times 100 \tag{1}$$

where V_0 is the change in droplet volume within 1 min for the pesticide alone and V_i is the change in droplet volume for the pesticide with adjuvant. There were three biological replicates for each pesticide.

2.4.7. Particle Size Measurements. For each pesticide formulation, the distribution of particle sizes was measured with a DP-02 laser particle size analyzer (Zhuhai Oumeike instruments Co., Ltd., Guangdong, China). A TeeJet 110−015 nozzle was located 1 m above the particle size analyzer, dispensing solution at a spray pressure of 0.3 MPa. The median volume diameter (DV_{50}) and the volume percentage of small

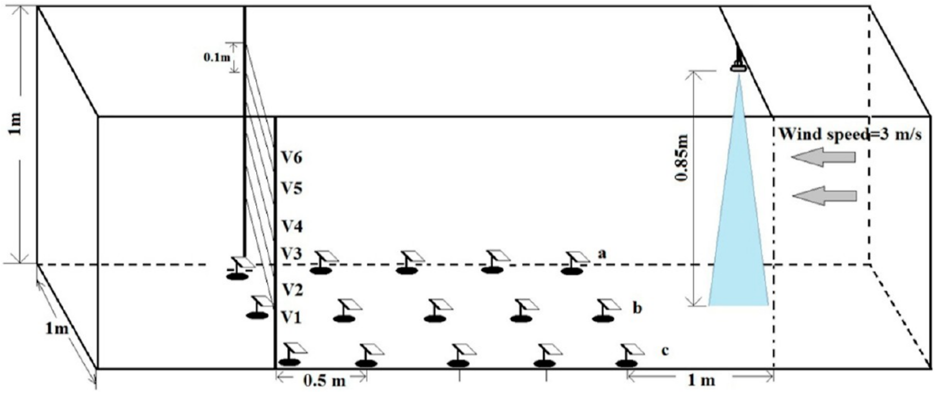

Figure 1. Schematic diagram showing the configuration of the wind tunnel test to measure droplet deposition.

Figure 2. Overview of the field experiment. (A) Location of the field experimental station (https://map.baidu.com/). (B) Overhead view of the cotton field used in this study (https://www.ovital.com/). (C) Image of the 3WQFTX-10 UAV used in the field test.

droplets (classified as those with a particle size <103 μm) were measured for each solution. The relative span (RS) was also calculated by eq 2 to evaluate droplet uniformity as described by Polli et al.[24]

$$RS = (DV_{90} - DV_{10})/DV_{50} \tag{2}$$

where small RS values correspond to better droplet atomization quality. There were three biological replicates per pesticide formula.

2.5. Droplet Deposition Measurements. Droplet movement processes were simulated in a wind tunnel to analyze the influence of each adjuvant on droplet deposition as previously described.[25] The wind tunnel was 5 m in length. A cross section of 1.0 × 1.0 m was used for this test (Figure 1). A TeeJet 110−015 nozzle was installed at 0.85 m above ground level to dispense the pesticide solution at a pressure of 0.3 MPa. The simulated wind speed (3 m s^{-1}) was selected from experimental field trials as the maximum observed wind velocity. Simulated wind continued for 2 s during this experiment.

Allura Red (Zhejiang Jigaode Pigment Technology Co., Ltd., Zhejiang, China), a water-soluble food dye with a recovery rate of ∼100%,[26] was used as a tracer to determine pesticide spray deposition. It was added at a rate of 6.25 g/L to each pesticide solution. Silica gel collapsible bulbs (2 mm in diameter) were used as droplet collectors to gather spray droplets from the air. Six vertical droplet collectors (designated V1−V6) were placed 3 m downwind of the spray nozzle, perpendicular to the direction of the airflow. V1 was placed 0.3 m above ground level and V2−V6 were placed above V1 at 0.1 m vertical intervals. Kromekote cards (30 × 80 mm) were used to collect droplets deposited on the ground. A total of 15 cards were placed on clips and arranged at 1.0, 1.5, 2.0, 2.5, and 3.0 m downwind of the nozzle. Three cards were distributed across the chamber in the horizontal direction at each distance, with 0.5 m between each card in each row (Figure 1).

When each spraying test was completed, the silicone tube collectors and Kromekote cards were collected and placed in separate zipped plastic bags. The cards were digitally scanned, and then the droplet density and coverage were analyzed with ImageJ software. To recover the Allura Red deposited on each silicone tube collector, 30 mL of ultrapure water was added to the bag, which was then shaken gently several times and ultrasonicated for 10 min. The eluent (5 mL per sample) was passed through a 0.22 μm filter to remove impurities. The Allura Red concentration of each sample was then measured on a Synergy HT microplate reader (BioTek Instruments, Inc., Winooski, VT, USA). The amount of Allura Red in the silicone tube collectors was calculated to assess droplet drift and deposition. There were four replicates of this experiment per treatment group.

2.6. Field Experiments. Field trials were carried out to establish the effects of each adjuvant on aphid control rates. The field trials occurred in May 2022 at the farm of the Institute of Cotton Research, Chinese Academy of Agricultural Sciences, Henan, China (36°05′10″N, 114° 30″60″ E) (Figure 2). The cotton variety "CCRI 79" was used at the seedling stage. The planting density of cotton was 55,000 plants/ha and the row spacing was 80 cm.

2.6.1. Pesticide Treatment. An electric-powered 3WQFTX-10 UAV (Anyang Quanfeng Aviation Plant Protection Technology Co., Ltd., Henan, China) was used for pesticide spraying (Figure 2C). It was operated at two heights above the canopy, 1.5 and 2.5 m, with a flight velocity of 4 m/s. At each height, 10 treatments were sprayed at a rate of 22.5 L/ha: CK1, 4/5CK1, 4/5CK1 + BDT, 4/5CK1 + WCH, 4/5CK1 + QR, CK2, 4/5CK2, 4/5CK2 + BDT, 4/5CK2 + WCH, and 4/5CK2 + QR (Table 1). To investigate differences between UAV-based and manual pesticide application, CK1 and CK2 were also manually sprayed using the MATABI Super Green16 electric air-pressure (EAP) knapsack sprayer (GOIZPERS Co., Ltd., Basque, Spain). The EAP sprayers released the pesticide at a rate of 450 L/ha and a pressure of 0.3 MPa. There were three replicate plots per treatment group, each consisting of a 60 × 16 m area of cotton field. There was a buffer zone of 10 m between plots. The weather during the experimental period was measured with a Kestrel 5500 Link micro-weather station (Kestrel Company, Portland, OR, USA) as previously described (Table S1and S2).[15]

2.6.2. Cotton Aphid CE Measurements. On 1, 3, and 7 d after pesticide application, the cotton aphid CE was measured.[16] A random five-point sampling method was used to survey the cotton aphid population size in each treatment plot, with six cotton plants surveyed at each time point. The number of cotton aphids per plant was recorded and the CE was calculated by eqs 3 and 4

$$D(\%) = ((N_a - N_b)/N) \times 100 \tag{3}$$

$$CE(\%) = (D_a - D_b)/(100 - D_b) \times 100 \tag{4}$$

where D is the insect dropping rate; N_a is the number of live insects before spraying; N_b is the number of live insects after spraying; D_a is the insect dropping rate in the treatment area; and D_b is the insect dropping rate in the control area.

2.7. Ladybird Beetle Egg Toxicity Assays. *Harmonia axyridis* (Pallas) (Coleoptera: Coccinellidae) individuals were provided by the Institute of Cotton Research, Chinese Academy of Agricultural Sciences. 2 day old ladybird eggs were immersed in aqueous solutions of QR or WCH for 30 s as described by Dong et al.[27] The tested concentrations of QR were 0.025, 0.05, 0.10, 0.20, and 0.40%, and the tested concentrations of WCH were 2, 3, 4.5, 6.75, and 10.13% (v/v). Double-distilled water served as the control group. Newly hatched larvae were removed every 6 h and used to calculate the hatching rate. There were three biological replicates per treatment group, with ∼20−30 eggs per biological replicate.

3. STATISTICAL ANALYSES

Statistical analyses were conducted in SPSS v16.0 (SPSS Inc., Chicago, IL, USA). For each parameter, the mean and standard error of the mean were calculated from at least three biological replicates. Differences between treatment groups were tested for statistical significance using Duncan's new multiple range test ($p < 0.05$). Data were visualized in Origin 2018 (Origin Lab, Northampton, MA, USA).

4. RESULTS AND DISCUSSION

4.1. Characterization of Base Pesticide Formulations.

To establish the general characteristics of the pesticide formulations, we first measured particle size through dynamic light scattering. The active ingredients of the conventional pesticides (acetamiprid EC and lambda-cyhalothrin EW) aggregated, forming large particles with an average size of 368.21 nm (Table 2). This was due to the poor water solubility of these compounds. However, the particles of the nanopesticide acetamiprid·lambda-cyhalothrin were smaller (average = 11.91 nm), likely because it had better water solubility and dispersibility in water. The recorded acetamiprid·lambda-cyhalothrin particle size (<100 nm) validated its status as a nanopesticide based on previously described classifications.[28]

Table 2. Particle Size of the Nanopesticide and Conventional Pesticide[a]

formulation	sample number	size/nm	average size/nm
5% acetamiprid EC + 2.5% lambda-cyhalothrin EW	1	357.44	368.21 ± 9.94 a
	2	359.12	
	3	388.06	
3.5% acetamiprid·lambda-cyhalothrin	1	11.85	11.91 ± 0.14 b
	2	11.71	
	3	12.18	

[a] Data in column 4 with different letters indicate significant differences ($p < 0.05$).

4.2. Adjuvant Effects on Pesticide Physicochemical Properties.

4.2.1. SST and DST. We next measured SST for each pesticide solution (Figure 3A,B). The SST values of CK1, 4/5CK1, 4/5CK1 + BDT, 4/5CK1 + WCH, and 4/5CK1 + QR were 33.28, 33.34, 31.39, 30.73, and 30.51 mN/m, respectively. These results demonstrated that the inclusion of a tank-mix adjuvant slightly reduced SST. The similar SST values of CK1 and 4/5CK1 showed that reducing the CK1 concentration did not significantly affect the SST. The SST values of CK2, 4/5CK2, 4/5CK2 + BDT, 4/5CK2 + WCH, and 4/5CK2 + QR were 37.25, 37.54, 33.87, 31.25, and 33.95 mN/m, respectively. Consistent with CK1, this indicated that the amount of CK2 in the formulation had little effect on SST but that the addition of an adjuvant significantly reduced it. This agrees with the ST results measured by Zhao et al.[29] who found that the difference in the dosage of the formulation product had no differentiated effect on the SST and DST.

We next analyzed DST for each sample from 15−5000 ms. The DST of the water control was approximately 72 mN/m over 5000 ms. At 15 ms, the DST values of CK1 and 4/5CK1 were 54.60 and 56.18 mN/m, respectively; the latter decreased to 34.90 mN/m within 5000 ms. The DSTs of 4/5CK1+BDT, 4/5CK1+WCH, and 4/5CK1 + QR decreased from 55.18, 56.41, and 56.28 to 32.83, 33.15, and 31.83 mN/m, respectively. The DST of 4/5CK2 decreased to 39.63 mN/m within 5000 ms; this was further reduced in the 4/5CK2 + BDT, 4/5CK2 + WCH, and 4/5CK2 + QR samples (38.13, 34.35, and 37.88 mN/m, respectively). WCH was thus more effective than BDT or QR in reducing the CK2 DST (Figure 3D).

4.2.2. Contact Angle. Liquid properties and leaf surface characteristics can affect the CA of a pesticide with respect to the leaf surface, which reflects the wetting ability.[30,31] To assess the potential impacts of adjuvants on the CAs of these pesticides, we therefore measured morphological changes in droplet appearance over time (Figure 4). Overall, we found that the CAs decreased rapidly. Notably, the CAs of CK1 and 4/5CK1 were lower on the adaxial than the abaxial leaf surfaces under identical treatment conditions. Similar trends were observed for CK2. These findings indicated that the adaxial cotton leaf surfaces were more readily wetted than the abaxial surfaces.

When UAVs are used to apply pesticides, tank-mix adjuvants are commonly added to reduce the CA and improve droplet wettability.[32,33] We therefore compared the CAs of each pesticide with and without the presence of adjuvant. The CAs of 4/5CK1 and 4/5CK2 decreased due to the ability of the tank-mix adjuvant in reducing SST (Figure 3A,B) and DST (Figure 3C,D). The CAs of 4/5CK1 + BDT were 27.10° on the adaxial leaf surface and 35.35° on the abaxial surface, lower than those of 4/5CK1 (33.7 and 38.02°, respectively) (Figure 4A,B). Both BDT and QR significantly reduced the CAs of CK1 and CK2 on the adaxial and abaxial leaf surfaces (Figure 4A−D). Furthermore, the CAs of 4/5CK1 + QR and 4/5CK2 + QR were <30.0° on the abaxial leaf surface within the observed time period (Figure 4B,D,F,H). These relatively low CA values demonstrated that pesticide solutions containing QR could achieve rapid wetting and spreading on cotton leaves.

4.2.3. Wetting and Penetration Times. The wetting and penetration times were next measured for each treatment (Figure 5A,B). The wetting time of CK1 were significantly longer than those of 4/5CK1 (71.35 and 66.92 s, respectively) (Figure 5A). The 4/5CK1 wetting time was reduced to 12.40, 6.49, and 29.86 s with the addition of BDT, WCH, and QR, respectively. The corresponding penetration times were reduced from 76.78 s for CK1 and 71.35 s for 4/5CK1 to 17.04, 12.39, and 34.54 s when BDT, WCH, and QR were added, respectively. The results were highly similar for CK2 (Figure 5B). This demonstrated that both the pesticide concentration and the presence of tank-mix adjuvants strongly affected the wetting and penetration times. This is consistent with previous statements that the addition of adjuvants could decrease the wetting and penetration time of two commercial herbicides.[22]

4.2.4. WA and Droplet Residual Patterns. WA is another commonly used metric to describe the droplet wetting and spread capabilities of a solution on a leaf.[34,35] We here found that the WAs of 4/5CK1, 4/5CK1 + BDT, 4/5CK1 + WCH, and 4/5CK1 + QR were 16.15, 17.26, 17.17, and 19.57 mm^2, respectively, on the adaxial leaf surface; the WAs of the same treatments were 14.35, 15.83, 17.59, and 15.57 mm^2,

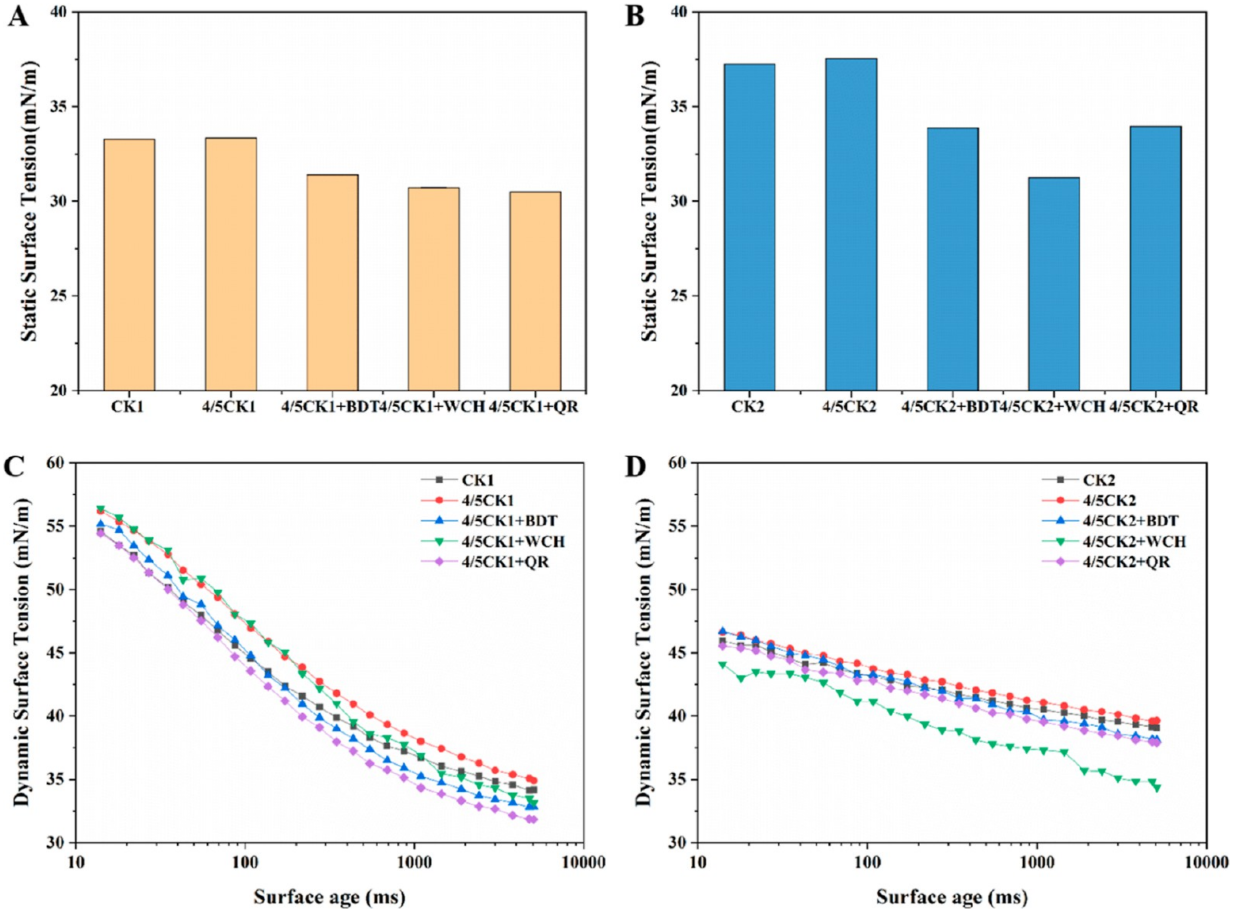

Figure 3. SST and DST of pesticide formulations. (A,B) SST values of the (A) CK1 and (B) CK2 treatments. CK1, 5% acetamiprid EC + 2.5% lambda-cyhalothrin EW; CK2, 3.5% acetamiprid·lambda-cyhalothrin. (C,D) DST values of the (C) CK1 and (D) CK2 treatments.

respectively, on the abaxial leaf surface (Figure 5C). These results showed that QR significantly increased the WA on the adaxial leaf surface, whereas WCH increased the WA on the abaxial surface. These results were consistent with our findings from the ST and wetting time assessments (Figures 3A,C and 5A).

The WAs of CK2 and 4/5CK2 were 14.93 and 14.14 mm^2, respectively, on the adaxial leaf surface. For CK2, the pesticide concentration therefore affected the WA. All three of the tank-mix adjuvants significantly increased the 4/5CK2 WA on the adaxial leaf surfaces (WA > 15 mm^2). Overall, the results thus showed that BDT, WCH, and QR significantly improved droplet WA on the adaxial leaf surface but had little effect on the abaxial leaf surfaces. The larger WAs of most treatment droplets on the adaxial compared to the abaxial leaf surfaces may have been due to the increased stomatal density on the abaxial side.[36] The stomatal uptake pathway is one of the most important pesticide entry routes into the leaves.[2] Thus, the larger number of stomata per unit area on the abaxial side corresponds to better pesticide absorption. Indeed, SEM images here showed that the stomata on the abaxial surface were open, allowing pesticide uptake (Figure 6B), whereas the stomata on the adaxial surface were closed (Figure 6A). This explains the reduced spreading and WA of the droplets on the abaxial side.

The "coffee-ring effect" (CRE) is a common phenomenon in which the evaporation of droplets containing suspended particulate matter from a solid surface leaves a circular deposition.[37,38] In the context of pesticide application, the CRE typically occurs when a drop of pesticide liquid dries on a leaf surface.[39] The heterogeneous distribution of particles caused by the CRE may decrease the coverage area of active ingredients, reducing the effective rate of pesticide utilization.[40] We therefore recorded the deposition state of the pesticides on cotton leaf surfaces after droplets had completely evaporated to determine whether the CRE occurred and could be ameliorated by the presence of an adjuvant (Figure 6C,D). Indeed, CK1 and 4/5CK1 droplets formed typical coffee-ring patterns on the leaf surface after evaporation (Figure 6C). The droplets containing BDT and WCH formed disk-shaped patterns, but wider rings or islands were observed after evaporation of droplets containing QR. Thus, droplets containing BDT or WCH did not produce the CRE, increasing the uniformity of residual distribution and potentially of pesticide efficacy. In contrast, 4/5CK2 droplets formed a uniformly disk-like profile on the leaf surface after complete evaporation (Figure 6D). The addition of adjuvants to the 4/5CK2 solution did not change the residue patterns. However, adjuvants did reduce the 4/5CK2 ST (Figure 3B,D), which inhibited droplet evaporation (Table 3) and increased the WA on the adaxial leaf surface (Figure 5D).

4.3. Droplet ER. We next measured the droplet ER of each treatment formulation to evaluate the antievaporation effect of adjuvants. The ERs of CK1-based droplets ranged from 0.13 to 0.17 μL/min. Compared to 4/5CK1 droplets, the average ERs of droplets containing BDT, WCH, or QR were slightly

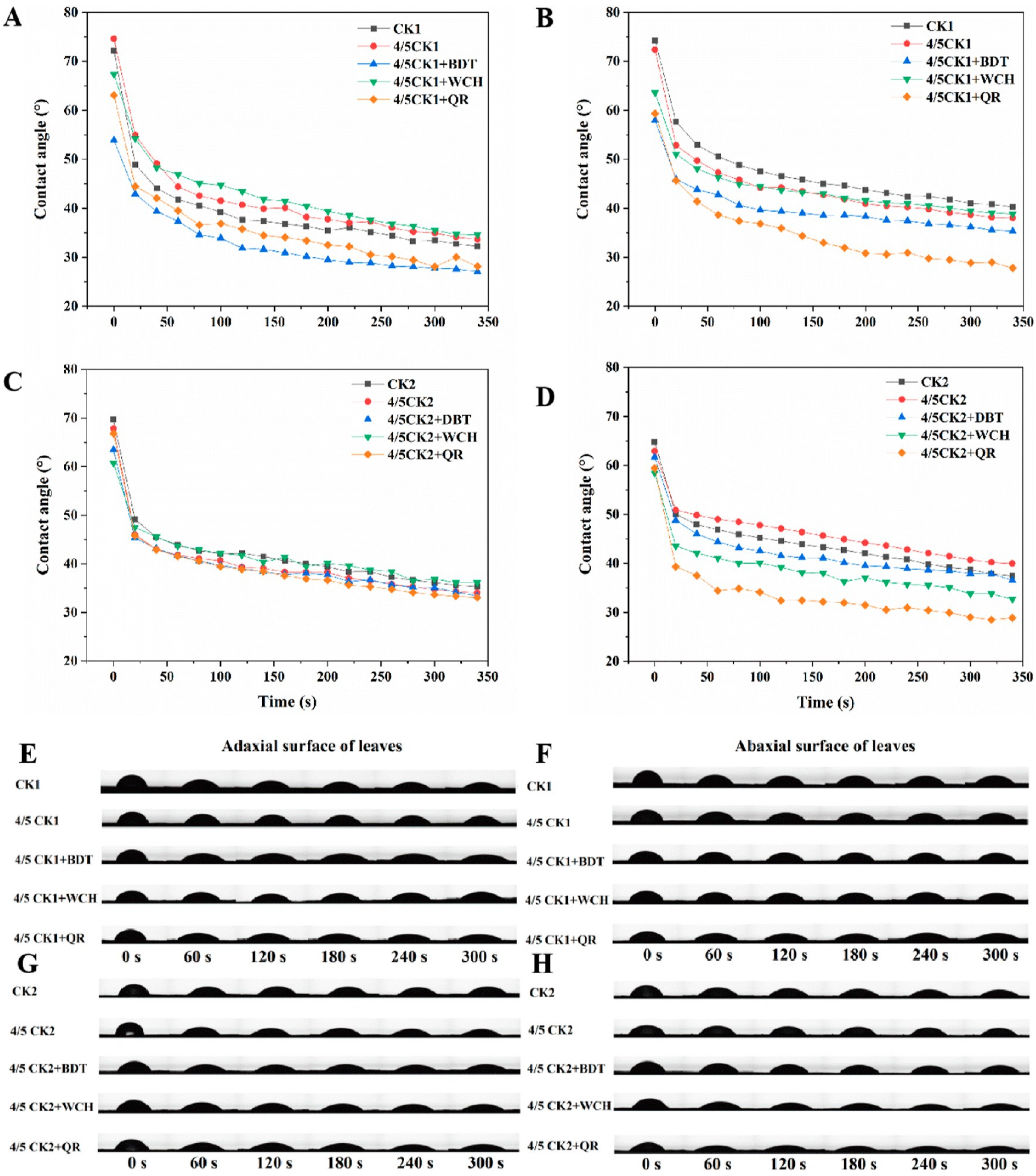

Figure 4. Changes in pesticide dynamic CA and droplet morphology on cotton leaves over time. (A,B) Dynamic CAs of CK1-based formulations on the (A) adaxial and (B) abaxial leaf surfaces. CK1, 5% acetamiprid EC + 2.5% lambda-cyhalothrin EW. (C,D) Dynamic CAs of CK2-based formulations on the (C) adaxial and (D) abaxial leaf surfaces. CK2, 3.5% acetamiprid·lambda-cyhalothrin. (E,F) Changes in CK1-based formulation droplet morphology on the (E) adaxial and (F) abaxial leaf surfaces. (G,H) Changes in CK2-based formulation droplet morphology on the (G) adaxial and (H) abaxial leaf surfaces.

decreased, but the differences were not significant. The ERs of CK2-based droplets similarly ranged from 0.12 to 0.18 μL/min, with no significant differences in ER between treatments with and without adjuvant. The inhibition rates of BDT, WCH, and QR ranged from 4.22 to 19.08 and 6.65 to 23.70% in CK1- and CK2-based formulations, respectively. Among the three adjuvants, QR was most effective in inhibiting evaporation.

4.4. Droplet Size Distribution.

Droplet size is one of the most important factors affecting spray retention, droplet

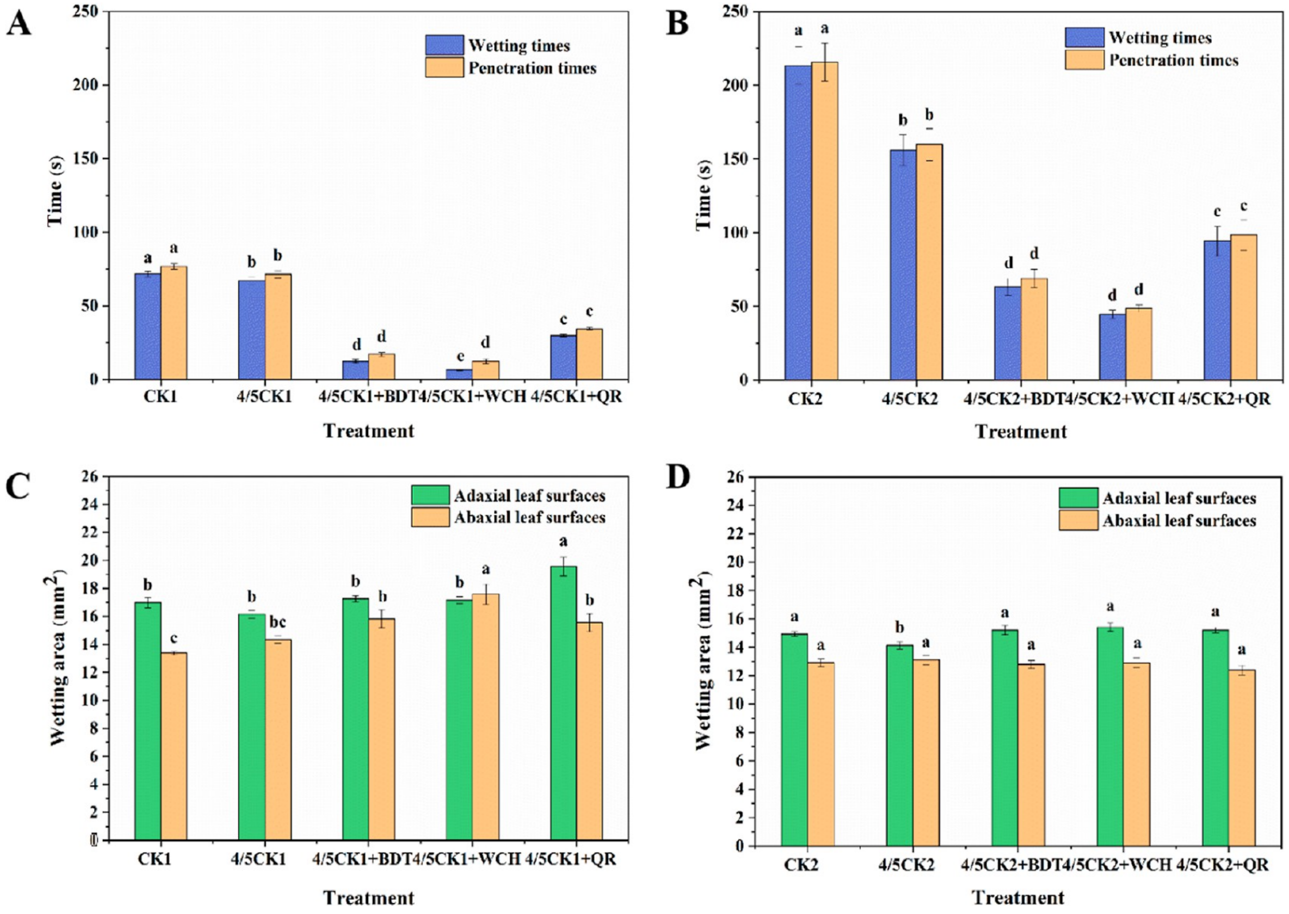

Figure 5. Wetting time, penetration time, and WA of each pesticide formulation on cotton leaves. (A,B) Wetting and penetration times of the (A) CK1 and (B) CK2 formulations. CK1, 5% acetamiprid EC + 2.5% lambda-cyhalothrin EW; CK2, 3.5% acetamiprid·lambda-cyhalothrin. (C,D) WA of the (C) CK1 and (D) CK2 formulations. Different letters indicate significant differences between each treatment ($p < 0.05$).

deposition, and drift.[41,42] In the context of aerial spraying, optimization of droplet size distribution contributes to reductions in droplet drift and promotion of droplet deposition to target plants. We therefore assessed the droplet size distribution of each pesticide formulation (Table 4). For both CK1 and CK2, changes in the dosage (to 4/5CK1 and 4/5CK2, respectively) had little effect on the droplet size distribution (Figures S1 and S2). In contrast, the DV_{50} was significantly higher and the percentage of smaller droplets was significantly lower for 4/5 CK1 + WCH than for 4/5CK1. The addition of QR also significantly decreased the percentage of smaller droplets. For CK2 formulations, 4/5CK2 + WCH had the highest DV_{50} and the lowest percentage of smaller droplets, whereas 4/5CK2+BDT had the lowest RS value. In conclusion, adding a tank-mix adjuvant increased the droplet size, reduced the number of small droplets, and decreased RS values to varying degrees; WCH caused the largest changes in each of these parameters. This finding is in accordance with the finding of Polli et al.[24]

4.5. Influence of Adjuvants on Droplet Deposition.

We next analyzed droplet deposition in a wind tunnel to simulate spraying in the field under windy conditions. The addition of BDT to CK1 had little effect on droplet deposition; however, the addition of WCH or QR decreased the amount of droplet drift at high positions (0.7 and 0.8 m above ground level) but increased the amount of droplets deposited at middle and low positions (0.3–0.6 m above ground level) (Figure 7A). For CK2, the addition of QR or WCH increased or decreased the total droplet deposition, respectively (Figure 7B). These results indicated that WCH had the strongest effect on antidrift performance, followed by BDT.

We also assessed the horizontal distribution of droplets at varying distances from the nozzle (Figure 7). The addition of BDT, WCH, or QR clearly increased droplet coverage and the deposition density of CK1, with WCH and QR having superior effects compared to BDT (Figure 7C,D). This may be because WCH and QR increased droplet size, decreasing the proportion of small droplets (Table 4). In CK2, addition of any of the three adjuvants increased the droplet coverage and deposition density compared to CK2 alone, further demonstrating that the adjuvants promoted droplet deposition (Figure 7E,F).

4.6. Adjuvant Effects on Aphid CE.

We next conducted a field experiment to assess the effects of adjuvants and spraying methods (UAV vs EAP) on cotton aphid CE. At an operating height of 1.5 m, the CEs of CK1, 4/5CK1, 4/5CK1+BDT, 4/5CK1+WCH, and 4/5CK1+QR 1 day after treatment (DAT) were 34.50, 36.27, 62.13, 54.19, and 60.01%, respectively. These findings demonstrated that the addition of BDT, WCH, or QR significantly increased the CE of 4/5CK1 1 DAT. Increases in time since pesticide application were correlated with increases in CE for each treatment and decreases in treatment-specific CE differences. 7 DAT, the CEs of 4/5CK2 + BDT, 4/5CK1 + WCH, and 4/5CK1 + QR reached 73.11,

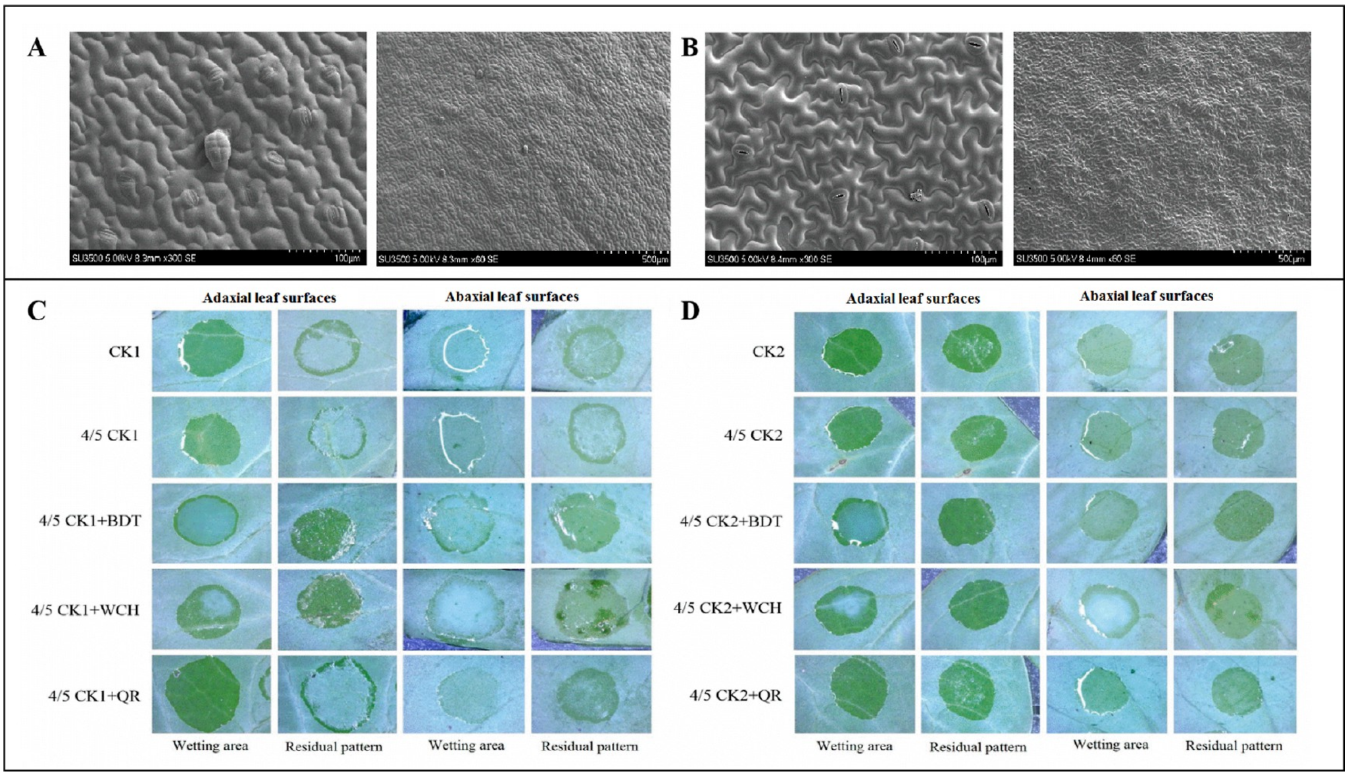

Figure 6. Cotton leaf surface morphology and wetting patterns. (A,B) SEM images of (A) adaxial and (B) abaxial leaf surfaces. (C,D) WAs and residual patterns of the (C) CK1 and (D) CK2 treatments. CK1, 5% acetamiprid EC + 2.5% lambda-cyhalothrin EW; CK2, 3.5% acetamiprid·lambda-cyhalothrin.

Table 3. Effects of Adjuvants on Droplet Evaporation Rate (ER) at 25 °C[a]

test	evaporation equation	coefficient of determination	ER/(μL/min)	evaporation inhibition rate/%
CK1	$y = -0.003x + 5.027$	0.95	0.16 ± 0.03 a	-
4/5CK1	$y = -0.004x + 5.008$	0.92	0.17 ± 0.01 a	-
4/5CK1 + BDT	$y = -0.003x + 5.017$	0.95	0.16 ± 0.01 a	4.22
4/5CK1 + WCH	$y = -0.003x + 5.021$	0.93	0.15 ± 0.00 a	10.04
4/5CK1 + QR	$y = -0.003x + 4.969$	0.96	0.13 ± 0.02 a	19.08
CK2	$y = -0.003x + 4.983$	0.91	0.18 ± 0.05 a	-
4/5CK2	$y = -0.003x + 4.925$	0.92	0.16 ± 0.01 a	-
4/5CK2 + BDT	$y = -0.002x + 4.952$	0.93	0.13 ± 0.01 a	18.30
4/5CK2+ WCH	$y = -0.003x + 5.033$	0.96	0.15 ± 0.01 a	6.65
4/5CK2 + QR	$y = -0.003x + 4.919$	0.98	0.12 ± 0.01 a	23.70

[a] Values presented as mean ± SE y in the evaporation equation indicate the droplet volume, x denotes the time recorded when the volume changes, and the slope of the equation represents the volume change rate of the droplets; data in column 4 with the same small letter are not significantly different ($p > 0.05$). The short solid line in the last column represents that the value was not calculated.

Table 4. Droplet Size Distributions for the Spray Dilutions[a]

formulation	DV_{50} (μm)	%V < 103 μm	RS
CK1	152.81 ± 0.50 abc	17.17 ± 0.24 ab	0.91 ± 0.01 a
4/5CK1	150.38 ± 1.38 c	17.91 ± 0.41 a	0.90 ± 0.00 ab
4/5CK1 + BDT	152.50 ± 0.85 bc	17.02 ± 0.46 ab	0.89 ± 0.02 ab
4/5CK1 + WCH	156.88 ± 0.74 a	15.83 ± 0.09 b	0.88 ± 0.01 ab
4/5CK1 + QR	154.49 ± 1.85 ab	15.87 ± 0.88 b	0.87 ± 0.01 b
CK2	133.35 ± 0.79 b	29.30 ± 0.52 a	1.09 ± 0.01 a
4/5CK2	137.00 ± 0.93 ab	28.17 ± 0.47ab	1.12 ± 0.02 a
4/5CK2 + BDT	140.37 ± 5.70 ab	24.18 ± 3.02bc	0.95 ± 0.01 b
4/5CK2+ WCH	143.75 ± 0.41 a	22.43 ± 0.31c	0.96 ± 0.00 b
4/5CK2 + QR	141.43 ± 0.89 ab	25.94 ± 0.74abc	1.09 ± 0.02 a

[a] Values presented as mean ± SE. Different small letters in the same column are significantly different ($p < 0.05$).

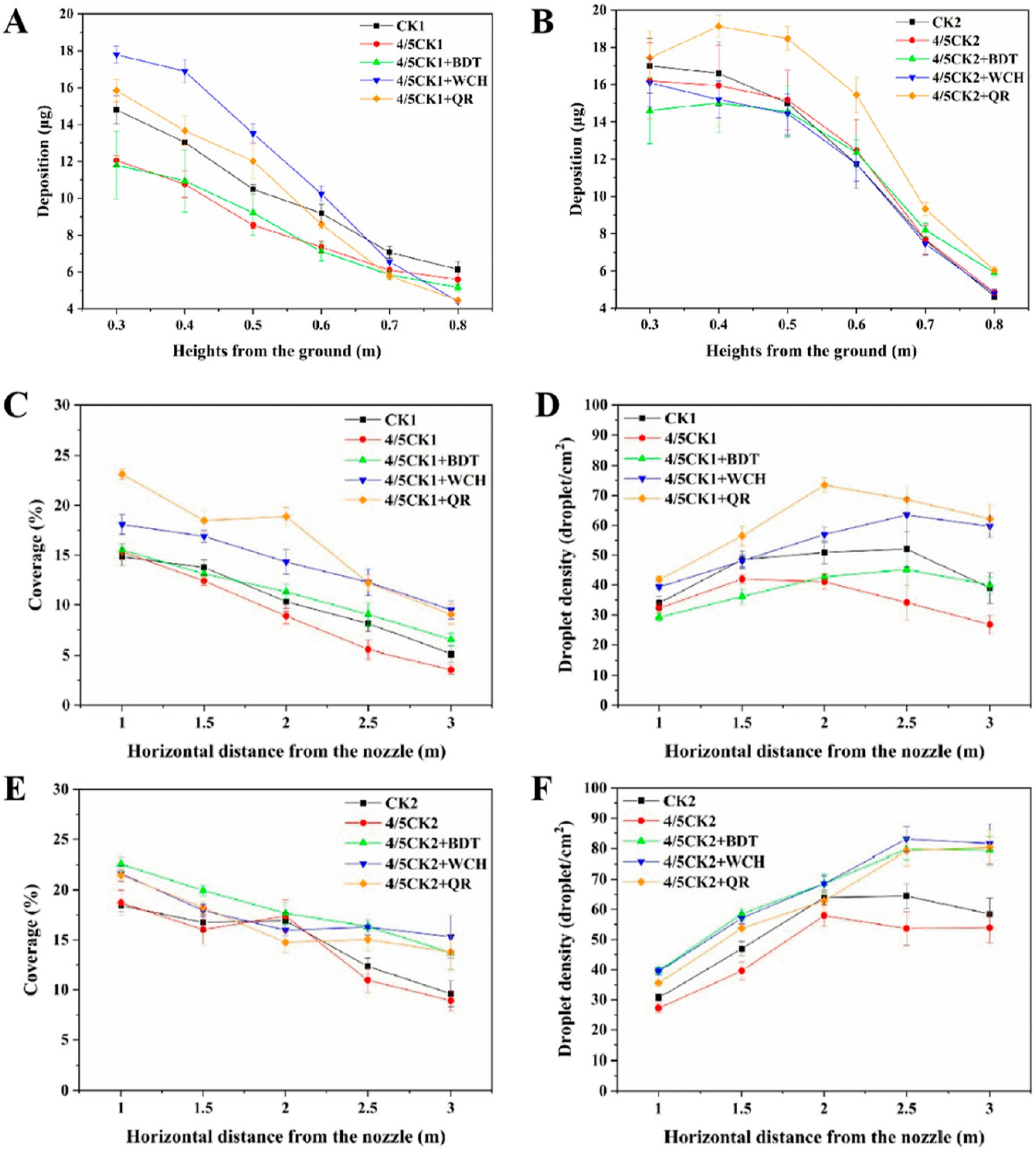

Figure 7. Droplet deposition at multiple heights and distances from the spray origin. (A,B) Droplet deposition between 0.3 and 0.8 m above ground level for (A) CK1-based and (B) CK2-based formulations. CK1, 5% acetamiprid EC + 2.5% lambda-cyhalothrin EW; CK2, 3.5% acetamiprid·lambda-cyhalothrin. (C,E) Droplet coverage at varying horizontal distances from the nozzle for (C) CK1-based and (E) CK2-based formulations. (D,F) Droplet density at varying horizontal distances from the nozzle for (D) CK1-based and (F) CK2-based formulations.

76.52, and 72.93%, respectively, comparable to the rates from the EAP treatment (88.09%) (Figure 8A). For CK2, the CEs of the 4/5CK2 + QR and the EAP sprayer treatments 1 DAT were 74.96 and 90.41%, respectively, significantly higher than the CE of 4/5CK2 (54.60%). 7 DAT, the CEs of 4/5CK2 + WCH (88.31%), 4/5CK2 + QR (85.25%), and the EAP sprayer (87.78%) were significantly higher than that of 4/5CK2 (66.63%) (Figure 8B). Thus, for both CK1 and CK2, the addition of WCH yielded the best CE against cotton aphid.

At an operating height of 2.5 m (Figure 8C), the CE of the EAP treatment 1 DAT was 86.98%, whereas the CE of CK1 was 36.26%. Thus, the CE of the pesticide formulation applied with a UAV sprayer was only 41.69% of the CE of the same formulation applied with an EAP sprayer. The CEs were 43.02% for 4/5CK1, 43.88% for 4/5CK1 + BDT, 59.19% for 4/5CK1 + WCH, and 63.86% for 4/5CK1 + QR. 7 DAT, the CEs of 4/5CK1 + BDT, 4/5CK1 + WCH, and 4/5CK1 + QR increased by 2.89, 3.13, and 13.53%, respectively. Moreover, the CE of 4/5CK1 + QR was comparable to that of the EAP treatment, indicating that QR significantly improved the pesticide CE of CK1. For CK2 (Figure 8D), the CEs of CK2 and 4/5CK2 1 DAT were 67.19 and 64.44%, respectively, both of which were lower than the CE achieved with the EAP sprayer (90.41%). The CEs of 4/5CK2 + WCH and 4/5CK2 + QR were 71.59 and 73.77%, respectively, comparable to that of the EAP sprayer. Thus, the addition of WCH or QR slightly

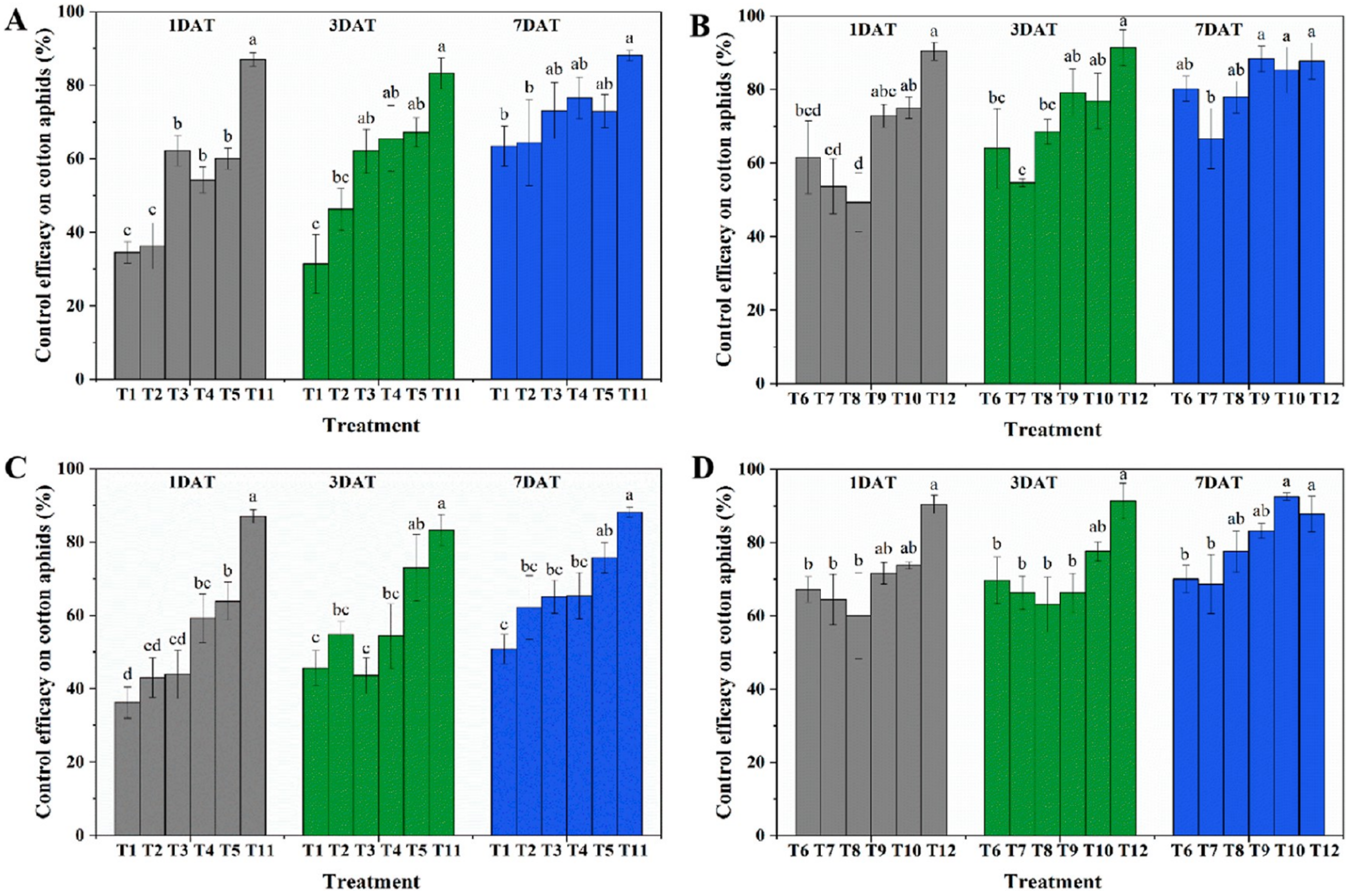

Figure 8. CE of several pesticide formulations against cotton aphids. (A,B) CEs of (A) CK1 and (B) CK2 treatments sprayed at a height of 1.5 m. CK1, 5% acetamiprid EC + 2.5% lambda-cyhalothrin EW; CK2, 3.5% acetamiprid·lambda-cyhalothrin. (C,D) CEs of (C) CK1 and (D) CK2 treatments sprayed at a height of 2.5 m. T1, CK1 sprayed with a UAV (UAV); T2, 4/5CK1 sprayed with a UAV; T3, 4/5CK1 + BDT sprayed with a UAV; T4, 4/5CK1 + WCH sprayed with a UAV; T5, 4/5CK1 + QR sprayed with a UAV; T6, CK2 sprayed with a UAV; T7, 4/5CK2 sprayed with a UAV; T8, 4/5CK2+BDT sprayed with a UAV; T9, 4/5CK2+WCH sprayed with a UAV; T10, 4/5CK2+QR sprayed with a UAV; T11, CK1 sprayed manually; T12, CK2 sprayed manually. Different small letters indicate significant differences between treatment on each DAT ($p < 0.05$).

improved the control effect of 4/5CK2, although the differences were not statistically significant. Overall, among the UAV-applied treatments, 4/5CK2 + QR had the best CE against cotton aphid. 7 DAT, the CEs of CK2 and 4/5CK2 were 70.04 and 68.60%, respectively, which were significantly lower than that of the EAP sprayer (87.79%). The CE of 4/5CK2 + QR (92.59%) was significantly higher than that of CK2 sprayed with the UAV, comparable to that of CK2 applied with the EAP sprayer. Thus, despite the 20% decrease in pesticide dosage of 4/5CK2 + QR compared to CK2, this formulation yielded the highest CE.

Overall, these results indicated that equivalent pesticide dosages were less effective when administered via the UAV than the EAP sprayer. This is consistent with prior observations (e.g., Wang et al.[43]). The decreased coverage area and number of droplets deposited on the leaves may account for the poor application effects of the UAV sprayer. In the process of spraying pesticides by UAVs, droplets are deposited below the aircraft under the influence of downwash air caused by the rotor. However, smaller droplets are susceptible to environmental crosswind. The existence of crosswind interferes with the downward movement of the smaller droplets, causing a "drift" to occur. Therefore, increasing droplet size and reducing the proportion of small droplets are key measures to reduce spray drift. Both indoor wind tunnel simulations and field experiments have demonstrated that adding a tank-mix adjuvant to a pesticide solution is an effective method of improving droplet deposition and reducing pesticide drift.[7,31,44] The goal of the present study was to test the effects of three adjuvants on two pesticide solution types, and we found that all three adjuvants increased pesticide efficiency against cotton aphids to varying degrees.

4.7. Comprehensive Adjuvant Analysis. ST, CA, wetting time, and penetration time are all important factors that together determine the permeability of a pesticide into a plant leaf.[2,45] A reduced ER also contributes to pesticide diffusion and wetting of the leaf surface.[46] Furthermore, increased droplet size and a reduced proportion of small droplets promote droplet deposition in a target region, thus improving pesticide efficiency against target pests.[17,47] To facilitate a clear understanding of the effects of each adjuvant on CK1 and CK2, we conducted a multiangle evaluation based on 15 metrics to integrate all of these parameters (Table 5).

The comprehensive analysis revealed that WCH promoted excellent pesticide wetting and permeability; it reduced ST, optimized the spray performance, promoted droplet deposition, and improved pesticide CE against aphids. QR exhibited a superior ability to reduce CA, inhibit evaporation, and promote droplet deposition, also improving the CE against aphids. Previous studies have shown that the plant oil adjuvant

Table 5. Evaluation of Three Tank-Mix Adjuvants on Two Formulations from Multiperspective[a]

metrics	CK1 (5% acetamiprid + 2.5% lambda-cyhalothrin)	CK2 (3.5% acetamiprid· lambda-cyhalothrin)
SST	QR < WCH < BDT	WCH < QR < BDT
DST	QR < BDT < WCH	WCH < QR < BDT
CA on the adaxial leaf surface	BDT < QR < WCH	QR < BDT < WCH
CA on the abaxial leaf surface	QR < BDT < WCH	QR < WCH < BDT
wetting time based on the canvas sheet	WCH < BDT < QR	WCH < BDT < QR
penetration time based on the canvas sheet	WCH < BDT < QR	WCH < BDT < QR
WA on the adaxial leaf surface	QR > BDT > WCH	WCH > QR > BDT
WA on the abaxial leaf surface	WCH > BDT > QR	WCH > BDT > QR
evaporation inhibition rate	QR > WCH > BDT	QR > BDT > WCH
droplet size	WCH > QR > BDT	WCH > QR > BDT
percentage of smaller droplets	WCH < QR < BDT	WCH < BDT < QR
drift deposition amount in wind tunnel	BDT < QR < WCH	WCH < BDT < QR
droplet coverage and density in wind tunnel	QR > WCH > BDT	BDT > WCH > QR
control effect against aphids in field at 1.5 m	WCH > BDT > QR	WCH > QR > BDT
control effect against aphids in field at 2.5 m	QR > WCH > BDT	QR > WCH > BDT

[a] < indicates that the value of the former metric is smaller than that of the latter, while > denotes that the value of the former metric is larger than that of the latter.

Table 6. Hatching Rate of Ladybird Eggs[a]

treatment	concentration (%)	hatching rate (%)
QR	0.025	67.37 ± 3.93 a
	0.05	77.60 ± 4.50 a
	0.10	68.89 ± 5.88 a
	0.20	64.50 ± 3.52 a
	0.40	63.25 ± 4.57 a
WCH	2	72.93 ± 7.42 a
	3	74.72 ± 2.65 a
	4.5	78.37 ± 3.83 a
	6.75	71.67 ± 10.93 a
	10.13	68.70 ± 1.42 a
water		76.87 ± 4.62 a

[a] Columns with the same letter are not significantly different ($p > 0.05$).

BDT reduces the CA, improves wetting properties, and increases droplet deposition on crop plants.[48] However, the effects of tank-mix adjuvants on pesticides are related not only to the adjuvant type but also to the concentration.[29,32,33] At the recommended concentration of 1.5%, BDT here exhibited more moderate effects on most parameters compared to WCH and QR. Future studies should assess the potential for increased BDT concentrations to exert more favorable effects on pesticide characteristics.

4.8. QR and WCH Toxicity to Ladybird Beetle Eggs. Finally, we sought to establish the safety of the tank-mix adjuvants in nontarget organisms. Based on the above comprehensive analysis, it can be concluded that adjuvant QR and WCH perform better. Therefore, we conducted an acute toxicity assessment to evaluate the environmental safety of these two adjuvants. The secondary consumer ladybird beetle (*H. axyridis*), a common insect predator, was selected as a model organism. At concentrations relevant to field applications, neither QR nor WCH exhibited obvious toxicity in ladybird beetle eggs. The lowest hatching rates (63.25 and 68.70%) were observed at the highest concentrations of QR and WCH, respectively (Table 6). However, these values were not statistically different compared to the control treatment. Working concentrations of QR and WCH were thus shown to be nontoxic to ladybird beetle eggs. Adjuvants play an important role in improving the physical and chemical properties and enhancing the efficacy of pesticides. With the increasing application in agriculture, the ecological toxicity and environmental safety risks of spray adjuvants are also exposed. Shannon et al.[49] reviewed the risks of spray adjuvants to bees and put forward some suggestions to reduce the risks of adjuvants to bees and other beneficial insects. In a recent study, researchers have shown that mineral oil adjuvant increased the ecotoxicity of herbicide metsulfuron-methyl to three nontarget soil invertebrate species, *Eisenia andrei*, *Enchytraeus crypticus*, and *Proisotoma minuta* on laboratory tests.[50] Our research indicated that the two adjuvants have no obvious adverse effects on the hatching rate of ladybird eggs within the tested concentration range. However, this study only tested the toxicity of adjuvants alone on the eggs. The ecological toxicity of adjuvants mixed with pesticides on eggs and other insect ages needs to be further studied in the future.

5. CONCLUSIONS

In conclusion, adjuvants can influence the physicochemical properties and spraying characteristics of pesticide diluents. The mineral adjuvant WCH had the best performance in improving the wetting and penetration ability. Moreover, WCH also significantly increased the droplet particle size and reduced the proportion of small droplets, which in turn decreased droplet drift and increased droplet coverage and density. Consistent with these characteristics, WCH showed the highest CE against cotton aphids when applied with a UAV at 1.5 m above the cotton canopy. The plant oil adjuvant BDT reduced the ST and CA and showed moderate wetting and penetration ability compared to WCH and QR. The addition of QR further reduced the ST and CA, increased the wetting ability, inhibited droplet evaporation, and improved spraying performance. Thus, a pesticide solution mixed with QR achieved the highest CE against cotton aphids when applied by a UAV at 2.5 m above the cotton canopy. Importantly, at relevant concentrations, neither WCH nor QR inhibited hatching of a nontarget natural enemy. Comprehensive analyses demonstrated that both WCH and QR improved pesticide characteristics, enhanced pesticide utilization efficiency, and improved pesticide CE. Increased utilization efficiency and reduced pesticide use (as demonstrated here) ultimately decrease pesticide runoff. In summary, the present study delineates a systematic method for assessing the effects of tank-mix adjuvants on the spraying characteristics and CEs of pesticides sprayed on cotton plants by UAVs. Furthermore, it clarifies the efficacy and safety of two common tank-mix adjuvants, validating their use in further studies and promoting practices that minimize environmental pollution.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c04301.

> Weather during the UAV spraying test at 1.5 m operation height, weather during the UAV spraying test at 2.5 m operation height, particle size distribution of spray dilutions in CK1 treatment groups, and particle size distribution of spray dilutions in CK2 treatment groups (PDF)

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Funding

This work was supported by the China Agriculture Research System, Agricultural Science and Technology Innovation Program of Chinese Academy of Agricultural Sciences and Independent project of the National Engineering Research Center of Cotton Biology Breeding and Industrial Technology (no. NERC010101).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors deeply express their thanks to Zhendi Hu, Xijun Deng, and Yue Liu for their valuable technical assistance.

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