Achieving High Efficacy and Low Safety Risk by Balancing Pesticide Deposition on Leaves and Fruits of Chinese Wolfberry (*Lycium barbarum* L.)

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ABSTRACT: Pesticide residue has become the main technical barrier that restricts the export of Chinese wolfberry. Can we achieve high efficacy and low safety risk by balancing pesticide deposition on the leaves and fruits of Chinese wolfberry? In this research, the structural characteristics and wettability of leaves and fruits of Chinese wolfberry at different growth stages were studied. The adaxial and abaxial surfaces of leaves were hydrophobic, whereas the fruit surfaces were hydrophilic. Adding spray adjuvant could increase the retention of droplets on the leaf surfaces of Chinese wolfberry by 52.28−97.89% and reduce the retention on the fruit surfaces by 21.68−42.14%. A structural equation model

analysis showed that the adhesion tension was the key factor affecting the retention of the solutions among various interface behaviors. When the concentrations of Silwet618, AEO-5, Gemini 31551, and 1227 were 2−5 times higher than their CMCs, the retention of pesticide solutions (pyraclostrobin and tylophorine) on Chinese wolfberry leaves significantly increased, and the control efficacies on aphids and powdery mildew also dramatically improved (65.90−105.15 and 41.18−133.06%, respectively). Meanwhile, the retention of pesticides on the fruit of Chinese wolfberry was reduced. This study provides new insights into increasing the utilization of pesticides in controlling pests and improving food safety.
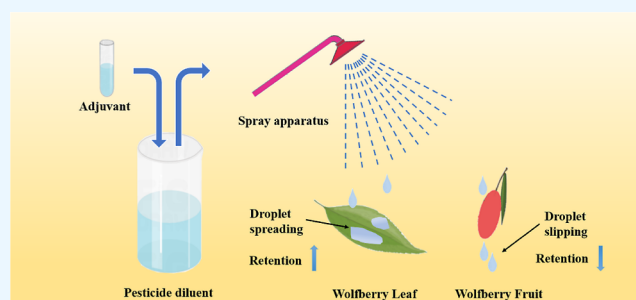
1. INTRODUCTION

Chinese wolfberry (*Lycium barbarum* L.) is a crop with economic, ecological, and social benefits in arid areas. It has been widely planted in Ningxia, Qinghai, and other regions of China.[1,2] Chinese wolfberry fruit has many health functions, such as promoting immune regulation, enhancing eyesight, clearing the liver, and exerting antitumor effects, and has become increasingly popular worldwide.[3−9] Chinese wolfberry fruit is currently exported to 105 countries and regions, of which Asia is the largest, followed by the European Union and the United States.[10]

In the growth process of Chinese wolfberry, diseases and insect pests are more common, which often affect the integrity and function of Chinese wolfberry leaves and lead to a significant decline in the yield and quality of Chinese wolfberry fruit but usually do not directly destroy the Chinese wolfberry fruit.[11,12] Growers often spray pesticides via conventional volume spraying to control diseases and insect pests, but due to the poor wetting ability of some pesticides, the control efficacy is not ideal, and the utilization rate of pesticides is lower, resulting in pesticide waste.[13] At the same time, the improper use of pesticides by some growers has caused many problems, such as excessive pesticide residues in fruits, which increase people's dietary risk.[14,15] Pesticide residues have

become the main technical barriers to trade and affect the export of Chinese wolfberry fruit.[16,17]

The retention and wetting behavior of liquids is a natural performance, which is common in many industrial and agricultural processes.[18−20] In the process of controlling crop diseases and insect pests by constant-volume pesticide spray, pesticide diluent is atomized by spraying equipment and then deposited on the surfaces of crop stems, leaves, flowers, and fruits through air transmission, thus allowing pesticides to play a role.[21] Each surface of crops has unique and complex surface characteristics, surface microstructure, apparent surface free energy (SFE), and so on, which will make pesticide droplets interact with them, leading to different wetting and retention performances and affecting the retention on the target surface, such as pepper fruit,[22] cucumber leaf,[23,24] and rice leaf.[25]

The retention behavior of the solution on the surface is affected not only by the surface characteristics but also by the characteristics of the solution. The contact angle and adhesion tension of the solution determine that the retention of the solution on the surface and are dependent on the surface tension.[26] In the process of pesticide application, after the spraying mode and surface are determined, the properties of the pesticide diluent can be regulated by adding adjuvant, which can affect the retention of pesticide on the crop surface and meet the specific needs of humans.[27,28] People usually hope that more pesticides can be deposited on the target surface, which will help to improve the control efficacy of pesticides on disease. However, because the amount of pesticide retention on the surface is closely related to the pesticide residue, this often leads to an increase in the retention of pesticides on the nontarget surface (such as fruit, flower, etc.), resulting in an increase in pesticide residues or even exceeding the limit.[29−31] For apples, oranges, and other types of large fruits, the bagging technique is commonly used to avoid the retention of pesticides on the fruits; however, it is not applicable to Chinese wolfberry because its fruit is small and dense.[32,33]

Researchers have found that using surfactants and oils adjuvants can increase the retention of liquids on hydrophobic surfaces, but on easily wetted surfaces, surfactant adjuvants will often cause excessive wetting, which leads to a decrease in retention instead.[34−36] Through the use of adjuvants can make droplets on different wetting properties of the surface to produce different changes, therefore, we expect to increase the retention of droplets on the leaf surfaces and reduce retention on the fruit surfaces of Chinese wolfberry. Therefore, increasing the retention of pesticides on Chinese wolfberry leaves while improving the control efficacy of pesticides and reducing the retention of pesticides on Chinese wolfberry fruits is expected and crucial.

In this paper, the surface characteristics and wettability of Chinese wolfberry fruits and leaves were studied, and their differences in wettability were tested. Pesticide diluents with different properties were obtained by using different kinds of adjuvants at different concentrations. The wetting, retention, and spreading behavior of each treatment on the surfaces of Chinese wolfberry fruit and leaf adaxial and abaxial were measured. Meanwhile, the structural equation model was used to evaluate the relationship between the retention of the solution at each surface and the properties of the solution and the index of wetting properties. The effect of adjuvants on the efficacy of pyraclostrobin in controlling Chinese wolfberry powdery mildew and tylophorine in controlling Chinese wolfberry aphids was also determined under field conditions.

2. MATERIALS AND METHODS

2.1. Materials. Chinese wolfberry fruits and leaves were collected from the planting base of Chinese wolfberry in Ningxia. The Chinese wolfberry fruits used in the test were divided into two varieties, "NQ1" and "NQ7". The same growing Chinese wolfberry fruits were collected when the fruits grew to 15 days, 30 days, and 45 days during the normal growth cycle of Chinese wolfberry. The leaves of Chinese wolfberry growing at the same time as the fruits for 15 days, 30 days, and 45 days were used in the test. All tested Chinese wolfberry trees had the same growth stage and growth characteristics. The leaves and fruits of Chinese wolfberry were collected in a Petri dish filled with wet filter paper and

temporarily stored in a refrigerator at 4 °C. The fresh materials collected on the same day were used in all experiments.

Pyraclostrobin (30% SC) was obtained from Shenzhen Noposion Agrochemicals Co., Ltd. Tylophorine (1% AS) was obtained from the Chinese Wolfberry Engineering Technology Research Institute of the Ningxia Academy of Agriculture and Forestry Sciences. Adjuvants, including Silwet618 [nonionic organosilicone surfactant; ethoxy-modified trisiloxane 92%, surfactant content 8%; Momentive Silicone Materials (Shanghai) Co., Ltd.], AEO-5 (nonionic surfactant; polyoxyethylene alkyl ether 75%, surfactant content 25%; Tianjin ZhongHe-ShengTai Commercial and Trading Co., Ltd.), Gemini 31551 (cationic surfactant; octadecylamide propyl dimethyl ammonium bromide 45%, surfactant content 55%; Zhengzhou Yihe Fine Chemicals Co., Ltd.), GY-Tmax (mineral oil; methyl soybean oil, linoleic acid, stearic acid, and oleic acid 85%, surfactant content 15%; Beijing Grand AgroChem Co., Ltd.), YSJZ (a mixture of oil and surfactants; epoxidized soybean oil, linseed oil, and methyl oleate 85%, surfactant content 15%; Shandong Agricultural University), and 1227 (cationic surfactant; dodecyl benzyl ammonium chloride 47%, surfactant content 53%; Jiangsu Four New Interface Agent, Science and Technology Co., Ltd.), were obtained. Formamide (99%), ethylene glycol (99%), and diiodomethane (98%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Deionized water was used to prepare the solution (pH 6.9 and hardness 0.01 mmol/L).

2.2. Methods. *2.2.1. Characterization of Chinese Wolfberry Fruit and Leaf Surfaces.* The macro Chinese wolfberry fruit and leaf surfaces were photographed by a digital camera, and the microstructure of each surface was studied by scanning electron microscopy (SEM, JSM-6610LV, Japan). The samples were sliced into small pieces, vacuum-dried, and sputter-coated with gold.[37]

The SFE is composed of dispersion components and polar components,[38] which can be obtained using formula 1

$$\frac{(1 + \cos\theta)\gamma_{lg}}{2\sqrt{\gamma_{lg}^d}} = \sqrt{\gamma_{sg}^d} + \sqrt{\gamma_{sg}^p}\sqrt{\frac{\gamma_{lg}^p}{\gamma_{lg}^d}} \tag{1}$$

where γ_{lg}^p and γ_{lg}^d are the polar components and dispersive components of the liquid, respectively, while γ_{sg}^p and γ_{sg}^d are the polar components and dispersive components of the solid, respectively, and θ is the contact angle of the solution at the target surface.

2.2.2. Preparation of Aqueous Solution. In order to accurately compare the effects of adjuvants on the properties of droplets and eliminate the interference of other substances on the test results, we prepared the aqueous solution of adjuvants for experiments. The six adjuvants were dissolved in deionized water, and the concentrations are shown in Table S1.

2.2.3. Retention of Solution on the Chinese Wolfberry Fruit and Leaf Surfaces. The retention of the solution was evaluated by the spraying method. Keeping the fruits drooping at 90°, leaves were placed on a homemade 45° slope for spraying to simulate the natural drooping state of the fruits and leaves. A Potter spray tower (Burkard Scientific Co., Uxbridge, UK) was used to spray solutions on the fruit and leaf surfaces. The retention was calculated according to formulas 2 and 3

$$\text{fruit retention (mg/g)} = (m_2 - m_1)/m_1 \times 1000 \tag{2}$$

$$\text{leaf retention } (mg/cm^2) = (m_4 - m_3)/s \times 1000 \quad (3)$$

where m_1 = the weight of the fruit before spraying solution, m_2 = the weight of the fruit after it was sprayed with a solution, s = the area of the whole leaf, m_3 = the weight of the leaf before spraying solution, and m_4 = the weight of the leaf after it was sprayed with a solution. The ambient temperature was 298.15 K, the relative humidity (RH) was 65%, and the samples were repeated at least 10 times.

2.2.4. Surface Tension of Solution Measurement. The surface tension of adjuvant solutions prepared by deionized water was measured by an automatic tensimeter (BZY-1, Shanghai Hengping Instrument and Meter Factory, China), three experiments were repeated for each treatment.[39] The relationship between the tested concentration and surface tension was evaluated, and the critical micelle concentration (CMC) of each adjuvant was then obtained.

2.2.5. Interfacial Behavior on the Chinese Wolfberry Fruit and Leaf Surfaces. 2.2.5.1. Contact Angles. Fresh and healthy wolfberry leaves and fruits were used as experimental materials. The Chinese Wolfberry leaves were cut into long strips of 0.5 cm × 2.0 cm to avoid the veins, put it on the glass sheet; the Chinese wolfberry fruits were cut into two halves from the middle, put the cut face down on the glass sheet, and select a relatively flat surface for the experiment. Droplets of 2 μL of the test solution were dripped on the fixed surfaces of Chinese wolfberry fruits and leaves, and the droplets were photographed by an image sensor on a contact angle measuring instrument (JC2000C2, Shanghai Zhongchen Digital Technology Apparatus Co., Ltd.), three experiments were repeated for each treatment. The contact angle of the test solution on the Chinese wolfberry fruits and leaves was obtained by analysis.[40]

2.2.5.2. Adhesion Tension, Adhesion Work, and Spreading Coefficient. The adhesion tension (Ta), adhesion work (Wa), and spreading coefficient (Cs) of the solution on the Chinese wolfberry fruit and leaf surfaces were calculated according to the corresponding surface tension of the solution and the corresponding contact angle,[41] which can be obtained using formulas 4−6

$$\text{Ta} = \gamma \cos \theta \quad (4)$$

$$\text{Wa} = \gamma(1 + \cos \theta) \quad (5)$$

$$\text{Cs} = \gamma(\cos \theta - 1) \quad (6)$$

where γ is the surface tension of the solution and θ is the contact angle of the solution at the target surface.

2.2.6. Correlation Analysis. To assess the direct effect of surface tension and contact angle on retention and the indirect effect on retention by adhesion tension, adhesion work, and spreading coefficient, a structural equation model (SEM) was constructed by IBM SPSS Amos. The data used for the variables in this model were standardized. Retention was the dependent variable, and contact angle and surface tension were independent variables. Adhesion tension, adhesion work, and spreading coefficient were set as mediator variables.[22]

2.2.7. Field Efficacy Trials and Phytotoxicity Evaluation. Field efficacy trials with Chinese wolfberry aphids and Chinese wolfberry powdery mildew were conducted at the Chinese wolfberry planting base of the Ningxia Academy of Agricultural and Forestry Sciences in mid-July 2022. The variety of Chinese wolfberry was "NQ1", in which plants were managed according to normal agronomic practices.

2.2.7.1. Experiment against Chinese Wolfberry Aphid. There were eight treatments (three replicates each) in the Chinese wolfberry aphid experiment: treatment 1, blank control area, sprayed with the same amount of water as the other treatments; treatment 2, tylophorine at 75 g a.i./ha; and treatments 3−8, tylophorine amended with Silwet618, AEO-5, Gemini 31551, GY-Tmax, YSJZ, and 1227 at 0.05, 0.05, 0.1, 0.25, 0.5, and 0.125 wt %, respectively.

Test plots (5 m × 6 m) were arranged in a randomized complete design. The spray volume was 650 L/ha. These treatments were applied using a backpack sprayer (MATABI−16) with a pressure of 0.3 MPa using conical nozzles (0.7 mm aperture). The flow rate of the sprayer was 350 mL/min, and the spray speed was 0.4 m/s.

They were sprayed in late July. Five branches from the eastern, southern, western, northern, and middle parts of each plant were selected. They were counted down from the top of the branches, a sign was placed on the 10th leaf and the number of insects on the marked leaf was counted. The population base was investigated 1 day before application, and the number of live insects was investigated on the 1st, 3rd, and 7th days after treatment. The reduction rate of aphids and control efficacy were calculated according to formulas 7 and 8

$$\text{reduction rate of aphid } (\%) = \frac{PT_1 - PT_2}{PT_1} \times 100 \quad (7)$$

$$\text{control efficacy } (\%) = \left(1 - \frac{RA_2 - RA_1}{1 - RA_1}\right) \times 100 \quad (8)$$

where PT_1 is the number of live insects before application, PT_2 is the number of surviving insects after application, RA_1 is the reduction rate of aphids in the blank control area, and RA_2 is the reduction rate of aphids in the pesticide treatment area.

2.2.7.2. Experiment against Chinese Wolfberry Powdery Mildew. There were eight treatments (three replicates each) in the experiment of Chinese wolfberry powdery mildew, which were as follows: treatment 1, blank control area, sprayed with the same amount of water as other treatments; treatment 2, pyraclostrobin at 150 g a.i./ha; and treatments 3−8, pyraclostrobin amended with Silwet618, AEO-5, Gemini 31551, GY-Tmax, YSJZ, and 1227 at 0.05, 0.05, 0., 0.25, 0.5, and 0.125 wt %, respectively.

The fungicides were sprayed first in mid-July and sprayed for a second time 7 days later. The initial amount of the disease was investigated 1 day before the application, and the control efficacy was investigated 3, 7, and 14 days after the last application. Ten branches were investigated in each plot, and 10 leaves were investigated from top to bottom. A total of 100 leaves were investigated in each plot. The disease severity was graded according to the percentage of disease spot area to the whole leaf area, using a rating from 0 to 9, with 0 representing no disease and 9 representing disease spot cover over 40% of leaves. The total number of leaves and the number of diseased leaves at all levels were recorded. The disease severity and control efficacy were calculated according to formulas 9 and 10

$$\text{disease severity } (\%) = \frac{\sum (N_1 \times \delta)}{N_2 \times 9} \times 100 \quad (9)$$

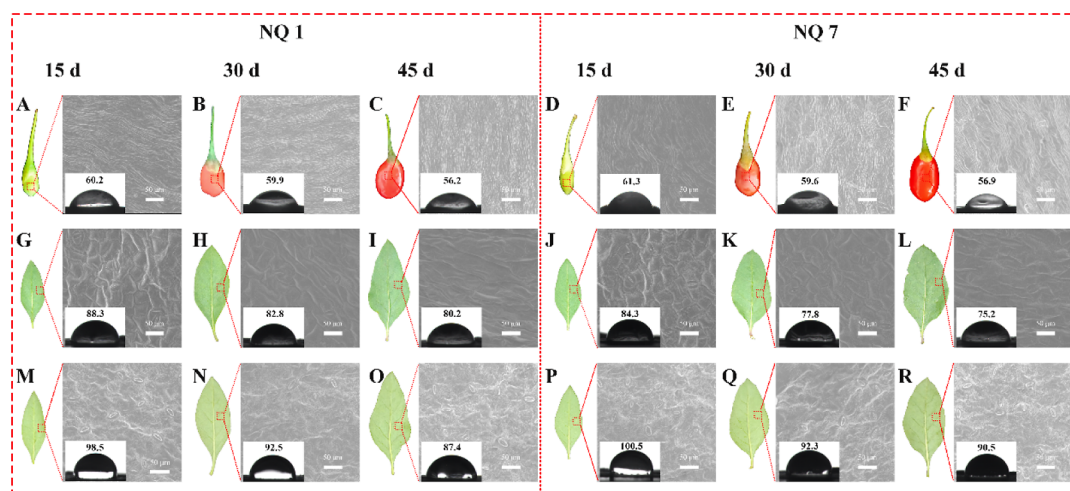$$\text{control efficacy } (\%) = \frac{DS_1 \times DS_4}{DS_2 \times DS_3} \times 100 \quad (10)$$

Figure 1. Photographs and SEM images, which show water contact angles: "NQ1" fruits (A−C) and leaf adaxial (G−I) and leaf abaxial (M−O) surfaces have 15 days, 30 days, and 45 days of growth; "NQ7" fruits (D−F) and leaf adaxial (J−L) and leaf abaxial (P−R) surfaces have 15 days, 30 days, and 45 days of growth. "NQ1" and "NQ7" are two varieties of Chinese wolfberry.
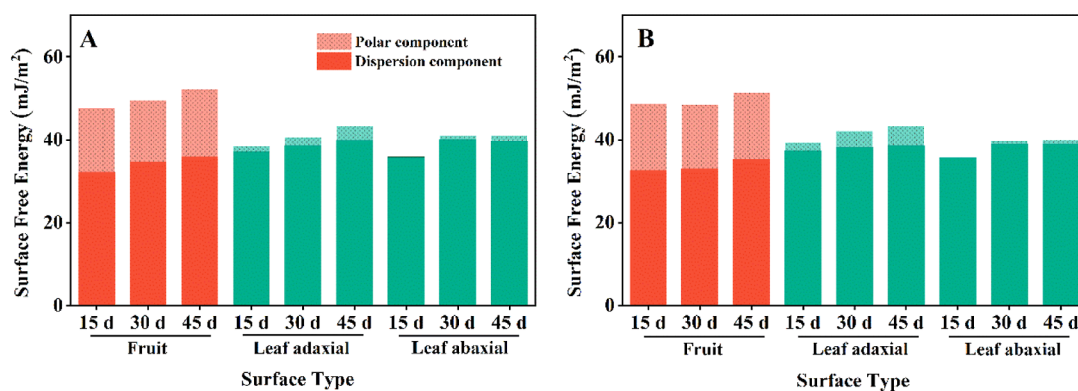

Figure 2. (A) SFE of Chinese wolfberry "NQ1" fruit and leaf surfaces after 15, 30, and 45 days of growth. (B) The SFE of Chinese wolfberry "NQ7" fruit and leaf surfaces after 15, 30, and 45 days of growth. Light colors represent polar component and dark colors represent dispersion component.

where N_1 is the number of diseased leaves in each scale, N_2 is the total leaf examined, δ is the disease scale, and DS_1 is the disease severity of the blank control area before application. DS_2 is the disease severity of the blank control area after application, DS_3 is the disease severity of the pesticide treatment area before application, and DS_4 is the disease severity of the pesticide treatment area after application.

2.2.8. Phytotoxicity Evaluation. The variety of Chinese wolfberry was "NQ1", and high-yield trees aged 5−6 years were selected to ensure that no pesticides were used 60 days before the safety test. Six kinds of adjuvant diluents were sprayed on Chinese wolfberry trees, and clear water was sprayed as a control. Four Chinese wolfberry trees were sprayed per treatment. The leaves and fruits of Chinese wolfberry were investigated four times on the 1st, 7th, 15th, and 30th days after treatment. A total of four times were investigated. One branch not less than 50 cm was selected from the eastern, western, southern, northern, and middle parts of the Chinese wolfberry trees to investigate all leaves and fruits.

2.2.9. Statistical Analysis. All data were analyzed using SPSS software (Version 20.0, IBM Corp., U.S.A.). The results were assessed using Shapiro−Wilk and Levene variance equality tests to ensure the normal distribution and

homoscedasticity of variances. The difference between each treatment was determined by variance analysis (ANOVA) using Tukey's tests at $p < 0.05$.

3. RESULTS AND DISCUSSION

3.1. Properties of Wolfberry Fruit and Leaf Surfaces. In the process of long-term evolution, plants gradually formed morphological characteristics adapted to their growth environment. Leaves and fruits are important plant organs that are exposed to open ground. The surface micromorphological characteristics of fruits and leaves show diversity, complexity, and stability, and their uniqueness affects the impact, wetting, and retention behavior of droplets on leaves and fruits.[42] In line with the principle of matching droplet characteristics and target surface specificity, fruit and leaf surface morphology, and SFE were studied to provide theoretical support for the safe and efficient utilization of pesticides on wolfberry fruit and leaf surfaces.

Two Chinese wolfberry varieties, "NQ1" and "NQ7", with more planting area were selected, and fruits and leaves with growing periods of 15 days, 30 days, and 45 days were collected and observed. As shown in Figure 1, the appearance of Chinese wolfberry fruits had an egg shape. In the process of fruit growth, the color changed from green to red. The leaves
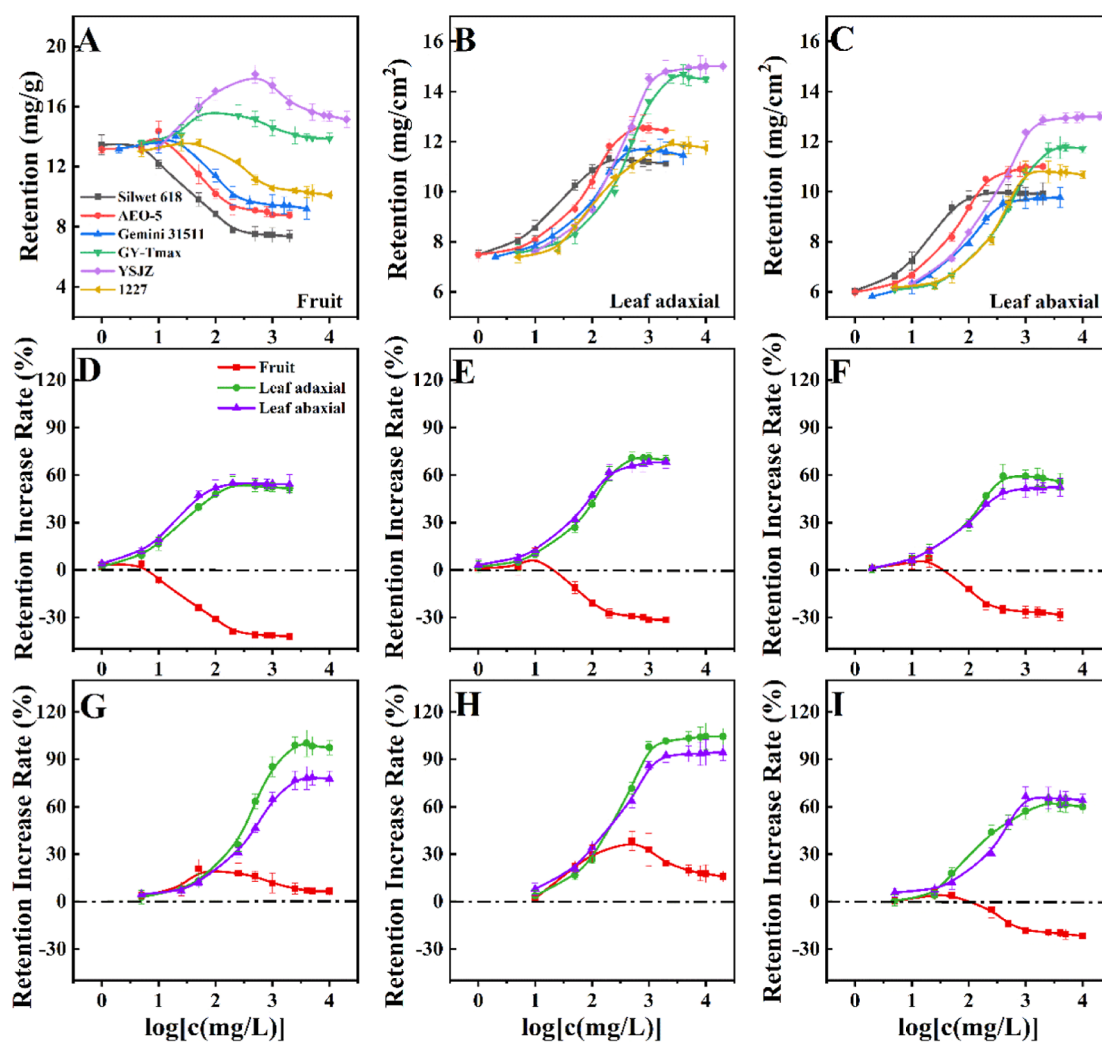
Figure 3. (A) Retention of six adjuvant solutions as a function of concentration on the fruit surfaces. (B) The retention of six adjuvant solutions as a function of concentration on the leaf adaxial surfaces. (C) The retention of six adjuvant solutions as a function of concentration on the leaf abaxial surfaces. The retention increasing rate of six adjuvant solutions as a function of concentration on fruit, leaf abaxial, and leaf abaxial surfaces: Silwet618 (D), AEO-5 (E), Gemini 31551 (F), GY-Tmax (G), YSJZ (H), and 1227 (I).

were long and oval in shape and green or light green in color. The leaf adaxial surfaces were smooth and slightly fleshy, and the vein was not obvious, but the leaf abaxial surface veins were obvious, and the color was slightly lighter than that of the adaxial surfaces. Observation by SEM showed that there was a thin layer of regular banded structure on the fruit surfaces, and the shorter the fruit growth cycle was, the denser the bands. The leaf shape gradually expanded with growth, but the change in the surface microstructure was not obvious. On the adaxial surface, the surface had a block structure with irregular arrangement, and the number of stomata was less than that on the adaxial surface. On the leaf abaxial surfaces, there were relatively many stomata distributed. An irregular banded structure was distributed between stomata, and the micro-structure was more abundant than that on the leaf adaxial surfaces.

We compared the difference in water contact angle on the fruit and leaf surfaces, as well as the difference between the two varieties. As shown in Figure 1, the stable contact angle of water was 56.2−61.3° on the fruit surfaces, 75.2−88.3° on the leaf adaxial surfaces, and 87.4−100.5° on the leaf abaxial surfaces. With the growth of fruits and leaves, the surface

microstructure changes slightly, resulting in a slight decrease in the stable contact angle, and there was no significant difference between the two varieties.

It has been pointed out that 65° is the boundary of the hydrophilic surface.[43] Therefore, the Chinese wolfberry fruit surface is a hydrophilic surface, the Chinese wolfberry leaf surface is a hydrophobic surface, and the leaf abaxial surface is more hydrophobic. The SFE parameters of fruits and leaves also showed this point, as shown in Figure 2. The SFE of fruit surfaces was higher than that of leaves, and the proportion of polar components was larger, showing hydrophilicity, while the SFE of leaves was lower, the proportion of polar components was very small, and the SFE of the leaf adaxial surface was higher than that of the abaxial surface, which showed hydrophobicity.

The liquid retention is closely related to the interfacial characteristics, and there are significant differences in the surface wettability between fruit and leaf surfaces, which may lead to differences in the wetting and retention behavior of droplets on the Chinese wolfberry fruit and leaf surfaces. The fruit and leaf of the Chinese wolfberry variety "NQ1" at the growing age of 30 days were selected as the model fruit and
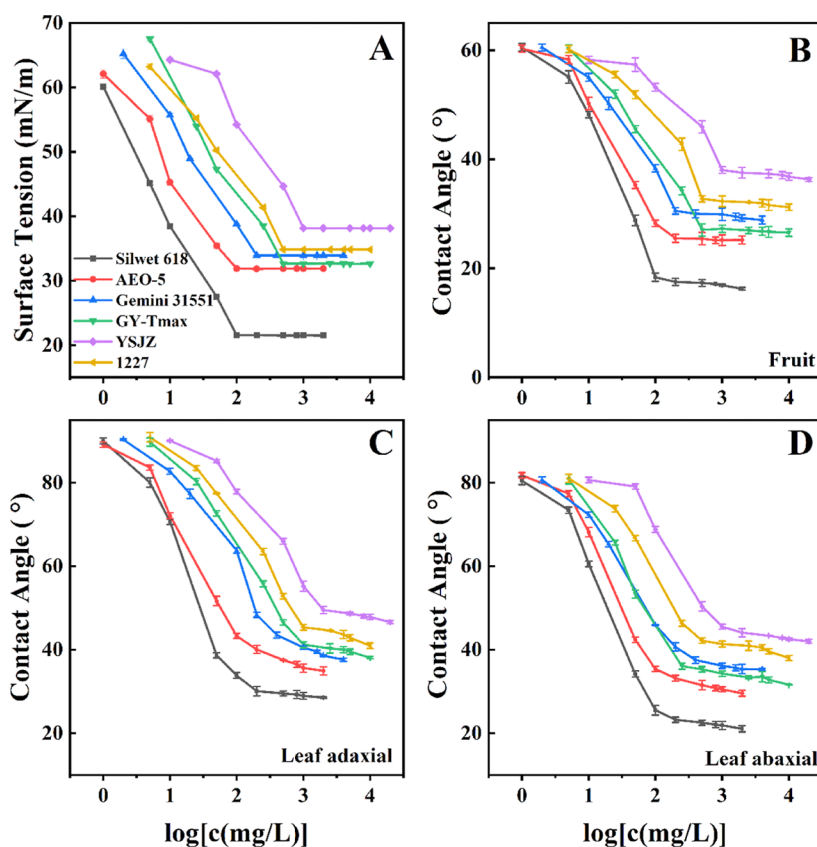
Figure 4. (A) Equilibrium surface tension of six adjuvant solutions as a function of concentration. The equilibrium contact angle of six adjuvant solution droplets as a function of concentration on fruit (B), leaf adaxial (C), and leaf abaxial (D) surfaces.

leaf (hereinafter referred to as fruit and leaf, respectively) to study the wetting and retention processes of solution on the Chinese wolfberry fruit and leaf surfaces.

3.2. Retention of Adjuvant Droplets on Fruit and Leaf. In addition to the characteristics of pesticides, the retention of pesticide diluents on the target surface is directly related to the control efficacy of pesticides, and it is also an important factor affecting pesticide residues on the surface of plant organs.[44] Through the use of adjuvants, researchers can increase the retention capacity of the pesticide diluent on the hydrophobic surface, thus increasing the control efficacy of the pesticide, but it was found that the use of adjuvants can also lead to excessive wetting of the solution on the easy-wetting surface, resulting in the loss and waste of pesticide.[35,36]

Figure 3A−C shows the retention of six adjuvant solutions on fruits and leaves. On the fruit surfaces, the six adjuvant solutions increased at first and then decreased. The inflection point mass concentrations of the six adjuvant solutions (Silwet618, AEO-5, Gemini 31551, GY-Tmax, YSJZ, and 1227) were 0.0005, 0.001, 0.002, 0.005, 0.002, and 0.0025 wt %, respectively. The critical mass concentrations from rapidly decreasing to flat were 0.02, 0.02, 0.04, 0.1, 0.1, 0.5, and 0.1 wt %, respectively. On the leaf surfaces, the six adjuvant solutions increased significantly at first and then tended to smooth with the increase concentration, and the inflection point was consistent with the inflection point on the fruit, and both adaxial and abaxial surfaces showed the same trend. When the mass concentration of adjuvants was 0.1 wt %, the highest retention was observed for YSJZ, and the retentions on adaxial and abaxial surfaces were 14.529 ± 0.179 mg/cm^{2} and 12.371

± 0.08 mg/cm^{2}, respectively, followed by GY-Tmax, AEO-5, 1227, Gemini 31551, and Silwet618.

On fruit surfaces, the effects of different adjuvants on solution retention were also different. Surfactant adjuvants Silwet618, AEO-5, Gemini 31551, and 1227 more easily reduced the retention, while oil adjuvants GY-Tmax and YSJZ increased more because of their lipophilic properties. When the mass concentration of adjuvants was 0.1 wt %, Silwet618 had the lowest retention, followed by AEO-5, Gemini 31551, 1227, and GY-Tmax, and YSZJ had the highest retention. Figure 3D−I shows that the retention increasing rates of the six adjuvant solutions on fruit and leaf surfaces were different. When the mass concentration of adjuvants was 0.1 wt %, the retention increasing rate of Silwet618 on fruit surfaces was −41.51%, while that on leaf adaxial and adaxial surfaces was 52.28 and 54.41%, respectively. The retention increasing rate of YSJZ on fruit surfaces was 32.80%, and the leaf adaxial and abaxial surfaces were 97.89 and 86.01%, respectively. This shows that different adjuvants had a greater impact on the retention performance due to their own properties.

The results showed that the retention of the solution was affected by the use of adjuvants, and different adjuvants showed different changes. Due to the difference in wettability between fruit and leaf surfaces, the use of surfactant adjuvants reduced the retention of solution on fruit surfaces and increased the retention on the leaf adaxial and abaxial surfaces. The use of oil adjuvants increased the retention of the liquid on the leaf surfaces more significantly. The retention of droplets was closely related to the wetting behavior of droplets on the surface. A clear understanding of the relationship between droplet retention and the parameters of wetting
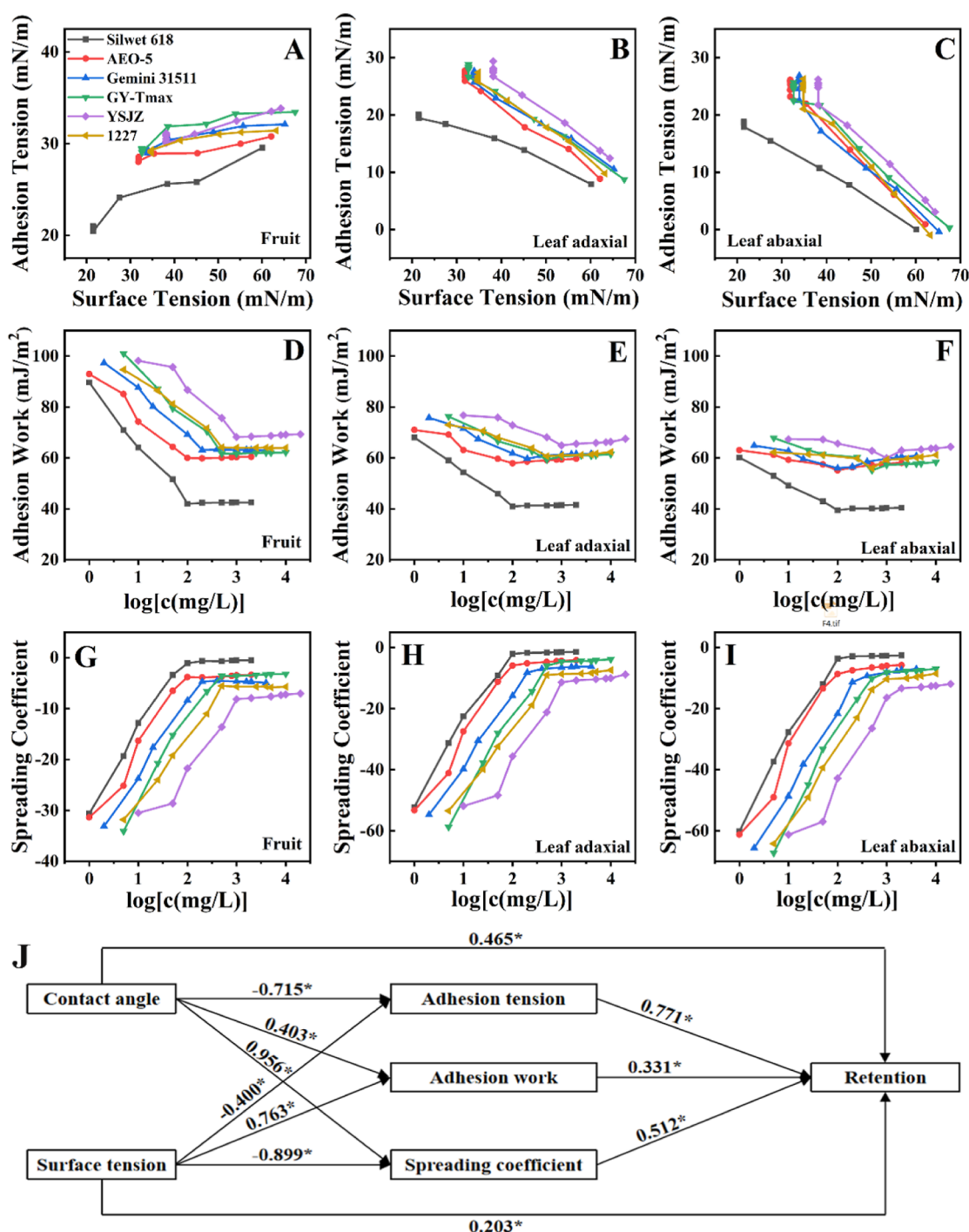
Figure 5. Relationship with adhesion tension and surface tension of six adjuvant solutions on fruit (A) and leaf abaxial (B) and leaf abaxial (C) surfaces. The adhesion work of six adjuvant solutions as a function of concentration on fruit (D) and leaf abaxial (E) and leaf abaxial (F) surfaces. The spreading coefficient of six adjuvant solutions as a function of concentration on fruit (G) and leaf abaxial (H) and leaf abaxial (I) surfaces. (J) Structural equation model of the relationship between wettability behavior and retention.

behavior can guide the selection and use of adjuvants in field applications. It improves the efficiency of pesticides at the same time and reduces the safety risk to nontarget parts.

3.3. Surface Tension of Adjuvant Solution. Surface tension is an important parameter to evaluate the physical properties of liquids. The number of surfactant molecules affects the surface tension, thus affecting the retention and wetting behavior of droplets.[45]

The surface tension of the liquid is an important factor affecting the wetting properties of the liquid. Figure 4A shows the relationship between the log10 value of the concentration of six adjuvants and the surface tension in this study. The surface tension of six kinds of adjuvant solutions decreased sharply with the increase in the concentration of adjuvant. When the concentration reached a certain value, the surface tension changed slowly, and an inflection point appeared; that is, the CMC of the adjuvant. The CMC is the lowest
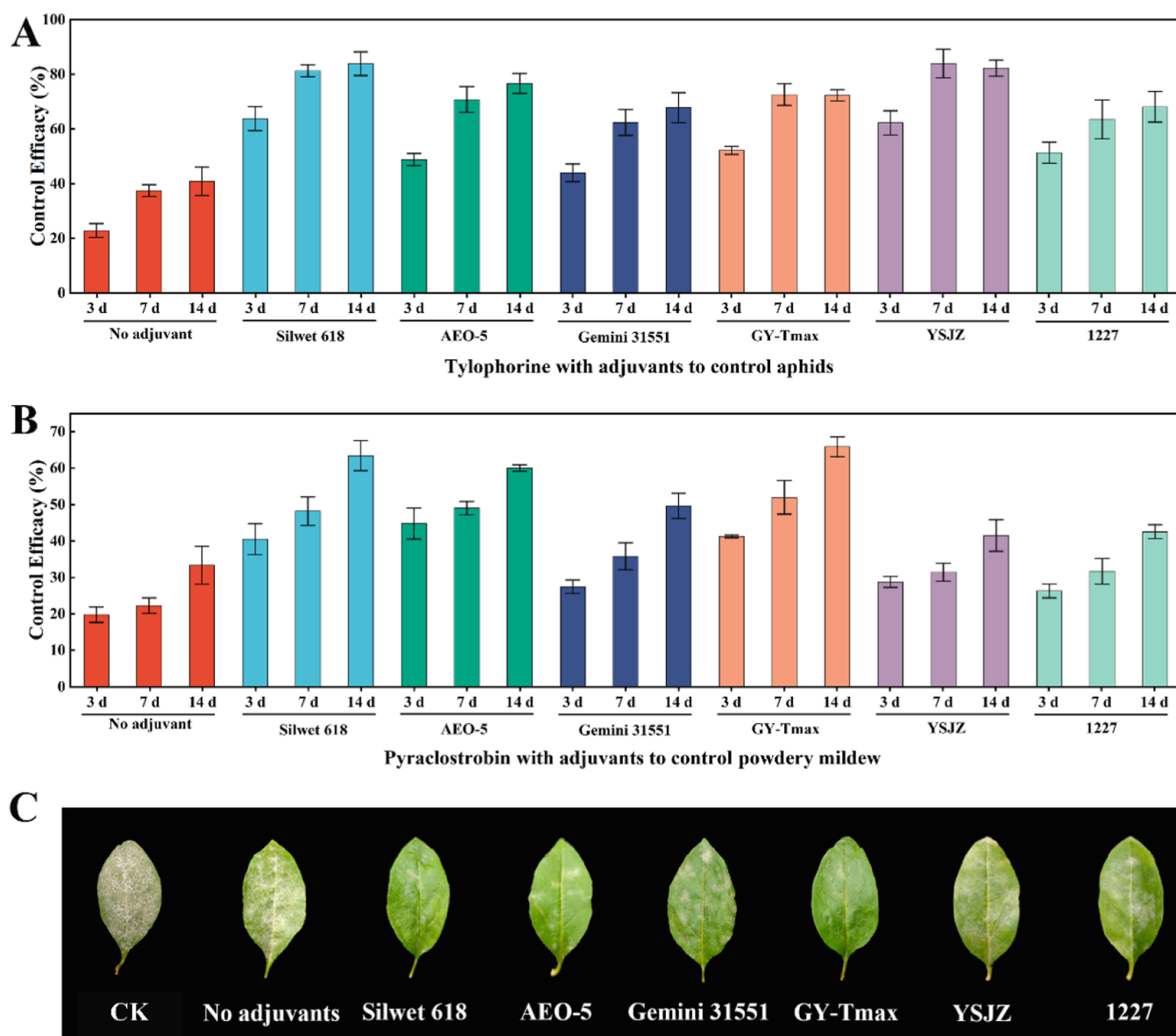
Figure 6. (A) Incorporating tylophorine with adjuvants to control Chinese wolfberry aphids under open-field conditions. (B,C) Incorporating pyraclostrobin with adjuvants to control Chinese wolfberry powdery mildew under open-field conditions.

concentration that causes surfactant molecules to form micelles in the solution.

In this study, the CMCs of six adjuvants (Silwet618, AEO-5, Gemini 31551, GY-Tmax, YSJZ, and 1227) were 0.01, 0.01, 0.02, 0.05, 0.1, and 0.025 wt %, respectively. The CMC can provide a reference for determining the optimum concentration range of the adjuvant.

3.4. Interface Behavior of Adjuvant Droplets on Fruit and Leaf Surfaces. Wettability is a macroscopic manifestation of interfacial interactions, which can be determined by measuring the contact angle of the solution.[46] The contact angle of the liquid on the target surface is an important index to measure the wetting retention performance. With the in-depth study of scientists, wetting models, such as Young's model, Wenzel model, Cassie–Baxter model, and Wenzel and Cassie–Baxter transition state model, have been continuously improved.

As shown in Figure 4B–D, with the increase in additive concentration, the contact angle decreased slowly at first, then decreased rapidly, and finally tended to equilibrium. The wettability of adjuvant Silwet618 was the best, followed by AEO-5, GY-Tmax, Gemini 31551, 1227, and YSJZ. The fruit and leaf surfaces showed similar trends. On the leaf surfaces, with the increase in the concentration of adjuvants, the contact angle decreased gradually. The wetting was in the Cassie–Baxter transition state at first and finally changed to the Wenzel state, which realized the hydrophilicity of the hydrophobic surface, thus increasing the retention performance of droplets on the leaf surfaces. On the fruit surfaces, the contact angle of water was less than 65°, which showed hydrophilicity to the fruit surfaces. With the increase in the concentration of adjuvants, the contact angle decreased greatly and was in a state of excessive wetting.

The trend of the contact angle was basically consistent with the overall trend of the surface tension. The decrease in the surface tension made it easier for the droplets to enter the micronanostructure of the surface, but the too-low surface tension also led to the excessive wetting of the droplets on the

wettable surface. This resulted in a decline in the ability of the surface to retain liquid. However, when the concentration of adjuvant exceeded its CMC, the contact angle of the droplets gradually tended to be smooth, but the retention on the fruit and leaf surfaces still changed rapidly; therefore, the contact angle or surface tension alone was not enough to reveal the retention properties of the adjuvant solution on the fruit and leaf surfaces.

Adhesion tension and adhesion work are two important indices to evaluate the affinity of the surface, which indicates the retention ability of the solution on different surfaces.[41] As shown in Figure 5A−C, the adhesion tension of adjuvant solutions on the fruit surfaces was positively correlated with the surface tension. With the increase in adjuvant concentration, the adhesion tension decreased, and the adhesion ability of droplets on fruits decreased. At the same time, under the dual influence of droplet gravity, the retention of adjuvant solutions on fruit surfaces showed a downward trend. Interestingly, the adhesion tension of the adjuvant solutions on the leaf adaxial and abaxial surfaces was negatively correlated with the surface tension, and the adhesion tension increased with the increase in the concentration of adjuvants, which increased the adhesion ability of the adjuvant solutions on the leaf adaxial and abaxial surfaces, and the retention ability of droplets on the leaf surfaces increased. As shown in Figure 5D−F, the adhesion work of six adjuvant solutions on fruit and leaf surfaces showed different trends with the change in adhesion tension. The adhesion work of YSJZ was the highest, followed by 1227, Gemini 31551, GY-Tmax, AEO-5, and Silwet618. On fruit surfaces, the overall trend decreased rapidly and then tended to balance with the increase in adjuvant concentration, while on leaf surfaces, the overall trend decreased slowly and then increased slowly.

The spreading coefficient is the parameter of the lateral diffusion driving force in wetting behavior.[47] Figure 5G−I shows the spreading coefficient of six adjuvant solutions on the surfaces between fruit and leaf with the increase in additive concentration. With increasing concentration, the spreading coefficient increased gradually, and the trend of lateral diffusion increased. The largest spreading coefficient was Silwet618, followed by AEO-5, GY-Tmax, Gemini 31551, 1227, and YSJZ.

As shown in Figure 5J, to explore the effect of different wetting parameters on retention during wetting, a structural equation model (SEM) of retention in six adjuvant solution systems was established. The contact angle (0.465) and surface tension (0.203) had a direct influence on retention. At the same time, there were indirect effects of contact angle and surface tension on disease severity that were mediated by adhesion tension (contact angle → adhesion tension: −0.715, surface tension angle → adhesion tension: −0.400, adhesion tension → retention: 0.771), adhesion work (contact angle → adhesion work: 0.403, surface tension → adhesion work: 0.763, adhesion work → retention: 0.331), and spreading coefficient (contact angle → spreading coefficient: 0.956, surface tension → spreading coefficient: 0.899, spreading coefficient → retention: 0.512). The results showed that adhesion tension was the key factor in determining the retention of six kinds of adjuvant solutions.

Therefore, for the hydrophobic leaf adaxial and abaxial surfaces, increasing the adhesion tension of the solution could increase the retention performance, and when the adhesion tension of the solution was greater than 20 mN/m, the effect of

promoting retention behavior was better. For the hydrophilic fruit surface, reducing the adhesion tension of the solution could reduce the retention on the fruit surface; when the adhesion tension was less than 30 mN/m, the solution was more likely to lose.

According to the CMC value and adhesion tension of each adjuvant, it is recommended that when the concentration of adjuvants is 2−5 times higher than their respective CMC, it can increase the retention of solution on leaf surfaces and reduce the retention on fruit surfaces.

3.5. Field Efficacy Trial and Phytotoxicity Evaluation.
The control efficacy of pesticides in the field can directly indicate the effect of adding adjuvants to regulate the retention properties of the solution on the use of pesticides. In the field experiment of this study, the concentration of each adjuvant was five times higher than its CMC. The mass concentrations of the six adjuvants (Silwet618, AEO-5, Gemini 31551, GY-Tmax, YSJZ, and 1227) were 0.05, 0.05, 0.1, 0.25, 0.5, and 0.125 wt %, respectively.

Figure 6A shows that after using adjuvants, the control efficacy of tylophorine on Chinese wolfberry aphids in the field was significantly improved, and the control efficacy of tylophorine added six kinds of adjuvants were 83.84, 76.62, 67.80, 72.33, 82.22, and 68.11%, respectively. The increasing rates of control efficacy were 105.15, 87.48, 65.90, 76.98, 101.17, and 66.66%, respectively. Interestingly, when six adjuvants were added to the solution containing pyraclostrobin, the field control efficacy against Chinese wolfberry powdery mildew was significantly increased (Figure 6B). The control efficacies of pyraclostrobin added six kinds of adjuvants were 48.19, 49.01, 35.83, 51.95, 31.47, and 31.69%, and the increasing rates of control efficacy were 116.20, 119.87, 60.73, 133.06, 41.18, and 42.17%, respectively. The pesticide diluent after adding adjuvants had excellent wetting performance, better wetting and retention on the leaf surfaces, and increased the retention of pesticide diluent on the leaf surfaces, thus greatly increasing the control efficacy (Figure S1B,C). From Figure 6C, we can see more intuitively the difference in the control effect of pesticide diluent with adjuvants on Chinese wolfberry powdery mildew. Due to the different characteristics of adjuvants, the effects of pesticides on the control of diseases and insect pests were also different. Surfactant adjuvants Silwet618, AEO-5, Gemini 31551, and 1227 have strong wetting and spreading ability, which can make the droplets spread rapidly on the surface of the leaves and penetrate into the microstructure of the leaves, so that the liquid on the surface of the leaves The retention is increased, thereby improving the control effect; the vegetable oil adjuvant GY-Tmax, and YSJZ has similar chemical properties to the leaf surface, which increases the affinity between the droplet and the leaf surface, and can better persist on the leaf surface, increasing the control effect, but at the same time, it will also increase the retention on the fruit surface. Therefore, when using adjuvants, we should reasonably select suitable adjuvants according to the objectives of prevention and control and improve the utilization efficiency of pesticides as much as possible. At the same time, it can also reduce the use of pesticides per unit area and further reduce the risk of pesticide residues (Figure S1A).

The application of pesticides plays a key role in ensuring the output and quality of agricultural products. Although the use of adjuvants can improve the control efficacy and utilization rate of pesticides, some adjuvants are also harmful to plants and
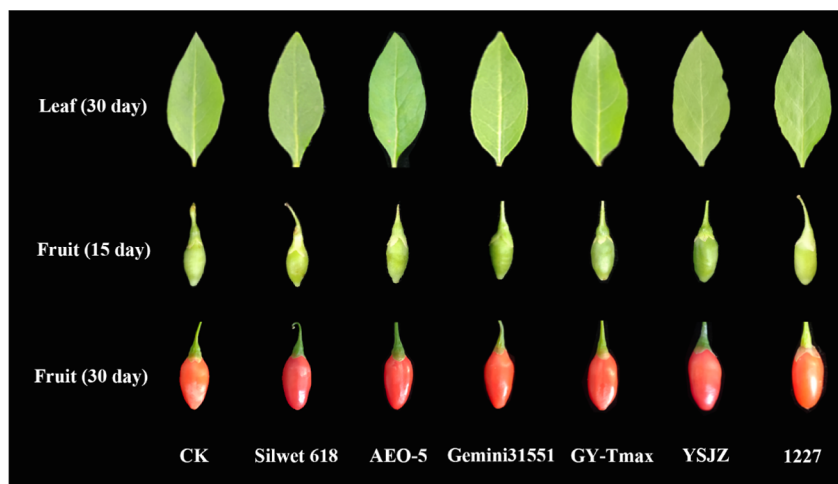
Figure 7. Effect of different adjuvant treatments on Chinese wolfberry leaf growth, fruit expansion, and coloring.

cause harm to the growth and development of plants. Therefore, it is very important to evaluate the phytotoxicity of adjuvants for their safe use. Phytotoxicity has many characteristics, including yellowing, local necrosis of leaves, fruit shedding, and even plant death.[48]

The phytotoxicity indices in this study mainly included leaf growth, fruit setting rate, fruit expansion, and coloring. The experimental results showed that different organs showed similar sensitivity to six kinds of adjuvants. Figure 7 shows that after treatment, the Chinese wolfberry fruits grew well and could develop and color normally. At the same time, the growth of leaves was not affected, and no phytotoxicity was observed, indicating that these adjuvants are safe for Chinese wolfberry trees and can be introduced into the production of Chinese wolfberry. The lack of phytotoxicity may be because the adjuvants used in this study reduced the retention of the solutions on the Chinese wolfberry fruit surfaces, while the Chinese wolfberry leaf surfaces contained a wax layer structure, which would not destroy the leaf surface structure at appropriate concentrations; therefore, it would not cause phytotoxicity.

4. CONCLUSIONS

In conclusion, adjuvants can regulate the wetting properties of pesticide diluents and adjust their retention on target plants. When the concentrations of Silwet618, AEO-5, Gemini 31551, and 1227 were 2−5 times higher than their CMCs, the retention of pesticide solutions on Chinese wolfberry leaves significantly increased, and the control efficacies on aphids and powdery mildew also dramatically improved. Meanwhile, the retention of pesticides on the fruit of Chinese wolfberry was reduced. This study provides a win−win strategy for improving crop food safety, increasing the control efficacy of pesticides and improving the efficiency of pesticide utilization.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c00581.

> Six adjuvants dissolved in deionized water at the indicated concentrations and retention of tylophorine amended with six adjuvants on Chinese wolfberry fruits and leaves (PDF)

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Notes

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