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# Formulation of Matrine Oil-Based Suspension Concentrate for Improving the Wetting of Droplets and Spraying Performance

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**Abstract:** Matrine is an efficient, low-toxicity, and environmentally friendly botanical pesticide; however, it is mainly applied as a soluble concentrate (SL) with a limited utilization rate that is unsuitable for ultra-low-volume spraying and unmanned aerial vehicles. Therefore, a matrine formulation (such as an oil-based suspension concentrate, OD) is more effective. In this study, matrine ODs were prepared with three kinds of emulsifiers (VO/02N, VO/03, and VO/01). The storage stability, suspensibility, viscosity, surface tension, contact angle, droplet density, fraction of coverage, maximum retention, indoor control, effect of adhesion tension, and adhesion work of matrine ODs were studied. All three types of matrine ODs had favorable stability, and the wetting and spraying performance of the matrine ODs were more effective than those of the matrine SLs. Among the three types of matrine ODs, the viscosity, wettability, spray performance, and maximum retention of the suspension made with emulsifier VO/03 were superior to those of the other two emulsifiers, and they were more effective in controlling *Spodoptera frugiperda*. Increasing the solution concentration improved the spreading velocity of the droplets on the solid surface and the wettability. The matrine OD prepared from emulsifier VO/03 had the most effective wettability and spraying properties, and it can be used for ultra-low-volume spraying and aerial application. This study offers new insights into the efficient use of plant-based pesticides.

**Keywords:** matrine; oil-based suspension concentrate; emulsifier; formulation; wettability; spray performance



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## 1. Introduction

Pesticides play a central role in preventing and controlling agricultural pests, weeds, and diseases and are thus an important means of improving agricultural production [1–4]. However, the pollution from pesticide residues is caused by the irrational use of chemical pesticides [5,6]. In contrast to synthetic pesticides, the development of environmentally friendly pesticides with high efficacy and low toxicity is crucial in ensuring the green and sustainable development of agriculture. The eco-friendly products represented by plant-based pesticides constitute important objectives for research and development in this field [7,8].

Matrine, a tetracyclo-quinolizidine compound, exists in various leguminous plants such as *Sophora flavescens* Ait., *S. alopecuroides* L., and *S. tonkinensis* Gapnep. Matrine is widely used in medicine to treat various diseases and can be used to control pests and diseases in agriculture because it has a wide spectrum of activities, including insecticidal, antibacterial, antifungal, and antiviral activities [9–13]. More significantly, matrine degrades easily in soil and water [14,15] and is nontoxic to nontarget organisms [16]. Therefore, matrine has attracted widespread attention as an environmentally friendly pesticide [17].

The fall armyworm (FAW, *Spodoptera frugiperda*) [18] is a major migratory pest. It can cause huge economic losses to corn, tobacco, and other crops after invasion and colonization [19,20]. The use of chemical pesticides to control *S. frugiperda* would not only rapidly produce resistance but would also create a series of environmental and ecological problems [21]. Therefore, it is particularly important to develop biopesticides such as matrine for FAW management.

Matrine is currently applied as a soluble concentrate (SL) formulation (it accounts for 88% of registered matrine pesticide varieties) [22] that is simple to process, safe, and convenient to use, and it has low toxicity and residue; however, this SL has a low utilization rate because of droplet vaporization, drift, and splash in the process of spraying [23]. Therefore, it is necessary to develop a matrine formulation with good wettability and strong deposition to improve the utilization rate and efficacy. An oil-based suspension concentrate (OD) has the advantages of high efficiency, safety, uniform droplets, and good wettability, and it can be directly used for ultra-low-volume spraying and unmanned aerial vehicles.

Emulsifiers play a key role in OD formulations, affecting their stability and wettability and even their application performance [24]. When the contact angle between the pesticide droplets and the leaf surface of the target plant is >90°, the leaf surface is hydrophobic, and the droplets can easily drop off, causing losses. Conversely, when the contact angle is <90°, the droplets can remain on the leaf surface [25], thus wetting the leaf and spreading on it. Liquid wettability on solid surfaces is used in areas such as oil recovery, waterproofing, and dyeing in agriculture [26]. A surfactant is added to a pesticide solution to wet the leaf surfaces and thereby delivers active ingredients to the plants, providing protection against pests and pathogens. Wetting agents are added to pesticide formulations to improve their wettability and to help reduce pesticide loss. Several emulsifiers can act as wetting agents to guarantee the stability of ODs and to improve the wetting properties [27]. Therefore, high-performance emulsifiers are required to improve the wettability of pesticide solutions while ensuring the stability of matrine ODs [28–31].

Improving wettability is recognized as an effective means of improving the rate of pesticide utilization. Additionally, the wetting state is not only related to the droplet size and diffusion rate but also the force of the droplet on the solid surface [32,33]. This study sought to achieve an optimal utilization rate of plant-based pesticide matrine and to reduce its negative impact on the environment. Three types of matrine ODs were prepared by using methyl oleate as a solvent oil and VO/02N, VO/03, and VO/01 as emulsifiers. The storage stability, wettability, suspension, viscosity, adhesion, spray performance, maximum retention, and indoor control effect of each type of formula were determined to evaluate the stability, wettability, and application performance of matrine ODs. Thus, this study could offer technical support for the development and utilization of efficient matrine formulation.

## 2. Materials and Methods

### *2.1. Experimental Materials and Instruments*

Matrine (80%) was purchased from Qingfengyuan Biologics Co., Ltd. (Bayannur, Inner Mongolia, China). Matrine soluble solution agent (SL; 1.0%) was made in the College of Horticulture and Plant Protection, Inner Mongolia Agricultural University (Hohhot, Inner Mongolia, China). Methyl oleate (solvent oil, the main component of matrine, is (*Z*)-9-octadecenoic acid methyl ester) solvent was purchased from Zibo Jinghe Biotechnology Co., Ltd. (Zibo, China). VO/01: the main component is 50% calcium dodecyl benzene sulfate (DBS-Ca) + 50% castor oil polyoxyethylene (BY-110); VO/02N: the main component is 50% calcium dodecyl benzene sulfate + 50% nonylphenol polyoxyethylene ether (OP-7); these two emulsifiers were purchased from Rhodia Feixiang Fine Chemicals Co., Ltd. (Zhangjiagang, China). VO/03: the main component is 50% calcium dodecyl benzene sulfate + 50% nonylphenol polyoxyethylene ether (OP-4); it was purchased from Cangzhou

Hongyuan Agrochemical Co., Ltd. (Cangzhou, China). Organic bentonite (thickener; the main component is montmorillonite), silica (stabilizer; the main component is $SiO_2$), and thickener and stabilizer were purchased from Kesai Agrochemical Holdings Co., Ltd. (Shandong, China).

### 2.2. Preparation of Matrine OD

A matrine OD was prepared according to the following formula ratio (calculated in 250 g): matrine, 21.9 g (7%); emulsifier (VO/03, VO/02N, or VO/01), 20 g (8%); thickener (organobentonite), 7.5 g (3%); stabilizer (silica), 5 g (2.5%); and solvent oil (methyl oleate), balanced for a total weight of 250 g. The ingredients were added into a beaker in their corresponding amounts, and the mixture was transferred into a sand mill (RTSM-0.2BJ, Shanghai Rute Electromechanical Equipment Co., Ltd., Shanghai, China) and ground at 10,000 rpm for 35 min until the particle size ($D_{50}$) was $\leq$5 μm.

### 2.3. Stability Test

The high- (54 ± 2 °C) and low-temperature (0 ± 2 °C) stability of different suspensions were tested to select the most suitable emulsifier for matrine ODs.

#### 2.3.1. High-Temperature Stability

The high-temperature stability test was operated according to the Chinese standard GB/T 19136-2021 [34]. Twenty grams of sample was added into the plug test tube and sealed. The samples were placed in a thermostat at (54 ± 2) °C for 14 days. The appearance of the solvent samples was observed, and the contents of the active ingredients were tested within 24 h.

The decomposition rate of the active ingredients was calculated according to Equation (1):

$$c = \frac{a - b}{a} \times 100\% \tag{1}$$

where

a—Effective content before high-temperature storage%;
b—Effective content after high-temperature storage%;
c—Decomposition rate of active ingredient%.

#### 2.3.2. Low-Temperature Stability

The low-temperature stability test was operated according to the Chinese standard GB/T 19137-2003 [35]. A total of 20 mL of matrine sample was sealed in a plug test tube and then stored at 0 ± 1 °C for 7 days. The appearance was observed after storage. Each sample was repeated four times.

#### 2.3.3. Suspensibility

According to Chinese standard GB/T 14825-2006, suspensibility refers to the content percentage of the active ingredient of a suspension compared to its original active ingredient after settling in a graduated cylinder of a specified height for a specified time [34]. The test was repeated three times.

Standard hard water (total concentration of $Ca^{2+}/Mg^{2+}$ is 500 mg/L) was also prepared according to Chinese standard GB/T 14825-2006.

#### 2.3.4. Viscosity

Viscosity was measured using an NDJ/SNB series rotary viscosimeter (28# rotor). Matrine OD (10 mL) was transferred into a sample cup and stirred at 40 rpm. The viscosity value was recorded when this had stabilized [36]. The test was repeated four times, and the average value was calculated.

## *2.4. Determination of Wettability*

### 2.4.1. Static Surface Tension (SST)

Surface tension is an essential property of liquids. Matrine SL and OD were diluted with deionized water 50-, 500-, and 1000-fold to form aqueous solutions (due to the low content of effective components in matrine SL, only 50-fold and 500-fold dilutions were used in this research), and the SST of each diluted solution was measured with an optical contact angle gauge (DSA-100, German KRUSS) [37]. Each sample was tested thrice, and the average value was calculated. The SST test was performed at 20 ± 1 °C.

### 2.4.2. Dynamic Contact Angle

To achieve a high utilization rate, droplets of the liquid pesticide must have an effective wettability to disperse and deposit rapidly on the leaf surfaces of the target plant. The dynamic contact angle of droplets on a solid surface is commonly used to determine the droplet wettability of pesticides [38,39]. The matrine OD was diluted 50-, 500-, and 1000-fold with deionized water. The solution was aspirated with a syringe needle of a $\varphi$ = 0.8 mm inner diameter, and the contact angle of each solution was measured with an optical contact angle measuring instrument, once per second for 0–4 min. The test was repeated four times, and the droplet shapes were photographed at 0, 1, 2, 3, and 4 min. The test was conducted at 20 ± 1 °C.

### 2.4.3. Droplet Density and Coverage

Water-sensitive test paper was used to determine the drip density. Three 3 × 4 cm water-sensitive test papers were fixed on tobacco leaves at different heights (10, 30, and 50 cm from the ground), and the matrine dilution was sprayed with a volume of 50 mL per 667 $m^2$ using a CNL-P05 sprayer (F110-03 nozzle); the spray height was 1.5 m. After spraying, the test paper was scanned (DJI MG-1/S/A/P, Shenzhen Dajiang Innovation Technology Co., Ltd., Shenzhen, China) [40], and the droplet deposition characteristics and coverage were calculated using droplet analysis scanner software (V1.2.4).

### 2.4.4. Maximum Retention

The tobacco leaves were cut into pieces and weighed ($m_0$) with an electronic balance. (Huifeng Green (Tianjin) Instrument Co., Ltd., Tianjin, China; the accuracy was 0.0001 g). Then, the leaf area (s) was measured with a leaf area meter (YMJ-B) (Zhejiang Top Instrument Co., Ltd., Hangzhou, China). The leaves (except the petioles) were completely immersed in the liquid for 10 s. The leaves were then suspended until the liquid stopped dripping; then, they were weighed ($m_1$) again [41]; each treatment was repeated 10 times. The maximum retention ($R_m$) of the leaves was calculated according to Equation (2):

$$R_m\ (\mathrm{mg/cm^2}) = (\mathrm{m_1} - \mathrm{m_0}) \times 1000/\mathrm{s} \times 100 \qquad (2)$$

## *2.5. Indoor Control Effect Test*

The control effect on *S. frugiperda* in tobacco was investigated at the Laboratory of the College of Horticulture and Plant Protection, Inner Mongolia Agricultural University (Hohhot, China). Test agents: 1.0% matrine SL (laboratory-made [42]) and 7.0% matrine OD (prepared in the laboratory, as above); deionized water was used as a control. Eight larvae (3rd instar) of *S. frugiperda* were cultured on tobacco leaves for 1 to 2 days, and the matrine dilution was sprayed at a dose of 50 mL/667 $m^2$ with a spray tower (PT-SL-12) [43]; each treatment was repeated four times. After 7 and 10 days of application, the number of live insects on each treated plant was checked, and the population decline rate and control effect were calculated according to the survey data.

*2.6. Determination of Adhesion Work and Adhesion Tension*

Adhesion work is a thermodynamic quantity reflecting adhesion strength. As a key factor, the adhesion strength is determined by the force between the molecules at the interface of the two phases [44].

The deposition rate of a pesticide spray correlates with the performance of the spray device, the surface tension of the pesticide droplets, and the surface free energy of the target plant. Additionally, the wettability of pesticides directly affects the deposition and diffusion of pesticide droplets on the plant leaf lamina. Therefore, understanding the interaction of pesticide droplets with the surfaces of target plants is critical. The difference between the adhesion work ($W_a$) of the droplets on the solid surface and the cohesive work ($W_c$) of the droplets determines the wetting process. $W_a$ depends on the contact angle, which is a visible dimension of the wettability of the solid. The adhesion tension ($\beta$) and contact angle ($\theta$) depend on the surface tension [45] ($\gamma_{LV}$) of the droplets and the solid interface. Using these parameters, the wettability of pesticide formulations and their aqueous solutions on certain solids can be predicted. The SST and contact angle of a solution on a solid were measured after 30 s with a DSA-100 optical contact angle gauge (Kruss, Germany). Adhesion tension and work may be calculated according to Equations (3) and (4), respectively:

$$B = \gamma_{LV} \times \cos\theta, \quad (3)$$

$$W_a = \gamma_{LV}(1 + \cos\theta) \quad (4)$$

where $\gamma_{LV}$ is the surface tension of the solution and $\theta$ is the contact angle.

## 3. Results and Discussion

*3.1. Influence of Emulsifiers on the Stability of Matrine OD*

The appearance of the matrine ODs prepared with different emulsifiers before and after high-temperature storage and cold storage did not observably change (Figure 1); so, the cold storage stability and high-temperature stability were qualified in appearance.

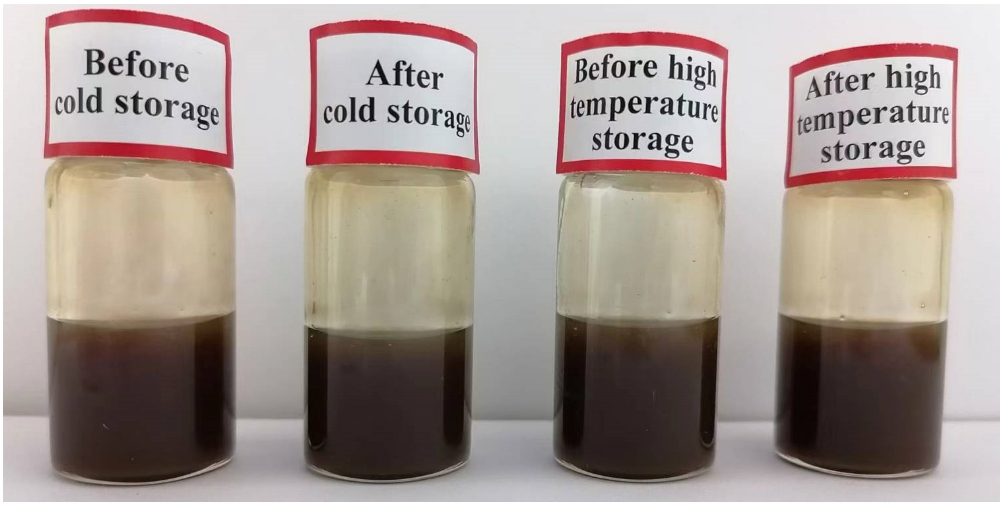


**Figure 1.** Appearance characteristics of matrine ODs.

No significant changes occurred in the active ingredient content and pH values of the matrine ODs prepared with different emulsifiers before and after high-temperature storage (Table 1). As the high-temperature stability of the pesticide formulas agreed with the national standard, the three types of emulsifiers could be used for preparing matrine ODs. The optimal emulsifier needs to be identified by the wettability of different matrine OD formulations.

**Table 1.** Influence of different emulsifiers on the high-temperature stability of matrine OD.

| Emulsifier | Usage of an Emulsifier | pH | | Active Ingredient Content (%) | | |
|---|---|---|---|---|---|---|
| | | Before High-Temperature Storage | After High-Temperature Storage | Before High-Temperature Storage | After High-Temperature Storage | Decomposition Rate (%) |
| VO/02N | 8% | 6.69 | 6.76 | 7.24 | 7.10 | 1.84 |
| VO/03 | 8% | 6.48 | 6.50 | 7.89 | 7.67 | 2.79 |
| VO/01 | 8% | 7.84 | 7.79 | 7.62 | 7.48 | 1.84 |

### 3.2. Suspensibility

Suspensibility is an important quality indicator that reflects the physical stability of pesticide suspensions. The high suspension rate can maintain the consistency of the concentration of the liquid sprayed by the pesticide, evenly deposit it on the target, and provide better efficacy [34,46,47]. Before heat storage, the suspensibility of the OD prepared with the three types of emulsifiers was >95% (Table 2), and it agreed with the relevant provisions of the national standard. Small variations were present in the suspensibility after 14 days of high-temperature storage at 54 ± 2 °C, but the three types of suspensions retained a high degree of suspensibility and were less affected by the elevated temperature (54 ± 2 °C), indicating that the three types of emulsifiers met the requirements of suspensibility for matrine ODs.

**Table 2.** Effect of different dosages of emulsifier on the suspensibility of preparation.

| Name of an Emulsifier | Use Level (%) | Suspensibility (%) | |
|---|---|---|---|
| | | Before High-Temperature Storage | After High-Temperature Storage |
| VO/02N | 8% | 99.09 | 98.25 |
| VO/03 | 8% | 99.33 | 98.89 |
| VO/01 | 8% | 99.17 | 98.64 |

### 3.3. Viscosity of Suspension

Emulsifier performances are critical to the stability of ODs; in addition to stabilizing the emulsion, the property of the emulsifier also determines the difficulty of emulsion formation and the functional properties of the final product [48]. Although a higher viscosity equates to a more stable suspension, too high a viscosity may adversely affect the preparation process and the use of the product. Consequently, a suitable viscosity is important to meet the requirements of stability and convenience. Among the three emulsifiers, the viscosity of VO/03 was significantly lower than that of VO/02N and VO/01 (Figure 2).

### 3.4. Wettability of Pesticide Droplets

The wetting behavior of ODs on the hydrophobic interface was evaluated by the surface tension and contact angle. The surface tensions of the matrine ODs made with the three types of emulsifiers were significantly lower than those of the matrine SLs and the control (deionized water), indicating that the added emulsifier may reduce the surface tension of the suspension (Figure 3). In addition, the surface tension decreased with the dilution multiple of the suspension. The surface tension of the suspension formulated with emulsifier VO/01 was significantly higher than those of the suspensions formulated with VO/02N, VO/03, and matrine SL, indicating that the wettability of the suspension with emulsifier VO/01 was poor. At the low dilution multiples (50-fold), the surface tension of the suspension formulated with VO/03 was the lowest (30.5 mN/m), while at the highest dilution multiples (1000-fold), the surface tension of the suspension formulated with VO/02N was significantly lower than those of the others, showing that emulsifier

VO/02N had greater diluent efficiency. Thus, the emulsifiers VO/02N and VO/03 both had good surface activity.

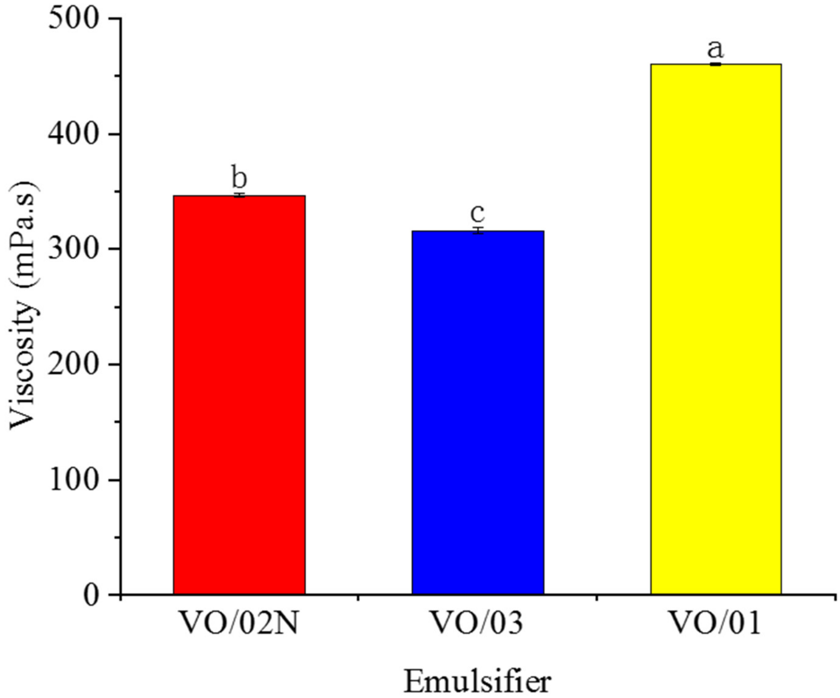


**Figure 2.** The effect of three emulsifiers on the viscosity of matrine ODs. Note: different lowercase letters indicate data that are significantly different between the same rows at the 0.05 level; the same is the case below.

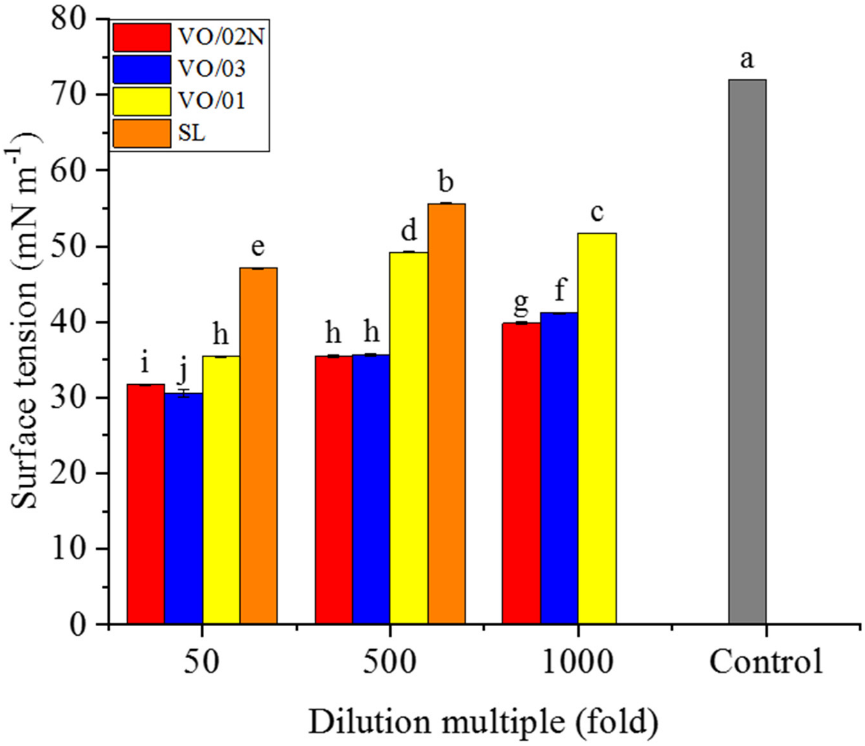


**Figure 3.** Effect of different dilution multiples of emulsifier solutions on the surface tension. Note: Different lowercase letters indicate data that are significantly different between the same rows at the 0.05 level.

The surface tensions of the suspensions formulated with emulsifier VO/02N and VO/03 were relatively similar, but the contact angle of the suspension formulated with VO/03 was less than that of the suspension formulated with VO/02N. This may be because the component of surface tension of the suspension formulated with VO/03 was closer to that of the solid surface free energy, and the interaction force between the pesticide droplet molecules and the foliage was reduced, thereby reducing the contact angle [49,50].

The contact angle is another important indicator in the assessment of the hydrophilicity and hydrophobicity of the suspension. It can intuitively reflect the wettability of pesticide droplets and the spreading and retention of droplets on the target surface, which is crucial to the improvement of the efficiency of pesticides [51]. The contact angle of the pesticide diluent varies with the change in the dilution multiple and the duration of the wetting times (Figure 4). The contact angles of the ODs made with VO/02N, VO/03, and VO/01 were significantly lower than those of the matrine SLs and the control (deionized water). The dispersion area of the suspension droplets grew gradually with the test time and spread out rapidly as the dilution multiple decreased. Under the same dilution multiple, the initial contact angle and equilibrium contact angle (i.e., the contact angle after 4 min) of the suspension formulated with VO/03 were less than those of the suspensions formulated with VO/02N, VO/01, or SL, indicating that the suspension formulated with emulsifier VO/03 had greater wettability on the hydrophobic interface. In particular, at low dilution multiples (50-fold), the contact angle of the suspension formulated with VO/03 was 40.3° at the start of the test and 7° at the end of the test, which was significantly lower than those of the other formulations, indicating that the suspension formulated with emulsifier VO/03 had good wettability and could spread quickly on the hydrophobic interface. Overall, considering the effects of the four emulsifiers on the surface tension and contact angle, emulsifier VO/03 had the most effective wettability, and the prepared matrine OD was easier to disperse and spread on the hydrophobic interface.

Based on the oil suspension stability and viscosity test results, the suspension formulated with emulsifier VO/03 had effective stability and wettability and lower viscosity. Thus, emulsifier VO/03 was the optimum emulsifier for the matrine OD.

Pesticide droplet atomization is an essential enabler of pesticide dose transfer. This is a key step in improving the utilization rate of pesticides and the target deposition efficiency of pesticide droplets [52]. Therefore, it is essential to explore the droplet deposition process for pesticide reduction and efficiency [53]. Consequently, we measured the effects of the three emulsifiers on droplet deposition (Figure 5). The average coverage of the suspension formulated with VO/03 was 18.3%, and the droplet density was 151 per $cm^2$. The droplet density and coverage of the suspension formulated with VO/03 were significantly higher than those of the other treatments and controls, although the coverage rate among the four preparations at the bottom of the crop (10 cm above the ground) did not significantly differ. Additionally, the droplet density and coverage rate among the treatments on the tobacco leaves at different heights did not significantly differ (except for the suspensions prepared with VO/01 and SL), indicating that emulsifier VO/03 had good wettability and could be uniformly deposited on tobacco leaves at different heights. Emulsifier VO/03 also increased the number of droplets and improved the droplet coverage rate, thereby improving the spray effect and achieving the best control effect. This result was consistent with the wettability measurement.

Although the droplet density and coverage of the suspension formulated with emulsifier VO/03 at different heights were significantly higher than those of the other treatments, the droplet density and coverage of the same agent did not differ at different heights. This may be because smaller tobacco plants were used in this experiment and because the indoor test was less affected by environmental factors (e.g., temperature and wind speed).

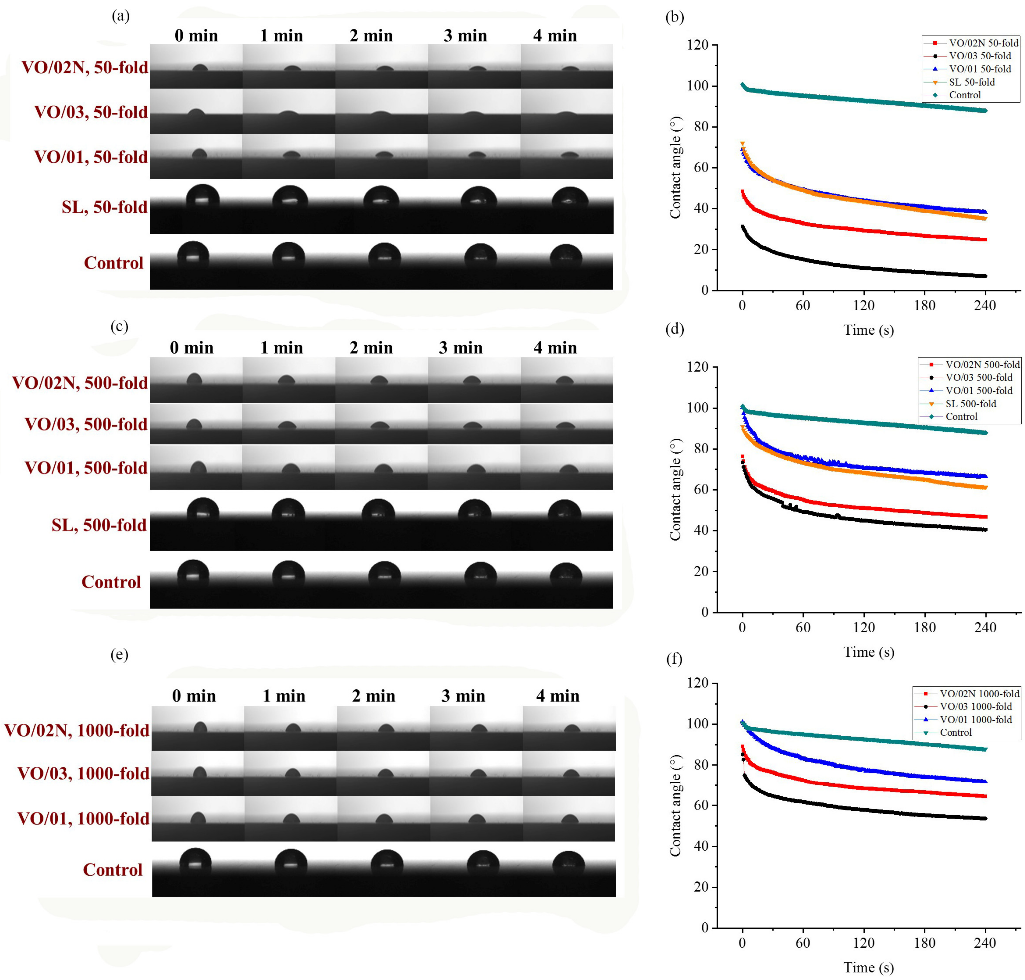


**Figure 4.** Contact angles of different dilution multiple of emulsifier solutions. (**a**,**b**) 50-fold diluted solution, (**c**,**d**) 500-fold diluted solution, (**e**,**f**) 1000-fold diluted solution.

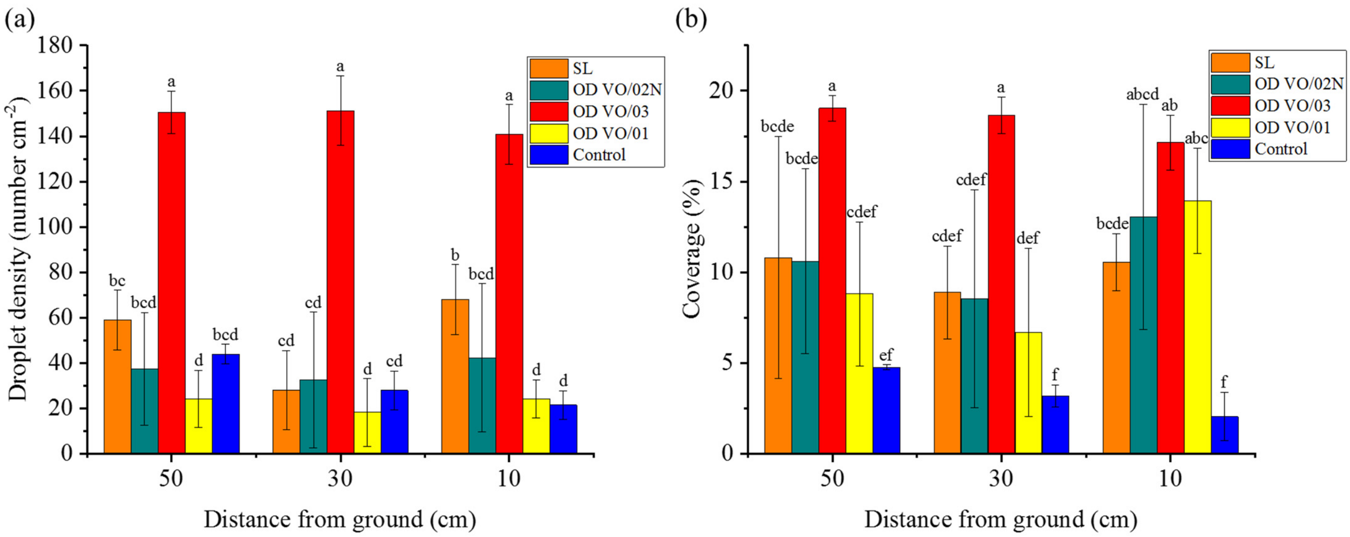


**Figure 5.** Distribution and coverage of spray droplets. (**a**) Droplet density, (**b**) Coverage. Note: Different lowercase letters indicate data that are significantly different between the same rows at the 0.05 level.

### *3.5. Maximum Retention of Matrine OD Droplets*

Increasing the retention level of the pesticide solution can help pesticide droplets to effectively wet the surface of plant leaf lamina, which can improve the contact probability between pesticides and pests. The retention of each preparation was higher than that of the water control (Figure 6). Among them, the retention of the suspension formulated with VO/03 was the highest, and it was significantly higher than that of the matrine SL or the suspension formulated with VO/02N. This indicated that emulsifier VO/03 had good wetting properties and could quickly spread droplets to the surface of the plant leaf lamina to achieve optimal activity.

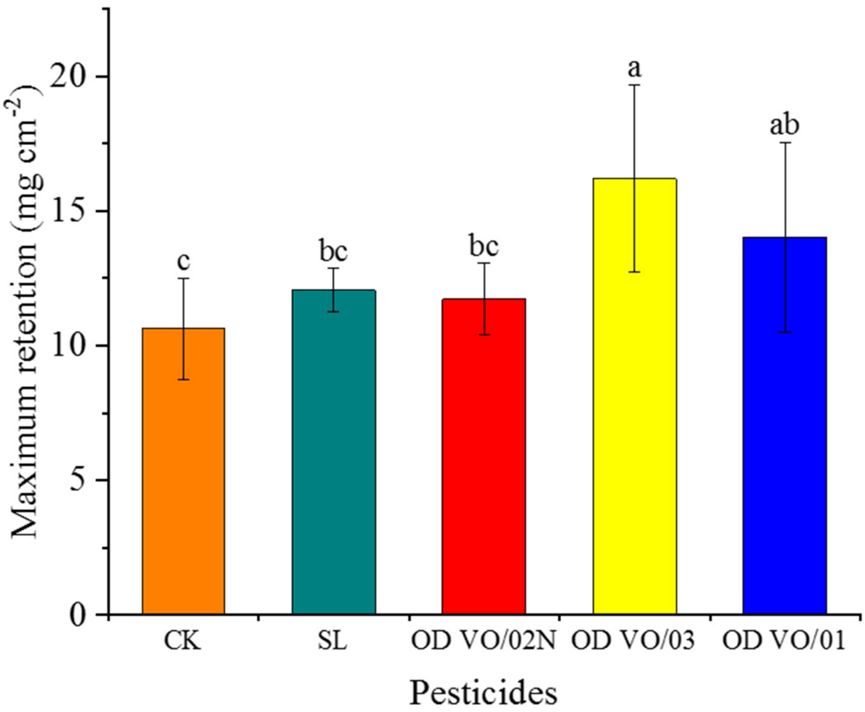


**Figure 6.** Maximum retention of each pesticide. Note: Different lowercase letters indicate data that are significantly different between the same rows at the 0.05 level.

A smaller surface tension will produce more retention of the pesticide formulation. In this study, the matrine OD formulated with VO/03 had the smallest surface tension and contact angle, and the maximum retention was also significantly higher than that of the matrine SL or the suspension formulated with VO/02N. However, the surface tension and contact angle of the suspension formulated with VO/01 were much higher than those of the suspensions formulated with VO/03 or VO/02N. Furthermore, the suspension formulated with VO/01 had a maximum retention second only to the suspension formulated with VO/03, and no significant difference was present in the maximum retention between the suspension formulated with VO/01 and the suspensions formulated with VO/03 and VO/02N. Considering the high viscosity of the suspension formulated with VO/01, it is speculated that the viscosity is another important factor affecting the maximum retention [41,54,55].

### *3.6. Pharmacodynamic Test*

Matrine had a specific control effect on *S. frugiperda* (Table 3). Seven days after application, the control effect of the suspension formulated with VO/03 on *S. frugiperda* was the highest (77.78%), although the difference between the treatments was insignificant. Ten days after application, the control effect of the suspension formulated with VO/03 on *S. frugiperda* was significantly higher than that of the suspensions formulated with VO/01 or matrine SL. Overall, the suspension formulated with VO/03 had the best control effect and demonstrated high persistence. This may be attributed to the good wettability and spray performance of emulsifier VO/03, which reduced the bounce and splash of the droplets during the deposition process, enabling the deposition of the active ingredients on the target crop leaves and insects to the greatest extent.

**Table 3.** Control effect of matrine on *S. frugiperda*.

| Treatment | Active Ingredient Rate (mL/hm$^2$) | Days after Treatment | | | |
|---|---|---|---|---|---|
| | | 7 d | | 10 d | |
| | | Population Decline Rate (%) | Efficacy (%) | Population Decline Rate (%) | Efficacy (%) |
| CK | - | 15.63 | - | 18.75 | - |
| SL | 50 | 71.88 | (66.66 ± 2.48) a | 68.75 | (61.54 ± 0.61) b |
| OD VO/02N | 50 | 75.00 | (70.37 ± 12.10) a | 72.39 | (65.50 ± 7.66) ab |
| OD VO/03 | 50 | 84.38 | (77.78 ± 8.55) a | 78.13 | (73.08 ± 7.69) a |
| OD VO/01 | 50 | 70.83 | (65.43 ± 8.56) a | 66.67 | (58.97 ± 2.18) b |

Note: Data are presented as mean ± SE; different lowercase letters indicate data that are significantly different between the same rows at the 0.05 level.

### *3.7. Wetting Mechanism of Matrine OD Droplets*

The effects of the three types of emulsifiers on the adhesion work ($W_a$) of the suspensions of varied dilution multiples are shown in Figure 7. Overall, the adhesion work increases with the decrease in the pesticide solution dilution multiple. The $W_a$ of the suspension formulated with emulsifier VO/03 significantly increased with the increase in *Wa*, which increased the adhesion force of the droplets on the solid surface. The $W_a$ of the suspension formulated with emulsifier VO/01 was greater than that of the suspension formulated with emulsifier VO/02N at high dilution multiples (1000-fold), but the opposite was the case at low dilution multiples (50-fold). The $W_a$ increased slowly as the dilution multiple decreased. The greater the adhesion work, the more easily and completely the droplets wet the solid surface. Based on the $W_a$, the matrine OD formulated with emulsifier VO/03 had better wettability on a hydrophobic interface.

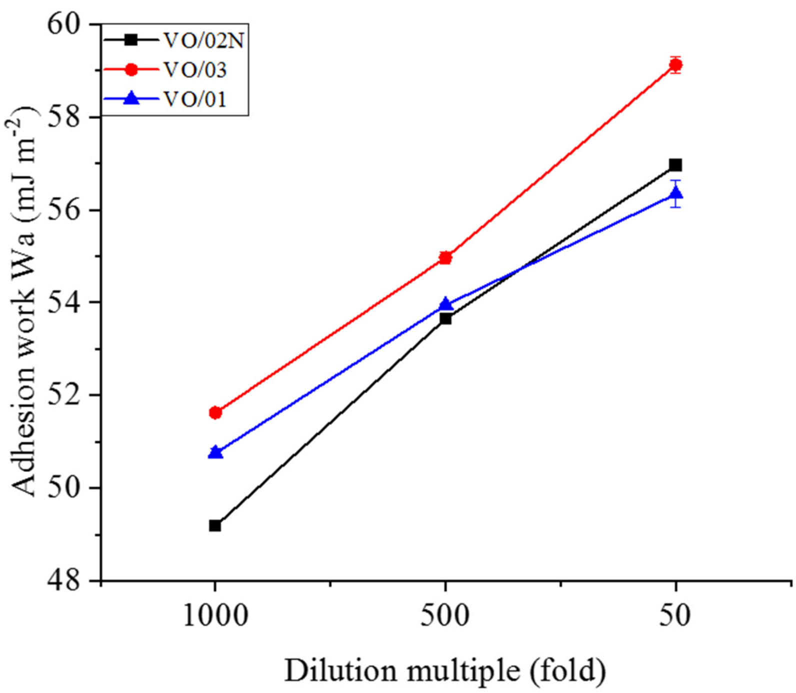


**Figure 7.** Effect of three emulsifiers with different dilution multiples on adhesion work ($W_a$).

The wetting behavior of pesticide droplets is widespread and has been used in many fields, especially for super-hydrophobic surfaces [56–58]. To better assess the wetting behavior of matrine ODs on a hydrophobic interface, the Wenzel equation and Cassie–Baxter model were used to study the relationship between the surface tension, contact angle, and adhesion tension of the dilution ratio of the suspension and the type of emulsifier (Figure 8). The wetting of pesticide droplets on solid surfaces can be divided into three stages. In the first stage, when the suspension is highly diluted (1000-fold), the droplets exhibit a non-wetting (Cassie–Baxter) state because an adsorption film has not yet been formed and the interfaces are super-hydrophobic [59–62]; the surfaces are generally rough, and the wetting and spreading of the droplets are likely to be influenced by surface flaws. During the diffusion process of the droplets, when the contact line comes across these flaws, the pinning force will prevent it from moving [59,63], providing an unsaturated adsorption membrane. At this point, the surface tension value is greater, and the adhesion tension is smaller. Such a super-hydrophobic test interface prevents the droplets from wetting and dispersing and is not conducive to adhering droplets to the solid phase interface. In the second stage, when the dilution of the suspension is reduced to a 500-fold dilution, the droplet gradually changes from a non-wetting (Cassie–Baxter) state to a wetting (Wenzel) state [41]. With the increase in the number of emulsifier molecules, the surface tension and contact angle gradually decreases, and the adhesion tension gradually increases. This may be due to the formation of an unsaturated adsorption film on the solid surface by the pesticide droplets, although these decreases or increases are slight. At this point, the droplets gradually break through the pinning effect of the target surface and replace the air layer in the three-dimensional structure, producing a semi-permeable process that effectively adheres to the solid surface. In the third stage, with a further decrease in the dilution ratio of the suspension (50-fold), a large number of emulsifier molecules are deposited on the solid phase interface, and the droplet completely breaks through the air layer in the three-dimensional structure and penetrates the depression of the solid surface to form a strong adhesion force. The droplets expand rapidly on the solid surface, achieving almost complete wetting while overcoming the pinning force and wet resistance force. At this point, the droplets exhibit a state of complete wetting (Wenzel).

Among the three types of emulsifiers, the VO/03 suspension had the highest adhesion tension and lowest surface tension and contact angle, whereas the adhesion tension, contact angle, and surface tension varied most significantly with the decrease in the dilution multiples. A clear turning point was present at the 50-fold dilution, showing that the wettability process of the suspension formulated with emulsifier VO/03 was sensitive to its dilution multiple. Thus, emulsifier VO/03 is the optimum matrine OD for wettability.

Previous studies have shown that OD is more homogenous for use in spraying and increased coverage on target leaf surfaces; thus, it notably reduces the pesticide dosage and the risk of pesticide pollution of the environment. Here, the formulation, wetting, and spray performance of matrine ODs were studied, and matrine products with favorable performances were developed, providing a new method for the green and efficient utilization of matrine plant pesticides.

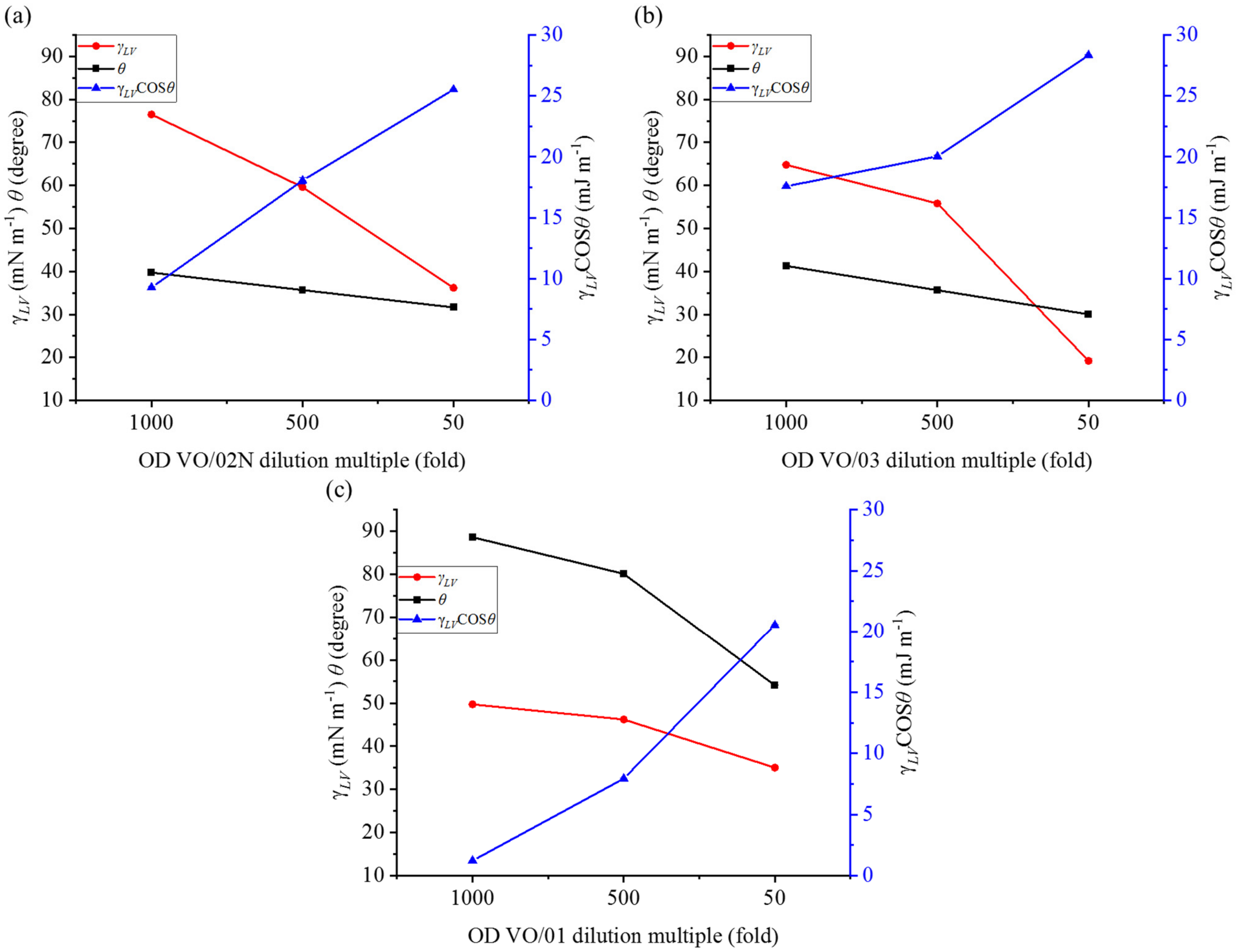


**Figure 8.** Relationship between the three emulsifiers and surface tension $\gamma_{LV}$, contact angle $\theta$, and adhesion tension $\gamma_{LV}$ cos$\theta$ of preparation at different dilution multiples. (**a**) OD VO/02N, (**b**) VO/03, (**c**) VO/01.

## 4. Conclusions

OD is a popular pesticide formula that has favorable wettability, strong adhesion, resistance to rain erosion, and a good utilization rate and is appropriate for ultra-low-volume and aviation spraying. In the absence of barrel additives, the change in pesticide formulation performance mainly depends on the selected emulsifier. Therefore, we selected three types of emulsifiers to prepare three matrine ODs and evaluated their stability, viscosity, suspension and wettability, spray performance, maximum retention, and control effect. These three types of emulsifiers improved the stability, wettability, and spray performance of the matrine ODs. Among them, the suspension formulated with emulsifier VO/03 had the most effective wettability, spraying performance, and control effect on *S. frugiperda*. The optimal formula for a matrine OD was determined as follows: matrine 21.9 g (7%); emulsifier (VO/03) 20 g (8%); thickener organobentonite 7.5 g (3%); stabilizer silica 5 g (2.5%); and solvent oil (methyl oleate), balanced for a total weight of 250 g.

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