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Effect of Adjuvants on the Wetting Behaviors of Bifenthrin Droplets on Tea Leaves

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Abstract: The hydrophobic epicuticle wax on fresh leaves of tea tree (Camellia sinensis (L.) O. Kuntze) leads to the loss of pesticide droplets, reducing efficacy. In this study, four adjuvants were selected to improve the diffusion and adhesion of bifenthrin droplets on the surface of tea leaves at different growth stages. The coupling effect of bifenthrin and adjuvants on the time-dependent and concentration-dependent wettability of droplets was investigated, and the difference in the wettability between bud and leaf was explained by observing the surface morphology. It was found that adjuvants effectively reduced the contact angle of droplets and accelerated the diffusion speed, and the above phenomenon became obvious with the increase in the adjuvant concentration. The wetting promotion of young leaves was more significant due to the reduced epicuticle wax and the greater roughness compared with fresh buds. The surface tension of the pesticide mixture was negatively correlated with the cosine of contact angle after adding the four adjuvants regardless of the growth stage of tea leaves. The contact angle of 0.2% Silwet L-77 decreased to 0° within 10 s, but the extreme wettability led to the decrease in adhesion with the increase in concentration. However, the wettability and adhesion on the surface of tea leaves were simultaneously suitable with more than 0.1% nonionic surfactant. The minimum concentration of the optimal adjuvant proposed in this study can provide an experimental basis and guide more efficient plant protection in tea gardens.

Keywords: adjuvant; bifenthrin droplet; contact angle; tea leaf; surface wetting; adhesion

1. Introduction

Pesticides and fertilizers are widely used in agricultural production due to their substantial agronomic and economic benefits [1]. The effective adhesion and diffusion of pesticide droplets on the surface of leaves can improve the efficiency of pest control [2]. However, pesticide droplets can easily fall off and poorly adhere because of the fluff and wax on tea leaves used to protect the buds against environmental damage and reduce transpiration [3]. Ineffective spraying occurs when pesticides insufficiently deposit on the hydrophobic surface of tea leaves [4]. Although increasing the spray quantity is preferred to improve the pesticide solution deposition in tea gardens, it can lead to serious pesticide wastage. As a consequence, excessive pesticides will increase the risk of residual pesticides in tea and cause environmental pollution [5].

Recently, spray additives have played an important role in the reformation of pesticide formulation and the control of crop pests. Jankú et al. [6] pointed out that spray adjuvants can significantly improve the wettability of droplets and increase deposition on target crops by altering the physical properties of pesticides, thus effectively reducing pesticide consumption [7,8]. Furthermore, as the major spray additives used in tea protection, surfactants [9,10], emulsified oils [11], and polymers [12,13] are widely used to promote diffusion by reducing the surface tension of droplets and the leaf–droplet interfacial tension caused by a special molecular adsorption property [14].
In recent decades, many scholars have focused on the effect of different additives on the spray deposition of various plant targets. For example, Van Zyl et al. [15] experimentally evaluated six different surfactants and oil adjuvants to improve foliar spray deposition. The results indicated that adjuvant concentration is essential for adequate deposition compared to other components. However, inadequate concentrations may not achieve the diffusion effect, which is required for the improvement of deposition volume and quality. Holloway et al. [16] quantitatively examined the retention and coverage of 10 commercially available tank-mix adjuvants on pea (Pisum sativum L.) and barley (Hordeum vulgare L.) leaves at different growth periods. Surfactants, especially silicone, caused the largest increase in spray coverage on both surfaces of pea and barley leaves compared with the emulsifiable oil and film former. Meanwhile, a study evaluated the dispersion and evaporation of single 300 mm diameter droplets amended with four spray adjuvants at different concentrations on four types of surfaces (abaxial and adaxial leaflet surfaces, petiole, basal stem) of soybean (Glycine max (L.) Merr.). The results showed that droplet-wetted areas increased with the increase in adjuvant concentrations nonlinearly and differed on the four surfaces: the abaxial surface had the largest wetted area, followed by the adaxial surface, the petiole, and then the basal stem [17]. Furthermore, Lin et al. [18] compared the wettability of pesticide droplets deposited at different positions (paraxial and distal to the veins, midvein, and secondary vein) on eucalyptus leaves and concluded that the wetted area was a minimum on the midrib, and the wetted area on the secondary vein was slightly larger than that on the interveinal area.

Adjuvants have positive effects on the wetting behaviors of pesticides, which can be attributed to chemical and physical characteristics. Furthermore, adjuvants can change the physicochemical properties of pesticide solutions, such as viscosity and surface tension [19]. The mechanism of the wetting state has been widely discussed by investigating the behavior of surfactant adsorption under equal conditions [14]. Cowles et al. [20] found that the surface tension of liquids substantially decreased with the increase in methylated silicone due to its superior surfactant properties. Solutions with a surface tension below 23 mN/m caused over 90% mortality of two-spotted spider mite (Tetranychus urticae Koch) in leaf dip bioassays. Decreased surface tension can increase the ratio between droplet coverage area and the amount of spray liquid required, reducing spray application rates and improving efficiency [21].

However, because of the complex physicochemical interactions between different pesticides and target crops, the effect and mechanism of adjuvants on the wettability of droplets vary from case to case. Presently, there is limited research on the wettability of tea leaves based on special pesticides and tea surface morphology. It is noted that the proportions of new buds and old leaves in tea trees vary with the seasons. New buds remain dormant in autumn and winter and germinate in spring [22]. Therefore, it is necessary to select a suitable type, concentration, and dosage of additives for specific application conditions.

Bifenthrin, a pyrethroid insecticide commonly used in tea gardens, has a broad insecticidal spectrum, low toxicity, low dosage, and short residual period. It can effectively control tea pests, such as lepidopteran larvae, small green leafhopper (Empoasca flavescens Fabricius), tea aphid (Toxoptera aurantii Boyer), and other tea garden pests [23]. For this compound, as well as most currently commercialized pesticides used in tea trees, little information is available on the investigation of the combined effects of leaf surface morphology and adjuvants on wetting behaviors.

The objective of this study was to investigate the effect of different types and concentrations of adjuvants on the wettability of bifenthrin droplets on the surface of tea leaves. Fresh buds and young leaves were chosen for the comparison of the surface morphology of tea leaves at different growth stages. Furthermore, this study proposed a method to improve the pesticide deposition on the surface of tea leaves to improve their plant protection efficiency in tea gardens.
2. Materials and Methods

2.1. Tea Type and Surface Morphology

The Rizhao green tea (bush-type tea tree with evergreen leaves), grown in Shandong Province, China, was used in this study. Among them, both mature leaves and new buds occur simultaneously on the tea tree. The mature leaves of this tea species are mostly elliptical, with leaf teeth on the margin of leaves. The surface structure at the interveinal area, secondary veins, and midrib on both the adaxial and abaxial surfaces can be clearly identified. Puckering on the leaves forms valleys along the veins on the adaxial surface and ridges on the abaxial surface [24]. The tea buds are curled, with a smooth membranous waxy layer on the front and fine fluff on the back (Figure 1).

![Image of tea leaves](image-url)

Figure 1. Fresh bud and young leaf on the canopy of tea tree.

Since the young leaves and buds on the tea canopy are the raw materials for tea manufacturing (Local Standard of Shandong Province, China: DB37/T 2709-2015 Product of Geographical Indication Rizhao Green Tea), they are the key targets for pesticide spraying during plant protection operations of Rizhao tea gardens in Shandong Province, China [24]. In addition, the fluff and wax on the surface of tea leaves will gradually fall off with the expansion of buds, resulting in higher hydrophobicity of fresh buds and young leaves than mature leaves. Therefore, it is necessary to improve the wettability and adhesion between fresh leaves and pesticide droplets.

Fresh leaves and buds growing on the same branch of the Rizhao green tea were picked for the wetting test. Then, the leaf surfaces were washed using deionized water and air-dried to ensure the freshness and cleanliness of the samples [25]. This was performed to prevent the change in surface microstructure caused by water evaporation and surface dust, which may affect the deposition of pesticide droplets on the surface. The surfaces of tea leaves and buds were observed with a 3D laser scanning microscope (KEYENCE, Osaka, Japan) with 400× magnification. Roughness was determined using VK Analyzer software to describe the leaf surface morphology in detail [26].

The leaf samples were placed flat on a glass slide, and the laser point of the lens was aimed at the region to be observed, avoiding the midrib and secondary vein. Three leaves and buds were selected, and three laser points were taken from each sample for repeated observations. Image-profile measurement (VK Analyzer) was used to analyze surface roughness in expert mode. A measurement area of 100 µm × 100 µm was randomly selected after noise detection, and the tilt correction value and surface roughness value were automatically obtained by the system. The measurement of each picture was repeated six times to obtain the mean and standard deviation.
2.2. Pesticide and Adjuvants

The pesticide used in this study was bifenthrin, 2-methylbiphenyl-3-ylmethyl(Z)-(1RS)-cis-3-(2-chloro-3,3,3-trifluoroprop-1-yl)-2,2-dimethylcyclopropanecarboxylate [27]. The dilution ratio of 10% bifenthrin EC ranged from 1:1000 to 1:6000 (V_water/V_10% bifenthrin EC = 1000–6000) based on the National Standard Guideline for the safe application of pesticides (GB/T8321.2-2000) [28]. Here, bifenthrin EC with a dilution factor of 3000 was used as the control group to explore the effects of different concentrations and types of additives on the wettability of droplets on the surface of tea leaves.

Details of the composition and source of the adjuvants used for the evaluation are summarized in Table 1. Each additive was mixed into a 10% bifenthrin diluent with concentration gradients of 0.01%, 0.05%, 0.1%, and 0.2% (3000 times bifenthrin diluent + 0.01%, 0.05%, 0.1%, and 0.2% adjuvants). Each sample (15 mL) was prepared in a centrifuge tube and used within 24 h to prevent the deactivation and decomposition of the reagents.

Table 1. Details of selected adjuvants listed.

| Trade Name | Registration Holder | Main Ingredient | Type | Possible Properties |
|------------|---------------------|-----------------|------|---------------------|
| Silwet L-77 | Momentive, USA      | Polyethoxylated heptamethyl trisiloxane | Organosilicone surfactant | Spreader |
| 6501       | Lion Brand, Singapore | Coconut oil diethanolamide | Nonionic surfactant | Detergent |
| JFC        | Hai-an, China       | Fatty alcohol polyoxyethylene ether | Nonionic surfactant | Penetrant |
| Greenwet 720 | Green-times, China | Compound oil | Emulsifiable oil | Anti-drift additive |

2.3. Surface Tension and Viscosity

The surface tension of the bifenthrin diluent with four adjuvants of four concentrations was measured using the Attension Sigma700 surface tension meter (Biolin, Göteborgu, Sweden). A highly sensitive balance was used to analyze the stress changes of the fully wetted platinum sheet when it was slowly immersed and pulled out from the liquid surface based on the Wilhelmy plate method to measure the surface tension of the solution accurately. The vessel filled with liquid was placed in a water bath at 25 °C to maintain a constant temperature during the measurement.

The NDJ-8S rotational digital viscometer (LICHEN, Shanghai, China) was used to determine the viscosity of the adjuvant—10% bifenthrin EC mixture. The No. 0 rotor with a viscosity range of 0–100 mpa·s was selected to accurately calculate the shear rate and low viscosity of the samples because of the large diameter of the cylindrical rotor. The rotor speed and conversion factor were set to 60 r/min and 0.1 mpa·s, respectively.

A total of 18 mixture samples were used during the experiments to obtain the surface tension and viscosity, which included four adjuvants of four concentrations, 3000 times solution of 10% bifenthrin EC, and pure water. Each sample was measured five times to ensure the repeatability of experiments, and the mean and standard deviation were obtained. Experimental data were analyzed by one-way analysis of variance (ANOVA), and differences in means were determined with Tukey’s honestly significant difference test (Tukey’s HSD) using IBM SPSS Statistics 26 software, with adjuvant type and concentration as class variables and individual measurements as samples. All significant differences were determined at the p = 0.05 level.

2.4. Contact Angle

Contact angle (θ) is the angle from the solid–liquid interface through the liquid interior to the gas–liquid interface at the junction of solid, liquid, and gas [29]. Contact angle is an important parameter for characterizing a surface and predicting its behavior in applications involving wettability and adhesion [30,31]. The surface is hydrophilic when θ is lower...
than 90°; otherwise, it is hydrophobic [32]. Here, the contact angle formed by a pesticide
droplet with an additive on the surface of tea was measured from side images of the droplet
profile, which was monitored as a function of time using the JC2000D3K contact measuring
instrument (POWEREACH, Shanghai, China). The instrument, experimental sample, and
measurement method are shown in Figure 2. Before the measurement, the tea leaves were
cut into strips of 5 mm × 300 mm (avoiding the main veins) and fixed flat on the glass
slide to make them shorter in the optical path direction, which was necessary to avoid light
blocking caused by uneven samples.

Figure 2. Schematic diagram of contact angle measurement process.

The microsyringe was placed above the leaf sample, and a sufficient volume of the
liquid droplet (3–5 µL) was formed at its tip by adjusting the control knob. The sample
platform was then slowly raised, and the measurement started once the droplet was gently
deposited on the leaf sample. After droplet deposition, the images were captured by a
charge-coupled device (CCD) camera at 0, 5, 15, 30, 60, and 90 s. JC2000D software was
used to calculate contact angles through the five-point fitting method (Figure 2). The five
points included two endpoints (a, b) on the contact line and three points (b, c, d) on the arc
line, ensuring that the baseline coincided with the contact line.

Each measurement was repeated three times by setting other droplets at different
positions on the same strip of leaf sample. The specific dripping positions are marked in
the upper right corner of Figure 2. The contact angle values of the 18 mixture samples
(four adjuvants at four concentrations, bifenthrin diluent, and pure water) on tea leaves at
two growth stages (fresh bud and young leaf) were obtained. Each mixture sample had
18 contact angle values on each surface, including six recording time points (0, 5, 15, 30, 60,
and 90 s) for three repetitions.

3. Results and Discussion
3.1. Surface Morphology and Roughness of Tea Leaves

The images of the fresh bud and young leaf observed by a 3D laser scanning micro-
scope are shown in Figure 3. The fresh bud had a stronger surface light reflection and a
smoother flat film-like waxy layer compared to the young leaf. In contrast, the surface of
young leaves had a larger roughness value, with wrinkled ridge-shaped cuticular folds,
which was caused by the falling process of the waxy layer and the maturing process of
the leaf venation, along with the growth of the tea leaves. Similarly, previous studies have
also shown that the total wax content of the surface of tea leaves is highest in fresh buds,
followed by young and mature leaves [33].
Table 2. Surface tension of bifenthrin diluent mixed with adjuvants in different concentrations.

| Concentration (%) | Surface Tension (mN/m) a |
|-------------------|--------------------------|
|                   | Silwet L-77 | 6501 | Greenwet 720 | JFC |
| 0                 | 45.436 (±0.473) a |  |
| 0.05              | 25.106 (±0.025) b | 27.400 (±0.030) b | 34.438 (±0.353) b | 43.897 (±0.499) b |
| 0.1               | 21.759 (±0.042) c | 26.939 (±0.032) bc | 32.980 (±0.130) c | 40.394 (±0.197) c |
| 0.2               | 21.087 (±0.044) d | 26.787 (±0.042) c | 31.759 (±0.063) d | 34.895 (±0.054) d |
|                   | 20.727 (±0.058) d | 26.848 (±0.017) c | 30.505 (±0.098) e | 32.805 (±0.070) e |
| F b               | 9631.434 | 5956.842 | 1874.348 | 1169.046 |
| DF                | 4 | 4 | 4 | 4 |
| p-value           | <0.0001 | <0.0001 | <0.0001 | <0.0001 |

a Means ± standard error (n = 5) followed by a different lowercase letter in each column are significantly different at p = 0.05 according to Tukey’s HSD. b ANOVA model: F-test statistics; DF—degree of freedom.

The surface tension of pure water was reduced by about 38% with bifenthrin, and the value tended to decrease as the adjuvant concentration increased. The minimum addition of selected additives can rapidly and significantly decrease the surface tension value. The trend gradually stabilized when the concentration was more than 100 ppm (0.01%). The surface tension of all additive mixtures approached the minimum when the concentration reached 1000 ppm.

The critical micelle concentration (CMC) of the mixed solution is the concentration corresponding to the inflection point where the surface tension value rapidly drops and gradually remains stable with the increase in concentration. The surfactant molecules can be enriched on the surface of the solution at an extremely low concentration due to the amphiphilic structure, resulting in an instantaneous drop in the surface tension of the mixed solution. The additive molecules do not aggregate on the surface with increased concentration but associate with each other in the solution to form a micelle suspension, preventing the surface tension of the mixed solution from further decreasing.
Although the surface tension values of the four adjuvants had similar trends, their variation ranges and gradients were quite different. For instance, the pesticide solution amended with a trace amount of trisiloxane Silwet L-77 decreased to the lowest surface tension value with the fastest speed among the four adjuvants with increasing concentration. A small amount of 6501 can rapidly reduce the surface tension of the pesticide mixture to below 27 mN/m. The compound oil Greenwet 720 and the nonionic surfactant JFC had a relatively weaker ability to reduce the liquid surface tension. In general, the effect of the nonionic surfactant molecule on the surface tension of the bifenthrin mixture was greater than with an oil adjuvant. Among the surfactants, the effect was greater in the organosilicon surfactant than in the nonionic surfactant.

The viscosity values of the mixed solution at different additive concentrations are listed in Table 3. After the same column of data, different lowercase letters indicate significant differences in \( p = 0.05 \) according to Tukey’s HSD. Clearly, although the viscosity of the bifenthrin solution varied significantly with concentrations of adjuvants, there was no clear trend in changes to it with increasing concentrations of the adjuvants. Therefore, the wetting and adhesion characteristics of the droplets mixed with the above adjuvants (surfactants and oil) on the surface of tea leaves were independent of the viscosity of the liquid. Most mechanistic studies of the underlying viscosity-induced wettability have focused on polymer additives. Polymer additives can significantly change the viscosity of liquids at very low addition levels [34]. Bertola [35] proposed the wetting mechanism of polymer droplets and concluded that the rebound of droplets was prevented by the dissipative force, which was generated from the polymer molecules stretching on the contact line. As a result, the deposition of droplets subsequently increased on the hydrophobic surface.

### Table 3. Viscosity of bifenthrin diluent mixed with adjuvants in different concentrations.

| Concentration (%) | Viscosity (mpa-s) \(^a\) | Silwet L-77 | 6501 | Greenwet 720 | JFC |
|-------------------|--------------------------|-------------|------|-------------|-----|
| 0                 | 0.982 (±0.007) ab        | 0.982 (±0.007) b | 0.982 (±0.007) a | 0.982 (±0.007) a |
| 0.01              | 0.956 (±0.014) c         | 0.954 (±0.016) c | 0.956 (±0.010) b | 0.976 (±0.008) ab |
| 0.05              | 0.968 (±0.012) bc        | 0.926 (±0.008) d | 0.976 (±0.010) a | 0.978 (±0.010) ab |
| 0.1               | 0.974 (±0.010) bc        | 0.928 (±0.007) d | 0.948 (±0.007) b | 0.958 (±0.012) bc |
| 0.2               | 1.003 (±0.006) a         | 0.998 (±0.011) a | 0.982 (±0.009) a | 0.946 (±0.010) c |

\( F \) \(^b\): 10.385, 41.484, 11.981, 10.051

\( DF \): 4, 4, 4, 4

\( p\)-value: 0.000102, <0.0001, <0.0001, 0.000126

\(^a\) Means ± standard error \((n = 5)\) followed by a different lowercase letter in each column are significantly different at \( p = 0.05 \) according to Tukey’s HSD. The comparisons between lowercase letters in the same column are statistically significant. \(^b\) ANOVA model: F-test statistics; DF—degree of freedom.

### 3.3. Contact Angle of Bifenthrin Droplets with Adjuvants on Tea Leaves

The images of the pure water droplet deposited on the surfaces of the fresh bud and young leaf of tea photographed by the optical contact angle measuring device \( (\theta_1 = 108.649^\circ, \theta_2 = 93.791^\circ) \) are shown in Figure 4. The steady state of the droplet could be due to the equilibrium of three interfacial tensions \( (\gamma_{sl}, \gamma_{lg}, \gamma_{sg}) \) at the junction of solid, liquid, and gas phases. The surface of the fresh bud was more hydrophobic with poorer wettability than the young leaf. Although the pure water droplets on the surface of the young leaf could not easily roll off, the contact area was not large enough to achieve a good wetting effect. This was due to the difference in the shape and thickness of wax on the surface of tea leaves of different ages. The thick and smooth hydrophobic waxy layer on the fresh bud increased the contact angle of pure water droplets on the surface.
Different types of adjuvants can further reduce the contact angle and accelerate the diffusion of droplets on the surface of tea leaves. Yu et al. [37] investigated two surface states based on the diversity of phenotypic genes in different leaves: wax deposition without hairs and hairy surface. The microroughness increased with increasing glandular trichomes, and then caused the wide spread of droplets.

The hydrophobic waxy layer gradually fell off with the growth of fresh buds, making it easy for adjuvant droplets to wet the surfaces. Moreover, with the increase in solid–liquid area under the droplet and around the contact line, the influence of adjuvant adsorption on the contact angle increased. Since the contact area between the adjuvant droplets and the rough leaf surface was larger than that of the smooth bud surface, the amplification effect of adjuvants on the wetting of young leaves was greater.

Previous studies have also shown that the surface morphology of target leaves was an important factor in wetting behaviors of pesticides by changing the rebound of droplets and spray run-off. Koch and Barthlott [36] assessed the superhydrophobic and superhydrophilic surfaces of plants and pointed out that cell sculptures and fine surface structure, such as folding of the cuticle or epicuticular waxes, can influence the wetting of plants. Yu et al. [37] investigated two surface states based on the diversity of phenotypic genes in different leaves: wax deposition without hairs and hairy surface. The microroughness increased with increasing glandular trichomes, and then caused the wide spread of droplets.

Among the four adjuvants, the contact angle of droplets with trisiloxane organosilicon Silwet L-77 decreased the most significantly with the change in concentration. According to the points corresponding to the initial time in Figure 5a,b, compared with the other three additives, the initial contact angle was the largest when the additive amount was small but decreased rapidly when the amount was more than 0.05%. The other three additives at the minimum concentration (0.01%) significantly decreased the contact angle of droplets at 0 s (65 ° ± 2.5°), but the decrease in the contact angle was not obvious, as the concentration increased at this moment. This result could be because the trisiloxane surfactant molecules with low concentration diffused inside the droplet and accumulated on the surface of the droplet at a slower rate than the other three additives.
Figure 5. Contact angles of 10% bifenthrin diluent with different concentrations of four adjuvants on the surface of fresh bud (a,c,e,g) and young leaf (b,d,f,h).
Moreover, Silwet L-77 and nonionic surfactant 6501 significantly decreased the contact angle of droplets on the surface of tea leaves over time, but there were differences between the above two adjuvants. The droplets mixed with Silwet L-77 rapidly expanded within 5 s, and the range of the contact angle greatly changed with the concentration. For instance, the pesticide droplets could only expand to a contact angle of about 60° at the 0.01% concentration, indicating partial wetting. Moreover, the contact angle could be rapidly reduced to 0° at the 0.2% concentration, indicating complete wetting. The concentration at this moment exceeded the critical wetting concentration (CWC) of Silwet L-77, a concentration above which a transition from partial wetting to complete wetting occurred at spreading over moderately hydrophobic surfaces [38]. This concentration was different in the leaves of the two growing stages due to the different surface morphology of the fresh bud and young leaf of tea. Similarly, some previous studies on rough surfaces also reported a similar phenomenon [33,39].

The contact angle of bifenthrin droplets with 6501 also rapidly decreased with time, reaching 47 ± 1.5° at a low addition amount (0.01%). As the concentration increased to 0.2%, the contact angle gradually decreased but did not decrease to an extreme state (0°) like Silwet L-77. The diffused trend of droplets with JFC and Greenwet 720 was similar. The droplets spread significantly within 15 s, after which the contact angle value decreased slightly, and the shape of droplets remained stable.

The wetting phenomenon of adjuvants is related to their ability to reduce the surface tension of the mixed solution. The increased Silwet L-77 can rapidly reduce the surface tension of the mixture to the lowest value, leading to its extreme wetting and spreading ability. The critical micelle concentration (CMC) of Silwet L-77 surfactant was lower than that of the other kinds of trisiloxane surfactants in the past determination [20], indicating that lower surface tension can be achieved through a small addition. The relatively higher surface tension of the bifenthrin mixture of Greenwet 720 and JFC at each concentration (Table 2) resulted in the equilibrium of droplets at larger contact angles than the other two surfactants.

### 3.4. Relationship between the Surface Tension and Contact Angle

According to the characterization of the balanced relationship between the three-phase interfacial tension ($\gamma_{sl}$, $\gamma_{lg}$, $\gamma_{sg}$) and the cosine value of contact angle ($\cos\theta$) in Young’s equation [40]:

$$\gamma_{sg} - \gamma_{sl} = \gamma_{lg} \cos\theta$$

the $\cos\theta$ formed by the deposition of droplets on tea leaves has a certain relationship with the surface tension of liquid. Here, the surface tension of the pesticide mixture (x value variable) and the $\cos\theta$ (y value variable) of droplets with four adjuvants deposited stably (60 s) on the surface of tea leaves at different concentrations were analyzed by regression. The fitted images and regression equations are shown in Figure 6.

There was a negative linear correlation between the two variables at the $p = 0.05$ level after adding the four adjuvants regardless of the growth stage of tea. The $\cos\theta$ value decreased with the increasing surface tension of the mixed solution. Moreover, the contact angle of adjuvant droplets on the fresh buds was larger than that on the young leaves under the same concentration, making the fitting straight lines representing the fresh buds below those representing the young leaves. The larger the absolute value of the slope of the fitted straight line, the more sensitive the $\cos\theta$ value changes with the surface tension of the mixed solution. Theoretically, the corresponding surface tension would be the minimum value required for the mixed droplets to spread on the surface of tea leaves if the straight line is extended to $\cos\theta = 1$. 

Figure 6. Relationship between $cos \theta$ and the surface tension of liquid. Each point represents the corresponding value of the four adjuvants at different concentrations. The straight line is the fitted image, and the specific equation is marked in the upper right corner of each figure: (a) Silwet L-77; (b) 6501; (c) JFC; (d) Greenwet 720.

Among the four graphs in Figure 6, the slope of the (b) line had the largest absolute value, indicating that the pesticide with nonionic surfactant 6501 can achieve the maximum reduction of the contact angle within the minimum change in surface tension. Compared with the other three adjuvants, the continuous extension of the straight red line (leaf) corresponds to the maximum surface tension value at the intersection of $cos \theta = 1$ (26.183 mN/m). It is predicted that when the surface tension is reduced to 26.183 mN/m, the droplets will completely spread on young leaves, and a smaller value (25.84 mN/m) is required for fresh buds.

3.5. Adhesion Tension and Work between Bifenthrin Droplets and Tea Leaves

The wetting process of pesticides on the surface of tea leaves can be divided into adhesion and spreading [41]. Whether pesticide droplets can effectively adhere to the surface of tea leaves is the key to the automatic wetting process. Moreover, not only the effective attachment but also the rapid diffusion of droplets is required to enhance pesticide efficacy, achieving the large coverage area and ideal plant protection effect.

The change value of the free energy $\Delta G$ during the wetting process can be calculated as [42]:

$$|\Delta G| = \gamma_{sg} + \gamma_{lg} - \gamma_{sl} = W_a$$  \hspace{1cm} (2)

$W_a$ represents the adhesion work, which is the minimum work required to pull the contacted solid and liquid away from the interface. The adhesion work reflects the binding capacity at the solid–liquid interface. The larger the $W_a$ value, the stronger the solid–liquid
bond. The adhesion tension reflects the wetting ability between solid and liquid, which can be calculated as:

$$\beta = \gamma_{sl} - \gamma_{sg}$$  \hspace{1cm} (3)

The larger the value is, the better it is for wetting.

The adhesion tension $\beta$ and adhesion work $W_a$ can be deduced from the relationship between the equilibrium contact angle and three interfacial free energies in Equation (1):

$$\begin{cases} \beta = \gamma_{lg} \cos \theta \\ W_a = \gamma_{lg}(1 + \cos \theta) \end{cases}$$  \hspace{1cm} (4)

The adhesion tension and adhesion work can be used to evaluate the wettability and adhesion of the adjuvant droplets when the surface tension of the mixture and the contact angle of droplets on the surface of tea leaves are available. The relationship between wetting and adhesion in adjuvant solutions can be obtained through this method [43].

The trends of the adhesion tension and work of bifenthrin droplets with different adjuvants on the surfaces of the fresh bud (a) and young leaf (b) changing with the concentration are shown in Figure 7. The adhesion tension value was negative when no adjuvants were added, indicating that the bifenthrin diluent was difficult to wet on the surface of tea leaves. Adding a small amount of adjuvant (0.01%) can rapidly increase the adhesion tension to a positive value and improve the wetting and spreading behavior of droplets. In addition, the adhesion work decreased with the increasing additive concentration, indicating that the adsorption between the droplets and tea leaves decreased with the improved wettability of the bifenthrin solution; that is, the pesticide can be easily lost from tea leaves.

![Figure 7](image-url)

**Figure 7.** Adhesion tension and adhesion work of bifenthrin droplets with different adjuvants on the surfaces of the fresh bud (a) and young leaf (b) vary with the concentration.
Therefore, the adhesion between droplets and tea leaves should also be considered in selecting adjuvants to improve the retention of pesticides. The bifenthrin droplets with organosilicon surfactant Silwet L-77 can rapidly spread on the surface of young leaves in a short time (Figure 8). However, it can easily cause the loss and waste of the pesticide due to the small adhesion work between the droplets and tea leaves. The bifenthrin diluent containing surfactant 6501 and JFC can show better wettability and adhesion on the surfaces of the fresh bud and young leaf, with a lower cost than Silwet L-77, resulting in better economics for large-scale pesticide spraying operations in tea gardens. Moreover, the adhesion tension and work tend to be stable when the concentration is greater than 0.1%. A similar phenomenon was observed in Zhu’s analysis of the adhesion of surfactant TX-100 droplets to the surface of rice (Oryza sativa) leaves. With the concentration increased around CMC, the adhesion tension stopped changing significantly [14]. The ideal wetting and adhesion effect can be achieved at this concentration, preventing pesticide residue in tea caused by excessive active agent content.

| Concentration (%) | 0s | 5s | 15s | 30s | 60s | 90s |
|-------------------|----|----|-----|-----|-----|-----|
| 0.01%             | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| 0.05%             | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |
| 0.1%              | ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) | ![Image](image16.png) | ![Image](image17.png) | ![Image](image18.png) |
| 0.2%              | ![Image](image19.png) | ![Image](image20.png) | ![Image](image21.png) | ![Image](image22.png) | ![Image](image23.png) | ![Image](image24.png) |

Figure 8. Deposition status of bifenthrin droplets with different concentrations of Silwet L-77 on the surface of young leaves over time.

4. Conclusions

Adjuvants can effectively reduce the contact angle and accelerate the spreading of bifenthrin droplets on the surface of tea leaves. Additionally, the wetting behavior of bifenthrin droplets varies with the type and concentration of adjuvants and is significantly affected by the change in tea surface morphology. Less hydrophobic wax and greater roughness on the leaf surface make it easier for adjuvanted bifenthrin droplets to wet the surface of young leaves than the fresh buds. However, in the above two growth stages, the same adjuvants have similar influences on the changing trend of the contact angle.

The contact angle decreases with the increase in adjuvant concentration. The wettability change is mainly due to the surface tension of the pesticide mixture altered by additive molecules. The trisiloxane surfactant is much better than the other three additives in reducing the surface tension of the bifenthrin diluent. The pesticide droplets with 0.2% Silwet L-77 can completely spread on tea leaves within 15 s. However, this extreme wetting phenomenon reduces the binding force between the two-phase molecules, leading to the loss of pesticides.

In contrast, the bifenthrin droplets with more than 0.1% nonionic surfactants 6501 and JFC have the desirable wettability and adhesion on the surfaces of fresh buds and young leaves. Moreover, the above two nonionic surfactants are cheaper than Silwet L-77, resulting in better economics for large-scale pesticide spraying operations in tea gardens. This study provides a strategy for spreading pesticides onto the hydrophobic surfaces of plants, thus improving their utilization rate and the effect on insect pest control.
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