Wettability on plant leaf surfaces and its effect on pesticide efficiency

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Abstract: A productive and sustainable agricultural system is essential to the existence of human beings. Although current agricultural practices can produce enough food for feeding nearly eight billion people, they cannot continue to do so sustainably without technological advancement. The amount of resources used in agriculture is staggering. Over three billion tonnes of crops are produced globally each year, requiring nearly four million tonnes of pesticides, 2.7 trillion cubic meters of water (about 70% of all freshwater consumptive use globally). How to improve the efficiencies of pesticides is a mostly concerned topic in sustainable agriculture. Wettability of plant leaf surfaces for retention, adsorption, and filtration of atmospheric pollutants, interception of precipitation, infection of pests and diseases have important implications. Therefore, understanding the interaction between the droplet and target crop leaf surface have significantly influences on pesticide utilization and pest control efficiency. This article summarizes the influences of leaf surface composition, morphology, and external environmental factors on leaf wettability. The chemical composition and structure of leaf surfaces are internal causes, including foliar wax content and morphology, foliar villus quantity, morphology and distribution, stomata and epidermal cell morphology and size, and leaf moisture status. External factors include pesticide composition and pesticide spraying methods that can also influence wettability. As a comprehensive result of the three-phase action of solid, gas, and liquid, wettability is the micro-foundation of understanding the plant interface relationship.

Keywords: wettability, pesticide efficiency, pesticide application, crop leaf morphology, leaf surface

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1 Introduction

Pests and weeds are associated with crop production, bringing great harm to agricultural production, and the data released by the Food and Agriculture Organization of the United Nations show that pests and weeds cause the world to lose a large amount of food each year, or about a third of its total output[1-2]. The use of chemical pesticides is an important method to control pests and weeds[3]. Norman E Borlaug, a Nobel laureate and renowned wheat breeder, said “without chemical pesticides, humans are at risk of starvation.” China is a large agricultural country with frequent occurrences of diseases and insect pests in the course of agricultural production. It is worth noting that, as the world’s largest producer and user of pesticides, the use of chemical pesticides per unit area in China is 2.5 to 5 times higher than the world’s average[4]. The threat of pesticides to environmental pollution and food safety is common in society. However, pesticides, as the most important and direct means of plant protection, can be sprayed to recover huge economic losses every year. Although pesticides can control diseases and insect pests, and bring many benefits to agriculture, pesticides and their metabolites are biotoxic and easily reside on the surface of agricultural products. Due to non-regulated uses of pesticides, the pesticide drift loss becomes serious, and the problem of not effective utilization of pesticides has attracted wide attention from general public. In China pesticide uses have many problems, such as high pesticide delivery and low effective utilization rate. Only 20% to 30% of the pesticide droplets sprayed can be deposited on the surface of crop leaves, which is much lower than the average of 50% in the developed countries[5]. The low efficiency in pesticide uses not only leads to a large amount of pesticide waste, but also causes a large amount of pesticide to be drifted to the non-target environment, resulting in plant, human and animal poisoning, environmental pollution, and the increase of pesticide residue in agricultural products. In the 1980s, the concept of pesticide utilization was developed internationally. The pesticide utilization rate refers to the proportion of the amount of pesticide deposited on the target to the total amount of pesticide used[6], that is, the deposition ratio:

Pesticide Utilization Rate = ([Amount of Pesticides Deposited on Crops]/[Total Amount of Pesticides Applied])×100%

The pesticide solution is liquid and spread over the surface of the crop leaves, thus realizing the infiltration and transmission of the effective components of the pesticides, so that the crop can be protected from the invasion of pests. Generally speaking, the whole farmland crop is regarded as the target, and the part of pesticide deposited on the crop is regarded as effective quantity. Studies have shown that a large amount of liquid in the leaf surface
or gather and lose, or bounce and fall, so that in the atmosphere, soil and water environment enrichment, seriously endanger the ecological environment. Therefore, detecting the effective wetting of pesticide droplets on crop surface is important to control the pesticide dosage\(^7\). By studying the effect of the wettability of plant leaves on the utilization ratio of pesticides, the utilization ratio of pesticide preparations should be greatly improved, the loss of pesticide preparations in use has been reduced, the dosage of pesticides has been reduced, the cost of processing, packaging, transportation and use of pesticide preparations has been reduced, and the cost have been remarkably reduced.

Therefore, the key technology is whether the pesticide can adhere to the leaf surface of the target crop and spread and deposit it quickly. This is of great significance to the efficient and rational use of pesticides, and is also the key technology to further improve the efficiency of pesticide use\(^8\). However, in practice, the pesticide solution is difficult to adhere to and spread on the surface of most crop leaves\(^9,10\). For example, the solution is difficult to adhere to rice, wheat, kale and other plant leaf surface and roll down, so pesticide utilization rates for these crops are low.

![Figure 1](image)

Figure 1  Schematic diagram of pesticide utilization

Finally, we need to consider the following problems: first, we need to find out some characteristics of pesticide solution itself (such as critical micelle concentration), correctly and scientifically grasp the mixed ratio of pesticide solution to water, dilute the solution to the optimum concentration, so as to improve the transfer efficiency of effective component metering in the solution; second, we need to observe the surface morphological characteristics of target crops, explore the micro-structure of leaf surface and the influence of surface free energy on the wettability of leaves; third, we need to find out the behavior of pesticide droplets on the leaf surface and the basic conditions for the wetting, spreading and holding of the solution on the leaf surface. Therefore, this paper explains the influencing factors of the wettability of plant leaf surface from the above three aspects, and the summary of these scientific research results is of guiding significance for our correct, reasonable and scientific uses of pesticides.

![Figure 2](image)

Figure 2  Scheme of pesticides wettability on plant leaf and pesticide efficiency

### 2 Determination of wettability and test methods

#### 2.1 Criteria

When the droplet is in contact with the surface of the object, the droplet is often not completely spread on the surface of the object, but forms a certain angle with the surface of the object, that is, the contact angle. The contact angle refers to the tangent of the gas-liquid interface made at the gas, liquid and solid three-phase intersection points. The angle between the liquid side and the solid-liquid junction line is a measure of the degree of wetting\(^11\). Usually, the contact angle can be measured in a more intuitive way. The wetting process is related to the interfacial tension of the object, when the liquid falls to equilibrium on the surface of the horizontal object, the formed contact angle and the interfacial tension are in accordance with the young’s formula below. Young’s formula describes the quantitative relationship between surface contact angle and surface tension between solid, liquid and gas\(^12\).

\[
\gamma_{sv} = \gamma_{sl} + \gamma_{tv} \cos \theta
\]

where, \(\gamma_{sv}\), \(\gamma_{sl}\) and \(\gamma_{tv}\) respectively represent the interfacial tension at the solid-gas, solid-liquid and liquid-gas interfaces, and represents the contact angle at the equilibrium state.

#### 2.2 Common Test Methods

There are many methods for measuring contact angle, which are roughly divided into angle measurement, force measurement and length measurement, but the accuracy, advantages and disadvantages of various methods are quite different\(^13\). The angle measuring method is simple and can be used to measure the droplet shape directly. The force measurement method obtains the contact angle by measuring the force, and the length measurement method obtains the contact angle by measuring the droplet shape size\(^14\). In the study of leaf wettability, angle measurement is the most commonly used contact angle measurement method\(^15\). The principle is to use various methods to directly observe the shape of the stable equilibrium droplet on the surface of the object, and to measure the angle indicated by the definition of contact angle. The operation step is to drop the droplet directly on the surface of the object or blow a small bubble at the solid-liquid interface, take the photo directly or then use the angle to determine the contact angle\(^16\). The method has the advantages of intuition, and has been sold at home and abroad.

![Figure 3](image)

Figure 3  Definition of Contact Angle

Although the measurement of contact angle seems relatively simple, it is difficult to get accurate and consistent measurement results because of the influence of many factors, such as surface roughness, surface adsorption capacity, gravity action, surface pollution situation, reading time, temperature and so on. In ecological studies, although some scholars have studied the wettability of plant leaves, the volume of droplets used by different researchers in the determination of contact angle ranges from 0.2 to 50 \(\mu\)L\(^17\). For conifers, the surface of leaves is small and generally small droplets are used. Broad leaf can be measured by...
larger droplets, but the contact angle of hydrophobic surface will be reduced under the influence of gravity, and the change of contact angle of hydrophilic surface is not obvious\textsuperscript{18}. A large number of studies have shown that the contact angle measured when the droplet volume is 1-10 μL is independent of the droplet volume\textsuperscript{19}.

Figure 4 Liquid wetting test card by Yuan et al

2.3 Testing of wettability of pesticide solution

Many farmland crops have undergone long-term evolutionary optimization, resulting in a variety of leaf surface structures suitable for survival, such as convex hulls, pits, stripes, grids, etc\textsuperscript{20}. These structures are crucial to the crops themselves, and it is these surface features that pose a variety of difficulties for pesticide sprays. The use of pesticides not only requires that the liquid medicine can adhere to the plant surface, but also can automatically spread to achieve the maximum coverage area, so as to achieve the best control effect\textsuperscript{21}. Plant wettability is very important to improve the utilization rate of pesticides and has become a research hotspot in recent years. Researchers studied the wettability of crops from various angles, such as contact angle, surface tension, spreading area, maximum leaf load and so on. It is generally believed that the larger the contact angle, the stronger the hydrophobicity of the leaf surface. The worse the wettability, the easier it is for the pesticide liquid roll down from the blade, resulting in the lower utilization ratio of pesticide. However, the smaller the surface tension, the better the wettability. Xu et al have shown that the contact angle decreases linearly with the decrease of the surface tension on the surface of PTFE\textsuperscript{22}. The hydrocarbon surfactants studied by Yuan Huizhu found that only when the surface tension decreased to a certain extent, the contact angle of the liquid on the leaf of the crop began to decrease significantly\textsuperscript{23}. As long as the concentration of new surfactants, such as carbon fluoride surfactants, reaches the critical micelle concentration (CMC), the contact angle of the liquid solution on the leaves will decrease rapidly\textsuperscript{24}. The larger the spreading area, the better the wettability. However, these determination methods all require specific instruments, which are usually not convenient for use in the field, especially not suitable for the rapid determination of the wetting of the solution on the surface of various crops by the pesticide sprayer in the field. Yuan et al designed a test card for the wettability of pesticide solution and evaluated its performance\textsuperscript{25}. It is concluded that the surface tension of the liquid and its contact angle on different crops can be reflected by spreading the liquid on the test card.

3 Factors influencing wettability of pesticide on plant leaf surface

3.1 Effects of plant leaf structure on wettability

The microstructure of plant leaf surface is closely related to the wetting and spreading of pesticide droplets on its surface.

3.1.1 Wax

Plant wax is a thin white layer covering the surface part of plant leaves. This structure can prevent excessive transpiration of water in leaves and invasion of mesophyll cells by microorganisms, which plays an important role in plants resistance to stress. However, wax is usually hydrophobic, since its main chemical components are the lipids of higher fatty acids and higher monohydric alcohols. The contact Angle is generally between 94°-109°. Therefore, the presence of waxy layer and the thickness of waxy layer directly affect the wettability of plant leaf surface.

As early as 1985, Haines et al\textsuperscript{26} found that locust and tulip trees with waxy covering on the leaf surface of plants had higher contact angles, while the leaves of brassica chinesis is with low waxy covering had smaller contact angles. Takamatsu et al\textsuperscript{27} also found that the wax content on the leaf surface of Japanese cedar changed due to the influence of different habitats and the extension of the growing season. In polluted environment, wax content decreased and wettability increased, while that of biennial cedar decreased and wettability increased compared with that of annual cedar. Steens’s group focus on the effect of wax content on wettability of plants. They found that the amount of waxy content in leaves would affect the behavior process of liquid droplets on the leaf surface, and liquid droplets were prone to spring and roll on the leaf surface with high wax content\textsuperscript{28}. According to Yang xiaodong’s result\textsuperscript{29}, bead-like waxy particles were found on the surface of doge’s tail grass and barngrass under scanning electron microscope, which resulted in their large contact angle and determined their hydrophobic characteristics. Wang huixia et al\textsuperscript{30} also found that the leaf contact angle of most species decreased significantly after the removal of epidermal wax, especially those with strong hydrophobicity. However, the contact Angle increased after wax removal on the back of poplar, peach tree, and huian tree. The increase in contact angle of species after waxy removal from leaf surfaces is generally less than 100°. The change of contact Angle after the removal of waxy leaf surface is related to the organic solvent destroying the leaf surface structure, physical properties, and the porous structure generated on the leaf surface.

3.1.2 Fluff

Leaf villi are the thinnest, softest, and most abundant structure in plants. For example, dandelion accounts for 95%-98% of the total wool fiber. The entire thickness of the pile is consistent. It has different shapes, such as curved, spiral, straight, curled, etc., making the duvet feel fluffy and dense, and forming a protective layer in the duvet that air is not easy to circulate. In 2002, Jiang lei\textsuperscript{31} research group of the Chinese academy of sciences further discovered that there were nano-structural hairs on the micron mastoid on the lotus leaf surface, and the multi-stage micro/nano structures and waxes on the lotus leaf surface led to the superhydrophobic and self-cleaning functions on the lotus leaf surface. Smith\textsuperscript{32} observed the leaf surface of soybean and found that wettability was related to the number and distribution mode of villi on the leaf surface. When there was less villi on the leaf surface, the contact angle on the leaf surface was small; when the leaf surface was covered with villi, the contact angle was large, resulting in high hydrophobicity. Through a large number of experiments, Neinhuis\textsuperscript{33} found that the wettability of leaf surface was affected by the villi, especially whether the villi surface was waxy. Generally speaking, there are two kinds of situations: in the dry environment, the number of fluff on the leaf surface of the plant is large, while in the humid environment, the number of fluff on the leaf surface of the plant is less, showing the opposite trend.
Moreover, the impact of environmental pollution will also affect the morphological dispersion density and quantity of foliar villi.

![The positive surface of aster foliage leaves](image1)
![Positive surface of flax blade of the chrysanthemum](image2)

**Figure 5** Plant leaves with fluff

### 3.1.3 Stomatal density

Stomata is the main outlet for water vapor to be discharged from from in vivo to in vitro during transpiration. They are also the channels through which photosynthesis and respiration interact with the outside air, thereby affecting the processes of transpiration, photosynthesis, and respiration and others. Stomata usually exist in the above-ground parts of the plant, especially on the leaf epidermis, and can also be seen on young stems and petals, but most submerged plants do not. Stomatal density and distribution have a great impact on plant life activities and are also one of the important reasons for the difference in wettability of plant leaves. It was found that the front and back of plant leaves have different wettability. Generally, the back contact angle is higher than the front contact angle, which showed the same trend with the distribution characteristics of stomata. Brewer and Nuñez observed that the denser the pores on a plant's leaf surface, the more hydrophobic it is. The research by Nagar et al. also showed that leaves with large stomatal density have strong hydrophobicity, but the linear relationship between stomatal density and wettability is not simple. In 2009, Shi hui et al. studied the morphological characteristics and water contact angle of leaf surfaces of a large number of plants and found that factors such as waxy, horny, stomatal, roughness and other factors on leaf surfaces would affect leaf wettability. In 2010, Wang huixia observed the morphological characteristics of the leaf surface of green plants and measured the water contact angle, analyzed the relationship between the wax, villi, stomata and other factors on the leaf surface and the contact angle value. They further analyzed the wettability of the leaf surface of plants and its influencing factors.

### 3.1.4 Leaf surface morphology

The plant epidermis refers to the outermost layer of cells in a plant. It is generally believed that the effect of leaf morphology on leaf wettability varies negatively with the gradient of epidermal cell protrusion. Barthlott and Neinhuis first began to pay attention to the characteristics of non-smooth surface of lotus leaves. By observing the microscopic morphological structure of lotus leaves, they found that there were micron-sized mastoid structures and waxy substances on the surface of lotus leaves, which led to the hydrophobic self-cleaning function of lotus leaves. In 2006, Jung et al. further studied the lotus leaf effect and found that the convex bodies on the blade surface were nanostructures rather than micron structures, which were more conducive to the analysis of the hydrophobic characteristics on the blade surface. Wang shujie et al. found that the epidermal cells were uneven and the contact angle on the surface of the waxy lotus leaves was large. The influence of epidermal cell morphology on leaf wettability was negatively correlated with the gradient of epidermal protrubance. Barthlott observed the leaf surfaces of a variety of superhydrophobic plants under scanning electron microscope, showing that the epidermal cell processes varied from 5 cm to 100 cm, but the contact angle did not change significantly. Therefore, it is believed that the morphological structure of epidermal waxy crystals and the waxing properties of villi may have more obvious influence on wettability.

![Stomata of plant leaf](image3)

**Figure 6** Stomata of plant leaf

### 3.1.5 Other

In addition to the factors mentioned above, leaf wettability is also related to leaf water status, leaf age, leaf position in the canopy, leaf epiphytes, plant growth altitude, pollutants and other factors.

### 3.2 Influence of surfactants for pesticides on wettability

With the development of pesticide science and technology, the dosage forms and varieties of pesticides have been increasing. Faced with a large variety of pesticides, how to properly select them has become a concern for pesticide users. Due to the protection of natural wax and fluff on the plant surface, water is difficult to be uniformly wetted. So pesticides cannot usually be used directly for the control of diseases and insect pests. Since semi-atomization when spraying pesticide, the high-speed spraying process can be completed only by rapidly reducing the dynamic surface tension of the system. When the pesticide droplets reach the surface of the leaf, they need to spread quickly and penetrate into the interstitial space of the tissue, so as to maximize the absorption of the drug effect, otherwise the pesticide liquid will fall to the ground after it reaches the leaf surface and waste pesticide. Surfactants help eliminate the micro-air barrier between fog drops and the leaf surface of plants, making the leaf surface of plants more hydrophilic. Therefore, adding a suitable surfactant to the pesticide solution can increase the spreading area of fog drops on the surface of crop leaves, thus accelerating the absorption rate of pesticide solution on plant leaves. Holloway studied the wettability of pesticide droplets on the surface of plant leaves. They found that for plant leaves with different contact angles, different surfactants could be added to improve the wettability of pesticide agents. Ramsdale et al. agreed that the surface tension of the solvent could be significantly reduced, so that the pesticide preparation could play a better wetting effect on the plant leaf surface. Jiang qingzhe et al. found that the critical surface tension is an important index to characterize the surface energy of a solid. Only when the critical surface tension of a solid is greater than the surface tension of a liquid can the liquid be well wetted on the solid surface. Since 2002, Gu zhongyan’s group have done a lot of research on how to make pesticide agents exert better wettability on plant leaves. They
finally\cite{50} showed that surfactants can reduce surface tension and change the behavior characteristics of pesticide agents on the surface of hydrophobic plants, so as to improve the wetting and spreading ability of pesticide solutions on plant surfaces. In recent years, Liu xiaoyan et al.\cite{51} found that adding silicone surfactants could effectively improve and enhance the wetting and diffusion properties of pesticide formulations on the surface of plant leaves.

![Figure 7 SEM figure of lotus leaf surface](image)

### 3.3 Effects of different application methods on wettability

Different formulations, different types, different control target ultimately lead to different application methods. Commonly used spraying methods include powder spraying, spraying, aircraft spraying, fumigation, poison bait, granulation method, seed treatment, soil treatment, film mulching application, and more than 10 kinds\cite{52}. During the pesticide use process, it is not possible to accurately grasp the dosage of the medicine and the characteristics of the target crops. Therefore, the amount of pesticide input is high and the target pertinence is poorly targeted, as the liquid cannot stay well on the leaf surface and wet. In view of the above problems, some researchers have studied the wetting characteristics of pesticides on leaf surfaces of different target crops. Among them, Xu Guangchun and others\cite{53} studied the wettability of the solution on rice leaves under large spray capacity and mist concentration. The critical surface tension of rice leaves was determined by using the Zisman chart method and compared with that of the 52 pesticides used in the field, which was determined by the national standard GB5549-90 method.

Spray method is one of the most important methods of pesticide application, and the utilization ratio of different spray methods is also different. The spray method has a great effect on the control effect. Jenson’s research\cite{54} shows that the spray head tilting forward or backward will improve the control effect of herbicide, and reduce the rate of ground loss of medicament effectively. When Foque and Braeckman\cite{55,56} studied the influence of nozzle type and spray angle on potted plants, they found that relative nozzle vertical ground spray, tilt spray can obtain higher deposition amount. Enhances the pertinence of the target application and improves the wettability of the plant leaves, thus improving the effective utilization of the liquid.

In China, when the pesticide field is used to control the diseases and insect pests of agricultural crops, the farmers generally use small manual spray apparatus and large capacity spray, and the blind operation is very common. At the present stage, the aviation application technology and the unmanned aerial vehicle equipment unceasingly enhances the pesticide application equipment level\cite{57}. These methods have many advantages, but there are also many problems. For example, UAV aerial spray can improve labor efficiency and reduce pesticide usage when spraying in a large area, but droplets drift seriously, which is easy to cause drug damage and cannot be popularized in the planting mode of strip segmentation in our country. Although electrostatic spray can increase the adhesion of droplets on the target surface and increase the wetting performance. It is expensive and needs special pesticide preparations to be matched, so it is seldom used in practice in our country.

In 2015, Yuan Huizhu et al.\cite{58} carried out the determination test of droplet deposition distribution and pesticide utilization ratio of different plant protection machinery in the corn field of Lanling County, Shandong Province, and selected 8 kinds of plant protection machinery including spray rod sprayer, plant protection UAV and manual sprayer.

The results showed that the spray volume of rod sprayer is large, the penetration of fog droplets is strong. With this mechanical application, there are more fog droplets deposited in different parts including the upper, middle and lower of the plant, and the wettability is good, spray volume of the rod sprayer is large, and the penetrability of the droplets is strong. However, because of the field operation, the excessive water consumption leads to the serious pesticide loss, which is not conducive to improving the pesticide deposition rate in the field operation, finally reducing the control effect on pests and diseases. Farmer self-made rod sprayer, the spray uniformity is poor, the loss is serious, and the wettability is poor. In the case of reduced water consumption of UAV spray, by spraying fine droplets (droplet size <100 μm), the number of droplets per unit area is increased and the wettability is increased, leading to the improved control effect. However, like the backpack motor sprayer and the mister, the spray operation is greatly affected by the operator and the spray uniformity is poor.

### 3.4 Other factors

The application of pesticides is a complex process, which is influenced by many factors. In addition to the several factors highlighted in this paper, the concentration of the pesticide liquid and the method of spraying also have an effect on the utilization rate of pesticides. For example, when the liquid concentration is close to the critical micelle concentration\cite{59}, the contact angle of the liquid on the plant leaf reaches the minimum value and the pesticide liquid can wet and spread well on the leaf surface. Water absorption rate of the plant leaves increases rapidly and then increases slowly with the increase of time, and finally tends to a stable value. While the water absorption rate decreases first and then tends to be stable with the extension of time. The high concentration gradient liquid does not directly affect the retention of the blade on the pesticide solution. When the pesticide droplet...
hits the surface of the target crop, the impact velocity, the impact angle, the liquid and the material on the surface of the droplet will also have an effect on the spreading process of the surface of the droplet, thus the pesticide efficiency.

4 Conclusions

Spraying pesticide liquid onto the surface of target crop leaves and smoothly adhering and adsorbing on the surface is a complex multi-factor process. Due to limited personal ability and time constraints, the following deficiencies still exist in this article. (1) This paper does not consider the spraying process of pesticide droplets, but assumes that the droplets can reach the leaf surface smoothly, and then mainly focuses on the change of some characteristic parameters of the droplets on the leaf surface. However, during the application process, the droplet cannot reach the blade surface smoothly because of the influence of the characteristics of the droplet itself, the external environmental factors (wind, temperature) and the inclination angle of the blade. (2) The change of individual droplets on leaf surface was studied, and the actual spraying process was a series of droplets. Therefore, the interaction between multiple droplets needs to be considered in future studies.

Note

Jingjing Wei, Yantao Tang and Meimei Wang contribute equally to this paper.

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