Adsorption characteristics of droplets applied on non-smooth leaf surface of typical crops

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Abstract: To further understand the adsorption characteristics of different-type leaf surfaces adsorbing pesticide droplets and reveal the adsorption mechanism of pesticide droplets on non-smooth leaves, non-smooth leaves of 12 kinds of typical target plants were investigated in this study. The parameters of surface morphological characteristics were measured, which include contact angle between leaves and water droplets, water holding capacity surface tension, polar component, dispersion component and other quantitative range of indicators and variation by modern means. The relationships between the indicators and water holding capacity were investigated respectively. The experimental results show that the number of trichomes, epidermal wax, morphology and distribution characteristics have influences on adsorption characteristics of the water droplets. There is a negative correlation between free energy of obverse side and the water holding capacity (R=−0.447) while the free energy of reverse side and the water holding capacity show a positive correlation (R=0.212). Also, there is a negative correlation between polar component of obverse side and the water holding capacity (R=−0.357) while the polar component of reverse side and the water holding capacity in plant leaves show a positive correlation (R=0.149). The research can provide a scientific theory for reasonable spraying of pesticide in the agricultural production, and can be a reference for the development of pesticide adjuvants and bionic pesticides.

Keywords: surface of plant leaves, adsorption characteristics, contact angle, water holding capacity, surface tension
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1 Introduction

The main reason for the low effective utilization of pesticide during spraying process in agricultural production is lack of spraying pertinence[1]. The key scientific point was whether pesticide droplets could form a good wetting on the leaf surface of target plants. A good wetting could improve spreading efficiency of pesticides[2]. Therefore, it is necessary to intensively study the adsorption and diffusion law of pesticide droplets on leaf surface and clarify the mechanism of pesticide adsorption and diffusion. The utilization efficiency of pesticides had a direct relationship with wetting and adsorption which were concerned with surface tension, contact angle and so on[3-9]. Early studies found that roughness, shape and number of attached villus affected adsorption capacity of leaves[10]. It was investigated that the adsorption capacity of seven-species conifers from the aspects of leaf surface

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cells and stomatal arrangement, surface convex and cross sectional shape[13]. Easy wetting fagus sylvatica leaves had strong adsorption capacity of the granules during the whole growth period, nevertheless the Ginkgo biloba leaves having “self-cleaning” characteristics was not easy to be wetted because of the special surface structure and hydrophobic wax on leaf surface according to Neinhuis and Barthlott[14]. Understanding the mechanism of adsorption of leaves was not enough only from the roughness, villus character, epidermal cells and stomatal arrangement and wettability etc. The surface free energy may be an important parameter which affects adsorption capacity of leaves, which was showed in the experimental results on Fraxinuschinensis, Syringa oblata and Popu-lus tomentosa by Wang et al.[15], Chen et al.[16] and Zhang et al.[17]. Many surface phenomena and surface properties including adsorption, wettability, anisotropy and cohesiveness had close relationships with mechanism of adsorption[18]. There is no report on the effect of leaf surface energy characteristics on pesticide adsorption. The effects of leave surface features such as villus, wettability, surface free energy, polar component and dispersion component on adsorption capacity were focused on in this study. Adsorption mechanism of pesticides on leaf surface was interpreted from wettability and surface energy characteristics of the leaves, which would provide scientific theoretical basis for reasonable and efficient pesticides spraying in agricultural production.

2 Materials and methods

2.1 Experimental materials

Plants: Cucumis sativus Linn, Solanum lycopersicum, Cucurbita moschata, Solanum melongena Linn, Semen canavaliae gladiatae, Fructus Capsici Capsicum frutescens L, Tropaeolum majus, Callistepohus Chinesis, V. amurensis Rupr, Cerasus pseudocerasus, Perilla frutescens, Cannabis sativa.

Experimental medicines: distilled water, diiodomethane.

Experimental instruments: Biological-microscope XSP-8CA (Shanghai Yongheng Optical Instrument Factory), JC2000A intravenous infusion contact angle/ interfacial tension measuring instrument (Shanghai Zhongchen Digital Technic Apparatus Company).

2.2 Experimental methods

2.2.1 Determination method of liquid holdup

The watch-glass was put on the scale and cleared. The qualities of leaves were recorded as m_1. The leaves were immersed in a beaker filled with tap water using tweezers. The leaves were removed and then placed in an electronic balance noting the reading of m_2 after 30 s (Until droplets were no longer dropped from leave surface). Each experiment was repeated 3-5 times and the liquid holdup would be averaged. Amount of liquid hold-up = $(m_2 - m_1)$/surface area (g/cm^2). The samples were placed on the loading platform of measuring instrument for static contact angle and interfacial tension (The measuring range is 0° to 180° and image magnification is 266 pixel/mm. The liquid was distilled water and the droplet size was 0.005 mL for the test parameter settings. The experiment was repeated several times and results were averaged). The liquid medicine was dropped on the sample with a 5 mL syringe (Droplets of 0.05 mL were adhered to the surface of the leaves and avoided dripping from the main veins).

The changes of droplets were observed on the screen. The photos and corresponding angles were recorded when the contact angle was maximal. The results would be averaged by statistical analysis.

2.2.2 Research methods of plant leaf surface characteristics

The contact angles including obverse and reverse of the 12 species were measured for liquid distilled and diiodomethane on the measuring instrument for static contact angle and interfacial tension under room temperature conditions. The surface free energy, polar component and dispersion component of leaves were accounted according to the Young Equation and Owens-Wendt-Kaelble law.

2.2.3 Measurement and calculation principles of surface free energy, polar component and dispersion component

The quantitative relationship between contact angle of equilibrium state and surface free energy of three-phase interface was derived according to the three-phase system illustrated in Figure 1,

The Young Equation:

$$\gamma_{sg} = \gamma_{s1} + \gamma_{1g}\cos\theta \tag{1}$$

where, γ_{sg} is the surface free energy of liquid, mJ/m^2; γ_{1g} is the surface free energy of solid, mJ/m^2; γ_{s1} is the interfacial free energy between the solid and liquid when the liquid saturated steam was balanced in the Equation, mJ/m^2. Surface free energy was divided into polar component (γ^p) and the dispersion component (γ^d) by Fowkes[19].

$$\gamma = \gamma^d + \gamma^p \tag{2}$$

Dispersion forces work only on the solid / liquid interface under the assumed conditions.

$$\gamma_{s1} = \gamma_1 + \gamma_s - 2\sqrt{\gamma_s^d\gamma_1^d} \tag{3}$$

The following conclusion can be obtained from combining (1) and (3):

$$\gamma_{s1}(1+\cos\theta) = 2\sqrt{\gamma_s^d\gamma_1^d} \tag{4}$$

Its application has been limited due to only the dispersion was considered. Owens et al.[20] expanded the following Equation from (3):

$$\gamma_{s1} = \gamma_1 + \gamma_s - 2\sqrt{\gamma_s^d\gamma_1^d} - 2\sqrt{\gamma_s^p\gamma_1^p} \tag{5}$$

γ_{s1} represents the function for geometric mean of dispersion component and polar component.

γ_s^p is the polar component of surface free energy of solid, mJ/m^2. γ_s^d is the dispersion component of surface free energy of solid, mJ/m^2. γ_1^p is the polar component of surface free energy of liquid, mJ/m^2. γ_s^d is the dispersion component of surface free energy of liquid, mJ/m^2.

The following conclusion can be obtained from Equations (1) and (5):

$$\gamma_1(1+\cos\theta) = 2(\sqrt{\gamma_s{}^p\gamma_1{}^p} + \sqrt{\gamma_s{}^d\gamma_1{}^d}) \tag{6}$$

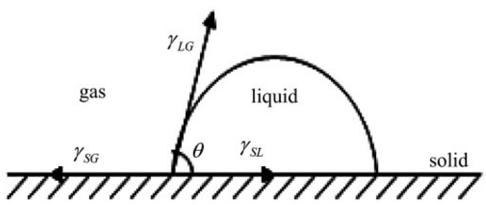


Figure 1 Equilibrium of droplets on the surface

The dispersion component and the polar components of surface free energy of the solid would be obtained according to the Equation (6) if the contact angles between solid surface and two kinds of detection solution were known. Solid surface free energy was calculated by the following Equation.

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{7}$$

Strongly polar and non-polar detection of liquid were required using this method to calculate the solid surface energy. The measured value γ_s^p would be higher if both the two kinds of detection liquid may form hydrogen bond (such as distilled water and glycerin).

The measured values of γ_s^d and γ_s were lower. Non-polar diiodomethane and strongly polar distilled water were selected as detection liquid based on the above research. Measurement results of surface free energy (γ_1), the polar component (γ_1^p) and the dispersion component (γ_1^d) for detection liquid were showed in Table 1.

Table 1 Surface free energy and its components of probe liquids

Probe liquid	Polar component γ_1^p/mJ·m^{-2}	Dispersion component γ_1^d/mJ·m^{-2}	Surface free energy γ_1/mJ·m^{-2}
Diiodmethan	2.3	48.5	8
Distilled water	51.0	21.8	72.8

2.3 Data processing

The experimental data were processed and analyzed using SPSS 11.5 (SPSS, Software Co, USA). Plant leaf surface free energy, polar component and dispersion component were calculated using Matlab 2009 and Visual C++ mixed programming. Related line graph, bar graph, line graph were plotted using Microsoft software Excel 2003.

3 Results and analysis

3.1 Surface free energy and its components of plant leaves

The water contact angle on leaf surface and diiodomethane contact angle of 12 species of plants were detected. The surface free energy (γ_1), the polar component (γ_1^p) and the dispersion component (γ_1^d) values of 12 species of plants were obtained by Matlab 2009. Statistical analyses were conducted by 2.1.3. The calculation results were shown in Table 2.

It can be seen that the obverse and reverse leaf surface wetting angles of 12 species of plants range from 40° to 140°. The obverse and reverse surface free energy range from 28 mJ/m^2 to 66 mJ/m^2. Obverse surface free energy of plant leaves is larger than the reverse surface free energy in most cases. The surface polar component of leaves ranges from 0.0038 mJ/m^2 to 48.50 mJ/m^2 and the surface dispersion component of leaves ranges from 12 mJ/m^2 to 49 mJ/m^2.

Table 2 Contact angle of water, surface tension and feature parameters on the surface of different plant leaves

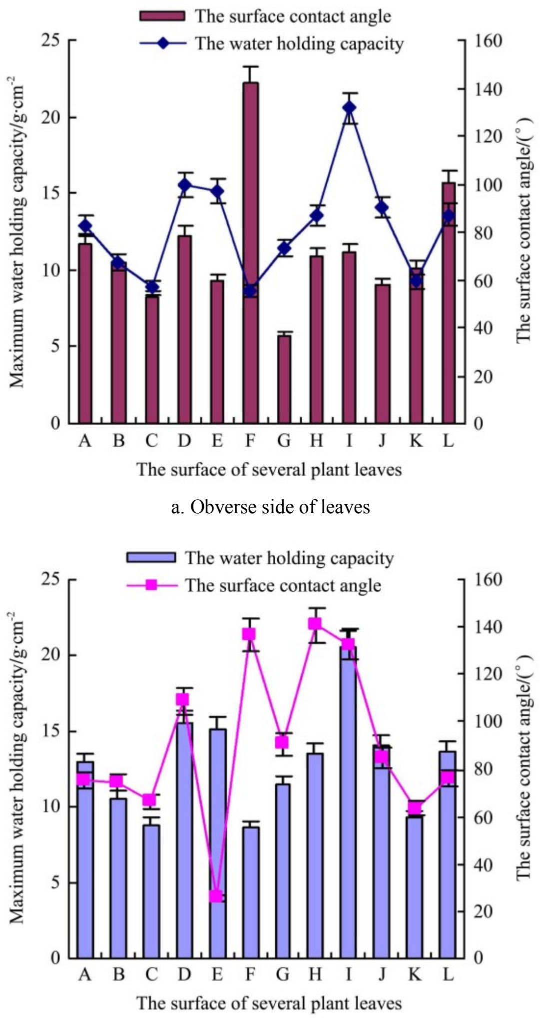
Plants		θ_1	θ_2	γ_s^p	γ_s^d	γ_s
Callistepohus Chinesis	1*	40.50	34.10	28.94	30.20	59.14
	2**	91.70	50.60	1.492	32.45	33.94
Solanum lycopersicum	1	55.95	59.60	25.84	19.24	45.08
	2	86.90	41.70	1.983	36.77	38.75
Cucumis sativus Linn	1	99.40	26.10	0.0929	48.84	48.94
	2	78.05	42.05	5.423	34.20	39.63
Solanum melongena L	1	81.85	52.30	5.313	28.90	34.21
	2	108.90	63.00	0.0006	28.18	28.18
Fructus Capsici Capsicum frutescens	1	67.35	51.40	13.82	26.15	39.96
	2	101.35	46.00	0.0038	38.04	38.04
Semen Canavaliae Gladiatae	1	59.95	43.95	17.12	28.86	45.98
	2	25.60	55.75	48.41	17.51	65.92
Tropaeolum majus	1	142.4	64.55	7.512	33.77	41.28
	2	135.95	94.75	0.7719	12.51	13.28
V.amurensis Rupr	1	95.85	37.35	0.1202	41.87	41.99
	2	75.60	40.40	6.368	34.52	40.89
Perilla frutescens	1	51.25	50.30	26.08	23.67	49.75
	2	69.20	31.30	8.395	37.61	46.00
Cerasus pseudocerasus	1	73.40	55.25	10.73	25.13	35.86
	2	132.45	67.25	3.701	29.99	33.69
Cucurbita moschata	1	34.50	52.60	40.60	20.02	60.63
	2	75.65	57.45	9.858	24.26	34.12
Cannabis sativa	1	69.65	52.40	12.48	26.04	38.53
	2	140.75	62.70	7.370	34.94	42.31

Note: θ_1 represents contact angles between water and leaves of different plants; θ_2 represents contact angles between diiodomethane and leaves of different plants; γ_s^p represents the polar component of the solid surface free energy; γ_s^d represents the dispersion component of the solid surface free energy; γ_s represents the solid surface free energy, $\gamma_s=\gamma_s^p+\gamma_s^d$; The data in the table is the average of 20 repeated experiments; *: 1 represents obverse side; **: 2 represents reverse side.

3.2 Correlation between surface wettability and water holding capacity of plant leaves

3.2.1 Relationship between the water contact angle and water holding capacity of obverse side

The experimental results were analyzed and shown in Figure 2a using of Microsoft Excel 2003. Obverse surface water contact angles of the selected 12 species of plants were different in the range of 35°-142°. Water contact angle of Tropaeolum majus leaves was up to 142° exhibiting strong hydropho-bicity. The minimum water contact angle of Callis-tepohus Chinesis leaves was 36° exhibiting strong hydrophilicity. Droplet contact angles of other 10 kinds of plants leaves were between 50° to 100°. The water holding capacity of 12 species of plant leaves ranged from 8 g/cm^2 to 21 g/cm^2. The maximum water holding capacity of cherry with pubescence was 20.57 g/cm^2. The minimum water holding capacity of Tropaeolum majus with gibbous surface and epid-ermis wax was 8.65 g/cm^2. The water holding capacity of other 10 kinds of plant leaves was between 9 g/cm^2 and 15 g/cm^2.



a. Obverse side of leaves

b. Reverse side of leaves

A: V.amurensis Rupr; B: Cucurbita moschata; C: Perilla frutescens; D: Solanum melongena L; E: Semen Canavaliae Gladiatae; F: Tropaeolum majus; G: Callistepohus Chinesis; H: Cannabis sativa; I: Cerasus pseudocerasus; J: Solanum lycopersicum; K: Fructus Capsici Capsicum frutescens; L: Cucumis sativus Linn.

Figure 2 Maximum water holding capacity and contact angle on the surface of several plant leaves

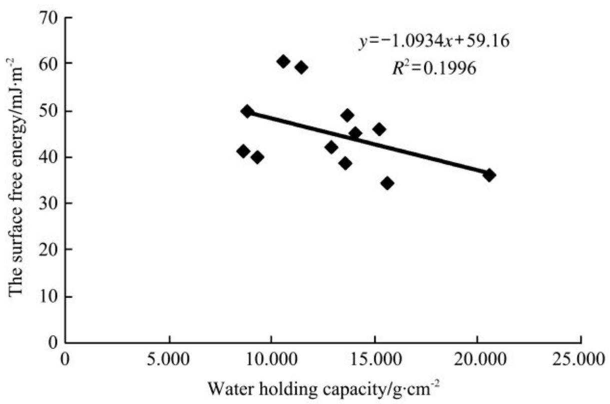
3.2.2 Relationship between the water contact angle and water holding capacity of reverse side

The statistical results were showed in Figure 2b.

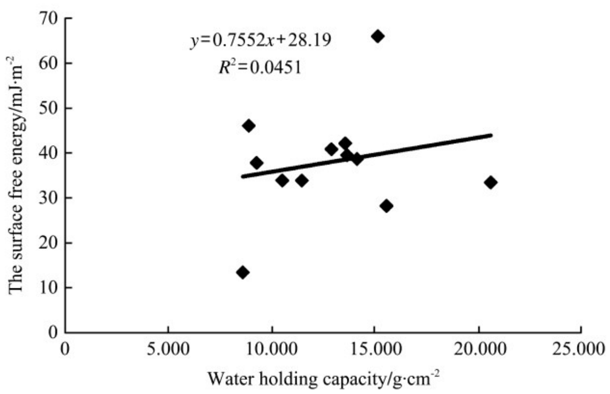
The reverse surface water contact angles of the selected 12 species of plants were different and ranged from 25° to 141°. Water contact angle of Callistepohus Chinesis leaves was up to 141° which showed strong hydrophobicity. The minimum water contact angle of Semen Canavaliae Gladiatae with pubescence was 26° exhibiting strong hydrophilicity. Droplet contact angles of other 8 kinds of plant leaves were between 63° and 91°. They were neither hydrophilic nor hydrophobic staying in intermediate state.

3.3 Relationships among water-holding capacity of plant leaves surface free energy, polar component and dispersion component

Relationship between surface free energy and water holding capacity of 12 species of leaves was obtained by statistical analysis using software. The statistical results were showed in Figure 3. It has negative correlation between free energy of obverse side and the water holding capacity (R=−0.4468). It has positive correlation between free energy of reverse side and the water holding capacity (R=0.2124).



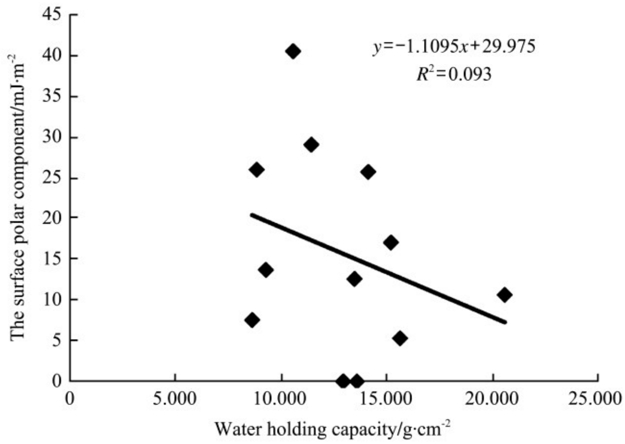
a. Obverse side of leaves



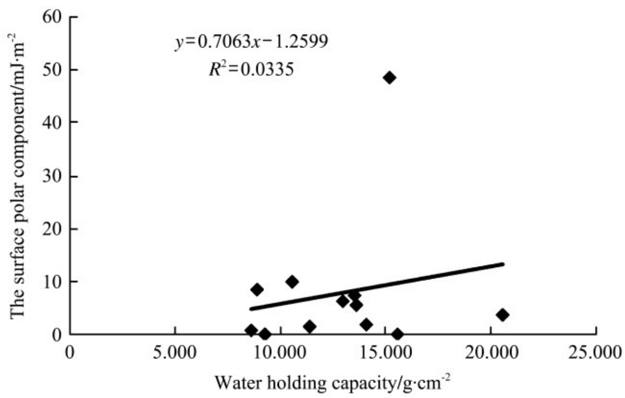
b. Reverse side of leaves

Figure 3 Relationship between surface free energy of plant leaves and water holding capacity

Relationship between surface polar component and water holding capacity was showed in Figure 4. It has negative correlation between polar component of obverse side and water holding capacity (R=−0.3035). It has positive correlation between polar component of reverse side and water holding capacity in plant leaves (R=0.1830).



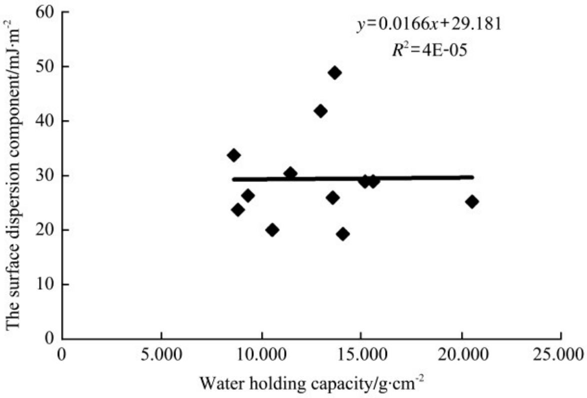
a. Obverse side of leaves



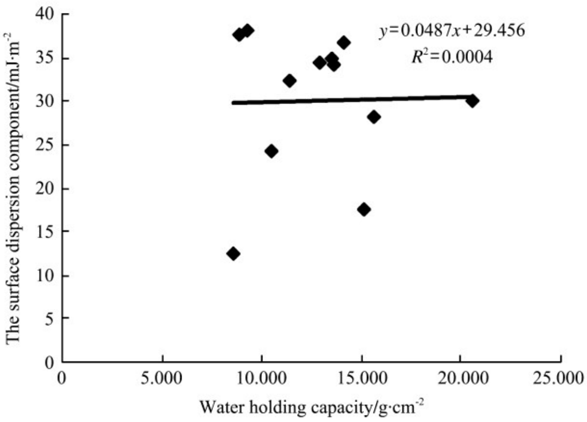
b. Reverse side of leaves

Figure 4 Relationship between surface polar component of plant leaves and the water holding capacity

Relationship between surface dispersion component and water holding capacity was showed in Figure 5. Relationship between surface contact angle and water holding capacity was showed in Figure 6. It has positive correlation between dispersion component of obverse side and the water holding capacity (R=−0.0465) while the dispersion component of reverse side and the water holding capacity has positive correlation in plant leaves (R=0.02). It has negative correlation between contact angle of obverse side and the water holding capacity (R=−0.1473) while the contact angle of reverse side and the water holding capacity has positive correlation in plant leaves (R=0.2119).

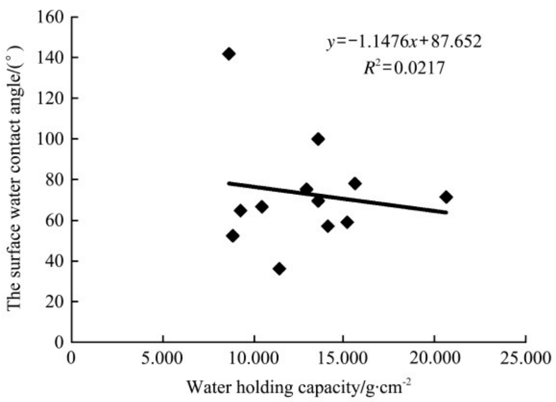


a. Obverse side of leaves

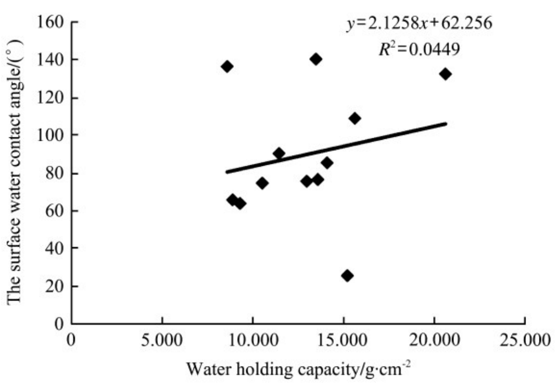


b. Reverse side of leaves

Figure 5 Relationship between surface dispersion component of plant leaves and the water holding capacity



a. Obverse side of leaves



b. Reverse side of leaves

Figure 6 Relationship between surface water contact angle of plant leaves and water holding capacity

4 Conclusions and discussion

1) The epidermal hair and epidermal wax distributed on the leaf surface directly affect the surface features (surface free energy, polar component, dispersion component) and retention characteristics of drops on leaf surface because of the difference on distribution of density, shape, texture and types .

2) The leaf surface of Tropaeolum majus has microstructure. The self-cleaning is due to mastoid on rough surface micro structure and surface wax. The combination of microstructure and nanostructure is the fundamental reason forming surface super hydro-phobic. And the superhydrophobic surface has a larger contact angle and smaller rolling angle. Water contact angle of Tropaeolum majus leaves was up to 142° exhibiting strong hydrophobicity. The leaf surface of Callistepohus Chinesis has conical burr. The minimum water contact angle of Callistepohus Chinesis leaves was 36° exhibiting strong hydrophilic-city. The maximum water holding capacity of cherry with pubescence was 20.57 g/cm^2. The minimum water holding capacity of Tropaeolum majus with gibbous surface and epidermis wax was 8.65 g/cm^2.

3) Surface morphology of plant leaves, wetting and retention characteristics of droplets are different. Water contact angle of Callistepohus Chinesis leaves was up to 141° exhibiting strong hydrophobicity. The minimum water contact angle of Semen Canavaliae Gladiatae with pubescence was 26° exhibiting strong hydrophilicity.

4) There is some correlation among surface free energy, polar component, dispersion component and water holding capacity. There is a negative correlation between free energy of obverse side and the water holding capacity while the free energy of reverse side and the water holding capacity show a positive correlation. There is a negative correlation between polar component of obverse side and water holding capacity while the polar component of reverse side and water holding capacity show a positive correlation in plant leaves. There is a positive correlation between dispersion component of obverse side and the water holding capacity while the dispersion component of reverse side and the

water holding capacity show a positive correlation in plant leaves.

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