Bangladesh J. Bot. **45**(5): 1027-1033, 2016 (December)

WETTING PROPERTY REPRESENTATION OF PESTICIDES ON THE CROP LEAF SURFACES

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Key words: Wetting property, Contact angle, Adhesion tension, Pesticides

Abstract

The research on the representation of wetting property of pesticide droplets applied on crop leaf surfaces would contribute to the improvement of pesticides applications. To further understand the wetting property of pesticides on crop leaves with all the aspects, relevant experiments were carried out. Firstly, the surface tension of validamycin aqueous solution with different concentrations was measured. As a result, critical micelle concentration of adjuvants in validamycin aqueous solution was 3.6364 g/l. Afterwards, the static contact angle of validamycin aqueous solution on crop leaf surfaces was obtained. It was obvious that when the concentration of validamycin aqueous solution was 3.6364 g/l, the static contact angle reached the minimum. Then, the correlations of adhesion tension β, adhesion work W_a, surface tension γ and contact angle θ were investigated. It was confirmed that there was a positive correlation between adhesion tension β and surface tension γ, adhesion work W_a and γ, also a negative correlation between β and contact angle θ, W_a and θ. When the concentration of alidamycin aqueous solution was 3.6364 g/l, the corresponding adhesion tension and adhesion work of pesticide droplets on crop leaf surfaces were obtained. At last, the dynamic contact angle of validamycin aqueous solution with different concentrations on crop leaf surfaces was measured. It proved that if pesticides were over diluted, the utilization efficiency of pesticides would be reduced a lot. It was of important significance for further research on wetting property of pesticide droplets on crop leaf surfaces which provided a basis for scientific pesticide applications.

Introduction

In China, pesticides which assist in reducing the incidence of pests and diseases are widely used in agricultural ptactices. The use of pesticides can reduce 15 - 40% loss of crops. However, during the process of spraying pesticides, only 20 - 30% of its deposit on plant leaves, far below the average 50% in developed countries. The level of retention of pesticide droplets on plant surfaces significantly affects the application efficiency of pesticides (Dong *et al*. 2015). In fact, the retention of pesticide droplets is closely related to the wetting ability of the pesticide on plant surfaces and the wettability of plant leaves. The special wettability of plant leaves provides a model for manufacturing functional surfaces (Liu *et al*. 2010, Koch *et al*. 2009). So the research on wettability of plant leaves is of great significance. In agricultural field, the wettability of plant leaves and the wetting ability of pesticides should be integrated into account. The correlation of the leaf surface features and wetness of leaves were studied by many researchers (Pandey *et al*. 2003, Yu *et al*. 2009, Kolyva *et al*. 2012, Koukos *et al*. 2015). The adjuvant has a significant influence on the wetting ability of pesticides. Gimenes *et al.* studied the effect of adjuvants on the dispersion of droplets applied on soybeans (Gimenes *et al*. 2013). Spanoghe *et al.* investigated the influence of agriculture adjuvants on spraying droplets spectra (Spanoghe *et al*. 2007). Moreover, the wetting ability is related to the surface characteristics of crop leaves (Xu *et al*. 2011, Wang *et al*. 2013) and surface tension of pesticide droplets (Knoche *et al*. 1992, Hollowayet *et al*. 2000,

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Kalin *et al*. 2014). The contact angle of pesticide droplets on leaf surfaces (Hurwitz *et al*. 2009, Fritsch *et al*. 2013), adhesion tension and adhesion work (Gu 2009) could be used as the characteristic parameters of representing the wetting property of the pesticide applied on crop leaf surfaces. The wettability representation of pesticides on target leaf surfaces were investigated.

Materials and Methods

Leaves of rice, corn and cucumber in the exuberant growth period were obtained as experimental samples (provided by College of Biological and Agricultural Engineering, Jilin University). Contact angle measuring instrument (HAD-HB) was used to measure the contact angle. The droplets were produced by micro injector fitted at the contact angle measuring instrument. All of the graphs were obtained by the software of Origin 8.0. A % validamycin aqueous solution was diluted into different concentrations. At 25ºC, a drop of the solution was dropped in a watch glass with a 1 ml injector, after that they were weighed with an analytical balance. The experiment was repeated 10 times, the weight of the watch glass was M, and then the mean weight of a droplet M_1 was obtained. To ensure same volume of each droplet, the force must be uniform in the process of experiments. In the control test, distilled water was used as an experimental material instead of validamycin. Also, the mean weight M_2 of the water droplet was obtained by 10 repeated tests. At last, the surface tension of validamycin aqueous solution was calculated according to the formula (Wang *et al*. 2010) described as follows:

$$\gamma = \gamma^*(H_2O)\cdot\frac{M_1}{M_2} \tag{1}$$

where γ was the distilled-water surface tension (25ºC), $\gamma^*(H_2O)$ the validamycin- solution surface, M_1 the weight of a drop of validamycin solution, M_2 the weight of a drop of distilled-water.

A 5% validamycin aqueous solution was diluted into low concentration (700 times dilution), moderate concentration (250, 275, 300 times dilution) and high concentration (50 times dilution). The leaves of rice, corn and cucumber were cut into 2.5 × 7.5 cm, and then stuck to the glass slide where environmental temperature was 25 ± 1ºC. Afterwards, the sample was placed on the loading platform of HAD-HB. The loading platform was adjusted to appropriate position so that the sample clearly appeared in the field of vision. Then, the droplet (0.005 ml) produced by micro injector dropped onto the sample. The static contact angle was recorded, and the average value of each plant and each concentration was obtained by 10 experiments. To obtain the dynamic contact angle, images of the droplet on the leaf were captured at setting intervals according to different plants. Then the corresponding dynamic contact angle was measured, the final result was the average value obtained by 10 reduplicative experiments.

The adhesion tension β and adhesion work W_a of the pesticide liquid on the leaf surface can be calculated based on the wetting equations (2) and (3)

$$\beta = \gamma\cos\theta \tag{2}$$

$$W_a = \gamma\left(\cos\theta + 1\right) \tag{3}$$

where β was the adhesion tension, W_a the adhesion work, γ the surface tension of the pesticide liquid and θ the contact angle of the pesticide liquid on leaf surface.

Results and Discussion

As shown in Fig. 1, at a low concentration, the surface tension of validamycin aqueous solution greatly decreased to the minimum with the concentration increasing. Then the surface tension increased and finally reached a certain level, as the concentration continues to increase. Usually to decrease the surface tension and ensure that pesticide liquid easily spreading on the leaf surface, various adjuvants were added to the pesticide. In fact, when the surface tension reached the minimum 36.24 mN/m, corresponding solution concentration (3.6364 g/l) was the critical micelle concentration of adjuvants in validamycin aqueous solution.

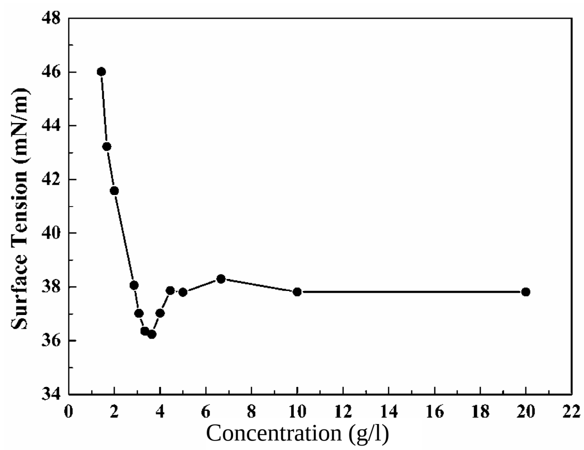

Fig. 1. The surface tension of validamycin aqueous solution with different concentrations.

It was observed that the contact angle of validamycin aqueous solution on the rice leaf was 127°~136° (Fig. 2). Meanwhile, the contact angle on the cucumber leaf and the corn leaf were 70°~93° and 49°~66°, respectively. From Fig. 2, it was confirmed that the contact angle decreased and then increased with increasing pesticide concentration. Moreover, when the concentration of validamycin aqueous solution was about 3.6364 g/l, the contact angle reached the minimum. That was to say, when the pesticide concentration was close to the critical micelle concentration, the pesticide liquid was much easier to spread on the leaf surface. Because of the influence of leaf-surface properties, the corresponding concentration was not fully equal to 3.6364 g/l.

In the spreading process, adhesion tension was defined as the force against surface tension, which reflected the ability of liquid replacing gas on the solid surface. The liquid automatically spread on the solid surface when the adhesion tension between the liquid and the solid was greater than the surface tension of the liquid. Therefore, adhesion tension was important parameter of judging the wettability of pesticide liquid on the target leaf. Moreover, the maximum work done by the system to the outside when changing from gas-solid and gas-liquid surfaces to liquid-solid surface was known as adhesion work. The greater the adhesion work, the more firmly the combination of the liquid and the solid. Therefore, adhesion work was an another important parameter to determine the wettability of the liquid on the surface of the leaf surface.

According to formula (3), the three dimensional diagram of adhesion tension, contact angle and surface tension was obtained by Origin 8.0. Similarly, based on formula (4) the three dimensional diagram of adhesion work, contact angle and surface tension was obtained.

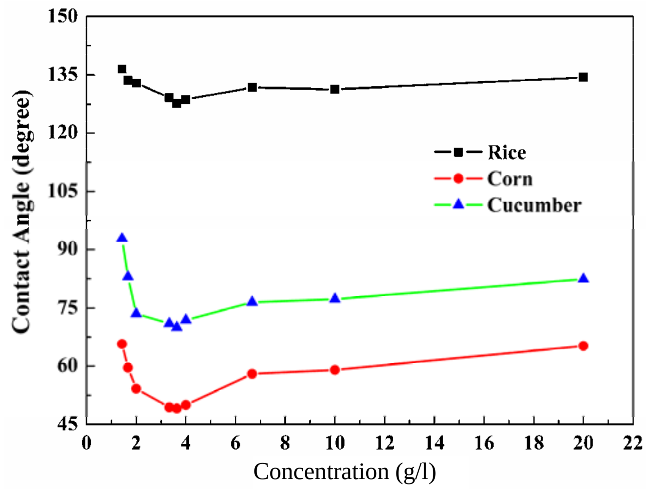

Fig. 2. The contact angle of pesticides with different concentration on crop leaf surfaces.

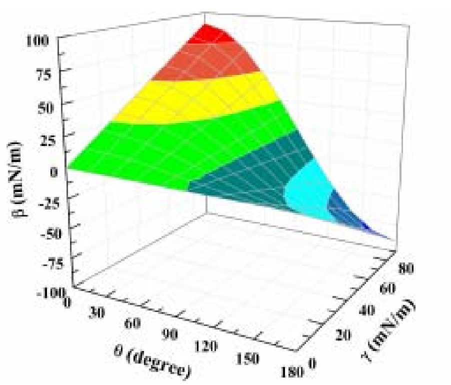

Fig. 3. The correlation of contact angle, surface tension and adhesion tension.

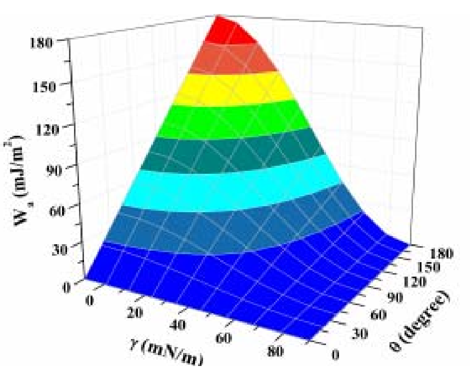

Fig. 4. The correlation of contact angle, surface tension and adhesion work.

Table 1. The characteristic parameters of the wetting property of the pesticide.

Crops	Contact angle (deg)	Adhesion tension (mN/m)	Adhesion work (mJ/m^2)
Rice	127.7	–22.16	14.08
Corn	49.1	23.73	59.97
Cucumber	70.2	12.28	48.52

As shown in Figs 3 and 4, contact angle θ was constant, when surface tension γ changed from 0 to 90 mN/m, adhesion tension β and adhesion work W_a increased. However, when γ was immovable, θ increased from 0 to 180°, β and W_a would decreased. Meanwhile, the adhesion tension and adhesion work were –90~90 mN/m and 0~180 mJ/m^2, respectively.

When the concentration of validamycin aqueous solution was 3.6364 g/l, the characteristic parameters of the wetting ability of the pesticide applied on typical crop leaf surfaces were shown in Table 1. Apparently, the adhesion tension showed a negative correlation with the contact angle and the adhesion work was positively correlated with the contact angle.

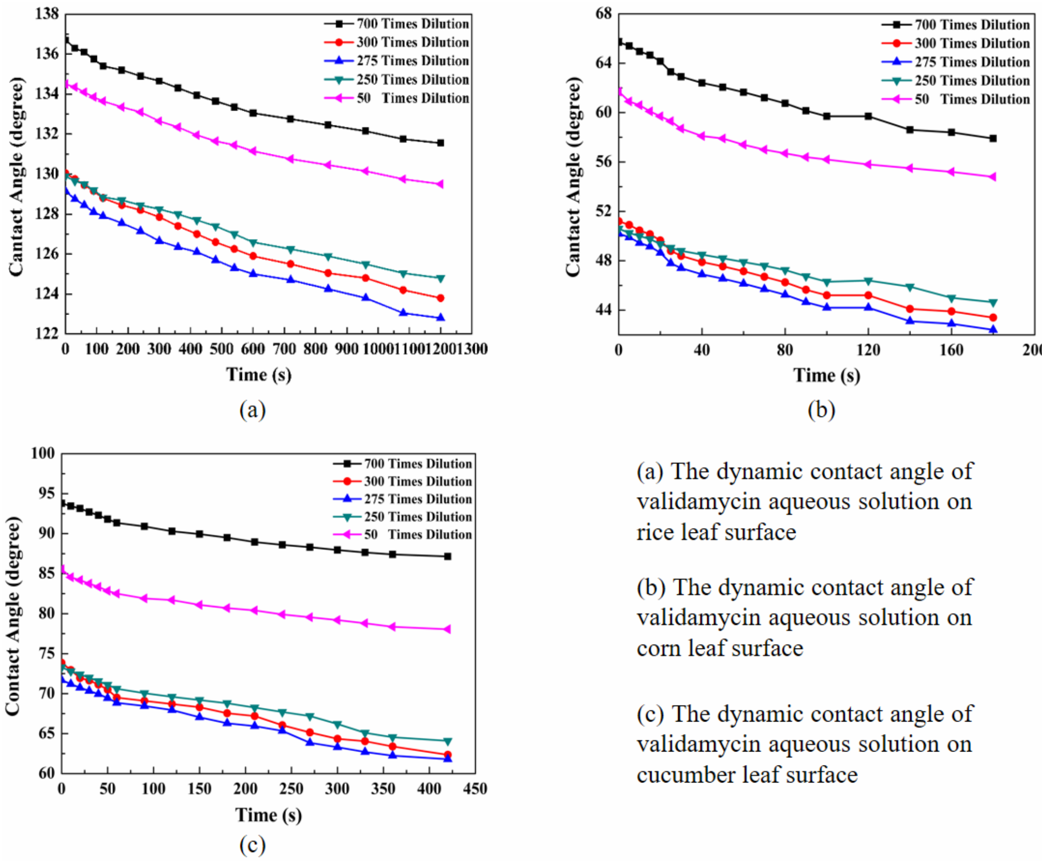

Fig. 5 The static contact angle of validamycin aqueous solution with different concentration on crop leaf surfaces.

The dynamic contact angle of validamycin aqueous solution on rice, corn and cucumber leaf surfaces was measured. The contact angle of the different-concentration pesticide on rice continuously decreased with time, but it was still much less than 90° at 20 min (Fig. 5a). It was obviously that the utilization ratio of the pesticide was very low. As for corn, the contact angle always was less than 90°, the greater the pesticide concentration, the smaller the contact angle (Fig. 5b). The contact angle of the pesticide on cucumber leaf was less than 90° when the dilution time was in a certain range. It indicated that plant leaves could be more easily wetted by the pesticide by changing the pesticide concentration. Obviously, the contact angle of low-concentration (700 times dilution), high-concentration (250, 275, 300 times dilution) pesticide on the crop leaf was significantly greater than that of moderate-concentration pesticide. In other word, when pesticide concentration was greater and less than the critical micelle concentration of the pesticide, the corresponding dynamic contact angle would increase. In China, pesticides were used with high-time dilution, which greatly reduced the concentration of the adjuvant in pesticides. So the wetting ability of pesticides would decrease and lead to the low utilization ratio of pesticides. Moreover, the wetting ability of validamycin aqueous solution on the corn leaf was greater than that of the cucumber leaf and far larger than that of rice leaf.

Critical micelle concentration (3.6364 g/l) of adjuvants in validamycin aqueous solution was obtained by measuring surface tension. Besides, when pesticide concentration was close to the critical micelle concentration, the contact angle reached to the minimum, the contact angle of the pesticide droplets on rice, corn and cucumber was 127.7, 49.1 and 70.2°. Moreover, there was a positive correlation between adhesion tension β and surface tension γ, adhesion work W_a and γ, also a negative correlation between β and contact angle θ, W_a and θ. When the concentration of alidamycin aqueous solution was 3.6364 g/l, the corresponding adhesion tension of rice, corn and cucumber was –22.16, 23.73 and 12.28 mN/m, respectively; the corresponding adhesion work was 14.08, 59.97 and 48.52 mJ/m^2, respectively. At last, when pesticide concentration was greater and less than the critical micelle concentration of the pesticide, the corresponding dynamic contact angle would increase a lot. If pesticides were overly diluted, the pesticide droplets would slip off the leaf surface and the utilization efficiency of pesticides was greatly reduced. It is significant for further research on wetting property of pesticide droplets on crop leaf surfaces. What is more, this provides the basis for scientific dilution of pesticides.

Acknowledgements

The work was financially supported by the "12th Five Year Plan" National Science and Technology in Rural Area (No. 2013AA103005-04 and No. 2012AA10A506-04), Changchun City Science and Technology Support Program (No. 14Nk002), Graduate Innovation Fund of Jilin University (No. 2016172) and Provincial Natural Science Foundation of Jilin. Authors are grateful to Key Laboratory of Bionic Engineering (Ministry of Education, China) for their technical assistance.

References

Dong X, Zhu HP and Yang XJ 2015. Characterization of droplet impact and deposit formation on leaf surfaces. Pest Manag. Sci. **71**: 302-308.

Fritsch A, Willmott GR and Taylor M 2013. Superhydrophobic New Zealand leaves: contact angle and drop impact experiments. J. Roy. Soc. New Zeal. **43**(4): 198-210.

Gimenes MJ, Zhu H, Raetano CG and Oliveira RB 2013. Dispersion and evaporation of droplets amended with adjuvants on soybeans. Crop Prot. **44**: 84-90.

Gu ZY 2009. Analysis of the relationship between hydrophilic or hydrophobic property of plant and action of pesticides solution on plants leaves. Jiangsu J. Agr. Sci. **25**(2): 276-281.

Holloway PJ, Ellis MCB, Webb DA, Western NM, Tuck CR, Hayes AL and Miller PCH 2000. Effects of some agricultural tank mix adjuvants on the deposition efficiency of aqueous sprays on foliage. Crop Prot. **19**(1): 27-37.

Hurwitz G, Guillen GR and Hoek EMV 2010. Probing polyamide membrane surface charge, zeta potential, wettability, and hydrophilicity with contact angle measurements. J. Membrane Sci. **39**(1-2): 349-357.

Kalin M, Polajnar M 2014. The wetting of steel, DLC coatings, ceramics and polymers with oils and water: The importance and correlations of surface energy, surface tension, contact angle and spreading. Appl. Surf. Sci. **293**: 97-108.

Knoche M, Noga G and Lenz F 1992. Surfactant-induced phytotoxicity: Evidence for interaction with epicuticular wax fine structure. Crop Prot. **11**(1): 51-56.

Koch K, Bhushan B and Barthlott W 2009. Multifunctional surface structures of plants: An inspiration for biomimetics. Prog. Mater. Sci. **54**(2): 137-178.

Kolyva F, Stratakis E, Rhizopoulou S, Chimona C and Fotakis C 2003. Leaf surface characteristics and wetting in *Ceratonia siliqua* L. Flora **207**(8): 551-556.

Koukos D, Meletiou Christou MS and Rhizopoulou S 2015. Leaf surface wettability and fatty acid composition of *Arbutus unedo* and *Arbutus andrachne* grown under ambient conditions in a natural macchia. Acta Bot. Gallica **162**(3): 225-232.

Liu KS, Yao X and Jiang L 2010. Recent developments in bio-inspired special wettability. Chem. Soc. Rev. **39**(8): 3240-3255.

Pandey S and Nagar PK 2003. Patterns of leaf surface wetness in some important and aromatic plants of western Himalaya. Flora **198**(5): 349-357.

Spanoghe P, Schampheleire MD, Meeren PVD and Steurbaut W 2007. Influence of agricultural adjuvants on droplet spectra. Pest Manag. Sci. **63**(1): 4-16.

Wang GL, Piao YS, Liang XJ, Zheng QR, Zhao Y and Dong YM 2010. Designing and practice for innovation of physical chemistry experiment mensuration of surface tension by drop-weight method. Guangdong Chemical Industry. **37**(11): 169-170.

Wang SJ, Zhang W, He HB, Wang WS, Zhang M and Hu XY 2013. Effection of typical plants leaves on pesticide wetting speciality and retentivity. Jilin Daxue Xuebao (Gongxueban) **43**(S): 564-568.

Xu LY, Zhu HP, Ozkan HE, Bagley WE and Krause CR 2011. Droplet evaporation and spread on waxy and hairy leaves associated with type and concentration of adjuvants. Pest Manag. Sci. **67**(7): 842-851.

Yu Y, Zhu H, Frantz JM, Reding ME, Chan KC and Ozkan HE 2009. Evaporation and coverage area of pesticide droplets on hairy and waxy leaves. Biosyst. Eng. **104**(3): 324-334.

(Manuscript received on 19 April, 2016; revised on 8 May, 2016)