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Study of The Effect of Concentration on The Level of Wetness in Chicory Leaves Using The ADSA-Overlay Method

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Abstract: It is challenging to distinguish between farmers and insecticides. Chemicals called pesticides are applied to eliminate pests in order to boost agricultural production for farmers. Using the Axisymmetric Drop Shape Analysis (ADSA)-Overlay approach, this study attempts to investigate the impact of the pesticide fipronil concentration on the degree of wetness in mustard leaves. The size of the contact angle between the mustard leaf surface and the pesticide solution determines the pesticide's wetting action. The cosine of the contact angle (θ) between the liquid insecticide and the solid surface determines the surface tension (γ). Sessile drop is the method used to assess surface tension. Chicory is the surface area that comes into touch with pesticide drops. At 25ºC samples containing 50 ppm were poured onto mustard leaves using a syringe. A digital microscope that was linked to a personal computer was used to capture sessile drop pictures. Three iterations of sessile drop imaging were conducted using samples at temperatures of 27, 29, 31, 33, and 35ºC. Samples of pesticide solution at concentrations of 75, 100, 125, and 150 ppm were photographed again. The reagent 50Sc pesticide's wetting level rises with an increase in fipronil content. As concentration increases, the reagent 50Sc insecticide solution's contact angle tends to get smaller.

Keywords: ADSA-Overlay, contact angle, mustard leaves, pesticides, surface tension.

INTRODUCTION

The relationship between farmers and pesticides is complex and often controversial. On one hand, farmers rely on pesticides to protect their crops from pests and diseases, and to enhance their productivity and profitability. On the other hand, pesticides pose risks to human health and the environment, and may have negative impacts on biodiversity and ecosystem services. Finding a balance between the benefits and costs of pesticide use is a challenge that requires careful assessment and management [1].

Pesticides are substances, chemical compounds (growth regulators and growth stimulants), microorganisms, viruses and other substances used to protect plants or plant parts of SNI 7313 : 2008 [2]. Each pesticide has a certain active ingredient which, when used, has a certain lethal dose for specific living creatures. Lethal dose is the minimum concentration required for a substance to kill certain organisms at a certain ratio [3]. The use of pesticides that are not the right type or dose will result in environmental pollution [4]. Pesticide use must be controlled to get maximum results with minimal risk. One of the factors that influences the effectiveness of pesticide use is the wetting effect of pesticides on plants. The wetting effect of the pesticide depends on the contact angle of the pesticide solution made. The smaller the contact angle of the pesticide solution on the leaf surface, the greater the wetting effect will be and the effectiveness of the pesticide will increase. The contact angle is influenced by the surface tension of the liquid, and the surface tension is influenced by the forces acting in the liquid such as van der Walls forces and hydrogen bonds. The internal force of a liquid is influenced by temperature, the greater the temperature, the smaller the internal force which causes the surface tension to be smaller [5]. The use of pesticides on plants should be done at certain times, when the temperature is optimal for the application of the pesticide. Research to find the most optimal pesticide concentration with the best wetting effect is needed to find out the right concentration of pesticide. One method for measuring good contact angles is Axisymmetric Drop Shape Analysis (ADSA).

ADSA is a method based on comparing drop shapes obtained from experiments with a mathematical model from the classical Laplace Equation. This method can be used for all liquid fluid systems that can be represented via the Laplace Capillarity Equation. The use of the ADSA method is recommended because this method can use digital image analysis which can significantly increase accuracy compared to analog methods [6]. Another advantage of ADSA is that this method is able to calculate contact angle, volume and surface area simultaneously.

This research has measured the surface tension of pesticide solutions with varying concentrations and measurement temperatures. Surface tension measurements were carried out using the ADSA-Overlay method and the drop shape used in the measurements was sessile drop. The surface area of the solid used as a contact medium with drops of the pesticide solution used is white mustard.

METHODS

Set of tools for determining contact angles

The ADSA-Overlay tool set is arranged according to figure 1. The syringe with the temperature control device is mounted on a holder clamp in a vertical position to the table. Sessile drops are placed on white mustard leaves by making the drops hang on the syringe, the drops are attached to the surface of the mustard leaves. The microscope that has been installed in such a way on another stand is connected with a computer with the ADSA-Overlay program so that the droplet image obtained is clear.

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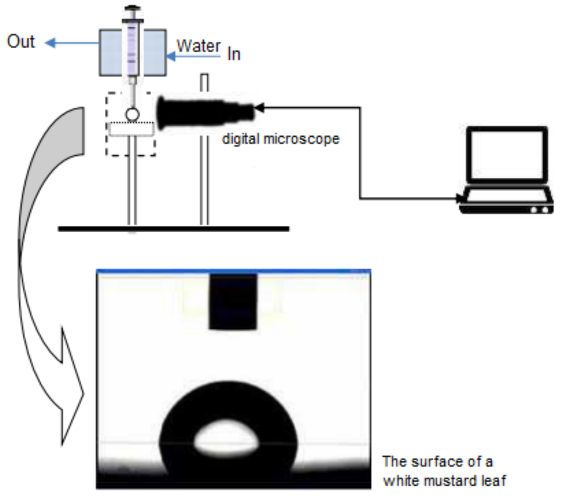

Figure 1. Set of tools for ADSA Overlay

Taking pictures of drop

Samples with a concentration of 50 ppm Fipronil (Reagent 50sc pesticide) were set at 25ºC and dripped using a syringe on mustard leaves. Sessile drop images were taken using a digital microscope (Dino-Lite Premier, 5 M) connected to a personal computer. The sessile drop image capture was repeated with samples at temperatures of 27º, 29º, 31º, 33º, and 35ºC for 3 repetitions, the image capture was repeated for reagent samples with an concentration of 75; 100; 125; 150 ppm.

Determination of contact angle

The Laplace Equation Plot is superimposed (overlaying) on the image that has been obtained. Plot the Laplace Equation by varying the b and c constants so that the plot obtained is as similar as possible to the profile image of the liquid drop obtained (fitting) (numerical method). The equations used in the ADSA-Overlay program are equations (10), (12), and (13) with the conditions of equation (14) [7, 8, 9]. Solving equations (10), (12), and (13) using the Runge-Kutta method to obtain the solution contact angle. The numerical calculation of the differential equation above was carried out using LabView 2012 software.

$$\frac{d\theta}{dz} = 2b + cz - \frac{\sin\theta}{x} \quad \text{.................................} (10)$$

$$c = \frac{(\Delta\rho)g}{\gamma} \quad \text{...} (11)$$

$$\frac{dx}{ds} = \cos\theta \quad \text{...} (12)$$

$$\frac{dz}{ds} = \sin\theta \quad \text{...} (13)$$

$$x(0) = z(0) = \theta(0) = 0 \quad \text{.............................} (14)$$

Therefore, the perfect shape of the Laplacian axis symmetric fluid-liquid interface curve can be obtained by simultaneously integrating the above set of equations (equations (10), (12), and (13) with predetermined b and c values. This value can be determined by the researcher or obtained from the results of previous images [6].

Determination of Optimal Reagent Pesticide Concentration

The optimal concentration of Reagent 50sc pesticide is determined by choosing the concentration with the smallest contact angle and the concentration closest to the application dose (50-150 ppm).

RESULT AND DISCUSSION

Theoretical curve fitting to sessile drop images

Sessile drop images were obtained by dripping fipronil solution on a flat area of chicory leaves. Figure 2 shows the dripping of the solution on chicory leaves. Sessile drops are obtained by dripping the solution using a needle at a distance of approximately 5mm from the surface of the mustard leaf. This is so that the drop does not break due to the momentum from the height it has when it falls from the syringe.

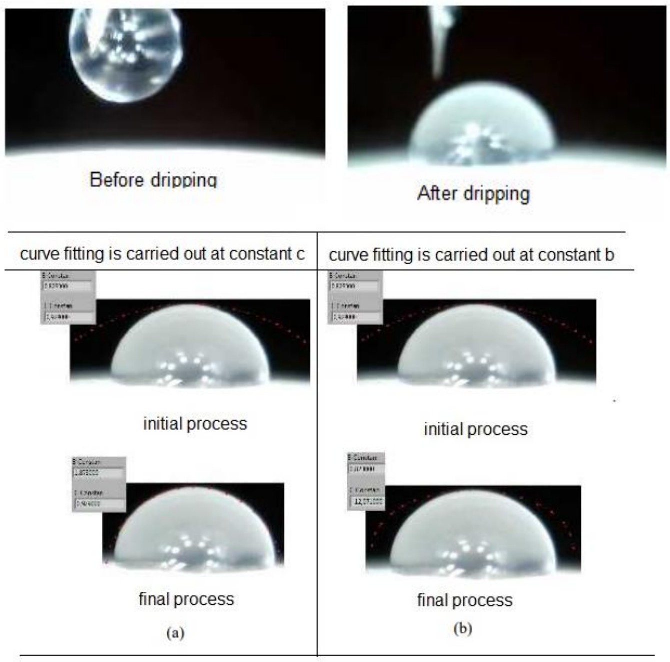

Figure 2. Process of dripping Fipronil solution on the surface of chicory leaves

The contact angle of the sessile drop was determined using the ADSA-Overlay program. The ADSA-Overlay program functions to match the theoretical curve to the sessile drop profile obtained. The theoretical curve is obtained from the Laplacian equation which is solved using numerical methods.

The results obtained are in the form of a Laplacian curve with a sessile drop profile. Fitting is carried out by aligning the critical point of the peak of the theoretical curve to the sessile drop profile. The position of the curve that has been determined is varied by the values of b and c so that the curve matches the profile of the experimental sessile drop.

Wetting Level of Regent Pesticide on the White Mustard Surface

The contact angle of a fluid droplet on a solid surface is determined by the internal force (force that occurs within the drop) and the external force (force that occurs outside the drop) of the fluid. The internal forces contained in a drop include van der Walls forces, dipole-dipole forces, and hydrogen bonds.

Internal forces in a solution occur between the molecules, the magnitude of the influence of internal forces on surface tension is influenced by the liquid molecules. Solutions have more than one type of molecule that makes up the droplets, the relationship between the types of molecules that make up the solution will affect surface tension.

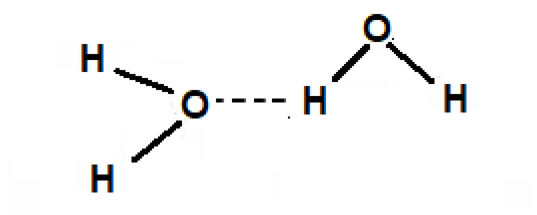

Figure 3. Hydrogen bonds that occur between water molecules

Hydrogen bonds in water occur due to polarity in water molecules as shown in figure 3. The fipronil solution has two types of molecules in it, namely fipronil and water. The internal forces that occur in fipronil solutions depend on the interactions between water and fipronil molecules. Fipronil which has an amide functional group which has high electronegativity allows hydrogen bonds to occur, but the chemical structure of fipronil shows that the fipronil molecule does not have strong polarity so the hydrogen bonds it has are relatively small compared to water. The hydrogen bonds that occur in the amide functional group are as shown in Figure 4.

In the samples used, the pesticide solution contained water and fipronil. Fipronil has low polarity compared to water, so the internal force relationship of the fipronil solution is smaller compared to pure water. The greater the ratio of fipronil in the solution, the smaller the internal force of the fipronil solution, this causes the surface tension of the solution to be smaller.

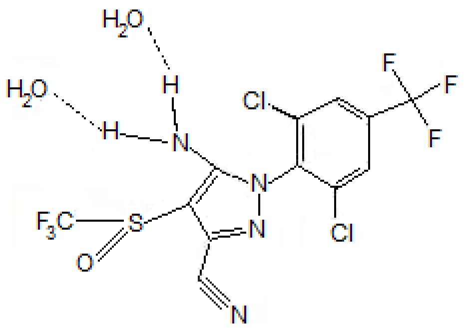

Figure 4. Fipronil experiences hydrogen bonds with water

The surface tension of the fipronil solution affects the contact angle that the solution droplets have. The greater the surface tension, the greater the contact angle. The influence of intermolecular interactions on sessile drops is shown in Figure 5. Fipronil, which has a smaller polarity compared to water, will reduce the internal forces in the solution, so that the surface tension is smaller. A small surface tension will cause the contact angle of the sessile drop to become small and the wetting effect to increase. Figure 5 shows the relationship between fipronil concentrations.

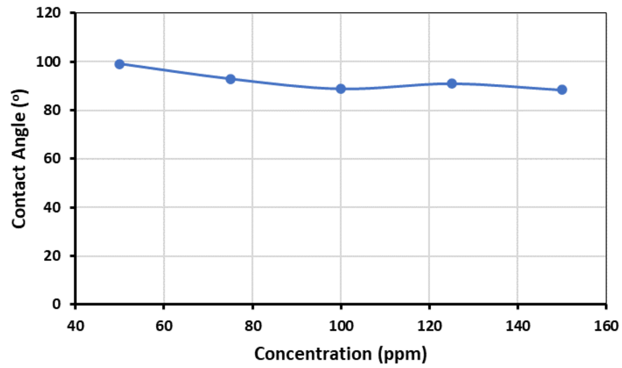

Figure 5. The effect of solution concentration on the contact angle at a temperature of 31°C.

With the contact angle produced by its sessile drop. Sessile drop of fipronil solution with a concentration of 150 ppm has the smallest contact angle. The forces involved in sessile drop equilibrium are shown in Figure 6 [10].

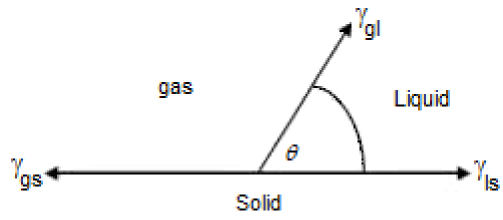

Figure 6. Force balance that occurs in a sessile drop, where:

γ_{lg} = surface tension of liquid-gas

γ_{gs} = interfacial tension of gas-solid

γ_{ls} = interfacial tension of liquid-solid

Surface tension is denoted by γ. The tension balance at the contact point of the three phases of Figure 6 follows Eq (16) [10 - 11]:

$$\gamma_{lg} = \frac{\gamma_{gs} - \gamma_{ls}}{\cos\theta} \quad (16)$$

From the equation above, assuming that the gas-solid interfacial tension (γ_{gs}) and the liquid-solid interfacial tension (γ_{ls}) remain constant, it can be determined that the greater the contact angle (θ) the solution has, the smaller the liquid-solid surface tension gas (γ_{lg}) owned [13].

The profile of a sessile drop is determined by the external and internal forces acting on the drop. External forces are forces that come from outside the droplet, for example gravitational force, and internal forces are forces contained within the droplet, for example Van Der Walls force. The internal forces that work in a sessile drop, as shown in Figure 6, result in attractive forces between the molecules. This attractive force causes the liquid droplets to become spherical and causes the contact angle of the droplets with the solid surface to become increasingly larger, as illustrated in Figure 6. The wetting effect of a liquid depends on the contact angle of the liquid with the surface of the solid. Figure 6 shows the wetting effect of 3 different liquids, (a) having a small wetting effect with a large contact angle and (c) having a large wetting effect with a small contact angle. The contact angle of the fipronil solution obtained in this study has a range of 85°-100° so the wetting level of the fipronil pesticide is not good [14].

Connection between Regent Pesticide Contact Angle and Temperature

Reagent 50sc pesticide uses the active ingredient fipronil which is toxic to insects. Pesticides become lethal to insects when the concentration used reaches a lethal dose. Lethal dose is a number used to indicate the level of toxicity of a substance. The lethal dose of regent pesticide for pests that attack white mustard is 50-150 ppm. The sample concentration used refers to the lethal dose of the regent 50sc pesticide, namely 50-150 ppm. The wetting rate of the regent 50sc sessile drop solution is influenced by the concentration and temperature of the solution. Concentration and temperature affect the internal forces acting on the sessile drop solution[15].

Internal forces such as Van Der Walls forces, dipole-dipole forces, and hydrogen bonds can be affected by temperature. The internal forces that occur between particles in a solution will cause the internal energy of the solution to decrease, resulting in the stability of the solution. With an increase in temperature, the solution particles will gain energy to release their bonds from the influence of internal forces [16]. So that the surface tension will decrease and the contact angle will become smaller. Figure 7 shows the effect of temperature on fipronil solutions at various concentrations.

As seen in Figure 7, the contact angle of the sessile drop of fipronil solution tends to decrease with increasing temperature. An increase in temperature causes the energy of molecules to increase so that the attractive forces between molecules decrease. This reduction in the attractive forces between molecules causes a decrease in the surface tension of the solution. The surface tension of the solution affects the contact angle of the sessile drop solution. The increase in contact angle in the 150 ppm fipronil solution is probably caused by differences in texture in the cross section of the mustard greens and the cooling equipment used. The contact angle obtained from this research has a value of more than 90° because the mustard plant used has a cuticle layer composed of wax molecules which are non-polar [17].

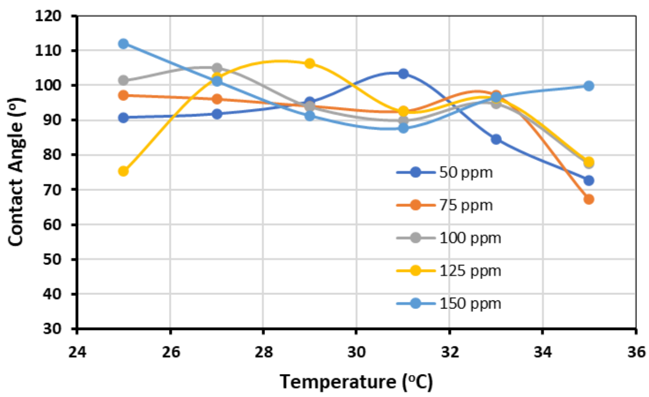

Figure 7. Effect of temperature on the contact angle of fipronil solution

CONCLUSION

The contact angle of the lethal dose of fipronil pesticide does not meet a good wetting level. The greater the pesticide concentration, the smaller the contact angle the sessile drop has (the wetting level increases). Increasing the temperature provides a better wetting effect on the fipronil solution.

In conclusion, determining the contact angle is crucial for a number of industrial operations and aids in assessing a solid surface's wettability. Better wetting and adhesion are indicated by a smaller contact angle, whereas worse wetting and decreased adhesion are indicated by a wider contact angle.

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