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Characteristics of Insecticide Formulation Using Surfactant Based on Palm Oil and Its Mortality Effect Against *Spodoptera litura*

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ABSTRACT

Pesticide should be formulated to keep bioactivity and to enhance efficiency and safety in application. Insecticide formulations consist of active ingredient and co-formulant. Most active ingredients are poorly diluted in water, so they need adjuvant such as surfactant. Surfactant will help to make a homogeneous solution between formula and water. Insecticide was formulated using emamectin benzoate as active ingredient and co-formulants such as xylene as solvent, surfactant DEA, APG and CTAC. DEA and CTAC surfactants were synthesized from palm oil derivates. They were palm oil methyl ester and palmityl alcohol. Insecticide was formulated using emamectin benzoate 15%, non-ionic surfactant (4%, 5%, and 6%) with DEA : APG ratio of 3:2, 1:1 and 2:3 and also cationic surfactant of 1%. Characterization of insecticide formulation showed that the best formulation of concentration nonionic surfactant was 6% with DEA : APG ratio of 2:3. The best characteristic of insecticide formulation was density of 0.9955 d/cm^3, surface tension of 27.42 dyne/cm, contact angle of 21.61, and particle size of 4.64 µm. This formula also caused mortality of *Spodoptera litura*, one of major insect pests on soybean, and showed as effective as commercial insecticide formula. The best insecticide concentration for application was 0.20% that caused 96% of larvae mortality at 24 hours after application.

Keywords: *APG, cationic surfactant, diethanolamide, mortality, nonionic surfactant*

1. INTRODUCTION

Plant pest and disease control using pesticides is one of the important strategies in plant protection field to keep quantitatively and qualitatively plant production. Most of pesticides used should be diluted with water before application. Unfortunately, most pesticide insecticide active ingredients including insecticide active ingredients are poorly diluted in water [1]. Therefore, pesticide active ingredients should be formulated to keep bioactivity and enhance efficiency and safety in application. Insecticide formulations consist of active ingredient(s) and co-formulant(s) [2]. Most of insecticide formulations that usually used by farmers are emulsifiable concentrate (EC), wettable powder (WP), solution concentrate (SL), suspension concentrate (SC), water dispersible granules (WG), and granule (GR) [3].

One of insecticide active ingredients that commercialized in Indonesia and usually used by farmers is emamectin benzoate. This active ingredient with chemical formula of $C_{56}H_{81}NO_{15}$ is macrocyclic lactone insecticide produced by the fermentation of the soil actinomycete, *Streptomyces avermitilis*. The mode of action of emamectin benzoate is by binding gamma aminobutyric acid (GABA) receptor and glutamate-gated chloride channel disrupting nerve signal within arthropods causing paralysis in insects [4]. In this study, emamectin benzoate has been chosen as an active ingredient that will be formulated by adding synthetic co-formulant or adjuvant. Emamectin benzoate is derivate from avermectin which has low toxicity to mammal, high efficiency, and more thermal stability than avermectin [5]. Unfortunately, this active ingredient has low solubility in water, it is about 24 mg/L [6]. Emamectin benzoate is usually formulated with high amount of solvent in the formulation of EC. This emamectin benzoate and solvent also have low solubility in water so it should be added with surfactant to enhance the formulation stability.

Surfactants are very important additives especially for forming homogeneous solutions of the nonpolar and polar phases. The function of surfactant is to reduce the surface tension of a solution. Surfactant is widely used in detergent, agrochemical, medicine and other products. Surfactants become a very important component in this product as they afford different properties and also make stable and homogeneous formulations possible [7]. In pesticide formulation, surfactants play the most important role to make homogeneous solution between formulation and water. There are several types of surfactant such as anionic, cationic, non-ionic and amphoteric surfactants. Among these surfactants that usually used in industry are anionic surfactants because they have good detergency, so it can be used in soap industry or petroleum industry. Non-ionic surfactant plays the most important role to stabilize insecticide solution. It has hydrophilic and hydrophobic, good adsorption, better to reduce surface tension, and high viscosity [8]. Non-ionic surfactant that can be used as adjuvant of pesticide is diethanolamide (DEA) and alkylpoliglucoside (APG). Diethanolamide can be synthesize from methyl ester of palm oil. Surfactant and Bioenergy Research Center (SBRC) of Bogor Agricultural University (IPB University) has already developed a technology to produce DEA with cheaper ingredient by using palm oil. DEA and APG have lowest surface tension value (20.97 dyne/cm and 21-22 dyne/cm) compared to other surfactants such as ethoxylate (23-25 dyne/cm), and lauryl betaine (31.17 dyne/cm) which is widely used in pesticides industry [9]. Both of surfactant are also produced from natural ingredient, so it will be more degradable than petroleumbased surfactant. Determining surfactant performance in insecticide formulation by analysing formulation characteristics such as density, surface tension, contact angle and particle size is important.

Insecticide effectiveness should be tested to insect pests. In this case, *Spodoptera litura*, an insect pest which is polyphagous such as soybean, chili, cabbage, rice, was used as test insect. In Indonesia, *S. litura* attack can cause loss of yield until 80% [10].

1.1. Materials and Methods

1.1.1. Chemical and Reagent

Emamectin benzoate was purchased from Asia Foresight-Care Group Ltd, Shanghai, China. Diethanolamide (DEA) nonionic surfactant was synthesized from palm oil metil ester, while alkylpoliglicoside C_{12}-C_{14} (APG) was purchased from BASF. Cetyl trimethyl ammonium chloride (CTAC) was synthesized from palmityl alcohol 98%.

1.1.2. Insecticide Formulation

Insecticide formulation used an active ingredient emamectin benzoate and co-formulant (solvent and surfactant). Concentration of active ingredient was 15%. Emamectin benzoate was dispersed in xylene, then stirred until transparent as an oil phase. Insecticide was formulated by using non-ionic surfactant at concentrations of 4%, 5% and 6% and cationic surfactant concentration was at 1%. DEA and APG were used with ratio surfactant of 3:2, 1:1 and 2:3. CTAC was used as cationic surfactant. This surfactant will be added in oil phase formulation. This formulation will be characterized to determine density, surface tension, contact angle, and particle size. The data of insecticide formulation will be analysed using completely randomized design with statistical analysis software (SAS).

1.1.3. Density

Density of insecticide formulation was measured using densitometer anton paar DNA 4500M. Insecticide formulation was diluted in water to get 1% solution. Sample will be injected using syringe and tested at temperature of 30º C.

1.1.4. Surface tension

Surface tension of insecticide was tested using spinning drop tensiometer. Insecticide formulation were diluted in water to get 1% solution. This sample was tested at temperature of 30 °C with spin rotation of 6000 rpm. The value of surface tension was measured from air bubble diameter in the tube.

1.1.5. Contact angle

Contact angle aimed to measured angle of liquid drop on leaves surface. Contact angle was analysed by diluted 1% of insecticide formulation in water. This sample was analysed using Phoenix 300 Contact Angle machine. Sample analysed by looking at the contact angle at the first drop and 10 minutes after. Soybean leaves were also used as the target of contact angle.

1.1.6. Particle size

Insecticide formulation was diluted in water to get 1% solution. Droplets were analysed using Microscope Leica ICC 50 HD. Samples were prepared in preparation glass and glass cover that have been cleaned using alcohol. Samples were put in preparation glass then covered using glass cover. Objects were observed under microscope and for adjustment of the lens, there are lighting adjusement, lens enlargement and also camera focus. Particle size will be measured by diameter measurement.

1.1.7. Data analysis

Data was analysed using completely randomized design with 2 factors (surfactants concentration and non-ionic surfactants ratio).

1.1.8. Effectiveness of insecticide formulation to Spodoptera litura

Insecticide formulations were tested to 3rd instar of *Spodoptera litura* larvae. Insecticide formulations were diluted in water with concentrations of 0.05%, 0.1% and 0.02%. Soybean leaves were dipped to this solution then given as larvae feed. Observations were carried out at 24, 48 and 72 hours after application. Larvae mortality data was analysed using completely randomized design with statistical analysis software (SAS).

1.2. Our Contribution

Many surfactants are synthetic compounds, this paper contributes in synthesizing the more environmental friendlier of surfactant made from plant chemical for pesticide formulation. Good pesticide formulation should fulfill several indicators/criteria, so this paper also describes several measurement of several indicators.

1.3. Paper Structure

The rest of the paper includes the methodology of our works with several references used. Other sections are the results of our works with short discussion and then we conclude this work in conclusion section. In the last section is reference list.

2. RESULTS AND DISCUSSION

2.1. Density

Insecticide formulation usually formed an emulsion. In emulsion density is the most important factor. Density is measured by divided mass and volume of sample [11]. Density differences caused formed two liquid phases. Two liquid phases in insecticide formulation consist of oil and water phases. The active ingredient contained in insecticide formulation usually cannot dissolve in water. The active ingredient is a chemical that has biological activity to target organism, but in application is needed to dissolve in co-formulant such as solvent, stabilizer, surfactant and many others chemical compound [9]. For application, insecticide usually is diluted with large amount of water, where will be hardly dissolved. Density differences caused there will be form two phased, if it had similar density, it will be more soluble.

Insecticide formulation shows average density of 0.9951-0.9959 g/cm^3 (Table 1). This average density shows stabilization of formulation in water. If the density is almost 1 g/cm^3, it means formulation can be dissolved in water. If density difference density between the two phases gets smaller, the emulsion formed will get better [12]. Surfactant concentrations and the ratio of non-ionic surfactants had a significant effect on the density of insecticide formulation. The formulation density value is quite good and shows the stability in the formation of emulsions between insecticide formulation and water. Ratio DEA and APG of 3:2 was significantly different from the 1:1 concentration, but the DEA ratio of APG 3:2 and 2:3, 1:1 and 2:3 were not significantly different. And also, surfactant concentration can significantly affect the formulation. Surfactants at 5% and 4% were not significantly different, but concentrations of 6% significantly from different with surfactant concentrations of 5% and 4%.

Table 1 Density of insecticide formulations in water

Surfactant concentration (%)	Density (g/cm^3)
DEA:APG Ratio (3:2)	
4	0.9956 ± 0.00ab
5	0.9959 ± 0.00a
6	0.9954 ± 0.00bc
DEA:APG Ratio (1:1)	
4	0.9955 ± 0.00b
5	0.9956 ± 0.00ab
6	0.9951 ± 0.00bc
DEA:APG Ratio (2:3)	
4	0.9955 ± 0.00b
5	0.9956 ± 0.00ab
6	0.9955 ± 0.00b

2.2. Surface Tension

Surfactants are organic compounds that have lipophilic and hydrophilic functional groups in their molecules [8]. Surfactant is a chemical that can decrease surface tension of insecticide formulation. Decreasing surface tension means stability of emulsion between formulation and water. Surfactant also will make formulation to have more contact with the plant. If the surface tension decreases, insecticide solution in water will spread on leave. Plants have surface where a wax actually cover the leaves. As adjuvant, surfactant will also help to wetting formulation on leaves.

Insecticide formulation using surfactant based on palm oil showed that more surfactant concentration in formulation will decrease surface tension of insecticide solution. Data also showed that by adding more APG surfactant will also decrease surface tension of insecticide solution (Figure 1). DEA:APG ratio of 3:2 was significantly different with 1:1 and 2:3. It also showed that surfactant concentration of 4%, 5% and 6% were significantly different. The best insecticide formulation is by using DEA and APG with ratio 2:3 and surfactant concentration of 6% with surface tension value of 27.42 dyne/cm.

2.3. Contact Angle

Contact angle is a way to measure angle of solid surface and tangent of droplet [13]. Measurement contact angle can give information about surfactant performance in pesticide formulation. Surfactant usually used as adjuvant and also as wetting agent. Leaves usually coated with wax, if water drop on the leaves, it usually run off from the leaves. Surfactant used to help pesticide formulation to stick on the leaves.

Contact angle will decrease if surfactant concentration increase. Increasing APG concentration will decrease contact angle of insecticide solution on the leaves (Figure 2). DEA:APG ratio and surfactant concentration significantly affect the contact angle of insecticide solution. It also showed that DEA:APG ratio of 2:3, 1:1 and 2:3 were significantly different, and surfactant concentration of 4% and 5% were significantly different with surfactant concentration of 6%. Data showed that the best treatment of insecticide formulation is by using DEA and APG with ratio 2:3 and surfactant concentration of 6% with contact angle value of 21.61°.

2.4. Particle Size

Particle size analysis is actually measurement of diameter size of emulsion droplet in water [9]. Surfactant has significant influence on particle size and dispersion of emulsion. If particle size decreases, surface and contact area on leaves will increase, so it can help to expand pesticide retention [14]. Uniformity of particle size also shows emulsion stability of insecticide formulation and water. Particle size uniformity means that formulation dispersed equally in water.

Particle size will decrease if surfactant concentration increases, so surfactant help formulation to form emulsion and dispersant in water. Increasing APG concentration will decrease particle size of insecticide formulation in water. Higher deviation standard insecticide solution means that variation of particle size and formulation did not disperse equally (Table 2).

Table 2 Particle size of insecticide formulation in water

Surfactant concentration (%)	**Particle size (μm)**
DEA:APG Ratio (3:2)	
4	6.25 ± 2.24a
5	6.04 ± 2.09ab
6	5.34 ± 1.8cd
DEA : APG Ratio (1:1)	
4	5.79 ± 1.6abc
5	5.62 ± 0.72bcd
6	5.52 ± 0.3cd
DEA:APG Ratio (2:3)	
4	5.68 ± 0.91bcd
5	5.22 ± 0.55d
6	4.64 ± 0.34e

DEA:APG ratio and surfactant concentration significantly affect contact angle of insecticide solution. DEA:APG ratio of 3:2 and 1:1 were significantly different with DEA:APG ratio of 1:1. It also showed that surfactant concentration of 4%, 5% and 6% were significantly different. Minimum particle size and deviation standard of insecticide formulation in water is about 4.64 ± 0.34 μm.

2.5. Effectiveness of Insecticide Formulation to *Spodoptera litura*

Spodoptera litura is an insect pest that occasionally causes heavy damage on soybean crops [15]. For testing purposes, the best insecticide formulations have been chosen from the previous results. The insecticide formulation containing 15% active ingredient. DEA:APG ratio of 2:3 and 6% surfactant was selected.

Insecticide formulation gave effective mortality effect to larvae. The best concentration of formulation is 0.20 % which shows comparatively mortality effect to the commercial insecticide formulation (Table 3). All concentration of insecticide formulation yielded high mortality effect at 48 hours after treatment and at 72 hours after treatment all larvae were died. The most effective concentration of insecticide formulation is 0.20 %.

Table 3 Mortality of *Spodoptera litura* treated with insecticide formulation's solution

Concen-tration (%)	**Mortality (%) at HAT**		
	24	**48**	**72**
Control	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
0.05	60.0 ± 7.1c	94.0 ± 5.5b	100 ± 0.0a
0.10	76.0 ± 8.9b	100 ± 0.0a	100 ± 0.0b
0.20	96.0 ± 5.4a	100 ± 0.0a	100 ± 0.0b
Commercial insecticide (emamectin benzoate 22%)			
0.10 %	96.0 ± 5.5	100 ± 0.0	100 ± 0.0

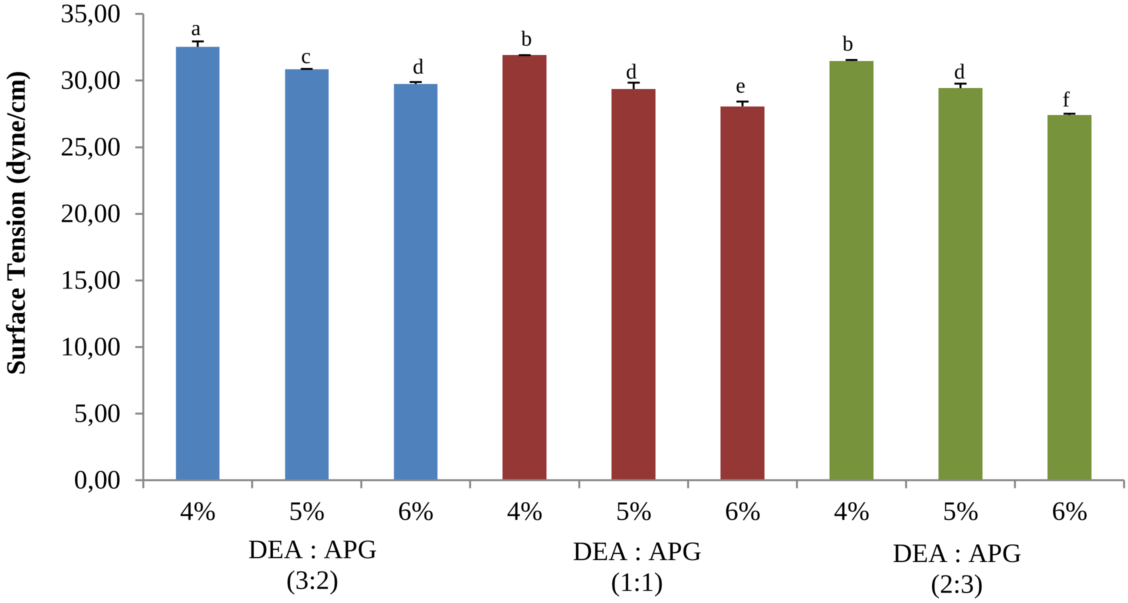

Figure 1 Surface tension of insecticide formulation in water ( ) DEA:APG ratio of 3:2, ( ) DEA: APG ratio of 1:1, ( ) DEA APG ratio of 2:3

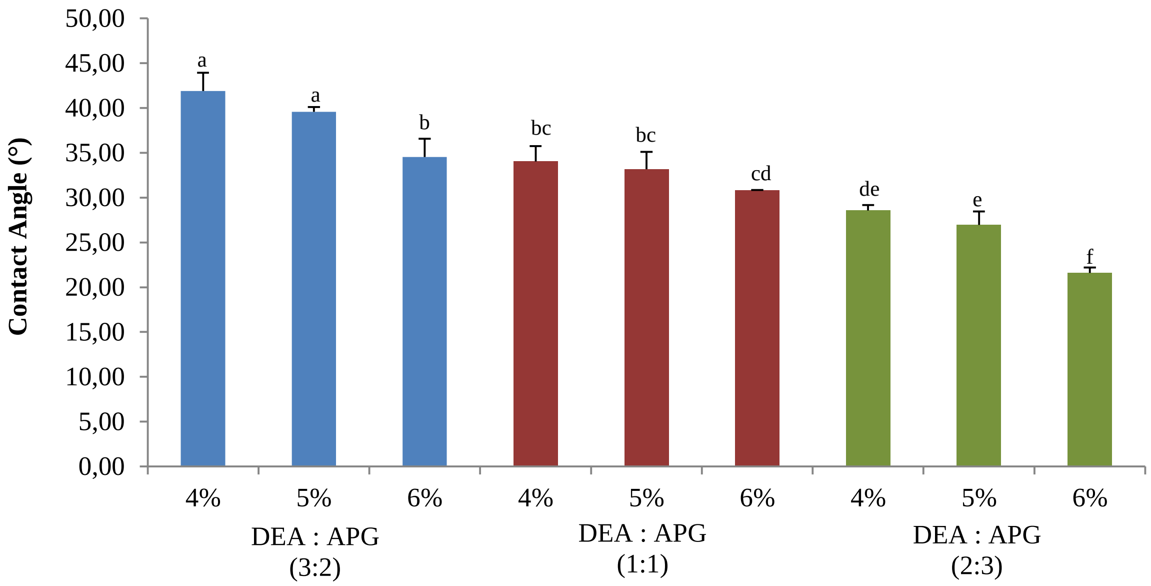

Figure 2 Contact angle of insecticide formulation in water ( ) DEA:APG ratio of 3:2, ( ) DEA: APG ratio of 1:1, ( ) DEA APG ratio of 2:3

3. CONCLUSION

Surfactant had significant influence in this formulation. Increasing surfactant concentration will increase the performance of insecticide formulation. Ratio of nonionic surfactant and surfactant concentration were significantly effect to characteristics of insecticide formulation. The best characteristics of insecticide formulation were density of 0.9955 d/cm^3, surface tension of 27.42 dyne/cm, contact angle of 21.61, and particle size of 4.64. The best insecticide formulation in this research contained non-ionic surfactant 6%, cationic surfactant 1% and DEA: APG ratio of 2:3. This formulation containing 15% emmamectin benzoate as an active ingredient gave high mortality effect to *S. litura* larvae and shows comparatively mortality effect to the commercial product which contained the same active ingredient.

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