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Research Article

Preparation of alphacypermethrin and fipronil emulsifiable concentrates using different concentrations of the modified polytrisiloxane (QS-302)

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Abstract: The present research aimed to enhance the efficacy of alphacypermethrin and fipronil insecticides formulated as an emulsifiable concentrate (EC) by adding varying concentrations of the modified polytrisiloxane (QS-302) as an adjuvant alongside the emulsifier blend. The formulations were subjected to emulsion and thermal stability tests according to the methods used by both the FAO and WHO to determine qualified pesticides. Using the residual thin film technique, the acute toxicity of prepared formulations was also assessed against adult rice weevil *Sitophilus oryzae* (L.). Generally, alphacypermethrin demonstrated greater effectiveness than fipronil, with LC_{50} values of 1.545 ppm for alphacypermethrin compared to 8.60 ppm for fipronil. When the QS 302 adjuvant was incorporated at a concentration of 7% into the EC formulations, the LC_{50} for fipronil decreased from 8.60 ppm to 5.98 ppm. Also, at a 14% addition of QS 302, the LC_{50} value dropped to 2.92 ppm. In contrast, the efficacy of alphacypermethrin against rice weevils diminished when QS 302 was mixed with the other components at the same concentration. This may be attributed to the enhanced pesticide penetration and distribution of fipronil, which was improved more than that of alphacypermethrin due to alterations in the hydrophobic-hydrophilic balance (HLB), ultimately affecting the solubilization and penetration of the insecticide through the rice weevil cuticle.

Keywords: emulsifiable concentrate, formulation, insects, polytrisiloxane

Introduction

Fipronil is a potent pyrazole insecticide, widely used against a large number of veterinary and agricultural pest species (Simon-Delso *et al.*, 2015) as well as used as a public hygiene insecticide (Rojas de Arias and Fournet, 2002; Xue *et al.*, 2009). It was recommended for use in locust control (Peveling, 2000; Peveling *et al.*, 2003). Also, it is commonly used as an insecticide on rice fields to control rice stem borers, brown plant hopper and rice water weevil at a rate of 30-100 g ai/ha. Additionally, alphacypermethrin is a broad-

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spectrum pyrethroid insecticide, effective for the control of chewing and sucking insects in a wide range of crops and animal husbandry at a concentration of 5-30 g active ingredient per ha (Saleem *et al.*, 1998).

Grain losses due to insect infestation during storage are considered a serious problem in developing countries such as Egypt. In particular, the rice weevil, *Sitophilus oryzae* (L.) is one of the most destructive insects infesting grain in Egypt. Fumigation methods by fumigants such as methyl bromide and phosphine are still widely used to control insects in commodities during storage. However, methyl bromide is banned because it is identified as ozone depletion. Insect resistance also developed to phosphine gas was reported by different countries that may have caused control failures.

Treating grain or storage structures with residual contact insecticides is the most effective means of preventing insect infestation. Insecticides used in such situations should meet certain criteria like 1ow mammalian toxicity, high efficacy against target insects and moderate degradation rate, allowing the least amount of residue while maintaining sufficient persistence for insect control (Soltan *et al.*, 2020). Spraying of storage with approved liquid residual insecticide after removal of food residues, as well as the treatment with appropriate insecticide protectant at the time of storage, may be desirable to reduce infestation problems (Daglish *et al.*, 2003; Nayak and Daglish, 2006). Nevertheless, repeated application of commercial insecticides belonging to particular chemical groups might lead to the emergence of resistant strains in several insect species in many countries. This resistance problem necessitates a search to evaluate alternative commercial insecticides belonging to another chemical group that is not rec and can be used in grain storage by application with normal mechanical liquid sprayers (Arthur, 2012). Another technique for reducing insecticide resistance and enhancing the biological activity of the insecticides is to develop new formulation types or improve formulation adjuvant technologies (Hazra *et al.*, 2013).

Combining anionic and nonionic surface-active agents is common in formulating emulsifiable concentrates containing toxic substances. Because the two types of emulsifiers work together synergistically, mixes of anionic and nonionic emulsifiers were the most effective for creating emulsifiable concentrates. (Mollet and Grubenmann, 2008). Additionally, the choice of solvent depends on its physical characteristics, such as its ability to save the active ingredient, its low phytotoxicity to plants, its inability to interact with the active ingredient or the emulsifier, and its flash point, which is typically greater than the lowest flash point of the component. Fipronil has a low solubility in water and non-polar organic solvents. Still, a high solubility in some polar organic solvents, such as acetone (545.9g/L at 20 °C), is useful for emulsifiable concentrate formulations because they are strong solvents. However, fipronil's solubility in water and non-polar organic solvents is not always sufficient to dissolve a sufficient percentage of a pesticide suitable for practical application (European Commission, 2011). Numerous silicon surfactant agents for material functionalization are currently being developed or are already available. Silicone surfactants are polymeric substances with polar components typically nonionic derivatives of polyoxyethylene and polyoxypropylene attached to a methylated, hydrophobic siloxane group. Since hydrophobic silicones have a stronger affinity for one another than for the surrounding polar or aqueous media, functionalizing silicones with silicone surfactants may have two additional benefits: (1) better surfactant adsorption to the interface if physisorption is investigated as a modification route; and (2) the potential mitigation of the association between silicone hydrophobicity and unfavorable biological adhesion (Busscher *et al.*, 1997; Yan *et al.*, 2006).

The present study emphasizes the role of formulation in improving pesticide efficacy by examining the effect of adjuvants such as modified polytrisiloxane (QS-302) against rice weevils to reduce insecticide's spraying amount, and ultimately save cost, Improve the efficiency of pesticide penetration extension and protect our environment.

Materials and Methods

Chemicals

Alphacypermethrin is α-cyano-3-phenoxybenzyl-3- (2,2-dichlorovinyl) -2,2-dimethyl cyclopropane carboxylate, a technical grade with 96.6% purity and its isomer ratios were 2.8% (R) (1S) Cis :97.2 % (S(1R) Cis, was obtained from Shell Research Ltd., Sittingbourne,UK. Fipronil is (±)-5-amino-1-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)- 4-trifluoromethylsulfinylpyrazole-3-carbonitrile (99.7% purity) was purchased from Sigma-Aldrich, USA.. Capstone™ FS-3100 is a nonionic fluoro-surfactant that provides exceptionally low surface tension in aqueous or solvent-based products and enables better wetting and spreading. It was purchased by DuPont company, USA. Modified polytrisiloxane (QS-302 is an organic silicone surfactant/adjuvant to Improve the efficiency of insecticide penetration extension and lasting a long time was provided by JangXi Tiansheng New Materials Co.Ltd, China**.**

Preparation of emulsifiable concentrate (EC) of aphacypermethrin and fipronil:

Three formulations of 10% emulsifiable alphacypermethrin concentrate and three formulations of 5% emulsifiable fipronil concentrate that has been considered in the present work are summarized in Table 1. Insecticides EC of alphacypermethrin and fipronil were prepared by using xylene as a solvent with dimethyl formamide anhydrous as a co-solvent, emulsifier blend, and modified polytrisiloxane (QS-302) as organic silicone surfactant/adjuvants to improve the efficiency of insecticides penetration extension and lasting a long time. These formulations are illustrated in Table 2.

Table 1 HPLC operating conditions for alphacypermethrin and fipronil.

Entries	Fipronil	Alphacypermethrin
Temperature	35 ˚C	40 ˚C
Detector	Multi variable wavelength ultraviolet detector	Multi variable wavelength ultraviolet detector.
Wavelength	280 nm	225 nm
Mobile phase	Acetonitrile 78% + Deionized Water 22%	Acetonitrile 70% + Methanol 10% + Deionized Water 20%
Flow rate	1 ml/min	1 ml/min

Table 2 Formulation of emulsifiable alphacypermethrin and fipronil concentrate.

Insecticide	Formulation code	Content
Alphacypermethrin	A1	Active ingredient 10 g/100 ml, Emulsifier 10 g /100 ml and Solvent and co-solvent (3:1 v/v) made up to 100 ml
	A2	Active ingredient 10 g/100 ml. Emulsifier 10 g /100 ml. modified polytrisiloxane 7 g/100ml and Solvent and co-solvent (3:1 v/v) made up to 100 ml
	A3	Active ingredient 10 g/100 ml. Emulsifier 10 g /100 ml. modified polytrisiloxane 14 g/100ml and Solvent and co-solvent (3:1 v/v) made up to 100 ml
Fipronil	F1	Active ingredient 5 g/100 ml, Emulsifier 5 g /100 ml and Solvent and co-solvent (3:1 v/v) made up to 100 ml
	F2	Active ingredient 5 g/100ml. Emulsifier 5 g /100 ml. modified polytrisiloxane 7 g/100ml and Solvent and co-solvent (3:1 v/v) made up to 100 ml
	F3	Active ingredient 5 g/100 ml. Emulsifier 5 g /100 ml. modified polytrisiloxane 14 g/100ml and Solvent and co-solvent (3:1 v/v) made up to 100 ml

Specification and optimum characteristics of emulsifiable concentrate:

In laboratory studies, the formulation samples were tested for important physical tests such as flash point, emulsion stability, viscosity, and chemical tests such as acidity and active ingredient according to FAO and WHO specifications (JMPS, 2010).

Physic*al* tests

The following tests were carried out on the prepared formulations of alphacypermethrin and fipronil.

Flash point

This is to ascertain the fire hazard from the formulation while in storage and transport. The sample under test was placed in the cup of Abel apparatus. The flashpoint was determined as the lowest temperature by applying a small test flame to the cup at regular intervals, causing vapor above the sample to ignite with a flash that occurred inside the cup (CIPAC, 1995a).

Emulsion stability

Initial emulsification

A 100 ml graduated cylinders are filled with 95 ml of standard water (composed of 342 ppm hardness, pH 6.0-7.0, and 80:20 Ca:Mg ratio). The remaining 100 ml cylinders are filled with five milliliters of emulsifiable concentrates. The cylinders containing emulsifiable concentrate and standard water are closed and then inverted once. The spontaneous formation of the emulsified mixture was observed visually after 30 seconds (CIPAC, 2003).

Emulsion stability and re-emulsion

This test can be conducted on emulsifiable concentrate (EC) and emulsion oil in water (EW) pesticide formulations according to CIPAC MT 36.3 (CIPAC, 2003). Emulsion characteristics are examined by mixing 5 ml of the formulation sample with WHO standard hard water in a 100 ml measuring cylinder, resulting in 100 ml of aqueous emulsion. To prepare hard water, 0.304 g of anhydrous calcium chloride and 0.139 g of magnesium chloride hexahydrate were dissolved in distilled water to a total volume of one liter. This corresponds to a total hardness equivalent to 342 ppm of calcium carbonate according to CIPAC MT 18 (CIPAC, 1995b). The cylinder was sealed with a stopper and turned upside down ten times. Afterward, the quantity of free oil or cream that had separated and settled at the top or bottom of the emulsion was noted. This observation occurred after the emulsion had been left to stand undisturbed for different intervals, specifically at the initial time, after 0.5 h, and at 24 h for re-emulsification.

Viscosity Test

The viscosity test was conducted according to CIPAC MT 192 (CIPAC, 2005b). This method is intended to characterize the flow behavior of liquid crop protection formulations. A sample is transferred to a standard measuring system (Capillary viscometer). The measurement is carried out under various shear conditions. The fluid sample temperature is kept constant at 20 °C throughout the test. The test is conducted again at a temperature of 40 °C. Two determinations at each temperature level were made as recommended. The apparent viscosities have been determined.

Chemical Tests

Acidity Test

The acidity test was carried out according to CIPAC MT 191(CIPAC, 2005a). 10 g of sample was weighed accurately into a dry conical flask and diluted with 100 ml water. The content of the flask was titrated immediately with the standard sodium hydroxide solution using methyl orange as an indicator. A blank reading with 100 ml of water was also determined.

$$\text{Acidity (as } H_2SO_4\text{) percent by mass} = 4.9\ (V-v)\ N/M$$

In the formula V is the volume in ml of standard sodium hydroxide solution is required for the test. v is the volume in ml of standard sodium hydroxide solution required for the blank determination. N is the normality of standard sodium hydroxide solution. M is the mass in g of the material test. When samples were tested using the above-prescribed method, acidity should be 0.05 percent by mass maximum.

Active Ingredient Test

The concentration of alphacypermethrin and fipronil was determined by HPLC with variable wavelength ultraviolet detector (VWD).

Instrumental and analytical conditions

High-Performance Liquid Chromatography (HPLC) Agilent 1260 HPLC Infinity system (Germany) was used for analysis with an Agilent variable wavelength ultraviolet detector. Separation was performed on analytical columns ZORBAX Eclips Plus (250 £.6 mm id, 5 mm particle size). Data was managed using HP Chemstation software.

Rice weevil culture and bioassay

In the laboratory, adult rice weevil, *Sitophilus oryzae* (L.), was reared as described by El-Kashan (1984). Each insecticide concentration was tested four times at 27 ± 1 °C and 70 % R.H. The surface deposit application method of Moustafa *et al.* (1980) was used to test the acute toxicity of insecticides against rice weevils via Petri dishes (9 cm diameter = 63.585 cm^2). The varied concentrations of the tested insecticides dissolved in acetone (from 0.01 to 0.2 $\mu g/cm^2$) were spread on the petri dishes and allowed to dry for an hour before use. Twenty lab-reared adults, both male and female, were placed in each Petri dish at the age of three weeks. They were then enclosed by plastic rings and incubated at room temperature. Two days later, the mortality counts were corrected based on Abbot's formula (Abbott, 1925). To compute the LC_{50} values, we used a probit analysis (Finney, 1971) using 95% confidence intervals, slope coefficients, and Chi-squares.

Results

Physical-Chemical Properties

The purpose of this study was to develop stable emulsifiable concentrates (ECs) containing alphacypermethrin and fipronil as active ingredients. Considering the properties of active ingredients and emulsifiers, we initially selected appropriate solvents and emulsifiers for the technical material. Through experimentation, a stable emulsion with the right balance of solvents and emulsifiers was developed that would provide the desired results during storage and application. Besides determining the stability of an insecticide, the effects of adjuvants such as modified polytrisiloxane on improving insecticide efficacy of developed formulations were evaluated. The physico-chemical characteristics of the emulsifiable concentrate formulations of fipronil and alphacypermethrin were gathered in the data given in Table (3).

All formulations passed physical tests, including flash point (above 24.5 °C, as per CIPAC MT 12 guidelines; CIPAC, 1995a) and emulsion stability. The stability tests conducted for the 10% emulsifiable alphacypermethrin concentrate and 5% emulsifiable fipronil concentrate formulations demonstrated stability after 2 hours, with cream or oil phase levels below the FAO or WHO standard specifications (JMPS, 2010). The re-emulsification tests after 24 hours also met these standards.

The acidity test results for all formulations were within the guidelines set by FAO and WHO (free acidity/alkalinity between 0.1% and 0.3%; CIPAC, 2005a; JMPS, 2010). The active ingredient content for alphacypermethrin formulations was around 10% ± 0.02, and for fipronil formulations, around 5% ± 0.012.

Surfactants, effective acidifiers, lowered the pH of water used for emulsification, preventing breakdown of active ingredients and improving stability. All formulations were chemically and physically stable after 14 days of tropical storage at 54 °C, meeting FAO/WHO specifications for tropical conditions (JMPS, 2010).

Acute toxicity against rice weevil

The mortality percentages of six insecticide formulations were evaluated on *Sitophilus* *oryzae* adults using a residual film method. LC_{50} values and regression line slopes are summarized in Table 4 and Figs. 1 and 2. All control groups had less than 5% mortality.

For alphacypermethrin formulations, toxicity rankings were as follows: A1 (without modified polytrisiloxane) > A2 (7% modified polytrisiloxane) > A3 (14% modified polytrisiloxane). The LC50 for A1 was the lowest (1.54 ppm), indicating the highest toxicity.

In contrast, fipronil formulations, toxicity increased with higher polytrisiloxane content: F3 (14% modified polytrisiloxane) > F2 (7%) > F1 (without polytrisiloxane). QS 302, a surfactant added to fipronil formulations, enhanced acute toxicity by 2–3 times based on its concentration, likely due to reduced surface tension and improved penetration.

Discussion

The physical and chemical properties of EC formulations are critical for ensuring performance in field applications. The results confirm that all tested formulations met FAO/WHO standards for flash point, emulsion stability, and acidity (CIPAC, 1995a; CIPAC, 2003). The stability under tropical conditions (14 days at 54 °C) suggests that these formulations are suitable for storage and use in diverse environments (JMPS, 2010).

Table 3 Physico-chemical properties of emulsifiable concentrate formulations of alphacypermethrin and fipronil.

Pesticide	Formulation	Test performance	Result	Standard result
Alphacypermethrin	A1 A2 A3	Emulsion stability	No creaming	Separation including creaming at the top and sedimentation at the bottom shall not exceed 2.0 mL
	A1	Flash point (ºC)	30	Flash point should be above 24.5 ºC
	A2		30.1	
	A3		30.4	
	A1	Viscosity (poise)	0.93	
	A2		0.84	
	A3		0.83	
	A1	Acidity (% w/w)	0.002	Acidity shall not exceed 0.05 percent by mass
	A2		0.0018	
	A3		0.001	
Fipronil	F1 F2 F3	Emulsion stability	No creaming	Separation including creaming at the top and sedimentation at the bottom shall not exceed 2.0 mL
	F1	Flash point (ºC)	30.4	Flash point should be above 24.5 ºC
	F2		30.3	
	F3		30.4	
	F1	Viscosity (poise)	0.88	
	F2		0.87	
	F3		0.84	
	F1	Acidity (% w/w)	0.0017	Acidity shall not exceed 0.05 percent by mass
	F2		0.0013	
	F3		0.0014	

Table 4 Residual toxicity of alphacypermethrin and fipronil formulations to the adults of the rice weevil.

Insecticide	EC formulations*	LC_{50} (µg/Cm^2)	Confidence limits (µg/Cm^2)	Slope	χ^2 (df)	Toxicity index**
Alphacypermethrin	A_1	0.024	0.011-0.037	1.434	5.097 (3)	100
	A_2	0.026	0.013-0.038	1.537	3.654 (3)	92.31
	A_3	0.047	0.030-0.065	1.566	5.909 (3)	51.06
Fipronil	F_1	0.135	0.121-0.152	4.923	7.641(3)	34.07
	F_2	0.095	0.075-0.012	2.287	5.575 (3)	48.42
	F_3	0.046	0.035-0.057	2.758	6.595 (3)	100

* A_1 and F_1 EC formulations without modified polytrisiloxane, A_2 and F_2 EC formulations mixed with 7% modified polytrisiloxane and A_3 and F_3 EC formulations mixed with 14 % modified polytrisiloxane. ** Relative to the highly toxic insecticide.

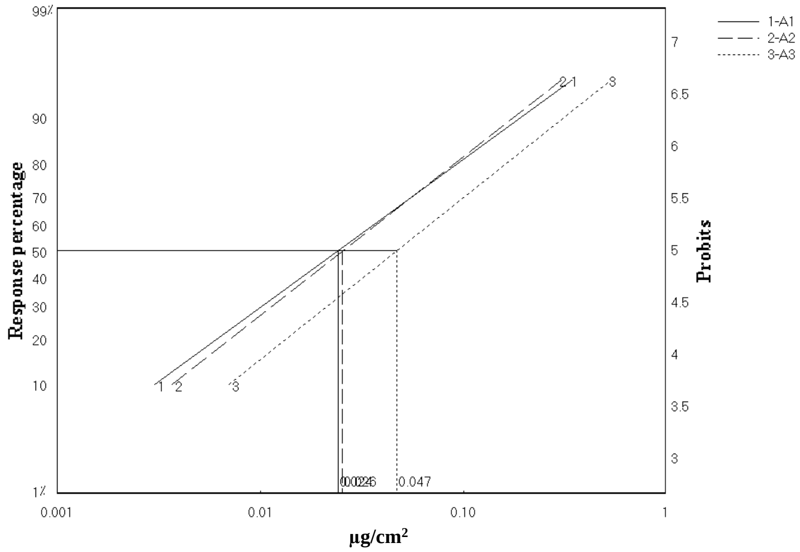

Figure 1 The Ld-P line of alphacypermethrin EC formulations (A1, A2 and A3) was bioassayed against *Sitophilus oryzae* after 48 h of exposure.

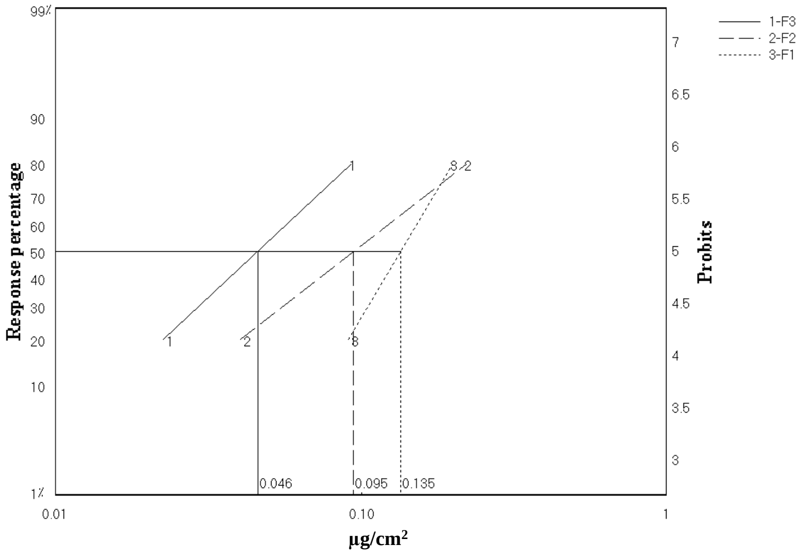

Figure 2 The Ld-P line of fipronil EC formulations (F1, F2 and F3) was bioassayed against *Sitophilus oryzae* after 48 h of exposure.

The use of acidifying surfactants to lower pH was effective in preventing the breakdown of active ingredients, enhancing the formulations' stability. Consistent active ingredient content (alphacypermethrin: 10% ± 0.02; fipronil: 5% ± 0.012) further underscores the reliability of these EC formulations. Emulsion stability and re-emulsification properties ensure the practicality of these formulations in agricultural settings, even in the presence of hard water or limited agitation (Feng *et al.*, 2018).

The acute toxicity results demonstrate the significant role of surfactants, particularly modified polytrisiloxane, in influencing insecticide performance. For alphacypermethrin, increasing polytrisiloxane content reduced toxicity, possibly due to changes in hydrophilic-lipophilic balance (HLB) affecting solubilization and penetration (Fainerman *et al.*, 2019). In contrast, higher polytrisiloxane content increased fipronil toxicity, likely due to enhanced surface tension reduction and penetration properties of QS 302 (Jiang *et al.*, 2011).

The enhanced spreading and wetting properties of QS 302 explain its effectiveness in fipronil formulations, aligning with findings that organo-silicone surfactants reduce surface tension below critical micelle concentration, thereby increasing penetration and acute toxicity (Chow *et al.*, 1989; Fainerman *et al.*, 2019; Jiao *et al.*, 2023). These results suggest that while QS 302 improves fipronil efficacy, its effect varies with the molecular structure of the active ingredient.

The higher toxicity of alphacypermethrin formulations without polytrisiloxane (A1) highlights the need to balance surfactant concentrations to optimize efficacy while minimizing environmental impact and cost. Further research on specific surfactant-pesticide combinations is necessary to refine formulation strategies, considering factors like molecular configuration and HLB to improve solubilization and penetration through insect cuticles (Jiang *et al.*, 2011).

The study supports the potential of QS 302 to reduce insecticide application rates by 20–30%, saving costs and reducing environmental risks. The ability of surfactants to enhance retention, spreading, and penetration makes them valuable in developing more efficient and sustainable pest control solutions.

Conclusion

This study demonstrated that the physicochemical properties of EC formulations of alphacypermethrin and fipronil could be modified by adding a commercially available modified polytrisiloxane (QS-302) as an adjuvant for EC formulations. Additionally, the inclusion of this adjuvant for use in the development of EC formulations may compromise not only the performance of the EC but also the efficacy of the insecticide against the target insect. It also helps reduce the amount and number of other additives in the formulation. For this reason, QS-302 can increase the penetration of fipronil into the cuticle of adult rice weevils, whereas other insecticides, such as alphacypermethrin cannot. This may be explained by the hydrophilic-lipophilic balance (HBL), which leads to solubilization and penetration of the insecticide in the rice weevil cuticle. It is best to consider specific data on each surfactant/pesticide combination in concluding a product's efficacy as a penetrate.

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تهیه کنسانتره امولسیون‌پذیر آلفاسای پرمترین و فیپرونیل با استفاده از غلظت‌های مختلف پلی‌تری سیلوکسان اصلاح شده (QS-302)

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چکیده: هدف پژوهش حاضر افزایش کارایی حشره‌کش‌های آلفاسای پرمترین و فیپرونیل فرموله شده به‌عنوان کنسانتره امولسیون‌پذیر (EC) با افزودن غلظت‌های مختلف پلی‌تری سیلوکسان اصلاح شده (QS-302) به‌عنوان یک ادجوانت در کنار مخلوط امولسیفایر بود. فرمول‌ها تحت آزمایش‌های امولسیونی و پایداری حرارتی با توجه به روش‌هایی که توسط FAO و WHO برای تعیین آفت‌کش‌های واجد شرایط استفاده می‌شوند، قرار گرفتند. با استفاده از تکنیک لایه نازک باقی‌مانده، سمّیت حاد فرمول‌های آماده شده روی حشرات کامل شپشه برنج *Sitophilus oryzae* (L.) آزمایش شد. به‌طور کلی، آلفاسای پرمترین اثربخشی بیش‌تری نسبت به فیپرونیل نشان داد، با مقادیر LC_{50} ۱/۵۴۵ پی‌پی‌ام برای آلفاسی پرمترین در مقایسه با ۸/۶ پی‌پی‌ام برای فیپرونیل. هنگامی‌که ادجوانت QS 302 در غلظت ۷ درصد در فرمولاسیون EC گنجانده شد، LC_{50} برای فیپرونیل از ۸/۶ پی‌پی‌ام به ۵/۹۸ پی‌پی‌ام کاهش یافت. هم‌چنین، با افزودن ۱۴ درصدی QS 302، مقدار LC_{50} به ۲/۹۲ پی‌پی‌ام کاهش یافت. در مقابل، اثر آلفاسای پرمترین در برابر شپشه برنج زمانی که QS 302 با سایر اجزاء در همان غلظت مخلوط شد کاهش یافت. این تأثیر ممکن است به افزایش نفوذ آفت‌کش و توزیع فیپرونیل نسبت داده شود که به‌دلیل تغییرات در تعادل آبگریز-آبدوست (HLB) بیش‌تر از آلفاسای پرمترین بهبود یافته است که در نهایت بر حل شدن و نفوذ حشره‌کش از طریق کوتیکول شپشه برنج تأثیر می‌گذارد.

واژگان کلیدی: کنسانتره امولسیون‌پذیر، فرمولاسیون، حشرات، پلی‌تری سیلوکسان