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Biodiesel Waste Based New Generation Formulation of Permethrin for Cockroach Control

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Permethrin Microemulsion, Nanoemulsion & Emulsifiable concentrate was formulated using biodiesel waste as an active dissolving solvent or as a carrier solvent. Process of stable emulsion development was optimized for parameters such as non-ionic surfactants concentration in micro and nanoemulsion and anionic surfactant concentration in emulsifiable concentration with high physical and chemical stability. Permethrin was analyzed by Gas chromatography using ECD and physical stability of emulsions was optimized in terms of shelf life of the product. The permethrin microemulsion (ME) ,Nanoemulsion (NE) and emulsifiable concentrate (EC) containing biodiesel waste of 20-100 ppm gave 30 -90 % mortality rates against *Periplaneta americana* (Order: Blattodea, Family: Blattidae) within 24 hours. The LD_{50} (Lethal dose) values recorded for the microemulsion, nanoemulsion and emulsifiable concentrate were 6.7646,10.385 & 46.7289 with biodiesel waste as a solvent or carriers for above formulations.

Keywords: Permethrin, Microemulsion, Nanoemulsion, Emulsifiable Concentrate, Hydrophilic-lipophilic Balance (HLB), Biodiesel waste, *Periplaneta Americana*

Introduction

A microemulsion is thermodynamically stable, and usually a transparent liquid solution. In pharmaceuticals, microemulsions are the objects of investigation in relation to drug delivery[2], because of their advantages (thermodynamic stability, ease of preparation, transparency, low viscosity, considerable potential for solubilizing a variety of drugs). The biodiesel production in India utilizes two main crops, karanja (*Pongamia pinnata*) and jatropha (*Jatropha curcas*) as major source of non-edible oils. Production of biodiesel generates 10% biodiesel waste liquid by volume approximately i.e. to say 10 kg of crude glycerol is generated as a by-product for every 100 kg of biodiesel produced. Majority of industrial products employ only purified glycerol as a raw material, and therefore bio diesel waste liquid is often discarded as a waste product. This liquid biodiesel waste creates disposal problems and in future, liquid biodiesel waste is likely to be produced in large amounts, with detrimental effects on the environment. Hence, there is an urgent need to convert crude glycerol into more valuable products. (Patent filed, Application No.: 2391/MUM/2008). In our previous research work, biodiesel has been used as a solvent for oil soluble synthetic pyrethroid based conventional formulations like emulsifiable concentrate[7]. The formulations thus developed were having improved storage stability. In this paper we have used biodiesel waste in new generation water based liquid formulation of synthetic pyrethroids to improve physical as well as chemical stability of formulation as well as to increase its efficacy as compared to conventional or solvent based formulation.

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Experimental section

Biodiesel waste (jatropha oil) from I.I.T Delhi, Permethrin (Technical, purity 93%) was purchased from United Phosphorous Limited, Mumbai, Polysorbate 80 (Tween 80) and Span 80 (sorbitan monooleate) from Merck India Limited.

Test insect

Cultures of *Periplaneta americana* were maintained at laboratory conditions, 60-70% RH, 27±1ºC and darkness i.e. 12:12 (L:D) h photocycle[8].

ATR-FTIR analysis

Infrared (IR) spectra were recorded on a Bruker alpha ATR-FTIR spectrophotometer using the attenuated total reflectance (ATR) technique, and values are expressed as gmax cm_1.

Preparation of microemulsion

Microemulsions and nanoemulsions prepared using these surfactants were formed spontaneously at 30 ◦C, and samples were normally prepared by diluting water/surfactant mixtures with oil, or by diluting oil/surfactant (Table 1) mixtures with water[9].

The surfactants used are Tween-80 (polysorbate-80) and Span-80 (Sorbitan monooletae). Emulsifiable concentrate formulation with and without biodiesel waste were prepared by method Wu *et al*[10].

Bioefficacy of chlorpyrifos microemulsion against *periplaneta americana* by contact toxicity bioassay

The efficacy of the emulsions thus formulated with and without biodiesel waste against the American Cockroach, *Periplaneta americana.* Contact toxicity bioassay was performed by applying selected doses of the microemulsions, nanoemulsions and emulsifiable concentrate (20, 40, 60, 80, 100 ppm) in the cages with the help of a microapplicator. 10 cockroaches were released in cages containing emulsion and mortality was observed after 24 hours. Each assay for different doses of the emulsion was performed 3 times. A control set was also maintained [11].

Results and Discussion

Discussion for ATR-FTIR

In biodiesel waste some additional peaks found at 1580-1740 cm-1.Peak at 1740cm-1 indicates the presence of carbonyl group of an ester. The absorbance bands of permethrin were located at 1730, 1086 and 949 cm-1[12]. In microemulsion formulation dissolution of permethrin in biodiesel waste was confirmed by the band at 1730,1086,949,1643 cm-1.The intensity of band was not sharp due to presence of surfactant aggregated[9] system in continuous phase (water approx 60%). ATR-FTIR spectrum of microemulsion clearly indicate, there is no chemical interaction between disperse and continuous phase and so it can be said that it is a physical mixture of both the two phases[12].

Table 1—Preparation of Microemulsion with varying concentration of Inert ingredients

Ingredients	EC 1(F1)	EC2(F2)	ME(F3)	NE(F4)
Permethrin	10	10	10	10
Solvent CIX	46		----	---
Biodiesel Solvent	---	78	3	3
Cyclohexanone	32	---	----	----
Surfactants (w/w)	10	10	20	15
Water	-----	-----	Upto 100	Upto 100

Discussion for insecticidal bioassay

The effect of permethrin was studied by preparing microemulsion, nanoemulsion and emulsifiable concentrate with and without biodiesel waste as a solvent or carrier and determining the LD_{50} of the emulsions. The emulsions were divided into four group i.e F1 to F4 (with biodiesel waste)(Table 1&3). The amount of biodiesel waste in microemulsion and nanoemulsion formulation was constant in recipe i.e. 3.0 % w/w (Table 1) but in emulsifiable concentrate it was 78% w/w. Biodiesel waste was used to solubilise

Table 2—Bioefficacy of Permethrin emulsions and estimation of LD_{50} values

S.No.	Sample Name	Concentration (ml)	Percentage Mortality	LD_{50} (mg/l)
1	EC (F1)	0.02	3.0	46.7299
		0.04	4.0	
		0.06	6.0	
		0.08	7.3	
		0.10	8.0	
		Control	0.0	
2	EC (F2)	0.02	3.0	54.9779
		0.04	4.0	
		0.06	5.0	
		0.08	6.7	
		0.10	7.2	
		Control	0.0	
3	ME (F3)	0.02	7.3	6.7646
		0.04	7.7	
		0.06	8.3	
		0.08	8.7	
		0.10	9.0	
		Control	0.0	
4	NE (F4)	0.02	6.33	10.385
		0.04	7.33	
		0.06	7.66	
		0.08	8.33	
		0.10	8.33	
		Control	0.0	

EC (F1) = Emulsifiable Concentrate of Permethrin with biodiesel waste
EC (F2) = Emulsifiable Concentrate of Permethrin without biodiesel waste
ME (F3) =Microemulsion of permethrin with biodiesel waste
NE (F4) = Nanoemulsions of permethrin with biodiesel waste

Table 3—Biodiesel waste composition

S.No.	Name of Ingredient	% of Ingredients
1.	Glycerol	40-50%
2.	Alcohol	0.2-1%
3.	Mono-, di-& tri-glycerides	1.5-3%
4.	Free Fatty Acid	1-2%
6.	Triglyceride Ester	0.1-0.2%
7.	Water	0.1-0.3%

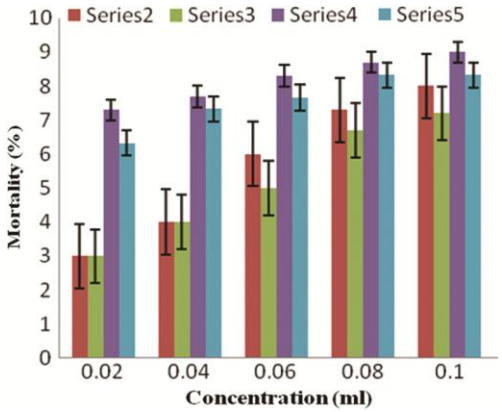

Fig.1—Graph between % mortality and concentration (in ml) for different formulations

permethrin in disperse phase, it did not show any insecticidal activity alone against cockroaches. When it was used in the microemulsion (ME) (F3) and nanoemulsion (F4) (Table 1) as disperse phase and as a carrier solvent for EC formulation (F1), the LD_{50} values decreased i.e 6.7646,10.385 & 46.7299 (Table 3) mg/l and mortality also increased i.e 90% for ME, 80% for NE and 80% for EC with biodiesel waste and 70% for EC (F2) without biodiesel waste, after 24 hours (Fig. 1). The variation of the toxicity of the ME, NE and EC of permethrin with and without biodiesel waste against cockroaches is shown in Figure 1. From the graph it can be seen that ME, NE and EC with biodiesel waste were more toxic and effective as compared to permethrin EC without biodiesel waste as a carrier solvent.Biodiesel waste contains some (Table 3) mono,di and tri glycerides, free fatty acids ,alcohol, Glycerol and methyl ester[7], and when permethrin is solubilised in biodiesel waste; the biodiesel waste fluxes the surfactant monomer continuously and these monomer assemble to form micelles which reduce the surface tension between the two layers and decrease the contact time with continuous phase (water) and stabilize the permethrin in water based emulsions. The use of biodiesel waste makes the emulsions more environments friendly and user friendly as compared to conventional petroleum based solvents.

Conclusion

The paper greatly emphasises on the efficient utilization of biodiesel waste or crude glycerol as a solvent or carrier or to replace the petroleum based hazardous, carcinogenic solvents to figure out environment friendly and cost effective product development work in new era. As Biodiesel waste creates disposal problem due to active constituents present in its own composition[7], hence by formulating the biodiesel waste with other ingredients, a sustainable and economically feasible green product can be developed.

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