Journal of King Saud University – Science 33 (2021) 101649

Contents lists available at ScienceDirect

Journal of King Saud University – Science

journal homepage: www.sciencedirect.com

Original article

Improvement of expired insecticides and their effectiveness against the cotton leafworm, *Spodoptera littoralis* (Boisd.)

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ARTICLE INFO

Article history:
Received 25 November 2020
Revised 11 September 2021
Accepted 6 October 2021
Available online 18 October 2021

Keyword:
Outdated
Obsolete insecticides
Disposal
Emulsifiers
Improvement
Efficiency
Spodoptera littoralis

ABSTRACT

Objectives: This study aimed to recycle some expired insecticides and evaluate their effectiveness against the cotton leaf worm, *Spodoptera littoralis* (Boisd.) as a tactic to dispose of these obsolete insecticides.
Methods: The physical and chemical characteristics of chlorpyrifos (Chlorzane 48% EC), malathion (Nasr-lathion 57% EC) and cyhalothrin (Lambda-cyhalothrin 5% EC) insecticides were determined. The active ingredients of the tested compounds were estimated by gas–liquid chromatography (GLC) equipped with a flame photometric detector GC/FPD and the insecticidal efficacy against the 4th instar larvae of the cotton leafworm, *S. littoralis* (Boisd.) was evaluated by the leaf dipping technique.
Results: The physical and chemical characteristics of the tested insecticides clarified that chlorpyrifos (Chlorzane 48% EC) succeeded in the stability of emulsion, while cyhalothrin (Lambda-cyhalothrin 5% EC) and malathion (Nasr-lathion 57% EC) failed the test, whether unexpired or expired. The emulsifiers, Tween 80 or Triton X-100 at a concentration of 20%, managed to improve the characterizations of the expired insecticides, cyhalothrin and malathion. Moreover, these emulsifiers investigated a promising increase in the efficiency of expired cyhalothrin against *S. littoralis*.
Conclusions: The emulsifiers, Tween 80 or Triton X-100 could be used to increase the efficiency of expired insecticides, especially cyhalothrin 5% EC, thus managing to apply and dispose of that outdated insecticide.

1. Introduction

The food and agriculture organization (FAO) defines obsolete pesticides as those that are no longer appropriate for use and thus need disposal, which include banned, outdated, unlabeled, and/or unknown pesticides, plus empty and contaminated pesticide tanks and contaminated soil entombed in ergonomically landfills or in a flat open area or closed pits (FAO, 2020b). The problem of obsolete pesticide stocks started to receive attention at the end of the 1980s (Dollimore and Schimpf, 2013). It is estimated that over 500,000 tonnes of obsolete pesticides are scattered throughout developing countries. Most (if not all) African countries have accumulated large amounts of obsolete persistent organic pollutants of 50,000 to 100,000 tonnes (pesticides and polychlorinated biphenyls) (Mansour, 2009). Improper disposal of outdated pesticides represents a big problem for public health and the environment because various of these pesticides are poisonous, kept in open or unprotected stores, seeped or corroded containers (Minh et al., 2006; Shalaby et al., 2018; FAO, 2020b). The seeping of pesticides into the ground contaminates groundwater and the soil. Poisoning of humans and animals can occur through direct or indirect contact with obsolete products and inhalation of vapors. Fire hazards may take place as a result of poor management of the stockpiles (Shalaby and Abdou, 2010; Hajjar, 2015; Norman and Fishel, 2017). Moreover, pest resistance to pesticides occurs due to variable used doses of expired products. The major causes of the obsolete pesticides' accumulation are the donation or purchase undue quantities of pesticides owing to commercial concerns or the lack of insufficient aid coordination, donation or buying of inappropriate pesticides, poor inventory management, and the non-disposal of banned and expired pesticides (Dvorská et al., 2012). The problem of outdated pesticides is very critical, so immediate action is required to get rid of the existing stocks and prevent more accumulations. High-temperature incineration is still the preferred

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.jksus.2021.101649
1018-3647/

technique as a permanent solution to dispose of toxic chemical wastes. The very problem of incineration is the release of polycyclic aromatic hydrocarbons and carbon soot, chlorinated dibenzo-dioxins and –furans, which are of a major concern for human health (Simeonov et al., 2014). However, there is no simple method of pesticides disposal that is safe, inexpensive and generally applies under prevailing conditions in developing countries (Mansour, 2009). Moreover, the preferred disposal option, high-temperature incineration, is ordinarily absent. The disposal of expired pesticides in developing countries in most cases requires repackaging, transmission to Europe and burning in specialized high-temperature hazardous waste ovens (Satyavani et al., 2011). This costs between $3000 and $4500 per tonne of waste (Hajjar, 2015). Pesticide formulation is a combination of active ingredient and other additives (formerly called inert ingredients). The emulsifier is a kind of adjuvant which is incorporated into the liquid to prevent the separation of the emulsion (Feng et al., 2018). The physical and chemical characteristics of pesticides can be used to specify the kind of adjuvant used and to ensure the quality of pesticides used. The current research aimed to improve expired insecticides and evaluate their efficacy against the cotton leafworm (*Spodoptera littoralis*).

2. Materials and methods

2.1. Insecticides

2.1.1. Chlorpyrifos

Two formulations of Chlorzane 48% EC (expired and unexpired) were used. The formulations were supplied by Kafr El-Zayat Pesticides and Chemicals Company, Kafr El-Zayat, Gharbia, Egypt.

2.1.2. Cyhalothrin

Two formulations of Lambda-cyhalothrin 5% EC (expired and unexpired) were supplied by Parijat Agrochemicals Company. Greater Kailash, New Delhi, India.

2.1.3. Malathion

Two formulations of Nasr-lathion 57% EC (expired and unexpired) were supplied by El Nasr Company for Intermediate Chemicals. Cairo-Alexandria Desert Road, km 28, Industrial Area, Abou-Rawash, Giza, Egypt.

2.2. Adjuvants

Tween 20 and Tween 80 were produced by El Nasr Pharmaceutical Chemicals Co., Egypt.

Span 20 and Triton X-100 were produced by Loba Chemie Pvt. Ltd., Wodehouse Road, Jehangir villa, Mumbai, India.

2.3. Physico-chemical properties of the tested formulations

2.3.1. Emulsion stability test

Anhydrous calcium chloride (0.304 g) and magnesium chloride hexahydrate (0.139 g) are thawed in distilled water and made up to 1 L to obtain standard hard water. The resulting water has 342 mg L^{-1} of hardness measured as calcium carbonate (Dobrat and Martijn, 1995). Standard soft water was obtained by mixing 100 mL of standard hard water with 900 mL of distilled water. The water hardness was 34.2 mg L^{-1}, calculated as calcium carbonate (Dobrat and Martijn, 1995). The emulsion stability test was performed in compliance with WHO standards (WHO, 1979). Inside 250 mL beaker, 75–80 mL of the examined water (distilled, soft, and hard water) was added. Five milliliters of the emulsifiable concentrate were added by a pipette, while stirring with a glass rod. The contents of the beaker were supplemented to 100 mL by adding the examined water with regular stirring. The cylinder was left for one hour at 30–31 °C and checked for any free oil or creaming layers. The amount of free oil, cream, or solid matter, if formed, should not exceed 2 mL.

2.3.2. Foam test

The emulsion stability test was also conducted to determine the amount of foam created after 5 min on the surface of the emulsion. The foam layer should not surpass 5 mL to pass the test (WHO, 1979; Dobrat and Martijn, 1995).

2.3.3. pH test

The test was performed in accordance with CIPAC standards (Dobrat and Martijn, 1995). One milliliter of the formulation being tested was estimated and transported to a measuring cylinder (100 mL) contained approximately 50 mL of the tested water. The cylinder was filled to 100 mL and shaken vigorously for 1 min. After that, it was allowed to settle. The pH of the supernatant liquid was estimated.

2.3.4. Storage stability test

2.3.4.1. Stability at 0 °C. The test was performed in accordance with CIPAC specifications (Dobrat and Martijn, 1995). The formulation of 100 mL was put in a measuring cylinder and poured into a glass flask. The glass bottle was tightly sealed and cooled for 7 days to 0 ± 2 °C, then the previous three tests were performed.

2.3.4.2. Stability at elevated temperature. The approach was established in compliance with CIPAC specifications (Dobrat and Martijn, 1995). The liquid formulation of 100 mL was placed into a glass flask. The glass bottle was tightly closed to avoid volume losses, and preserved for 14 days in an oven at 54 ± 2 °C. The stored specimens were cooled to ambient temperature, then emulsion stability, foam and pH examinations were conducted.

2.4. Determination of the active ingredients of the tested compounds

A series of concentrations for each insecticide was prepared by diluting the commercial formulation with hexane. The solution was injected into GLC equipped with a flame photometric detector, GC/FPD. GC analysis was conducted on a PAS-1701 (Agilent, Folsom, CA) fused silica capillary column of 30 m length, 0.32 mm id., and 0.25 μm film thickness. The oven temperature was programmed from an initial temperature of 160 (2 min hold) to 210 °C at a rate of 5 °C min^{-1} and was maintained at 210 °C for 3 min and raised to 240 °C at a rate of 5 °C min^{-1} and was maintained at 240 °C for 1 min and raised to 270 °C at a rate of 20 °C min^{-1} and was maintained at 270 °C for 10 min. The injector and detector temperatures were maintained at 240 and 260 °C, respectively. Nitrogen was used as a carrier at a flow rate of 3 mL min^{-1}. The hydrogen and air flow rates were 75 and 100 mL min^{-1}, respectively. Peaks were identified by comparison of sample retention time values with those of the corresponding pure standard compounds. Under these conditions, the retention time values of malathion, chlorpyrifos and cyhalothrin were 7.33, 8.132 and 18.05 min, respectively.

2.5. Bioassay test

A laboratory strain of the cotton leafworm *Spodoptera littoralis* (Boisd.) was maintained under constant conditions of 25 ± 1 °C and 70 ± 5% relative humidity and kept off any contamination by chemicals till the time of study in order to obtain a susceptible and homogenous strain as described by Eldefrawi et al. (1964). A series of concentrations for each insecticide was prepared by diluting the commercial formulation with water. Castor-bean leaves were dipped in each concentration for 30 s, then left to dry. The fourth-instar larvae were confined with treated leaves in Petri dishes (15 cm in diameter). Untreated leaves were dipped in water only (as a control). Four replications (each of 10 larvae) were tested for each concentration. The mortality percentages were recorded after 48 h of treatment. Mortality data was subjected to Probit analysis to calculate the lethal concentration values (LC_{50}) of the examined compounds. The toxicity index was determined according to Sun (1950) as follows:

$$\text{Toxicity index} = \frac{LC_{50}\,\text{of the most effective compound}}{LC_{50}\,\text{of the tested compound}} \times 100$$

2.6. Statistical analysis

The average mortality percentage was corrected using Abbott's formula (Abbott, 1925). The results of the bioassay were statistically analyzed according to the method of Finney (1971) to obtain the LC_{50} values, using a computer software, SPSS 25 (SPSS, 2017). The values of LC_{50} were considered significantly different if the 95% confidence limits did not overlap.

3. Results

3.1. Physico-chemical properties of the studied formulations

The emulsion stability results of the tested formulations before storage, after cold and heat tropical storage were shown in Table 1. The test was implemented with three types of water, distilled, soft and hard water. The data of emulsion stability of the unexpired insecticides revealed that chlorpyrifos 48% passed the test, whether before or after storage with all tested water. On the other hand, cyhalothrin failed the test before and after storage with distilled water. Moreover, malathion failed the test before and after storage with hard water. In general, chlorpyrifos (unexpired) passed the emulsion stability, while cyhalothrin and malathion failed the test. Concerning the emulsion stability of the studied expired formulations, once again, chlorpyrifos passed the emulsion stability, while cyhalothrin and malathion failed the test. The separation layers of the expired formulations were higher than their equivalents of unexpired formulations.

The foam formation results of the tested unexpired and expired formulations before storage, after cold and heat tropical storage with distilled, soft and hard water were recorded in Table 2. The results revealed that all evaluated formulations traversed foam formation.

The pH of all tested unexpired and expired formulations before storage, after cold and heat tropical storage were elucidated in Table 3. The pH of chlorpyrifos unexpired formulation was 6.6 before and after cold storage and 6.5 after heat storage. The pH of the expired formulation decreased to 4.2 before and after cold storage and 4.3 after heat storage. Chlorpyrifos unexpired passed the pH while the expired formulation failed the test. Similarly, the pH of cyhalothrin expired was lower than that of the unexpired formulation. It is noteworthy that the expired cyhalothrin formulation passed the pH while the unexpired failed the test. On the other hand, the pH of malathion expired formulation was higher than that of the unexpired formulation. Generally, both malathion unexpired and expired formulations failed the pH test.

3.2. Improving the expired tested compounds

One of our study's goals is to enhance the physical and chemical characteristics of the expired formulations in order to solve the problem of how to dispose of expired formulations. At the same time, attempt to benefit from these expired formulations by making them valid for application, hence protecting the environment from pollution and saving a lot of money. Chlorpyrifos expired formulation passed all the previous physico-chemical properties; therefore, no attempts were made to repair the compound. The emulsion stability of the enhanced expired formulations was summarized in Table 4. Among 20 preliminary trials of the enhanced formulations, five formulations passed successfully through the emulsion stability using distilled water. These five formulations were:

1. Cyhalothrin (5%) + Tween 80 (15%).
2. Cyhalothrin (5%) + Tween 80 (20%).
3. Cyhalothrin (5%) + Triton X-100 (20%).
4. Malathion (57%) + Tween 80 (20%).
5. Malathion (57%) + Triton X-100 (20%).

Then, the emulsion stability of these five successful enhanced formulations was achieved before storage, after cold and heat tropical storage with distilled, soft and hard water (Table 5). All successful enhanced formulations passed the test as the creaming layers did not exceed 2 mL, except the formulation of Lambda-cyhalothrin (5%) + Tween 80 (15%) as the creaming layer was 2.5 mL after cold storage with distilled water. There were not any observed creaming layers in the case of Lambda-cyhalothrin (5%) + Tween 80 (20%) or Lambda-cyhalothrin (5%) + Triton X-100 (20%) formulations, whether before storage, after cold or heat tropical storage with distilled, soft or hard water.

The foam formation results of successful enhanced formulations before storage, after cold and heat tropical storage with distilled, soft and hard water were demonstrated in Table 6. The results revealed that, all the studied formulations passed the foam formation, where the foam layers ranged from zero to 2.5 mL.

Table 1
Emulsion stability of the unexpired and expired formulations.

Formulations	State	Emulsion stability (separation mL)								
		Before storage			After cold storage			After heat storage		
		D.W	S.W	H.W	D.W	S.W	H.W	D.W	S.W	H.W
Chlorpyrifos	Unexpired	1	0.5	0	1	1.5	0.1	1.7	0.5	0
Cyhalothrin		4	1.5	1.5	4.2	1.5	1	3.7	1.5	2
Malathion		0	0.5	4	0	1	4.5	1	0.5	4
Chlorpyrifos	Expired	1.8	1	0.5	2	2	1	2	1	0.5
Cyhalothrin		4	3	1.5	4.5	3	3.5	4	3	2.5
Malathion		5	6.5	6.5	5	6.5	6.5	5.5	6.5	6.5

D.W = distilled water; S.W = soft water; H.W = hard water.

Table 2
Foam formation of the unexpired and expired formulations.

Formulations	State	Foam (mL)								
		Before storage			After cold storage			After heat storage		
		D.W	S.W	H.W	D.W	S.W	H.W	D.W	S.W	H.W
Chlorpyrifos	Unexpired	4	3	0	1.5	3.5	0	3	3.8	1.5
Cyhalothrin		0	0.5	0	0	0	0	1	2	0.5
Malathion		3	5	2	2	3	1	3	2.5	1.5
Chlorpyrifos	Expired	3	5	3	2	4	1.5	5	5	3
Cyhalothrin		1.5	2	0.5	1	0	0	2.5	3	1.5
Malathion		4.5	5	2	2	3	1	3	4.5	2.5

D.W = distilled water; S.W = soft water; H.W = hard water.

Table 3
pH of the unexpired and expired formulations.

Formulations	State	pH		
		Before storage	After cold storage	After heat storage
Chlorpyrifos	Unexpired	6.6	6.6	6.5
Cyhalothrin		7.5	7.4	7.4
Malathion		3.5	3.4	3.5
Chlorpyrifos	Expired	4.2	4.2	4.3
Cyhalothrin		5.5	5.4	5.5
Malathion		7.3	7.3	7.2

Table 4
Emulsion stability of the enhanced expired formulations.

Formulations	Emulsifier	Conc. of emulsifier (%)	Separation (mL)
Cyhalothrin	Tween 20	5	5
	Tween 80		4
	Triton X-100		4
	Span 20		6
	Tween 80	10	3
	Triton X-100		3
	Tween 80	15	2
	Triton X-100		2.3
	Tween 80	20	0
	Triton X-100		0
Malathion	Tween 20	5	6
	Tween 80		3.5
	Triton X-100		5
	Span 20		9
	Tween 80	10	3.8
	Triton X-100		4.1
	Tween 80	15	2.5
	Triton X-100		2.8
	Tween 80	20	1
	Triton X-100		1.5

3.3. The active ingredient of the studied compounds

The measured quantities of the active ingredient (A.I) of the tested compounds were shown in Table 7. Chlorpyrifos (unexpired) revealed deterioration of the A.I by 6.02% relative to the standard insecticide (A.I = 45.11 and 48% for the unexpired and standard chlorpyrifos, respectively). A slight deterioration of the A.I of the expired compound occurred (3.52%) relative to chlorpyrifos unexpired. On the other hand, the expired cyhalothrin loss was 43.25% of A.I relative to the unexpired compound. A greater degradation of the expired malathion was observed (89.65%) relative to the unexpired insecticide (A.I = 5.03, 48.6 and 57% for the expired, unexpired and the standard malathion, respectively).

3.4. Efficiency of the improved expired insecticides against the cotton leafworm

The data presented in Table 8 revealed that the median lethal concentration (LC_{50}) amount of the expired chlorpyrifos (48% EC) was not significantly different from the unexpired compound against 4th instar larvae of the cotton leafworm. The LC_{50} of the unexpired and expired formulations were 15.47 and 17.08 ppm, respectively. Further, the efficiency of the expired chlorpyrifos was 90.57% relative to the unexpired one. Similarly, the unexpired cyhalothrin was not significantly different from the expired chlorpyrifos. On the other hand, the toxicity of the expired cyhalothrin insecticide decreased sharply (LC_{50} = 187.07 ppm). The addition of some adjuvants to the expired cyhalothrin improved its efficiency, where the effectiveness resulted from adding Tween 80 and Triton X-100 increased from 10.59% to 46.31 and 44.39%, respectively. On the other hand, the expired malathion exhibited 87.12% loss of efficiency relative to the unexpired compound (the

Table 5
Emulsion stability of the successful enhanced formulations.

Formulations	Emulsion stability (separation mL)								
	Before storage			After cold storage			After heat storage		
	D.W	S.W	H.W	D.W	S.W	H.W	D.W	S.W	H.W
Cyhalothrin (5%) + Tween 80 (15%)	2	1	0.5	2.5	1	0.5	2	1	0.7
Cyhalothrin (5%) + Tween 80 (20%)	0	0	0	0	0	0	0	0	0
Cyhalothrin (5%) + Triton X-100 (20%)	0	0	0	0	0	0	0	0	0
Malathion (57%) + Tween 80 (20%)	1	1.5	1.5	1	1.5	2	1.5	1.5	1.5
Malathion (57%) + Triton X-100 (20%)	1.5	1.7	1.9	1.5	2	2	2	1.7	1.5

D.W = distilled water; S.W = soft water; H.W = hard water.

Table 6
Foam formation of the successful enhanced formulations.

Formulations	Foam (mL)								
	Before storage			After cold storage			After heat storage		
	D.W	S.W	H.W	D.W	S.W	H.W	D.W	S.W	H.W
Cyhalothrin (5%) + Tween 80 (15%)	1	2	0	0	0	0	2	2.5	1
Cyhalothrin (5%) + Tween 80 (20%)	1	1.5	0	0	0	0	1.5	2	0
Cyhalothrin (5%) + Triton X-100 (20%)	1	1.5	0	0	0	0	1	2	0.5
Malathion (57%) + Tween 80 (20%)	0	0	0	0	0	0	0	0	0
Malathion (57%) + Triton X-100 (20%)	1	1.5	0	0	0	0	1.5	2	0

D.W = distilled water; S.W = soft water; H.W = hard water.

Table 7
The amount of active ingredients (%) of tested insecticides.

Insecticide	Retention time (min)	Standard	Unexpired	Expired	A.I%* unexpired	A.I%** expired
Chlorpyrifos	8.132	48	45.11	43.52	93.98	96.48
Cyhalothrin	18.05	5	4.67	2.65	93.4	56.75
Malathion	7.33	57	48.6	5.03	85.26	10.35

[*] The active ingredient (A.I) percentage of the unexpired insecticide relative to the standard one; ** The A.I percentage of the expired insecticide relative to the unexpired one.

Table 8
Toxicity of different formulation states (unexpired, expired, improved) on *Spodoptera littoralis.*

Treatments	State	LC_{50}[a] (ppm)	95% Confidence limits (ppm)		Slope[b] ± *SE*	Intercept ± *SE*	$(x^2)^d$	Toxicity index (%)
			Lower	Upper				
Chlorpyrifos	Unexpired	15.47	13.55	17.94	1.99 ± 0.25	−2.37 ± 0.29	3.51	100
	Expired	17.08	11.67	35.96	1.96 ± 0.25	−2.42 ± 0.29	8.23	90.57
Cyhalothrin	Unexpired	19.82	10.66	27.92	2.41 ± 0.25	−3.12 ± 0.35	10.02	100
	Expired	187.07	143.67	242.35	3.07 ± 0.36	−6.99 ± 0.82	7.01	10.59
	Improved (Tween 80)	42.80	33.48	50.48	4.54 ± 0.48	−7.41 ± 0.80	8.16	46.31
	Improved (Triton X-100)	44.65	35.42	53.24	4.76 ± 0.48	−7.86 ± 0.81	9.25	44.39
Malathion	Unexpired	456.86	290.36	637.16	1.83 ± 0.24	−4.88 ± 0.66	5.41	100
	Expired	3546.53	2552.77	9212.71	1.35 ± 0.36	−4.80 ± 1.15	0.78	12.88
	Improved (Tween 80)	2193.41	1854.81	2963.01	1.74 ± 0.35	−5.82 ± 1.12	4.92	20.83
	Improved (Triton X-100)	2220.86	1913.93	2843.05	2.03 ± 0.36	−6.82 ± 1.15	4.47	20.57

[a] The concentration causing 50% mortality. [b] Slope of the concentration-mortality regression line ± Standard Error. [c] Intercept of the regression line ± Standard Error. [d] *Chi* square value.

LC_{50} values of the unexpired and expired compounds were 456.86 and 3546.53 ppm, respectively). However, the efficiency of the improved compound by Tween 80 and Triton X-100 increased against the 4th larval instar of *S. littoralis* to 20.83 and 20.57%, respectively.

4. Discussion

The results of the physical and chemical characteristics of the unexpired insecticides revealed that the cream layer formed by chlorpyrifos did not exceed 2 mL. On the other hand, it transcends that value for cyhalothrin and malathion. The permissible limit for emulsion stability shall not exceed 2 mL of creaming separation layer (Dobrat and Martijn, 1995). Similar results were obtained for the expired insecticides, where chlorpyrifos was the only one which passed the test. Emulsion stability is specifically linked to the degree of emulsion tightness and the bonding power between the continuous and dispersed phases (Mohyaldinn et al., 2019). In addition, the emulsion becomes stable when the emulsifiers are added to the two-phase systems due to the slowing down of emulsion breaking such as coalescences (Mohamed et al., 2017).

The foam layers formed by the unexpired and expired insecticides did not exceed 5 mL. The permissible limit of foam layer volume should not surpass 5 mL (Dobrat and Martijn, 1995). All the foam layers of the expired insecticides were higher than the corresponding values of the unexpired.

The pH of chlorpyrifos unexpired were near seven, whereas the related values of the expired insecticides were slightly less than 4.5. Chlorpyrifos and cyhalothrin expired insecticides decreased the pH, while the opposite was observed for malathion. These results are consistent with Satyavani et al. (2011) who found that the pH of expired and unexpired formulations displayed major changes in pH. Unharmed pH of the spray solution should be through a range of 4.5 to 7.0 (Halcomb, 2012). Salem et al. (2016) and Sammour et al. (2018) reported that most pesticides are steadier when the pH ranges from 5.5 to 7.0. Pesticides may be exposed to alkaline hydrolysis, where pH higher than seven triggers chemical deterioration of many pesticides (alkaline hydrolysis). Therefore, it reduces the potency of the pesticide's A.I (Fishel, 2002; Abdel-Aziz et al., 2018).

Trials have been achieved in the current research to repair expired insecticides. The emulsifiers of Span 20, Triton X-100, Tween 20 and Tween 80 were used. Five formulations succeeded among twenty preliminary experiments of emulsion stability with distilled water. Span 20 does not manage to reform any formulations. The emulsifiers do their actions by decreasing the surface tension of the spray droplets, making the area of pesticide coverage larger, which increases the exposure of pests to pesticides (Cassiday, 2014). According to the previous literatures, the hydrophile-lipophile balance (HLB) values of the studied emulsifiers of Span 20, Tween 20, Tween 80, and Triton X-100 were 8.6, 16.7, 15.0, (Aboud et al., 2016; Lindner et al., 2018) and 13.4 (Housaindokht and Pour, 2012), respectively. The HLB number is utilized to calculate the proportion of the hydrophilic and hydrophobic groups of the surfactant molecules. HLB values greater than ten indicate water preference (hydrophilic), while values under ten indicate an affinity for lipids and organic solvents (Charcosset, 2012). The law HLB value of Span may explain the failure of the compound to improve the studied insecticides, where they are all O/W (oil in water emulsions).

The physico-chemical properties of the repaired formulations were accomplished before and after storage with distilled, soft and hard water. Only Lambda-cyhalothrin (5%) + Tween 80 (15%) failed the physical and chemical characteristics between the five repaired formulations. This failed formulation passed the previous characteristics when Tween 80 concentration was increased to 20%. Tween 80 or Triton X-100 emulsifiers at 20% concentration managed to repair each of cyhalothrin and malathion insecticides.

The current research revealed that the deterioration of the expired chlorpyrifos was slight, while the loss of the expired cyhalothrin A.I was a little less than 50%. Similarly, a greater degradation was recorded for the expired malathion A.I. by 90%. These results were in accordance with FAO (2020a) who reported that the pesticide A.I can change chemically and breakdown into compounds that may no longer possess pesticidal action, thus reducing the concentration of the parent A.I.

The results indicated that the toxicity of the expired chlorpyrifos was not significantly different from the unexpired insecticide. These findings confirm the results of the physical and chemical characteristics of expired chlorpyrifos. The insecticidal efficiency of chlorpyrifos showed similarity to that reported by Abdelgaleil et al. (2019) who stated that the toxicity of chlorpyrifos against the third larval instar was 12.34 ppm. The present research elucidated that the enhancement process for expired cyhalothrin raised the insecticidal efficacy nearly 5-folds. Moreover, the study revealed a great deterioration occurred in the expired malathion. However, the addition of some adjuvants to expired malathion improved its efficiency by about 2-folds. These findings were in accordance with Abdelgaleil et al. (2018) who clarified that the combination of adjuvants with chlorpyrifos and cyhalothrin insecticides improved the efficiency and the persistence of these insecticides.

5. Conclusion

Obsolete pesticides are a major public health and environmental concern. The shortage of efficient management and accessible techniques for the disposal of expired pesticides are linked to the majority of developing countries. Incineration seems to be the current practical choice for the disposal of outdated pesticides. However, there are environmental concerns about its use due to the release of toxic chemicals. Therefore, attempts to find alternative methods for the disposal of obsolete pesticides. The process of adding adjuvants to obsolete pesticides may be important to enhance the efficacy of these expired compounds. The expired formulations of cyhalothrin 5% EC and malathion 57% EC could be reused by enhancing these formulations with Tween 80 (20%) or Triton X-100 (20%). However, further studies are required to ensure the low risk of the enhanced compounds on mammals, as well as their low persistence in nature.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was a part of project titled "Prevention Practices for Occupational Workers from Adverse Effects of Pesticides and the safe Disposal of Expired Compounds" funded by Academy of Scientific Research and Technology, Egypt during 2016 – 2018. Authors are thankful to Academy of Scientific Research and Technology, Egypt, for funded this project.

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