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Chemical Stability and Byproducts Identification of Hexythiazox Emulsion Concentrate under Thermal Storage, Hydrolysis, and Photolysis in Egyptian Clay Soil

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IN THE PRESENT study, the stability of hexythiazox in the formulation of Efdal hekzarun 5% EC after accelerated hot storage for 14 weeks at 35, 40, 45, and 54 °C, forced acidic and alkaline hydrolysis for 7 days in 1.0, 0.1, and 0.01N in HCl and NaOH, and photolysis in clay soil of Egypt for 14 days was investigated. The results showed that the active ingredient decreased by 18.15% after 14 weeks of storage at 54 °C. However, the decline within the same time period ranged between 5-10% at 35, 40, and 45 °C, respectively**.** Thus, hexythiazox storage complied with FAO specification after more than 14 weeks at 35°C and not after more than 9, 8, and 4 weeks at 40, 45, and 54°C, respectively. The data showed that the degradation rate of hexythiazox was dependent on its initial concentration and increased progressively as temperature increased. Furthermore, the shelf life of hexythiazox after storage at 54°C was found to be approximately 1/5 that of its shelf life after storage at 35°C. The kinetics of hexythiazox degradation under the studied conditions followed the first-order model, being dependent upon its initial concentration. The shelf life ($t_{0.95}$) and half-life ($t_{1/2}$) of hexythiazox in forced alkaline solutions were less than those in acidic solutions. The results revealed that hexythiazox is a non-persistent pesticide in soil; it decomposed rapidly in Egyptian clay-loam soil, with an 80.53% reduction in 14 days at ambient conditions and a half-life ($t_{1/2}$) of 5.75 days. This is due to soil pH (8.59), organic matter (1.92), and the molecular structure of hexythiazox, which contains chromophores such as ethylene and carbonyl groups; it may be sensitive to direct photolysis by sunlight because it absorbs wavelengths longer than 290 nm. According to the GC/MS analysis, hexythiazox was degraded to different byproducts after specified conditions. The benzene and cyclohexane rings remain stable under different applied conditions; however, the thiazolidine ring is cleaved and opened during thermal and forced acidic hydrolysis and remains stable after alkaline hydrolysis and soil photolysis. The contraction reaction is unique to the forced alkaline hydrolysis and photolysis of hexythiazox in clay-loam soil; thus, two products were identified: 4-chloro-2-(cyclohexanecarboxamido) benzoic acid and 3-cyclohexyl-1-methyl-1-(2-phenylethyl) urea; the latter one and 4-methyl-5-phenylthiazolidine-2-one were identified in the forced alkaline hydrolysis of hexythiazox.

Keywords: Hexythiazox; accelerated hot storage; clay soil; GC/MS; degradation; shelf-life; half-life.**1.**

Introduction

Hexythiazox is regarded as an acaricide and insecticide with non-systemic mode of action. It is nymphicidal, larvicidal, and ovicidal in nature. Hexythiazox is classified as a mite growth inhibitor by the Insecticide Resistance Action Committee (IRAC) due to its widespread usage in agriculture and horticulture to prevent the eggs and larvae of several phytophagous mites on vegetables, fruits, cotton, pepper, and flowers. It is administered to plants at any stage of growth, from budding to fruiting (IRAC, 2023). Thiazolidine group is the foundation of hexythiazox. Commercial chiral insecticide hexythiazox is composed of the enantiomers (4S, 5S)-hexythiazox and (4R, 5R)-hexythiazox in a 1:1 ratio (Zhang *et al.*, 2024).

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The stability, effectiveness, residual transfer, and safety assessment of pesticides in the environment will all be impacted by their environmental behaviours, which include soil degradation, hydrolysis, photolysis, sorption and desorption, and leaching (Zhou *et al.*, 2021).The rate at which pesticides degradation, are turned into degradation products, or are partially or totally mineralized is a significant element in determining how long pesticides will be present in the environment. This degradation could be caused by an abiotic mechanism such as hydrolysis or photolysis, or it could be caused by a biotic process such as biodegradation. Photolysis is the mechanism by which photons from sunlight break down pesticide molecules (Ahmad *et al*., 2023). Forced degradation evaluates pesticide stability in severe situations, providing insight into storage and shelf life (Mansour *et al*., 2024a). Forced degradation studies reveal the chemical behaviour of the parent compound, which aids in the development of formulation and packaging as well as the generation of degraration products in much less time, typically a few weeks.

In recent studies, agricultural chemical hydrolysis is understood as a process involving the breakdown of pesticides through interaction with water's functional groups. This is accompanied by microbial degradation, photolysis, and other water-related reactions. These processes are critical in understanding pesticide dissipation, particularly under varying environmental conditions, such as temperature, pH, and light exposure, which influence their stability and persistence in agricultural settings. (Crovella and Paiano, 2023). The pH value, acid concentration, and exposure duration in an acidic media influenced quinclorac hydrolysis. The hydrolysis rate of quinclorac increased with decreasing pH and HCl concentration with exposure duration, and vice versa (Mansour *et al*., 2023).

Pesticide hydrolysis is essentially a nucleophilic substitution reaction, in which nucleophilic groups (H_2O or OH) attack the core electrophilic groups (C, N, S, P, etc.) of the pesticide molecules and replace the leaving groups, producing a variety of hydrolytic products. Meanwhile, numerous elements influence the hydrolytic process, including pesticide properties and environmental parameters (such as pH, water temperature, and clay minerals) (Zhou *et al*., 2023). The pH value and hardness of water sources in agricultural regions may vary, making it essential to analyze the water before pesticide application. This analysis helps determine the concentrations of cations and anions, as both water pH and hardness influence the pesticide's effectiveness. Additionally, these factors can affect various physical properties, including emulsion stability, re-emulsification, and dispersion stability (Mansour *et al*., 2024b).

The presence of photocatalysts such as TiO_2, H_2O_2, and KNO_3 has been shown to further affect the photodecomposition process. Among these, TiO2 was the most effective in promoting the degradation of hexythiazox, significantly enhancing its breakdown under UV light exposure. This is consistent with the findings of earlier studies where TiO_2 acted as a photocatalyst, facilitating the generation of reactive species that accelerate the degradation of the pesticide. These findings suggest that, under controlled conditions with TiO_2, the decomposition process of hexythiazox can be manipulated, which may be useful for reducing its persistence in the environment (Gireesh *et al.,* 2022*)*

The dissipation of Hexythiazox in soils, both aerobic and anaerobic, has been studied with varying results, reflecting the different environmental factors that influence its persistence. In aerobic conditions, Hexythiazox is generally more stable, though its degradation can occur through microbial activity and other soil processes. Several studies have found that in sandy loam and other soil types, the dissipation half-life of Hexythiazox can vary significantly, ranging from 21 to 43 days. These results highlight that the pesticide’s persistence depends on the specific soil type, moisture content, and temperature conditions (Heben, 2023). Moreover, its degradation products in aerobic soils are considered persistent but are typically less mobile in the soil, potentially accumulating in the upper soil layers.

Hexythiazox's environmental behavior in soils also depends on its interaction with various soil components. It is known to form complexes with organic matter, which can affect its mobility and persistence. This can lead to Hexythiazox being less prone to leaching in the soil, especially in clay-rich soils where it tends to bind more strongly. Its dissipation in these soils is often governed by both chemical processes, such as hydrolysis, and biological degradation, which can reduce the amount of active ingredient over time (Mandal, 2023).

Agricultural productivity is the primary factor influencing global food production. Soil can filter and buffer organic and inorganic components, either removing contaminants from the environment or isolating pollutants from organisms (El-Ramady *et al.,* 2024). Microbial activity in soil can reduce the demand for inorganic fertilizer treatments. High levels of potentially toxic elements (PTEs) in soil can harm human health. Using hyper-accumulator plants can be a cost-effective and environmentally beneficial technique to increase desired

levels of contaminants in soil l (El-Shwarby *et al*., 2022). As a result, recent research was carried out to analyze and evaluate the stability of hexythiazox under forced thermal, acidic and basic hydrolytic conditions, as well as to investigate its photolysis in Egyptian clay-loam soil. Additionally, the degradation products of this pesticide will be identified by GC/MS in order to perhaps illuminate the degradation pathways. Finally, the analytical results obtained under the conditions of the experiment will be utilized to calculate the shelf-life and half-life periods for this pesticide.

2. Material and methods

2.1 Materials

♦ The certified reference standard of hexythiazox with a purity of 99.54% was provided by Dr. EhrenstorferTM Gmbh (Augsburg, Germany).

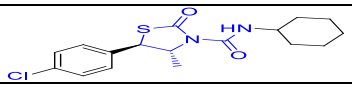
♦ The hexythiazox formulation utilized in the study was Efdal hekzarun 5% EC, which was readily available on the Egyptian market. The chemical and physical properties of hexythiazox (FAO/WHO, 2009) are provided in **Table (1).**

♦ Acetonitrile, methanol, and water were HPLC-grade solvents used in the study and were obtained from Sigma-Aldrich.

♦ QuEChERS (Quick Easy Cheap Effective Rugged Safe) extraction kits (4.0g MgSO4, 1.0g NaCl, 1.0g sodium citrate tribasic dihydrate, and 0.50g sodium citrate dibasic sesquihydrate).

♦ QuEChERS clean-up kits (25 mg PSA sorbent and 150mg MgSO4) were acquired from Sigma-Aldrich to evaluate hexythiazox in soil samples.

Table 1. Chemical and physical properties of hexythiazox.

ISO common name	**Hexythiazox**	
IUPAC name	(4RS,5RS)-5-(4-chlorophenyl)-N-cyclohexyl-4-methyl-2-oxo-1,3-thiazolidine-3-carboxamide	
CA name	Trans-5-(4-chlorophenyl)-N-cyclohexyl-4-methyl-2-oxo-3-thiazolidinecarboxamide	
Chemical class	Thiazolidinecarboxamide	
Pesticide group	Acaricide, Insecticide	
CAS Registry number	78587-05-0	
CIPAC number	439	
Structural formula		
Molecular formula	$C_{17}H_{21}ClN_2O_2S$	
Molecular weight	352.88 g/mol	
Melting point	105.4°C (378.6 K)	
Solubility in organic solvents	Solvent	g/L
	n-Hexane	4.64
	n-Heptane	4.63
	Dichloromethane	619
	Acetone	159
	Toluene	233
	Xylene	230
	Methanol	17.6
	Ethanol	22.1
	Acetonitrile	34.5
	Ethylacetate	148
Solubility at 25°C in deionized water	0.12 mg/L	
Relative Density	1.2829 g/cm^3 (1282.9 kg/m^3) at 20°C	
Minimum active substance purity	976 g/Kg	
Mode of action	Non-systemic with contact and stomach action. Mite growth inhibitor affecting CHS1.	

2.2 Methods

2.2.1. Calibration curve of hexythiazox using HPLC-DAD

A stock solution of the hexythiazox standard (400µg/mL) in acetonitrile was prepared in a 50 mL volumetric flask and stored at-18°C. The pesticide calibration plot was generated using HPLC (Agilent Technologies 1260 infinity system) with four quaternary pumps (G1311B, G1316A, G1315D, and G1328C), a thermostated column compartment, and a DAD detector at concentrations of 10, 25, 50, 100, 150, 200, 250, 300, and 350µg/mL. The chromatographic separation was carried out using an Agilent C18 chromatographic column (4.6 mm ID x 150 mm x 4 m). As shown in **Fig. (1)**, hexythiazox was detected at 235 nm with a retention time of 3.917 min. Isocratic elution was performed using a mobile system containing water (+1% H3PO4), methanol, and acetonitrile (5:5:90) at a flow rate of 1 mL/min and injection volume of 5 µL.

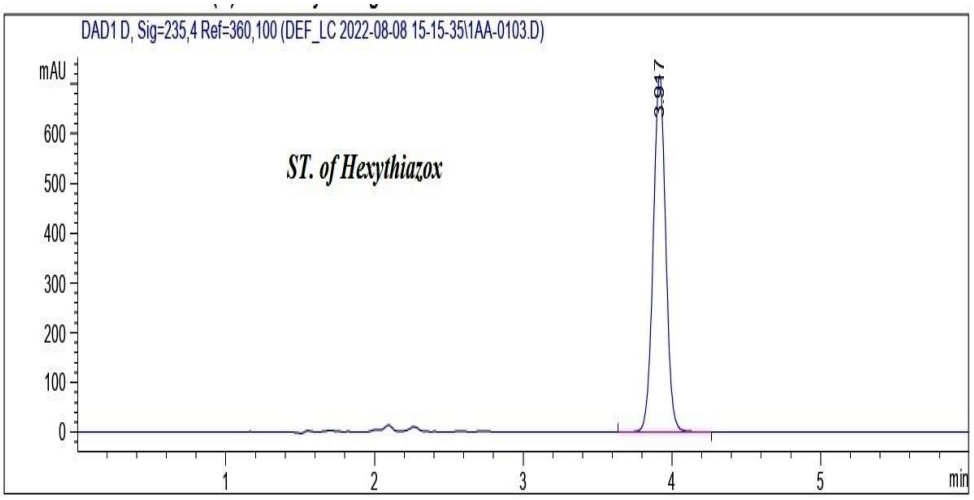


Fig. 1. The HPLC chromatogram of hexythiazox standard (400µg/mL).

2.2.2 Thermal and hydrolytic degradation of hexythiazox

● Accelerated hot storage

The accelerated hot storage procedure was carried out in accordance with CIPAC MT 46.1 (1995). 50 mL of the formulation were placed in a glass bottle and exposed to temperatures of 35°C, 40°C, 45°C, and 54°C for a range of times (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14 weeks) in a dark electric oven with a temperature control system. Following withdrawal, each individual sample was evaluated using HPLC to determine the concentration of active component and GC/MS to identify the degradation products.

● Forced acidic and alkaline hydrolytic studies

Forced hydrolysis studies were performed at room temperature in acid and basic solutions to allow the chemical/pesticide to breakdown as a result of contact with water according to (Mansour *et al*., 2023 and Mansour *et al*., 2024a). This study used (0.01N, 0.10N, and 1.0N) HCl and (0.01N, 0.10N, and 1.0N) NaOH to perform acid and alkaline hydrolysis, respectively **Fig. (2).**

● Acidic hydrolysis studies

10 mg of hexythiazox was mixed with 2 mL of suitable concentrations of HCl (0.01N, 0.10N, and 1.0N) in 25 mL volumetric flasks and left at room temperature for 1, 3, 5, and 7 days. Before analyzing the sample, it was neutralized with 2 mL of an acid-equivalent concentration of NaOH to prevent further degradation and the solution was diluted, and filtered through a 0.45 nylon syringe filter.

● Alkaline hydrolysis studies

10 mg of hexythiazox was mixed with 2 mL of suitable concentrations of NaOH (0.01N, 0.10N, and 1.0N) in 25 mL volumetric flasks and left at room temperature for 1, 3, 5, and 7 days. Before analyzing the sample, it was neutralized with 2 mL of a base-equivalent concentration of HCl to prevent further degradation and the solution was diluted, and filtered through a 0.45 nylon syringe filter.

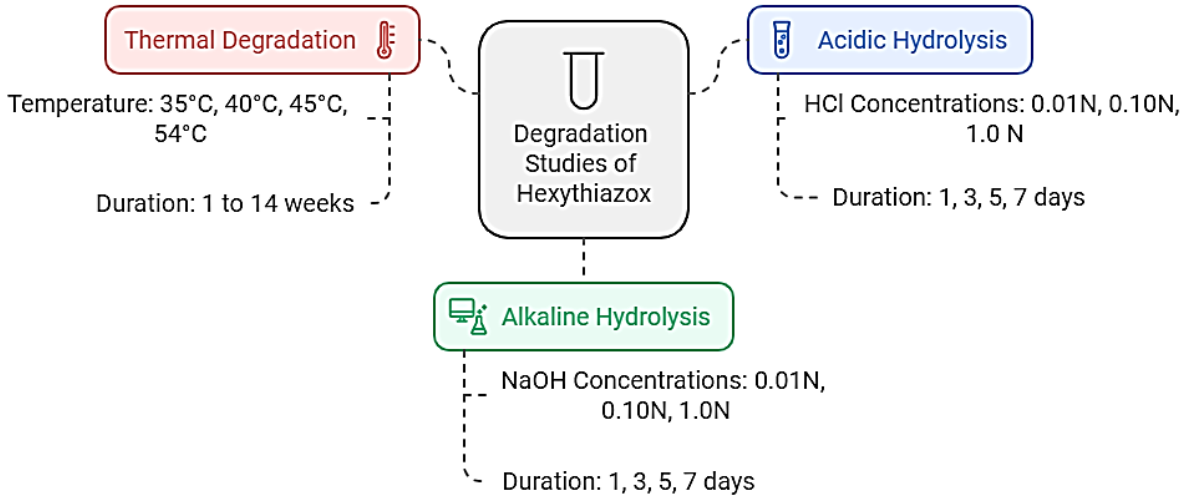


Fig. 2. Methodology flowchart for hexythiazox during thermal and forced hydrolysis.

2.2.3. Photolysis of hexythiazox in clay soil

10 g of soil was weighed and spiked with 100 µg/mL of the pesticide formulation in a Petri plate. The contents were evenly put on the dish and left in the sun for 1, 3, 5, 7, 14, and 21 days. After each interval as in **Fig. (3)**, the contents of each petri dish were transferred to a covered 50 mL centrifuge tube, and 10 mL of acetonitrile was added. The contents were vortexed for 1 min to ensure maximum sample-solvent interaction. The components were vortexed for 1 min again after adding QuEChERS extraction pouch kits. The extracts were centrifuged at 4000 rpm for 10 minutes, and the supernatant layer was transferred to a tube containing a QuEChERS clean-up kit. The tube contents were vortexed for 1 minute before centrifugation at 4000 rpm for 10 minutes. Prior to analysis, the acquired residue was filtered through a 0.45 nylon syringe filter.

2.3. Kinetic studies

After each experimental method, the kinetics of hexythiazox dissipation/degradation was determined using the appropriate reaction rate equation. The data collected were utilized to calculate the degradation rates constant, half-life, and shelf-life times.

2.4. The identification of degradation products

The degradation products of hexythiazox were identified by using an Agilent 7890 B, 5977 A MSD gas chromatography with an Agilent mass spectrometric detector, direct capillary interface, and fused silica capillary column (30 m 0.025 mm HP-5-0.25 micron -60 to 325/325^{o}C). Samples were injected using helium as the carrier gas in a pulsed split mode with a split ratio of (10:1), split flow of 10 mL/min, and flow rate of 1 mL/min. The solvent delay was 4 min, with a 1 µL injection volume. The temperature scheduled for the GC started at 50°C for 0.5 min, then increased to 190°C at a rate of 10°C/min with a 1 min hold time, then to 220°C at a rate of 10°C/min with a 1 min hold time, and lastly to 300°C at a rate of 10°C/min with a 2 min hold time at 300°C. The temperature of the injector was held constant at 280°C. The product was found using NIST and Wiley mass spectral data bases.

3. Results

3.1. Calibration curve for hexythiazox standard

As determined by HPLC at working concentrations of 10, 25, 50, 100, 150, 200, 250, 300, and 350µg/mL, the calibration curve for hexythiazox is depicted in **Fig. (4)**. The plot of the concentration vs. observed peak area was linear, with a correlation coefficient (R^2) of 0.99875.

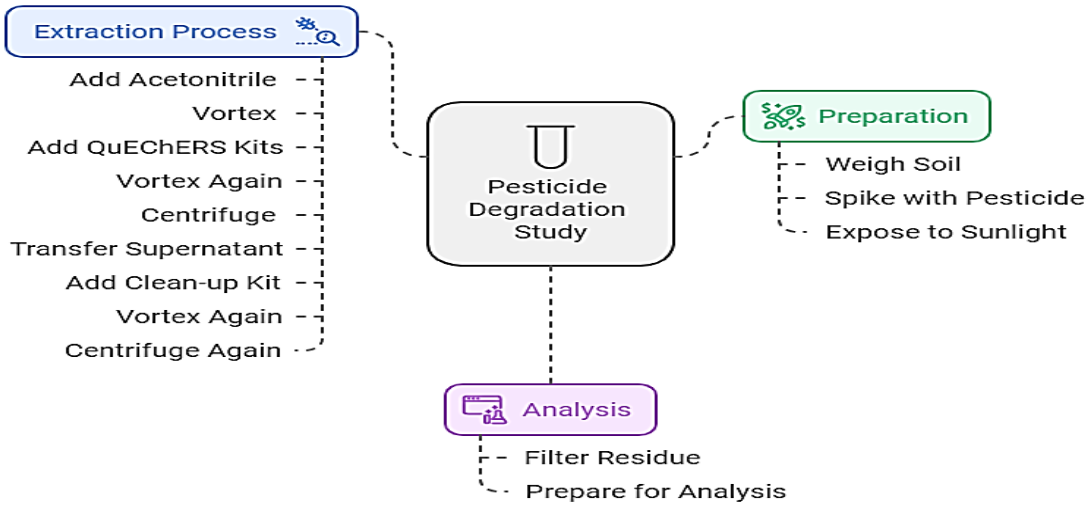


Fig. 3. Methodology flowchart for hexythiazox determination after soil photolysis.

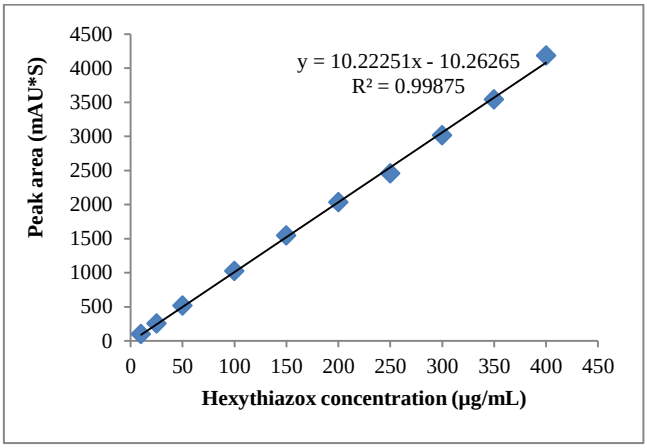


Fig. 4. Standard Calibration curve for hexythiazox using HPLC.

3.2. Thermal conditions stability of Hexythiazox (active ingredient) in formulation of Efdal hekzarun 5% EC

Table (2) demonstrate results of the accelerated thermal degradation of hexythiazox in Efdal hekzarun 5% EC during thermal storage. The active component decreased by 18.15% after 14 weeks of storage at 54°C. However, the decline within the same time period ranged between 5-10% at 35, 40, and 45°C, respectively.

3.3. Forced hydrolytic degradation of hexythiazox in (Efdal hekzarun 5% EC)

3.3.1. Effect of acidic hydrolysis

The data in **Table (3)** show hydrolysis of hexythiazox in 0.01, 0.10 and 1.0N HCl. The data illustrate that after 7 days of hydrolysis in 1.0N HCl, the active ingredient in Efdal hekzarun 5% EC lost 74.98%. However, throughout the same time period, the active ingredient loss in 0.10 and 0.01N HCl was 71.29% and 67.54%, respectively.

3.3.2. Effect of alkaline hydrolysis

The data in **Table (4)** show the alkaline hydrolysis of hexythiazox in 0.01, 0.10 and 1.0 N NaOH. The data illustrate that after 7 days of hydrolysis in 1.0 N NaOH, the active ingredient in Efdal hekzarun 5% EC lost 87.84%. However, throughout the same time period, the active ingredient loss in 0.10 N and 0.01N NaOH was 81.26% and 75.29%, respectively.

Table 2. Effect of storage at 35, 40, 45 and 54°C on the a.i. stability of Efdal hekzarun 5% EC.

Storage period (week)	35°C		40°C		45°C		54°C	
	Conc. (µg/mL)	Loss %	Conc. (µg/mL)	Loss %	Conc. (µg/mL)	Loss %	Conc. (µg/mL)	Loss %
Initial	394.98	0	394.98	0	394.98	0	394.98	0
1	393.54	0.36	392.53	0.62	392.06	0.74	389.85	1.30
2	392.08	0.73	389.51	1.38	389.13	1.48	384.67	2.61
3	391.21	0.93	387.52	1.89	386.33	2.19	379.58	3.90
4	390.48	1.14	384.95	2.54	383.37	2.94	374.48	5.19
5	388.57	1.62	382.50	3.16	380.52	3.66	369.42	6.47
6	387.45	1.91	380.17	3.75	377.68	4.38	364.17	7.80
7	385.96	2.28	377.68	4.38	374.88	5.09	358.99	9.11
8	384.34	2.69	375.51	4.93	371.95	5.83	354.10	10.35
9	383.78	2.84	372.90	5.59	369.23	6.52	348.81	11.69
10	382.24	3.23	370.29	6.25	366.15	7.30	343.71	12.98
11	380.09	3.77	367.81	6.88	363.34	8.01	338.50	14.30
12	378.95	4.06	365.63	7.43	360.50	8.73	333.40	15.59
13	376.29	4.73	363.11	8.07	357.46	9.50	328.31	16.88
14	373.89	5.34	360.42	8.75	354.38	10.28	323.29	18.15

Table 3. Hexythiazox degradation rates in 0.01, 0.10 and 1.0 N HCl.

Concentration of reagent (N)	Storage period (Days)	Conc. of Hexythiazox (µg/mL)	Degradation rate (%)
0.01 N HCl (pH=2)	0	394.98	0
	1	363.13	8.06
	3	257.90	34.71
	5	190.28	51.83
	7	128.20	67.54
0.10 N HCl (pH=1)	0	394.98	0
	1	347.03	12.14
	3	244.63	38.07
	5	162.74	58.80
	7	113.40	71.29
1.0 N HCl (pH=0)	0	394.98	0
	1	341.81	13.46
	3	227.47	42.41
	5	150.12	61.99
	7	98.84	74.98

Table 4. Hexythiazox degradation rates in 0.01 N, 0.1 N and 1.0 N NaOH.

Concentration of reagent (N)	Storage period (Days)	Conc. of Hexythiazox (µg/mL)	Degradation Rate (%)
0.01 N NaOH (pOH= 2, pH=12)	0	394.98	0
	1	354.29	10.30
	3	242.48	38.61
	5	161.14	59.20
	7	97.60	75.29
0.10 N NaOH (pOH= 1, pH=13)	0	394.98	0
	1	330.22	16.40
	3	221.36	43.96
	5	133.17	66.28
	7	74.00	81.26
1.0 N NaOH (pOH= 0, pH=14)	0	394.98	0
	1	327.63	17.05
	3	192.93	51.15
	5	100.29	74.61
	7	48.01	87.84

3.4. Kinetics of the forced degradation of hexythiazox

3.4.1. Thermal degradation of hexythiazox.

Figs. (5, 6, 7, and **8)** show plots of ln C of hexythiazox vs. time during 14 weeks of storage at 35, 40, 45, and 54°C. The plots revealed a linear relationship, with R^2 values ranging from 0.99254 to 0.99909. **Table (5)** provides the kinetic parameters calculated from these figures.

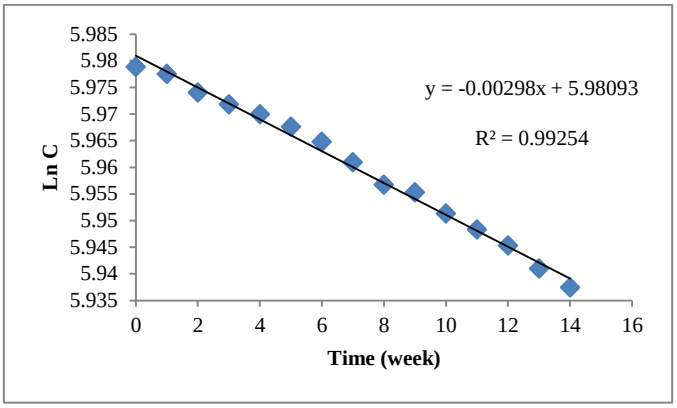


Fig. 5. A plot of ln C vs. time (weeks) for. hexythiazox degradation after 35°C storage.

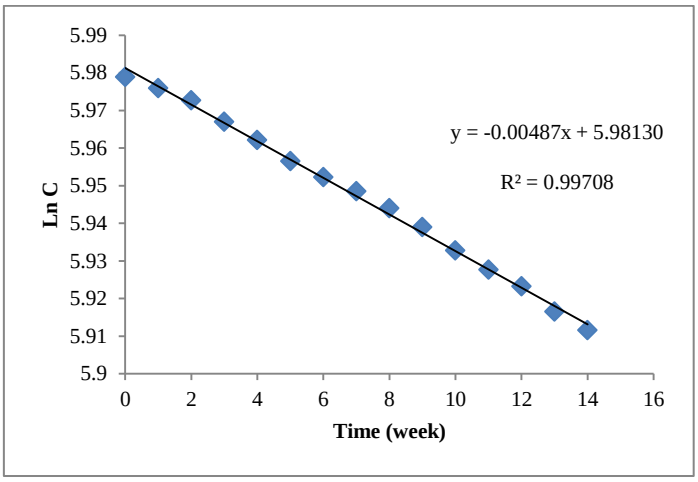


Fig. 6. A plot of ln C vs. time (weeks) for hexythiazox degradation after 40°C storage.

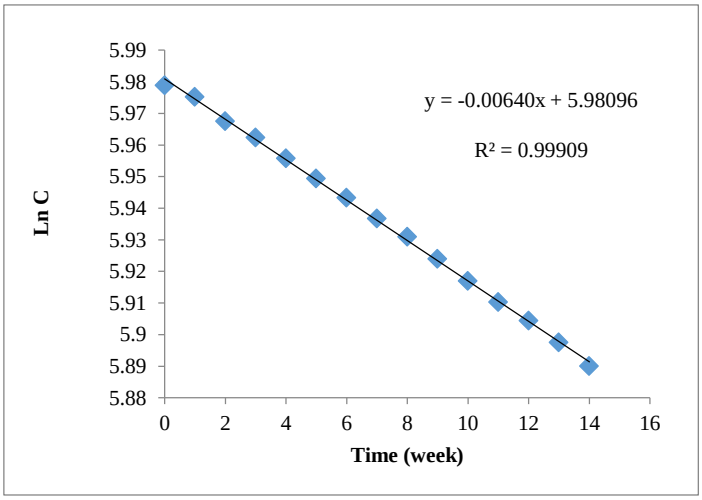


Fig. 7. A plot of ln C vs. time (weeks) for hexythiazox degradation after 45°C storage.

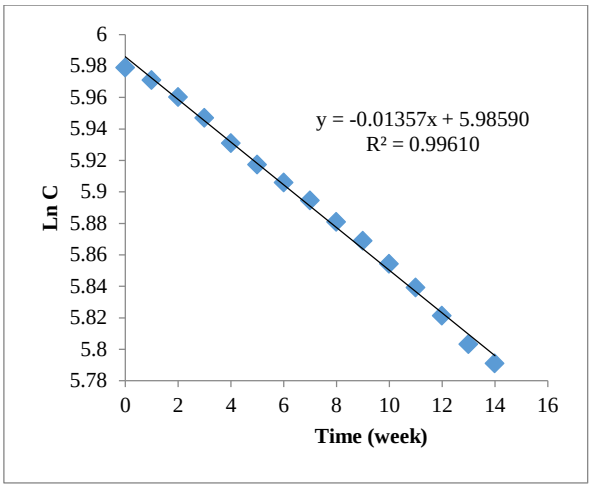


Fig. 8. A plot of ln C vs. time (weeks) for hexythiazox degradation after 54°C storage.

Table 5. Kinetic parameters for the thermal degradation of hexythiazox after storage at 35, 40, 45 and 54°C.

Pesticide	Storage temperatre (°C)	Linear regression equation	R^2 coefficient	Degradation rate (K) ($week^{-1}$)	Shelf-life $t_{0.95}$ (week)
Hexythiazox (Efdal hekzarun 5% EC)	35	y = - 0.00298x+5.98093	0.99254	2.98×10^{-3}	17.21
	40	y = - 0.00487x+5.98130	0.99708	4.87×10^{-3}	10.53
	45	y = - 0.00640x+5.98096	0.99909	6.40×10^{-3}	8.01
	54	y = - 0.01357x+5.98590	0.99610	13.57×10^{-3}	3.78

3.4.2. Acidic hydrolysis of hexythiazox

The natural logarithm of hexythiazox concentration in acidic solutions, ln C vs. time (days), yielded a straight line with an intercept of ln [C_0], indicating that acidic hydrolysis of hexythiazox followed first-order kinetics, as shown in **Figs. (9, 10, and 11).** The plots possess a slope of (-k), which corresponds to the degradation constant in (day^{-1}) and R^2 coefficient values ranging from 0.99328 to 0.99840. The predicted kinetic parameters of acidic hydrolysis of hexythiazox are provided in **Table (6).**

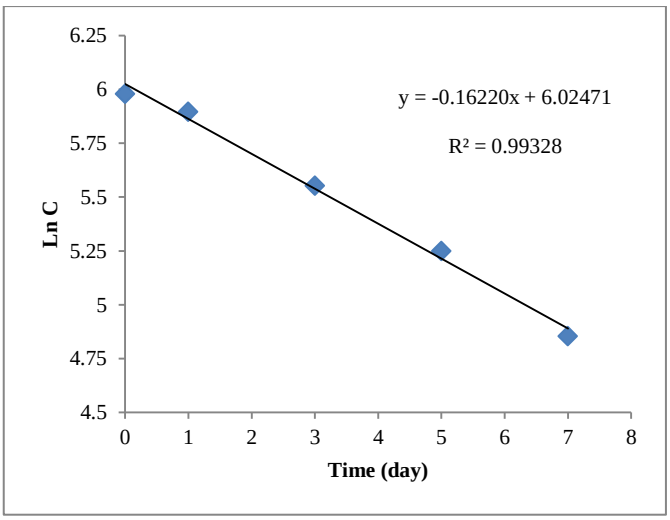


Fig. 9. A plot of ln C vs. time for the acidic degradation of hexythiazox in 0.01 N HCl

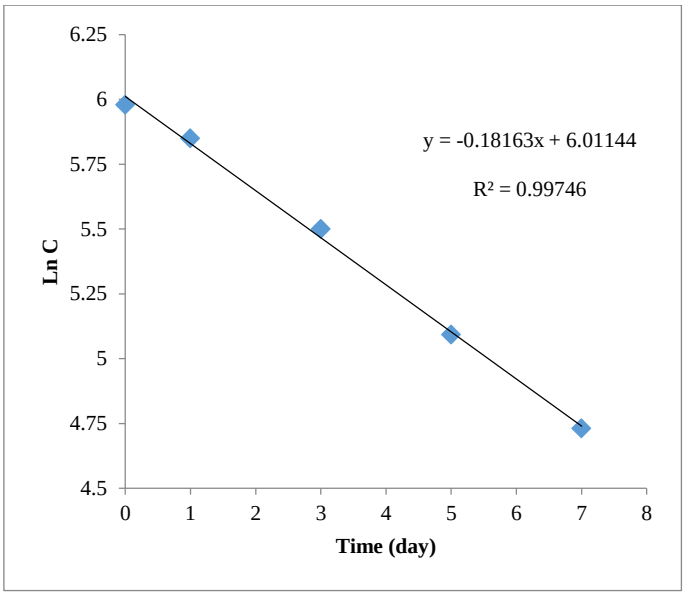


Fig. 10. A plot of ln C vs. time for the acidic degradation of hexythiazox in 0.10 N HCl

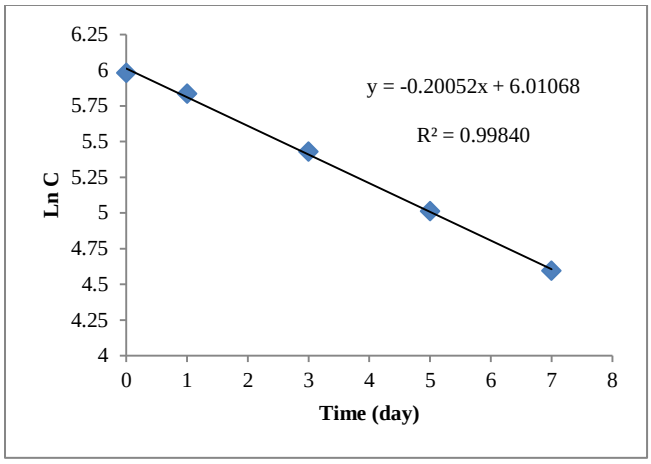


Fig. 11. A plot of ln C vs. time for the acidic degradation of hexythiazox in 1.0 N HCl.

Table 6. Degradation kinetic parameters of hexythiazox in acidic solutions.

Conc. of HCL	Linear regression equation	R^2 coefficient	Degradation constant (K) (day^{-1})	Shelf-life $t_{0.95}$ (day)	Half-life $t_{1/2}$ (day)
0.01 N	y = -0.16220x + 6.02471	0.99328	16.220×10^{-2}	0.32	4.27
0.10 N	y = -0.18163x + 6.01144	0.99746	18.163×10^{-2}	0.28	3.82
1.0 N	y = -0.20052x + 6.01068	0.99840	20.052×10^{-2}	0.26	3.46

3.4.3. Alkaline hydrolysis of hexythiazox

The natural logarithm of the hexythiazox concentration in the alkaline solutions (ln C) vs. time (days) yielded a straight line with an intercept of ln [C_0], indicating that alkaline hydrolysis of hexythiazox followed first-order kinetics, as shown in **Figs. (12, 13,** and **14**). The plots possess a slope of (-k), which corresponds to the degradation constant in (day^{-1}) and R^2 coefficient values ranging from 0.99065 to 0.99160. The predicted kinetic parameters of the alkaline hydrolysis of hexythiazox are provided in **Table (7)**.

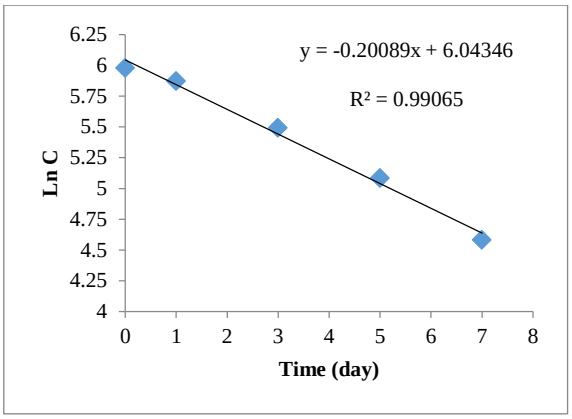


Fig. 12. A plot of ln C vs. time for the alkaline degradation of hexythiazox in 0.01 N NaOH.

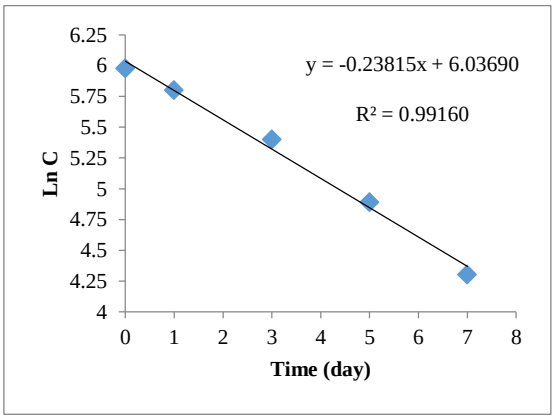


Fig. 13. A plot of ln C vs. time for the alkaline degradation of hexythiazox in 0.10 N NaOH.

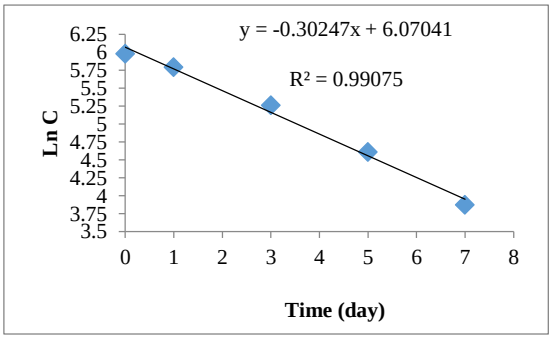


Fig. 14. A plot of ln C vs. time for the alkaline degradation of hexythiazox in 1.0 N NaOH.

Table 7. Degradation kinetic parameters of hexythiazox in alkaline solutions.

Conc. of NaOH	Linear regression equation	R^2 coefficient	Degradation constant (K) (day^{-1})	Shelf life $t_{0.95}$ (day)	Half-life $t_{1/2}$ (day)
0.01 N	y = -0.20089x + 6.04346	0.99065	20.089×10^{-2}	0.26	3.45
0.10 N	y = -0.23815x + 6.03690	0.99160	23.815×10^{-2}	0.22	2.91
1.0 N	y = -0.30247x + 6.07041	0.99075	30.247×10^{-2}	0.17	2.29

3.5. Identification of hexythiazox degradation products using GC/MS

3.5.1. Thermal degradation products and pathways

Following 14 weeks of storage at 54°C, a sample of Efdal hekzarun 5% EC was subjected to GC/MS analysis in order to identify thermal degradation products using the Wiley and NIST mass spectral databases. The identified degradation products along with their structures and masses are provided in **Table (8)**. The forced thermal degradation pathways of hexythiazox provided in **Fig. (15)** may be explained as follows:

Step A: The product isocyanatocyclohexane (**P_1**) may be formed by cleaving the C-N bond that binds the cyclohexane formamide to the thiazolidin-2-one ring.

Step B: The formamide, N-methyl-N-phenyl- (**P_2**) may be formed by binding methyl formamide with a phenyl ring.

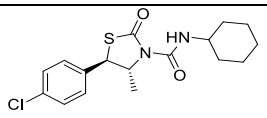
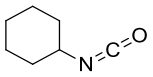
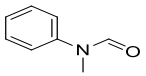
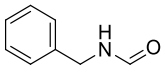
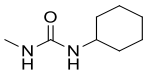
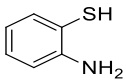
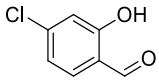
Step C: The product N-Benzylformamide (**P_3**) may be formed due to the binding of the formamide group to methylbenzene.

Step D: N-Cyclohexyl-N'-methylurea (**P_4**) may be formed by cleaving the N-C bond in thiazolidin-2-one and combining the CH_3 group with the amino group.

Step E: The formation of benzenethiol, 2-amino- (**P_5**) (m/z=125) is caused by the loss of chloride from phenyl as well as the binding of the H_2S and NH_3 groups as a result of the thiazolidine-2-one ring fragmentation to the phenyl.

Step F: Due to hydrolexation at position 2 in the benzene ring and CO binding to position 1, the product Benzaldehyde, 4-chloro-2-hydroxy- (**P_6**) is produced

Table 8. The identified thermal degradation products of hexythiazox at 54°C using GC/MS.

Product	Common name	RT (min)	Structure	m/z
P_0	Hexythiazox	25.133		352.2
P_1	Isocyanatocyclohexane	6.416		125.1
P_2	N-methyl-N-phenylformamide	10.387		135.1
P_3	N-benzylformamide	10.484		135.1
P_4	1-cyclohexyl-3-methylurea	13.963		156.1
P_5	2-aminobenzenethiol	16.430		125.0
P_6	4-chloro-2-hydroxybenzaldehyde	19.382		156.0

2.5.2. Acidic hexythiazox degradation products and pathways

A neutralized sample was analyzed using GC/MS after 7 days of forced acidic hydrolysis of hexythiazox to identify possible degradation pathways and significant hydrolytic products. The identified degradation products, along with their structures and masses, are provided in **Table (9).** The forced acidic hydrolytic pathway of hexythiazox in **Fig. (16)** may be explained as follows:

Step 1: The hydrolysis of the thiazolidine ring and cleaving of the C-N bond between the cyclohexane and formamide groups lead to the binding of urea at 1C in the phenyl ring to form 1-(4-chlorophenyl) urea (**P_1**) and the binding of urea with the methyl group liberated from the thiazolidine ring to form 3-methylurea (**P_4**).

Step 2: The product isocyanatocyclohexane (**P_3**) may be formed by cleaving the C-N bond that binds the cyclohexane formamide with a thiazolidin-2-one ring.

Step 3: The product 2-Methyl propionamide (**P_5**) may be formed through the binding of formamide with ethane and then attaching methyl at position 2.

Step 4: The product cyclohexylamine (**P_8**) is formed as a results of cleaving the N-C bond which binds cyclohexane with formamide group.

Step 5: Thiazolidine are hydrolyzed in acidic or basic aqueous solutions to form aldehyde, amino thiol, isothiocyanate, and mercaptal. Hence, the degradation products benzaldehyde (**P_2**), ethyl isothiocyanate (**P_6**), 2-aminobenzenethiol (**P_7**) and butanedioic acid, mercapto- (**P_9**) are formed.

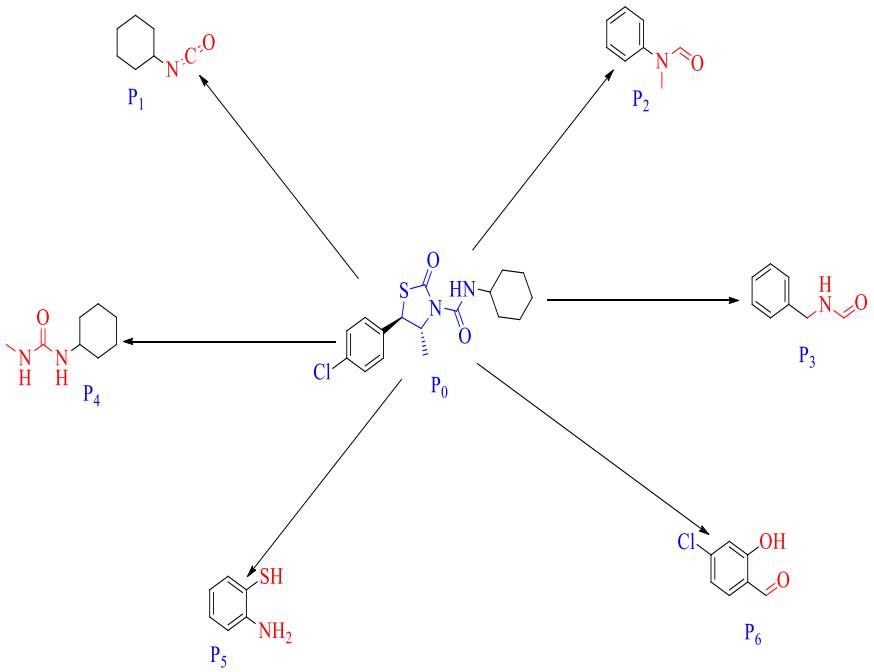
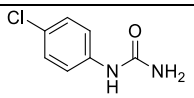
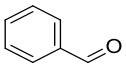
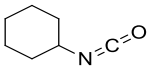
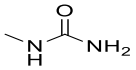
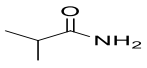
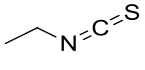
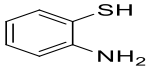
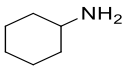
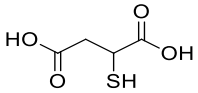


Fig. 15. The thermal degradation pathways of hexythiazox at 54°C.

Table 9. The identified degradation products of hexythiazox hydrolysis in acidic solutions.

Product	Common name	RT (min)	Structure	m/z
P_1	1-(4chlorophenyl)urea	4.876		169.9
P_2	Benzaldehyde	5.592		106.0
P_3	isocyanatocyclohexane,	6.576		125.1
P_4	3-methylurea	9.803		73.9
P_5	2-Methylpropionamide	12.755		87.0
P_6	Ethyl isothiocyanate	12.904		87.0
P_7	2-aminobenzenethiol	16.430		125.0
P_8	cyclohexylamine	23.055		99.1
P_9	Butanedioic acid, mercapto-	28.960		150.0

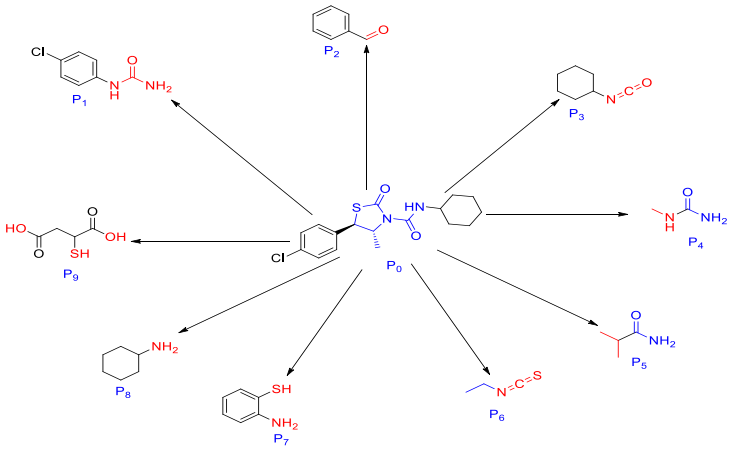


Fig. 16. The forced acidic hydrolytic pathway of hexythiazox.

2.5.3. Alkaline hexythiazox degradation products and pathways

A neutralized sample was analyzed using GC/MS after 7 days of forced alkaline hydrolysis of hexythiazox to identify possible degradation pathways and significant hydrolytic products. The identified degradation products, along with their structures and masses, are provided in **Table (10)**. The forced alkaline hydrolytic pathway of hexythiazox in **Fig. (17)** may be explained as follows:

1- The product benzene, 1-isocyanato-2-methyl- (**P_1**) may be formed by binding methyl and cyanato groups to the benzene ring in positions 2 and 1, respectively.

2- The formation of isocyanatocyclohexane (**P_2**) may occur through the cleaving of the C-N bond that connects cyclohexane formamide to the thiazolidin-2-one ring.

3- The contraction reaction may occur between N-cyclohexylformamide and N-methyl-2-phenylethanamine results in 3-Cyclohexyl-1-methyl-1-(2-phenylethyl) urea (**P_3**).

4- Hydroxylation in the benzene ring at 2C and at iminomethyl, as well as substitution of the chlorine atom with the methyl, may lead to the formation of 2-Hydroxy-5-methylbenzaldehyde oxime (**P_4**).

5- The product thiourea, N, N'-bis(1-methylethyl)- (**P_5**) may be formed by the binding of methyl ethyl to NH_2 groups in thiourea.

6- The 4-methyl-5-phenylthiazolidine-2-one (**P_6**) may be formed when the C-N connection between cyclohexylformamide and thiazolidine is broken followed by the loss of chlorine atom.

7- 3-methylthiazolidine (**P_7**) is generated by the attaching of methyl to nitrogen in the thiazolidine ring after losing CO and cleaving the connection between thiazolidine, 4-chlorobenzene, and cyclohexylformamide.

8- The hydrolysis of thiazolidine in strong alkaline lead to the formation of Propane, 2-methyl (**P_8**), 1-chloropropane (**P_{12}**) and ethyl chloride (**P_{13}**).

9- The product N-Methyl-cyclohexylamine (**P_9**) may be produced by the cleaving of N-C bond that binds cyclohexane to formamide, followed by the binding of the methyl to the amine.

10- N-methylacetamide (**P_{10}**) and acetamide (**P_{11}**) are formed by cleaving the connection between the cyclohexyl, formamide and thiazolidine.

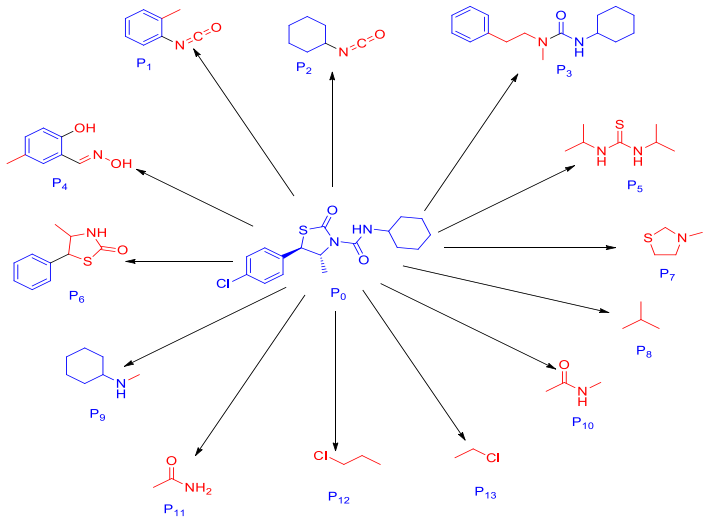
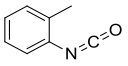
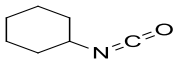
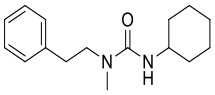
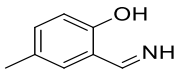
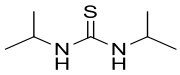
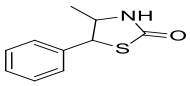
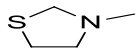
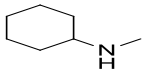
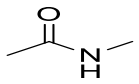
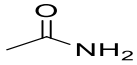
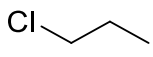


Fig. 17. The forced alkaline hydrolytic pathway of hexythiazox.

Table 10. The identified degradation products of hexythiazox hydrolysis in alkaline solutions.

Product	Common name	RT (min)	Structure	m/z
P_1	Benzene, 1-isocyanato-2-methyl-	5.014		133.1
P_2	isocyanatocyclohexane	6.925		125.1
P_3	3-cyclohexyl-1-methyl-1-(2-phenylethyl)urea	8.315		260.0
P_4	2-hydroxy-5 - methylbenzaldehyde oxime	8.985		151.1
P_5	Thiourea, N,N'-bis(1-methylethyl)-	10.581		160.1
P_6	4-methyl-5-phenylthiazolidine-2-one	11.268		193.1
P_7	3-methylthiazolidine	12.286		102.8
P_8	Propane,2-methyl	12.412		57.9
P_9	N-methylcyclohexanamine	12.618		113.1
P_{10}	N-methylacetamide	12.733		72.9
P_{11}	acetamide	13.477		58.9
P_{12}	1-chloropropane	19.176		77.9
	64.0	20.858		

2.6 Dissipation of hexythiazox in clay-loam soil

The Soil, Water, and Environment Research Institute (SWERI) in Giza, Egypt, analyzed the physical and chemical properties of typical Egyptian soil prior to investigating hexythiazox breakdown in soil. According to **Table (11)**, the soil was clay-loam with low organic matter content. In addition, the pH of the research soil was alkaline. **Table (12)** show the dissipation of hexythiazox in clay-loam soil. The results demonstrated that the active ingredient was reduced by 80.53% during 14 days at ambient conditions.

3.6.1. Kinetic study of hexythiazox dissipation in the soil

As in prior cases of degradation, hexythiazox dissipation in clay-loam soil followed first order kinetics and depended on concentration. When ln C was plotted vs. time, a straight line was produced with an R^2 coefficient of 0.99026 and a slope of (-k) in **Fig.(18)**. The half-life ($t_{1/2}$) of hexythiazox degradation in the clay-loam soil was determined to be 5.75 days, based on the data in **Table (13).**

Table 11. Chemical, mechanical and physical properties of soil used in the hexythiazox dissipation study.

Chemical properties				
Organic matter %	1.92			
Soluble cations (mg/L)	K^+	Na^+	Mg^{2+}	Ca^{2+}
	24.24	311.51	68.75	190.38
Soluble anions (mg/L)	SO_4^{2-}	Cl^-	HCO_3^-	CO_3^{2-}
	454.84	655.83	61.02	---
Available macro-elements (mg/Kg soil)	N	K	P	
	69.00	183.00	8.34	
Available micro-elements (mg/Kg soil)	Cu	Fe	Mn	Zn
	0.046	0.876	0.342	0.152
Mechanical properties				
Soil texture	Clay %	Silt %	Sand %	
Clay	44.76	16.25	38.99	
Physical properties				
Saturation percentage (SP)	Electrical conductivity(ds/m)		pH (1:2.5- soil: water)	
62.99	2.91		8.59	

Table 12. Dissipation of hxythiazox 5% EC in clay-loam soil.

Exposure Periods (day)	Conc. of Hexythiazox (µg/mL)	Dissipation rate %
0	98.62	0
1	93.56	5.13
3	77.41	21.51
5	63.46	35.65
7	43.29	56.10
14	19.20	80.53

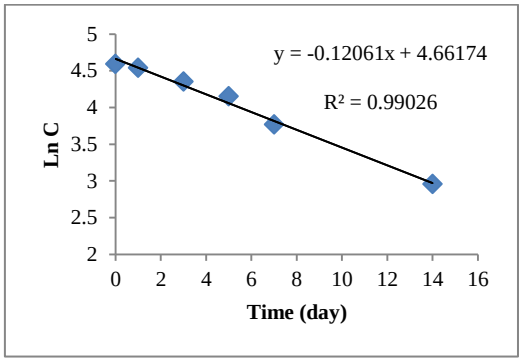


Fig. 18. A plot of ln C vs. time for the photolysis of hexythiazox in clay-loam so

Table 13. Kinetic parameters of hexythiazox photolysis in clay-loam soil.

Linear regression equation	R^2 coefficient	K value (day^{-1})	$t_{1/2}$ (day)
y = -0.12061x +4.66174	0.99026	12.061×10^{-2}	5.75

3.6.2. GC/MS identification of the degradation products of hexythiazox in soil

Following a study of the photolysis of hexythiazox in clay-loam soil, a soil sample was examined using GC/MS to identify the degradation products and determine the possible degradation pathway using Wiley and NIST mass spectrum databases**.** The identified degradation products with their structures and masses are provided in **Table (14)**. The photolysis degradation pathway of hexythiazox in clay-loam soil **Fig.(19)** can be explained as follows:

Step 1: The interaction between methanethiol and acetamide results in the formation of alpha.-(methylthio) acetamide (**P_1**).

Step 2: The contraction reaction between cyclohexanecarboxamide and 4-chlorobenzoic acid in position 2 of the benzene ring results in 4-chloro-2-(cyclohexanecarboxamido) benzoic acid (**P_2**).

Step 3: Acetamide binds to 4-chlorobenzene after cleaving the bond between cyclohexane and formamide to form the N-(4-chlorophenyl) acetamide (**P_3**).

Step 4: After cleaving the bond between cyclohexane and formamide and losing chlorine, the product benzyl isocyanate (**P_4**) is produced by reacting isocyanatomethane with benzene.

Step 5: After cleaving the C-N bond between cyclohexylformamide and the thiazolidine, 2-(4-chlorophenyl) thiazolidine (**P_5**) is produced.

Step 6: Following the cleavage of the N-C bond that binds cyclohexyl to formamide, the N-hydroxycyclohexylamine (**P_6**) is produced via a hydroxylation process at the amino group.

Step 7: The product N-methyl-cyclohexylamine (**P_7**) may be formed by cleaving the N-C bond that binds cyclohexane to the formamide group, followed by binding the methyl group to the amine.

Step 8: The product (R)-3-(benzoylamino)-2-methylpropanoic acid (**P_8**) may be formed via the interaction of benzamide with 2-methyl propanoic acid, which is formed during thiazolidine degradation.

Step 9: Benzene, 1-isothiocyanato-4-methyl (**P_9**) is formed by the binding of thiocyanato to the benzene and the replacement of chlorine with methyl.

Step 10: The contraction reaction between N-cyclohexylformamide and N-methyl-2-phenylethanamine produces 3-Cyclohexyl-1-methyl-1-(2-phenylethyl) urea (**P_{10}**).

Step 11: Acetamide, N-methyl-N-phenyl- (**P_{11}**) may be formed after acetamide binds to the benzene and then the methyl group attaches to the amino in acetamide.

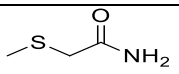
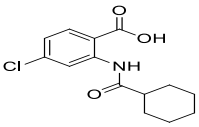
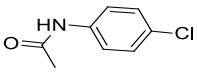
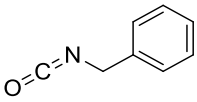
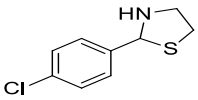
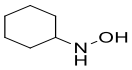
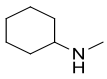
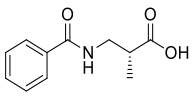
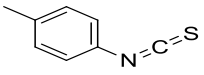
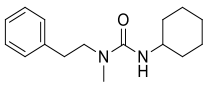
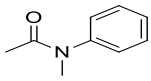
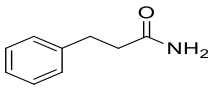
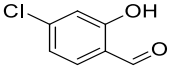
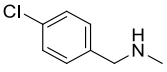
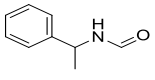
Step12: The reaction between formamide and ethyl benzene produces phenylpropanamide (**P_{12}**).

Step 13: The product benzaldehyde, 4-chloro-2-hydroxy- (**P_{13}**) may be produced due to hydrolexation and CO binding at positions 2 and 1,respectively in the benzene.

Step 14: When dimethyl amine binds to 4-chlorobenzene, the product N-(4-chlorobenzyl)-N-methylamine (**P_{14}**) is produced.

Step 15: After the breakdown of thiazolidine, the product formamide, N-(1-phenylethyl)- (**P_{15}**), is produced by the binding of acetamide to 1-chloro-4-ethylbenzene**.**

Table 14. The identified degradation products of hexythiazox photolysis in clay-loam soil

Product	Compound	RT (min)	Structure	m/z
P_1	alpha.-(Methylthio)acetamide	8.275		104.9
P_2	4-chloro-2-(cyclohexanecarboxamido) benzoic acid	9.906		281.1
P_3	N-(4-chlorophenyl)acetamide	13.317		169.0
P_4	benzyl isocyanate	13.694		133.1
P_5	2-(4-chlorophenyl)thiazolidine	16.103		199.0
P_6	N-hydroxycyclohexylamine	16.309		115.1
P_7	N-methyl-cyclohexylamine	16.778		113.1
P_8	(R)-3-(Benzoylamino)-2-methylpropanoic acid	17.402		207.1
P_9	Benzene, 1-isothiocyanato-4-methyl	17.83		148.8
P_{10}	3-cyclohexyl-1-methyl-1-(2-phenylethyl)urea	18.306		260.0
P_{11}	Acetamide, N-methyl-N-phenyl-	18.483		148.9
P_{12}	phenylpropanamide	18.586		148.9
P_{13}	Benzaldehyde, 4-chloro-2-hydroxy-	18.998		156.0
P_{14}	N-(4-chlorobenzyl)-N-methylamine	19.519		154.8
P_{15}	formamide, N-(1-phenylethyl)-	25.384		149.0

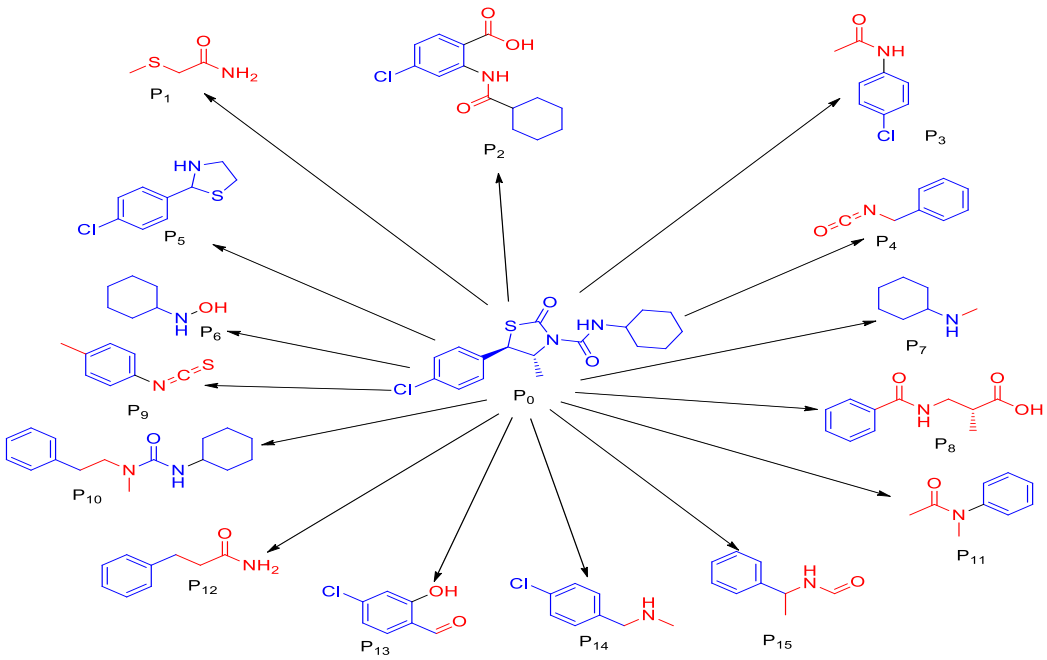


Fig. 19. The photolysis degradation pathway of hexythiazox in clay-loam soil.

4. Discussion

As per the FAO/WHO (2010), the average reduction of a pesticide's active component throughout storage for 2, 6, 8, and 12 weeks at 35, 40, 45, and 54°C should not exceed 5% of its average original concentration. Thus, hexythiazox storage complied with FAO specification after more than 14 weeks at 35°C and not after more than 9, 8, and 4 weeks at 40, 45, and 54°C, respectively. Hexythiazox has 1 hydrogen bond, a donor, and 3 hydrogen bonds, an acceptor, based on its chemical composition. The main distinction between hydrogen bond donor and acceptor is that the hydrogen bond donor includes the hydrogen atom that participates in the hydrogen bond formation, whereas the hydrogen bond acceptor contains lone electron pairs.

The hydrogen bond is responsible for a variety of the chemical and physical features of compounds containing N, O, and halogen atoms such as F, Cl, Br and I that appear unique when compared to other similar structures. In particular, intermolecular hydrogen bonding is responsible for water's high boiling point (100°C) in comparison to the other hydrides with significantly weaker hydrogen bonds (Sabin, 1971). Furthermore, the chemical composition of hexythiazox pesticide reveals that it contains p-chlorophenyl, which makes the pesticide environmentally stable, at high temperatures or in the presence of light, as well as preventing oxidation reactions that occur in the acidic and alkaline environments. One or more chlorine atoms substitute for hydrogens on carbon, as in the structure of hexythiazox and DDT. These chlorinated hydrocarbons do not exist in nature. The majority of them have one characteristic: environmental persistence. Tan (1983) and O'Neil (2006). Overall, the obtained results are consistent with Coromandel (2021), which reported that the hexythiazox was stable for two years when stored at a normal temperature.

The obtained results indicate that the hydrolysis of hexythiazox was influenced by pH values, acid concentration, and exposure time in the acidic aqueous solution. Furthermore, it was observed that the hydrolysis rate of hexythiazox decreased as the pH of the acidic medium increased i.e. the HCl concentration decreased. Schröder E. and Lübke K. (2014) reported that the formyl group and the thiazolidine ring were cleaved under acidic hydroletic conditions (0.5 N methanolic hydrochloric acid, 60 hours at room temperature), and this is in accordance with the current findings as the rate of hexythiazox hydrolysis increased in concentrated acidic solutions. The hydrolysis of the thiazolidine ring to form aldehyde, amino thiol, isothiocyanate, and mercaptal in acidic or basic aqueous conditions causes the hexythiazox to be unstable (Pesek and Frost (1975); JECFA (1994)). This is consistent with the findings of the current investigation, which show that hexythiazox is unstable in strong acidic solutions. The reaction includes C-S bond breaking and proceeds via the production of an iminium thiolate zwitterion intermediate as shown in **Fig. (20).**

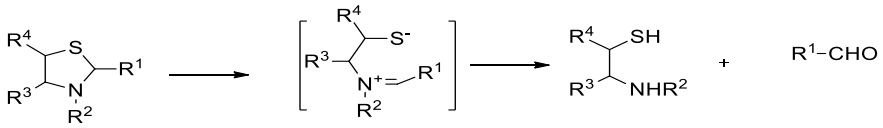


Fig. 20. Hydrolysis of thiazolidine ring in acidic and basic solution.

FAO (2011) reported that about 1 to 10% of the initial concentration of hexythiazox declined at pH 4 (90°C for 20 min) and pH 5 (100°C for 60 min). About 50% of the parent comound was hydrolyzed at pH 6 (120°C for 20 min). PT-1-3, the only significant product, was discovered in levels equal to 48.4% of the starting concentration. As well, ECHA (2017) reported that hexythiazox degraded slowly in the alkaline (pH 9) aqueous solutions under sterile circumstances at room temperature (22°C), whereas it was found to be stable under neutral (pH 7) and acidic (pH 5) conditions. At 22°C and pH 9, the hydrolytic half-life of hexythiazox ranged from 370 to 504 days. Alkaline hydrolysis of hexythiazox increased in 1.0 N NaOH compared to 0.10 and 0.01 N NaOH. This indicates that the increased concentration of OH^- ions in the solution facilitated the degradation of this molecule. As, the thiazolidine ring degraded and opened in a strong alkaline solutions like NaOH (Pesek and Frost (1975); JECFA (1994)). The hydroxylation takes place in both urea parts after the hydrolysis of the molecule. According to the EPA (2007), hexythiazox was hydrolytically stable in aqueous solutions with pH ranging from 5 to 9 and somewhat persistent when exposed to light. As well, EFSA (2019) studied the hydrolysis of hexythiazox in water at different pH values (pH 5, pH 7, and pH 9) and at different temperatures (22, 50, and 70°C), concluding that the degradation of hexythiazox was pH and temperature dependent. Whereas the hexythiazox was stable between pH 5-7 with a half-life of more than 500 days and even at pH 9, at 70°C the same degradation level reached over 300 days, 12 days, or less than 5 hours in buffer solutions of pH 5, 7, or 9, respectively.

The data showed that the degradation rate of hexythiazox was dependent on its initial concentration and increased progressively as temperature increased. Furthermore, the shelf life of hexythiazox after storage at 54°C was found to be approximately 1/5 that of its shelf life after storage at 35°C.However, the shelf-lives of hexythiazox after storage at these elevated temperatures were compatible with the duration of time recommended by the FAO/WHO. The current results are consistent with Mansour *et al.* (2018), who reported that there was a positive relationship between temperature, the intensity of light, length of storage periods, and the degradation rate of active ingredients.

The data show that an acidic or alkaline medium affects the half-life and shelf life of hexythiazox as they increase progressively when the acidity or alkalinity of the medium decreases. The kinetics of hexythiazox degradation under the studied conditions followed the first-order model, being dependent upon its initial concentration. The shelf life ($t_{0.95}$) and half-life ($t_{1/2}$) of hexythiazox in forced alkaline solutions were less than those in acidic solutions.

According to the GC/MS analysis of hexythiazox samples after thermal, forced acidic and alkaline hydrolysis, hexythiazox was degraded to different byproducts; one of them, isocyanatocyclohexane, was identified in thermal, forced acidic and alkaline hydrolysis, while 2-aminobenzenethiol was identified in thermal and forced acidic hydrolysis. The benzene and cyclohexane rings remain stable under different applied conditions; however, the thiazolidine ring is cleaved and opened during thermal and forced acidic hydrolysis and remains stable after alkaline hydrolysis. The contraction reaction is unique to forced alkaline hydrolysis of hexythiazox; thus, two products were identified: 3-cyclohexyl-1-methyl-1-(2-phenylethyl) urea and 4-methyl-5-phenylthiazolidine-2-one.

The obtained results showed that hexythiazox was degraded rapidly in Egyptian clay-loam soil because hexythiazox's molecular structure contains chromophores such as ethylene and carbonyl groups; it may be sensitive to direct photolysis by sunlight because it absorbs wavelengths larger than 290 nm and that are consistent with EPA (2007) which stated that hexythiazox degradation was most rapid (half-lives of a few weeks or less) in aerobic soil and water when photolysis is possible.

The dissipation and degradation of Hexythiazox emulsion concentrate in alkaline clay soil with the provided characteristics will depend on several key factors such as soil texture, organic matter content, pH, cation and

anion composition, and available macro- and micronutrients. Here's an explanation of the role of these soil properties in the behavior of hexythiazox:

1. Soil pH (8.59 – Alkaline):

♦ Effect on Hexythiazox: The pH of 8.59 indicates that the soil is alkaline. Hexythiazox is a miticide that is typically more stable in slightly acidic to neutral pH conditions and that are consistent with Sparks (2003), who stated that at higher pH levels, the pesticide may become less soluble or more prone to degradation due to changes in its chemical structure.

♦ Degradation: Alkaline conditions may accelerate the hydrolysis (breakdown by water) of hexythiazox, especially if the pesticide contains functional groups that are sensitive to changes in pH (like ester groups or amides). This could result in a faster breakdown of the pesticide in the soil as found in FAO/WHO (2009).

♦ Effect on Persistence: The higher pH in this soil might lead to the quicker dissipation of hexythiazox, reducing its persistence and effectiveness as a pesticide, but also reducing the risk of long-term accumulation in the soil.

2. Clay Soil Texture:

♦ Water Retention and Adsorption: Clay soil has fine particles that retain water and may also adsorb pesticides like hexythiazox more readily due to its high surface area. This could initially slow the dissipation of the pesticide as it becomes trapped in the soil matrix as stated by Laird (1997).

♦ Slow Release: However, over time, the pesticide may slowly leach out into the soil solution, depending on water movement and whether the pesticide binds strongly to clay particles. Clay also has a relatively high cation exchange capacity (CEC), which may influence how tightly the pesticide is bound to the soil and affect its mobility and degradation.

3. Saturation Percentage (62.99%):

♦ Soil Moisture and Leaching: The high saturation percentage of 62.99% indicates that the soil has a significant amount of water, which may help in leaching the pesticide down through the soil profile.

♦ Influence on Degradation: High soil moisture can enhance microbial activity (if oxygen levels are sufficient) and facilitate the hydrolytic degradation of hexythiazox. However, poor drainage and the water-retention nature of clay could cause slower movement of hexythiazox, limiting its exposure to microorganisms and slower biodegradation.

4. Organic Matter (1.92%):

♦ Soil Microbial Activity: Organic matter provides food for soil microbes, which can accelerate biodegradation of hexythiazox. With 1.92% organic matter, microbial populations may be somewhat limited, but enough organic material is present to support degradation processes (Bollag and Liu, 1990).

5. Soluble Cations and Anions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, CO_3^{2-}, Cl^{-}, SO_4^{2-}):

♦ Calcium (Ca^{2+}) and Magnesium (Mg^{2+}): The high concentrations of Ca^{2+} (190.38 mg/L) and Mg^{2+} (68.75 mg/L) suggest that the soil has a significant presence of these divalent cations, which could affect the solubility and mobility of hexythiazox. Calcium and magnesium ions could compete with hexythiazox for binding sites on soil particles, potentially influencing the pesticide's retention or leaching behavior and this agreement with Sparks (2003).

♦ Sodium (Na^{+}): The relatively high level of Na^{+} (311.51 mg/L) in the soil could lead to the formation of sodium salts of hexythiazox, making the pesticide more soluble in water, and thus more prone to leaching and dissipation from the soil and this agreement with Goring *et al*., (1975)

♦ Chloride (Cl^{-}) and Sulfate (SO_4^{2-}): The presence of these anions can interact with hexythiazox and may influence its mobility. Chloride can act as a counterion, potentially enhancing the solubility of hexythiazox in the soil solution, leading to faster leaching as stated by FAO/WHO (2009).

6. Available Macro- and Micro-Elements (P, K, N, Zn, Fe, Mn, Cu):

♦ Nutrient Availability: The availability of macronutrients like phosphorus (P) and potassium (K), as well as microelements like zinc (Zn), manganese (Mn), iron (Fe), and copper (Cu), will influence microbial populations and their activity in degrading hexythiazox and this consistent with Bollag and Liu (1990) who stated that if certain microbial groups use these nutrients for metabolism, they may enhance microbial degradation of the pesticide.

7. Environmental Conditions and Microbial Activity:

♦ Soil Microbes: The organic matter content, available nutrients, and moisture levels are conducive to microbial activity, which is a key factor in the biodegradation of hexythiazox. However, high saturation in clay soils with limited oxygen may slow down aerobic microbial degradation processes, leading to more anaerobic decomposition, which may not be as efficient for pesticide breakdown.

ECHA (2017) reported that hexythiazox had a half-life of 7.8 to 56.0 days (geometric mean: 23.7 days) in soil under aerobic conditions at normal temperatures of 20^{o}C while the half-lives values of the main metabolites of hexythiazox varied from 6.6 to 25.0 days for PT 1-9, 9.1 to 264.2 days for PT-1-2, and 10.7 to 54.1 days for PT 1-3.

The results are consistent with EPA (2007), which stated that the parent hexythiazox half-life ranged from 8 to 25 days in aerobic soil metabolism tests, depending on soil type, while the overall hazardous residual half-life was predicted to be around 41 days. The half-life of the parent hexythiazox under field conditions ranged from 5 to 26 days. MacBean (2010), reported that half-life of hexythiazox in clay-loam soil was 8 days, and the molecule was oxidized to the corresponding hydroxy, resulting in minor hydroxylated cyclohexyl metabolites.

The Pesticides can be categorized as either non-persistent (half-life< 30 days), moderately persistent (half-life between 30 and 100 days), or persistent (half-life >100 days) based on their half-lives (Gavrilescu, 2005). According to the previously specified classification, findings suggest that hexythiazox is a non-persistent pesticide in the soil.

Overall, Patnaik (2007) found that certain chemical compounds exhibit hazardous properties due to the presence of specific functional groups. For example, lower molecular weight aldehydes are more toxic than the higher molecular weight aldehydes, aliphatic amines have low to moderate toxicity, and organic isocyanates are extremely reactive due to significant unsaturation in the isocyanate functional groups. The majority of isocyanates are harmful to one's health**.** These in accordance with the current results as hexythiazox degrades to a variety of byproducts, some of which are toxic:

● Aldehydes (4-chloro-2-hydroxybenzaldehyde and benzaldehyde).

● Aliphatic amines (cyclohexylamine, N-methyl-cyclohexylamine and N-hydroxycyclohexylamine).

● Organic isocyanates (benzyl isocyanate, benzene, 1-isothiocyanato-4-methyl and benzene, 1-isocyanato-2-methyl-).

In conclusion, the kinetics of hexythiazox degradation in the Egyptian clay-loam soil followed the first-order model, being dependent upon its initial concentration, similar to that of thermal and forced hydrolysis. According to the GC/MS analysis of hexythiazox after soil photolysis, hexythiazox was degraded to different byproducts; two of them, N-methyl-cyclohexylamine and 3-cyclohexyl-1-methyl-1-(2-phenylethyl)urea, were also identified in the neutralized sample after alkaline hydrolysis while benzaldehyde, 4-chloro-2-hydroxy-, was identified after thermal conditions. The benzene, cyclohexane and thiazolidine rings remain stable after the soil photolysis. The contraction reaction is unique to the photolysis of hexythiazox in clay-loam soil like the forced alkaline hydrolysis as the studied soil was alkaline; thus, two products were identified: 4-chloro-2-(cyclohexanecarboxamido) benzoic acid and 3-cyclohexyl-1-methyl-1-(2-phenylethyl)urea; the latter one was also identified in the forced alkaline hydrolysis of hexythiazox.

5. Conclusion

In this research, the accelerated hot storage at different temperature, hydrolytic (acidic and alkaline) conditions and photolysis of hexythiazox 5% EC in clay soil were investigated. The results showed that the thermal storage of hexythiazox complied with FAO specification after more than 14 weeks at 35°C and not after more than 9, 8, and 4 weeks at 40, 45, and 54°C, respectively. The data showed that the degradation rate of hexythiazox was dependent on its initial concentration and increased progressively as temperature increased. Furthermore, the shelf life of hexythiazox after storage at 54°C was found to be approximately 1/5 that of its shelf life after storage at 35°C. The shelf life ($t_{0.95}$) and half-life ($t_{1/2}$) of hexythiazox in forced alkaline solutions were less than those in acidic solutions. The results revealed that hexythiazox is a non-persistent pesticide in soil; it decomposed rapidly in Egyptian clay-loam soil, with an 80.53% reduction in 14 days at ambient conditions and a half-life (t1/2) of 5.75 days. According to the GC/MS analysis, hexythiazox was degraded to different byproducts after specified conditions. The contraction reaction is unique to the forced alkaline hydrolysis and photolysis of hexythiazox in clay-loam soil.

6. Conflicts of interest

"There are no conflicts to declare".

7. Acknowledgments

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