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A Study of Quinclorac Degradation during Thermal and Forced Hydrolysis and Soil Photolysis

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IN THE PRESENT study, the stability of quinclorac as (Queen 75% WG) during the forced thermal degradation at temperatures, forced acidic and alkaline hydrolysis, and soil photolysis was investigated. The results indicate that the maximum active ingredient degradation of quinclorac (5.57%) was achieved during storage at 54°C after 14 weeks. During the same time period, however, the reduction was modest, ranging between 1.5- 3% at 35, 40, and 45°C, respectively. The shelf life of quinclorac after storage at different temperatures was consistent with the time period recommended by FAO/WHO. The acidic hydrolysis of quinclorac improved the shelf-life and half-life to 5.40 and 72.96 days, respectively, which is almost four times that of 1.0 N HCl. However, in alkaline conditions, the shelf-life and half-life of quinclorac were lowered to 1.02 and 13.73 days, respectively. Increasing the alkaline concentration to 1.0 N NaOH further reduced these results to 0.44 and 5.95 days, respectively. Generally, the kinetics of quinclorac degradation followed a first-order model that was reliant on its initial concentration. Furthermore, the half-life of quinclorac dissipation was determined to be 124 days in local clay-loam soil (with organic matter of 1.92%) and a significant saturation percentage of 62.99% and hence it is considered a persistent herbicide. The degradation products of quinclorac were identified by GC/MS and may be attributed to decarboxylation, dechlorination, hydroxylation, and the substitution of chlorine with a hydroxyl group.

Keywords: Quinclorac; forced thermal degradation; acidic hydrolysis; alkaline hydrolysis; soil photolysis; degradation products.

1. Introduction

Quinclorac is a highly selective synthetic auxin used primarily to control weeds in rice crops as well as other agricultural crops. It was first registered as a soil- or foliar-applied herbicide for annual grass and broadleaf weed control in 1992 (Lym, 2016). The IUPAC name of quinclorac is (3, 7-dichloro-quinolone-8-carboxylic acid), which is quinoline-8-carboxylic acid with chlorine atoms in place of the hydrogen atoms at positions 3 and 7. It is considered a combination of an organochlorine compound and a monocarboxylic acid.

Auxins are natural plant hormones found at the tips of plant roots and shoots that regulate the amount, type and direction of plant growth. Auxin herbicides are classified into seven groups: phenoxy-carboxylic acids, benzoic acids, pyridine carboxylic acids, pyridyloxy-carboxylic acids, quinolone carboxylic acids, pyrimidine carboxylic acids, and aryl pyridine carboxylic acids, all of which have carboxylic acid functionality. The use of dichloroquinoline derivatives as herbicides, including quinclorac, was first patented in 1982 by BASF under German Patent DE 3108873 and name of BAS 514 H.

Essentially, quinclorac is a selective herbicide with auxin activity resembling indolylacetic acid. It works systemically and is being absorbed by germinating seeds, the root system and partially through leaves to regulate and slow down plant growth. It has been used for pre- and post-emergence control of *Echinochloa* spp. as well as other weeds including *Aeschynomene* spp., *Sesbania spp*. and *Ipomoe*a spp. in direct-seeded and transplanted rice.

Thermal stability is an essential property to assess the performance of a chemical after exposure to high temperatures. For pesticides, this thermal stability affects its structural groups, side branching, compensators, the molecular weight as well as aromatic content (Alshamsi *et al*., 2015). As well,

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forced degradation demonstrates the pesticide stability in a short period of time and under severe environments to provide information regarding storage conditions and shelf life. There are several elements that influence the molecular quality with time and intensity of degrading events such as acid and alkaline hydrolysis (Devrukhakar and Shankar, 2020)**.** Pesticides also undergo photo, chemical and microbial degradation in which its molecular links may be either broken or exhibit an internal conversion. Most pesticides are extremely sensitive to photolysis due to their structural properties (Meng *et al*. 2022). However, in order to initiate a photochemical reaction, a pesticide must absorb a specific wavelength to be elevated to an excited state. The stability, effectiveness, residual transfer, and safety assessment of pesticides in the environment will all be impacted by their environmental behaviours, including the soil degradation, hydrolysis, photolysis, sorption and desorption, and leaching (Zhou *et al*., 2021). The rate at which pesticides degrade, are turned into the degradation products, or are partially or totally mineralized is a significant element in determining how long the 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).

Elevated quantities of potentially toxic elements (PTEs) in soil pose a risk to human health. Using hyper-accumulator plants may be an eco-friendly and cost-effective way to achieve more desired levels of these pollutants in soil (El-Shwarby *et al*., 2022).

Pesticide hydrolysis is essentially a nucleophilic substitution reaction, in which the 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, hydrolytic processes are influenced by numerous factors, including pesticide properties and environmental parameters such as pH value, water temperature, and clay minerals (Zhou et al., 2023).

The photocatalytical degradation of quinclorac under sunlight in the presence of H_2O_2 and [(R,R)-(N,N′-bis(3,5,3′,5′-tetra-tert-butylsalicylidene)-1,2-cyclohexanediaminato] manganese(III) acetate (Mn (III) salen). They found that 91% degradation of quinclorac was obtained after 240 minutes in pure water. The degradation products identified indicated that there was a cleavage of quinclorac molecule involving hydroxylation along with the breaking of the C=N link on the pyridine ring and hydroxylation of the benzoic ring. They also affirmed that hydroxyl and superoxide radicals were the main reactive species in this reaction (Yang *et al*., 2018).

The impact of temperature and moisture on the half-life and dissipation of quinclorac in soil under greenhouse conditions using Northern Great Plains soil examined by Lym (2016). He found that quinclorac 50% dissipation time (DT_{50}) was dependent on several factors including soil type, moisture content, temperature, and especially organic matter (OM). The dissipation time (DT_{50}) for quinclorac in four types of soils from the Northern Great Plains varied from 21 to 112 days and it increased with the soil moisture content. However, in low organic matter soils, moisture had a lesser impact. Moreover, the dissipation rate increased with temperature in all four soils. As well, an average DT_{50} of 38 days was exhibited in soil with higher OM (6%), 45% moisture content and at 16ºC.

Quinclorac's environmental behavior in acidic paddy soil under rice (*Oryza sativa L.*) field conditions and assessed the danger that its residues would affect the next tobacco crop (*Nicotiana tabacum L.*) quantified by Zhong *et al*. (2018). At seven days after transplanting the seedlings, rice was sprayed once with quinclorac 50% WP at 562.5, 375.0, or 187.5 g a.i. ha^{-1}. In rice field soil, quinclorac decomposed using first-order kinetics and had a half-life of 28.29–30.27 days.

A nanocomposite of nZVI/ATP was created with nanoscale zero-valent iron (nZVI) supported on attapulgite (ATP) for activating peroxymonosulfate (PMS) and producing reactive free radicals for quinclorac elimination. Quinclorac was degraded chemically into five main compounds via hydroxyl substitution, oxidation, and ring-cleavage. Finally, the majority of the breakdown products were mineralized into inorganics such CO2, H2O, or other substances. nZVI/ATP-PMS proved to be a highly efficient catalytic degradation system for eliminating quinclorac residues in aqueous solution (Ding *et al*., 2019)**.**

The detection method of quinclorac in rice plants, paddy soil, and paddy water using Liquid chromatography tandem triple quadrupole mass spectrometry developed by Siqi *et al*. (2020). The data demonstrated that quinclorac had a good linear connection in the linear range from 0.01 to 1 mg/L ($R \geq 0.999$). The range for quinclorac quantification was 0.0125–0.05 mg/kg. The average recovery rates

ranged from 85% to 112% when quinclorac spiked at 0.05, 0.2 and 1 mg/kg in soil and plants and at 0.0125, 0.05 and 0.25 mg/kg in field water. The range of the relative standard deviations (RSD, n=6) was 1.1% to 9.3%. A plot experiment was used to confirm the method's reliability. Rice seedlings were treated with a 375 g/hm^2 dosage of quinclorac via spraying. Quinclorac was quickly decomposed in rice plants, according to the results. Qinclorac dissipation rate was 94% after 21 days of application. Quinclorac, however, dissipated slowly in soil and water from paddy fields. Only 33% and 45% of the treated areas had dissipated after 21 days.

Global food production is mostly determined by agricultural productivity. Soils are a source of nutrients for plant growth. These nutrients directly improve crop yields and resistance to biotic and abiotic stressors (Elramady *et al*., 2021) therefore the current research study the fate of quinclorac in caly soil. Furthermore, increased microbial activity in the soil may lower the need for inorganic fertilizer applications (Taha *et al*., 2018).

The objective of this study is to investigate the fate of quinclorac during forced thermal, acidic and alkaline hydrolysis as well as its photolysis in Egyptian clay-loam soil. In order to elucidate the degradation pathways, the degradation products of this herbicide will be identified using GC/MS. Finally, the analytical results will be used to quantify the shelf-life and half-life periods for this pesticide under the applied experimental conditions.

2. Material and methods

2.1 Materials

- Quinclorac (purity of 98.89%) certified reference standard was obtained from Dr. Ehrenstorfer^{TM} Gmbh (Augsburg, Germany).
- Quinclorac formulation (Queen 75% WG), which is readily accessible on the Egyptian market, was used. The chemical and physical properties of quinclorac are provided in **Table (1)**.
- HPLC grade acetonitrile and methanol were acquired from Sigma-Aldrich.
- QuEChERS (Quick Easy Cheap Effective Rugged Safe) extraction kits (4g $MgSO_4$, 1g NaCl, 1g sodium citrate tribasic dihydrate, and 0.5 g sodium citrate dibasic sesquihydrate) and clean-up kit (25 mg PSA sorbent and 150 mg $MgSO_4$) were purchased from Sigma-Aldrich for quinclorac evaluation and determination in soil samples.

2.2 Methods:

2.2.1. Calibration curve of quinclorac using HPLC

A stock solution of the quinclorac standard (400 µg/mL) was prepared in acetonitrile in a 50 mL volumetric flask and kept at -18°C. Quinclorac concentrations (10, 25, 50, 100, 150, 200, 250, 300, and 350 µg/mL) were utilized to prepare the standard calibration curve using HPLC (Agilent Technologies 1260 infinity system) which is equipped with four quaternary pumps (G1311B, G1316A, G1315D, and G1328C), a thermostated column compartment, and a DAD detector. The chromatographic separation was performed using an Agilent C18 (4.6 mm ID x 150 mm x 4 µm) chromatographic column. Isocratic elution was carried out using a mobile system comprised of water (+1% H_3PO_4): methanol: acetonitrile (5:5:90) at a flow rate of 1 mL/min and an injection volume of 5 µL. The chromatogram for quinclorac is shown in **(Fig. 1)** indicating a retention time of 1.903 min at 210 nm.

2.2.2 Forced thermal and hydrolytic degradation of quinclorac

●Thermal Degradation studies

Accelerated high temperature storage procedure was carried out in accordance with CIPAC MT 46.1. About 20 g of the pesticide formulation was placed in glass beakers that were introduced into an electrical oven at following temperatures (35, 40, 45 and 54ºC) in the dark. One beaker was utilized for each temperature, and the oven temperature was regulated in order to allow for the withdrawal of the samples at the predetermined period of (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14 weeks) per temperature. Following withdrawal, each individual sample was analyzed by HPLC to identify the concentration of active ingredient and by GC/MS to identify the thermal degradation products of the tested pesticide.

● Forced hydrolytic studies

Forced hydrolytic studies were conducted using acid and base aqueous media at room temperature. This allowed for the monitoring of the tested pesticide breakdown as a result of its interaction with water.

● Acidic hydrolysis studies

In 25 mL volumetric flasks, about 10 mg of quinclorac were mixed with 2 mL of appropriate concentrations of HCl (0.01 N, 0.1 N, and 1.0 N). The flasks were left at room temperature for 1, 3, 5, and 7 days. After each period, the sample was neutralized with 2 mL of NaOH with an acid-equivalent concentration to prevent further degradation. The solution was then diluted and filtered through a 0.45 nylon syringe filter before being analysed.

● Alkaline hydrolysis studies

In 25 mL volumetric flasks, about 10 mg of quinclorac were mixed with 2 mL of appropriate concentrations of NaOH (0.01 N, 0.10 N, and 1.0 N). The flasks were left at room temperature for 1, 3, 5 and 7 days. After each period, the sample was neutralized with 2 mL of HCl with a base-equivalent

concentration to prevent further degradation. The solution was then diluted and filtered through a 0.45 nylon syringe filter before being analysed.

2.2.3. Soil photolysis

About 10 g of soil sample was put in a petri dish. Each sample was spiked with 100 µg/mL of the pesticide formulation and the content was spread uniformly and exposed to sunlight for 1, 3, 5, 7, 14 and 21 days. After each period, the contents of the petri dish were transferred into a capped 50 mL centrifuge tube and 10 mL of acetonitrile were added to it. The contents were vortexed for 1 minute to ensure the maximum sample-solvent interaction. QuEChERS extraction pouch kits were then added to the mixture, and the sample was vortexed again for 1 min. The mixture extract was centrifuged for 10 min at 4000 rpm and the supernatant layer was transferred to a tube containing a QuEChERS clean-up kit. The tube contents were then vortexed for 1 min and centrifuged at 4000 rpm for 10 min. Finally, the obtained residue was filtered through a 0.45 nylon syringe filter before being analyzed.

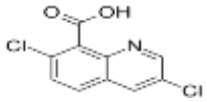
2.3. Kinetic studies

The kinetics of quinclorac dissipation/ degradation was determined after each experimental procedure using the appropriate model rate equation. The results obtained were used for the calculation of the degradation rate constants; half-lives and shelf-lives accordingly.

2.4. Identification of the degradation products

Degradation products of quinclorac from each experimental procedure were identified using GC/MS) Agilent 7890B, 5977A MSD (with a direct capillary interface and fused silica capillary column (30 m × 0.025 mm HP-5-0.25 µm) from 60 to 325 ºC. The samples were injected at a flow rate of 1 mL/min in a pulsed split mode with a split ratio of (10:1) and a split flow mode using 10 mL/min and He as carrier gas. The solvent delay was set at 4 min and the injection volume was 1 µL. The GC oven temperature was programed to start at 50 °C for 0.5 min then raised to 190 °C at a rate of 10 °C /min with a 1 min hold time. The temperature was then raised to 220 °C at a rate of 10 °C/min with a 1 min hold time and, finally, it was elevated to 300 °C at rate of 10 °C/min with a 2 min hold time at 300 °C. The temperature of the injector was set at 280 °C. The NIST and Wiley mass spectral database was used for the identification of the resulting peaks and relating it to the corresponding fragment weight and structure (**Figure 1**).

Table 1. Chemical and physical properties of quinclorac.

ISO common name	Quinclorac	
IUPAC name	3,7-dichloroquinoline-8-carboxylic acid	
CA name	3,7-dichloro-8-quinoline carboxylic acid	
Chemical class	Quinolinecarboxylic acids	
Pesticide group	Herbicide	
CAS Registry number	84087-01-4	
CIPAC number	493	
Structural formula		
Molecular formula	$C_{10}H_5Cl_2NO_2$	
Molecular weight	242.1 g/mol	
Melting point	The melting point quinclorac pure (99.8%): 272.4-276.9°C. The melting point of quinclorac technical (purity 98.7) at atmospheric pressure is 279.9°C.	
Solubility in organic solvents at 20°C	Solvent	g/L
	n-Heptane	0.003
	Toluene	0.006
	Dichloromethane	0.5
	Acetone	2.8
	Ethylacetate	0.9
	Methanol:	2.7
Solubility in water at 20ºC including effect of pH	Quinclorac, pure: 80.1 mg/L at pH 3 61.5 mg/L at PH 6.1	Quinclorac, (purity 99.8%): 0.072 g/L at pH 5.5 (deionized water)75.9 g/L at pH 10.3(NaOH, 0.1 Mol/L)

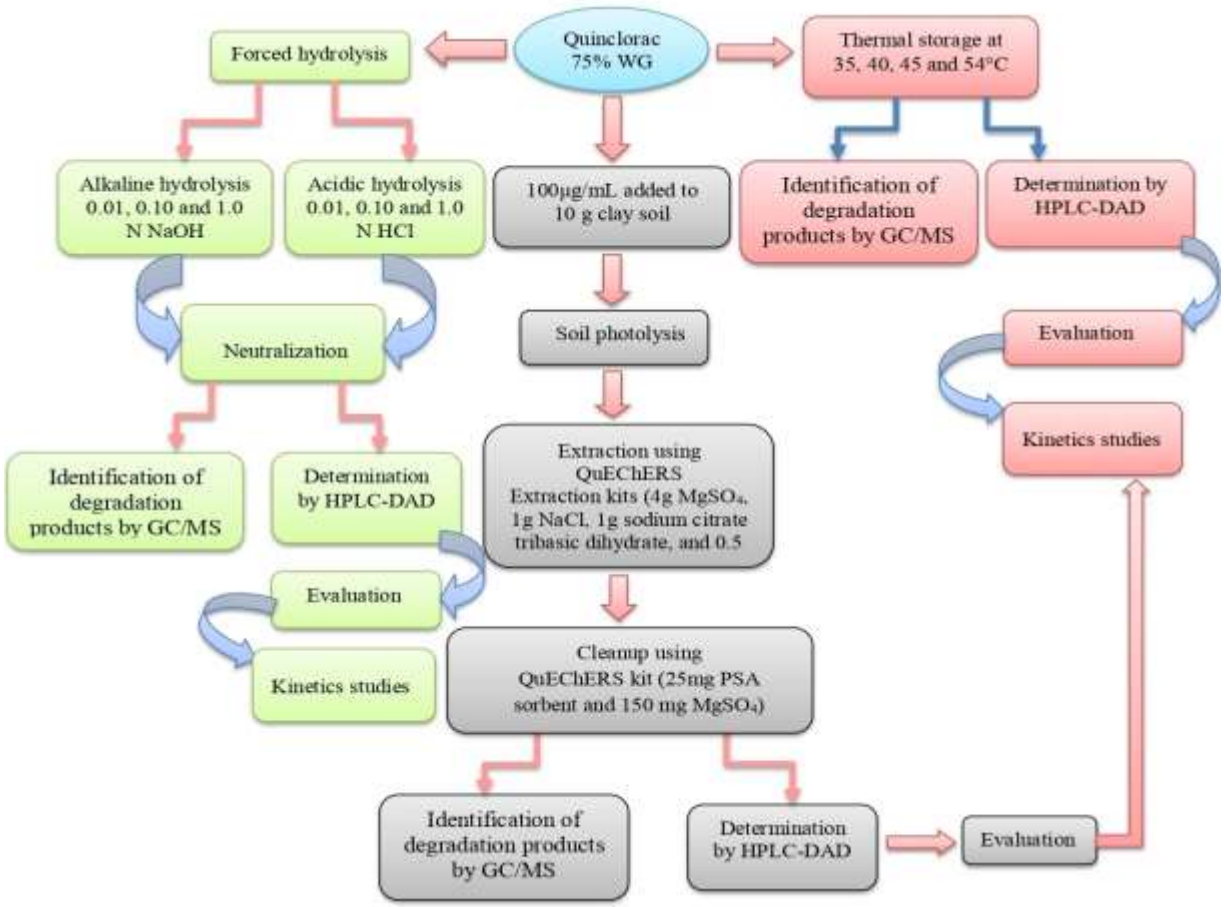


Fig. 1. Methodology flowchart for quincolrac determination.

3. Results

3.1. Calibration curve for quinclorac standard.

The standard calibration curve for quinclorac working concentrations of 10, 25, 50, 100, 200 and 300 µg/mL and the measured peak area (mAU*S) using HPLC is shown in **(Figs. 2 and 3).** The correlation coefficient (R^2) was 0.99846 indicating the linearity of the applied method for the tested concentration range.

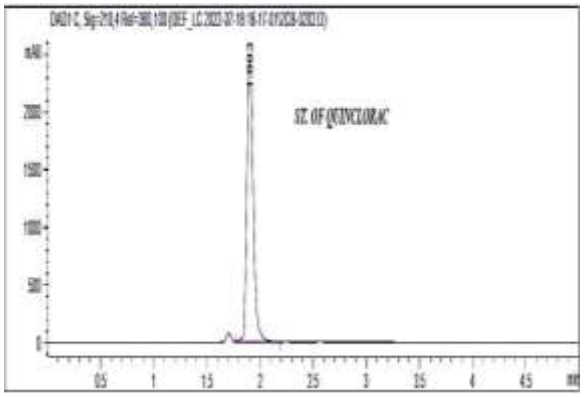


Fig. 2. The HPLC chromatogram of quinclorac standard (400µg/mL).

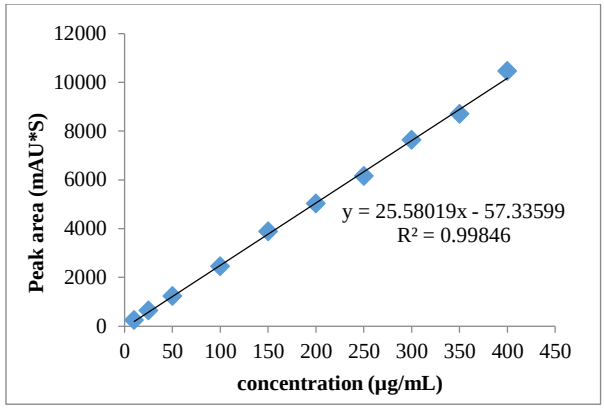


Fig. 3. Standard Calibration curve for quinclorac using HPLC.

3.2. Thermal conditions stability of quinclorac (active ingredient) in Queen 75% WG formulation:

Table (2) shows the results obtained for the forced thermal degradation of the active ingredient of Queen 75% WG during the predefined thermal storage conditions. The results show that the active ingredient was significantly degraded (5.57%) after storage at 54 °C for 14 weeks. However, the

reduction was modest at 35, 40, and 45°C ranged between 1.5- 3% for the same period.

3.3. Forced hydrolytic (acidic and alkaline) degradation of quinclorac in (Queen75% WG).

3.3.1. Effect of acidic hydrolysis

The data in **Table (3)** reveal that the acidic hydrolysis of the active ingredient in Queen 75% WG after 7 days in 1.0 N HCl exhibited a loss of 25.55 %. However, over the same period, the loss in 0.1 N and 0.01 N HCl reached 9.48% and 6.60%, respectively.

Table 2. Effect of storage at 35, 40, 45 and 54 °C on the stability of a.i. of Queen 75% WG.

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	399.53	0	399.53	0	399.53	0	399.53	0
1	399.12	0.10	398.95	0.15	398.57	0.24	398.23	0.33
2	398.58	0.24	398.39	0.29	398.01	0.38	396.75	0.70
3	398.35	0.30	397.80	0.43	397.25	0.57	395.51	1.01
4	397.75	0.45	397.24	0.57	396.59	0.74	393.92	1.40
5	397.28	0.56	396.62	0.73	395.82	0.93	392.12	1.85
6	397.05	0.62	395.98	0.89	394.66	1.22	390.69	2.21
7	396.53	0.75	395.37	1.04	394.01	1.38	388.75	2.70
8	396.10	0.86	394.64	1.22	393.44	1.52	387.03	3.13
9	395.81	0.93	393.90	1.41	392.28	1.81	385.59	3.49
10	395.42	1.03	393.12	1.60	391.52	2.00	383.71	3.96
11	394.98	1.14	392.30	1.81	390.63	2.23	382.40	4.29
12	394.51	1.26	391.44	2.02	389.79	2.44	380.47	4.77
13	393.87	1.42	390.54	2.25	388.89	2.66	379.07	5.12
14	393.24	1.57	389.65	2.47	387.72	2.96	377.28	5.57

3.3.2. Effect of alkaline hydrolysis

The data in **Table (4)** reveal that the alkaline hydrolysis of the active ingredient in Queen 75% WG exhibited a 60.53% loss after hydrolysis in 1.0 N NaOH for 7 days However, over the same period, in 0.1 N and 0.01 N NaOH the loss was 37.88% and 29.95%, respectively.

Table 3. Quinclorac degradation rates in 0.01 N, 0.1 N and 1.0 N HCl.

Concentration of reagent	Storage period	Conc. of Quinclorac (µg/mL)	Degradation Rate (%)
0.01 N HCl (pH= 2)	0	399.53	0
	1	394.31	1.31
	3	386.93	3.15
	5	380.55	4.75
	7	373.17	6.60
0.10 N HCl (pH= 1)	0	399.53	0
	1	391.92	1.90
	3	381.82	4.43
	5	374.12	5.46
	7	361.65	9.48
1.0 N HCl (pH= 0)	0	399.53	0
	1	389.94	2.40
	3	358.13	10.36
	5	328.40	17.80
	7	297.47	25.55

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

Concentration of reagent	Storage period	Conc. of Quinclorac (µg/mL)	Degradation rate (%)
0.01 N NaOH (pH =12, pOH =2)	0	399.53	0
	1	382.80	4.19
	3	338.94	15.17
	5	314.66	21.24
	7	279.88	29.95
0.1 N NaOH (pH =13, pOH =1)	0	399.53	0
	1	371.46	7.03
	3	316.74	20.72
	5	280.15	29.88
	7	248.19	37.88
1.0 N NaOH (pH =14, pOH =0)	0	399.53	0
	1	364.18	8.85
	3	293.13	26.63
	5	233.40	41.58
	7	175.71	56.02

3.4. Kinetics of the forced degradation of quinclorac

3.4.1. Thermal degradation of quinclorac

Plots of ln [C] of quinclorac vs. time (weeks) of storage at 35, 40, 45, and 54°C for 14 weeks are shown in **Figs. (4, 5, 6 and 7)**. The plots demonstrate that there was a linear relationship between the quinclorac concentration and time with R^2 ranging from 0.99201 to 0.99858. The kinetic parameters calculated from these figures are provided in **Table (5)**.

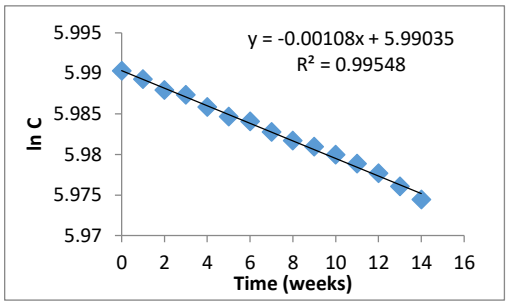


Fig. 4. A plot of ln C vs. time (weeks) for quinclorac degradation after 35°C storage

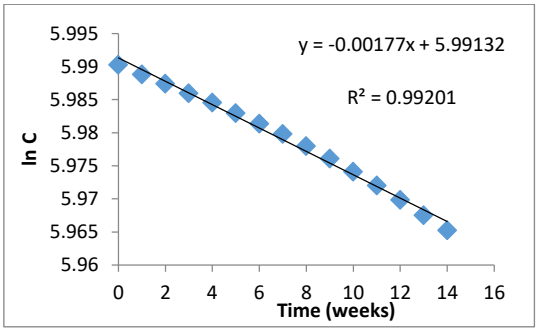


Fig. 5. A plot of ln C vs. time (weeks) for quinclorac degradation after 40°C storage.

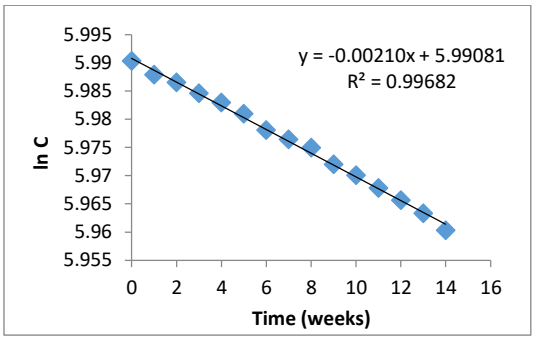


Fig. 6. A plot of ln C vs. time (weeks) for quinclorac degradation after 45°C storage.

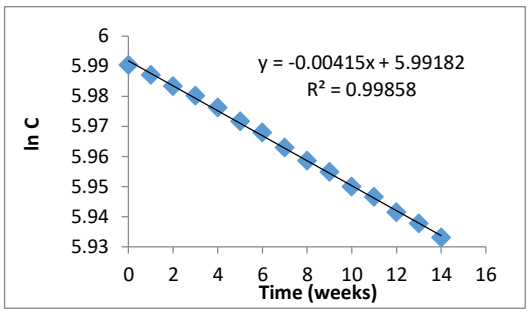


Fig. 7. A plot of ln C vs. time (weeks) for quinclorac degradation after 54°C storage.

3.4.2. Acidic hydrolysis of quinclorac

Figs. (8, 9, and **10)** demonstrate that plot of quinclorac concentration ln [C] vs. time (day) indicating that acidic quinclorac hydrolysis followed the first-order kinetics. The slope of the plots was (-k) which is the degradation constant was provided in (day^{-1}). **Table (6)** provides the calculated kinetic parameters for quinclorac hydrolysis.

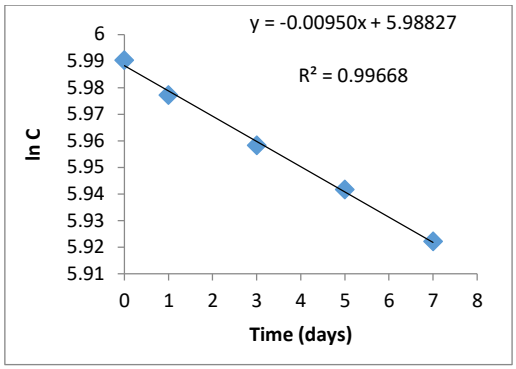


Fig. 8. A plot of ln C vs. time for the acidic degradation of quinclorac in 0.01 N HCl

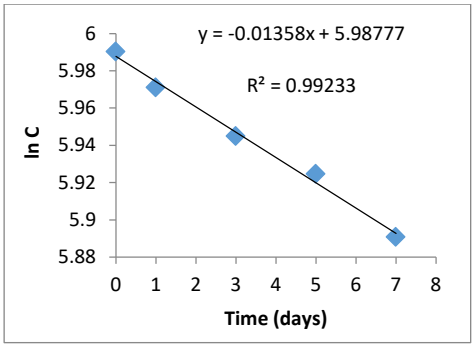


Fig. 9. A plot of ln C vs. time for the acidic degradation of quinclorac in 0.1 N HCl

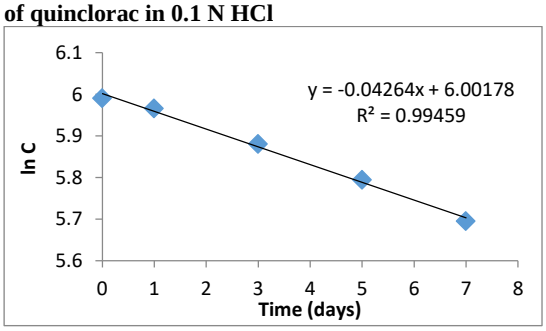


Fig. 10. A plot of ln C vs. time for the acidic degradation of quinclorac in 1.0 N HCl

3.4.3. Alkaline hydrolysis of quinclorac

Figs. (11, 12, and **13)** demonstrate that the natural logarithm of quinclorac concentration ln [C] vs. time (day) produced a straight line with an intercept of ln [C_0], indicating that the alkaline hydrolysis of quinclorac followed the first-order kinetics. The slope of the plots provided (-k), which refers to the degradation constant in (day^{-1}). **Table (7)** provides the overall kinetic parameters. **Table (7)** also shows that the calculated shelf life and half-life of quinclorac in 1.0 N NaOH were reduced to approximately 1/2 that of its shelf life and half-life in 0.01N NaOH.

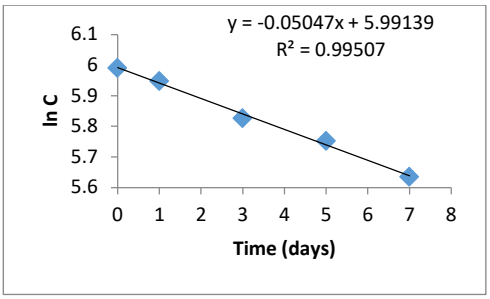


Fig. 11. A plot of ln C vs. time for the alkaline degradation of quinclorac in 0.01 N NaOH

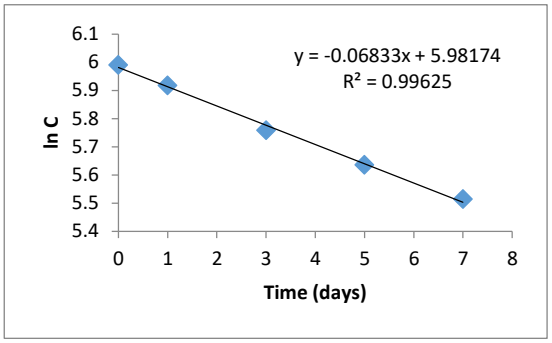


Fig. 12. A plot of ln C vs. time for the alkaline degradation of quinclorac in 0.1 N NaOH

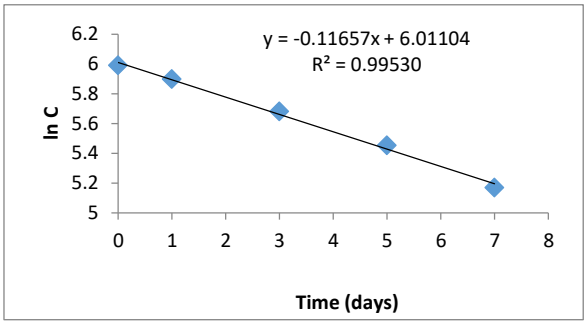


Fig. 13. A plot of ln C vs. time for the alkaline degradation of quinclorac in 1.0 N NaOH.

3.5. Identification of quinclorac degradation products using GC/MS

3.5.1. Thermal degradation products and pathways

A sample of quinclorac formulation (Queen 75% WG) was analyzed after 14 weeks of storage at 54°C to identify the thermal degradation products by GC/MS using Wiley and NIST mass spectral data bases. **Table (8)** provides the detected degradation products/ fractions as well as their relative structures.

According to the obtained data, the forced thermal degradation pathways of quinclorac, provided in **Fig. (14),** may be explained as follows:

- **Step A** involves the formation of 3,7-dichloroquinoline (**P_1**) as a result of decarboxylation of quinclorac **(P_0).**

- **Step B**, 7-chloro-8-quinolinecarboxylic acid (P_2) is formed as a result of dechlorination at position 3. The formation of quinoline with one chloride atom is in agreement with Lewis (2004) who mentioned that when quinclorac if heated to breakdown may release toxic vapors of nitrogen oxides and chlorine.

Table 5. Kinetic parameters for the forced thermal degradation of quinclorac 75% WG after storage at 35, 40, 45 and 54 °C.

Temp.	Linear regression equation	R^2 coefficient	K ($week^{-1}$)	Shelf-life $t_{0.95}$ (week)
35°C	y = -0.00108x + 5.99035	0.99548	1.08×10^{-3}	47.49
40°C	y = -0.00177x + 5.99132	0.99201	1.77×10^{-3}	28.98
45°C	y = -0.00210x + 5.99081	0.99682	2.10×10^{-3}	24.43
54°C	y = -0.00415x + 5.99182	0.99858	4.15×10^{-3}	12.36

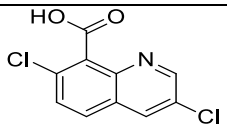
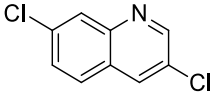
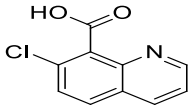
Table 6. Degradation kinetic parameters of quinclorac in acidic solutions.

Conc. of HCl	Linear regression equation	R^2 coefficient	K (day^{-1})	Shelf-life $t_{0.95}$ (day)	Half-life $t_{1/2}$ (day)
0.01 N	y = -0.00950x + 5.98827	0.99668	9.50×10^{-3}	5.40	72.96
0.10 N	y = -0.01358x + 5.98777	0.99233	13.58×10^{-3}	3.78	51.04
1.0 N	y = -0.04264x + 6.00178	0.99459	42.64×10^{-3}	1.20	16.26

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

Conc. of NaOH	Linear regression equation	R^2 coefficient	K (day^{-1})	Shelf-life $t_{0.95}$ (day)	Half-life $t_{1/2}$ (day)
0.01 N	y = -0.05047x + 5.99139	0.99507	50.47×10^{-3}	1.02	13.73
.1 N0	y = -0.06833x + 5.98174	0.99625	68.33×10^{-3}	0.75	10.14
N1.0	y = -0.11657x + 6.01104	0.99530	116.57×10^{-3}	0.44	5.95

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

Product	Common name	RT	Structure	m/z
P_0	Quinclorac	19.765		241.1
P_1	3,7-dichloroquinoline	22.597		197.1
P_2	7-chloro-8-quinoline carboxylic acid	34.184		206.9

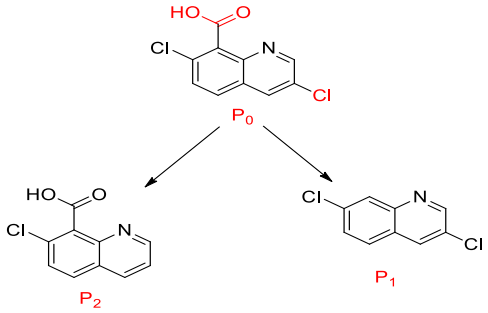
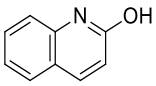
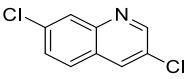
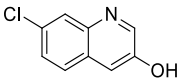
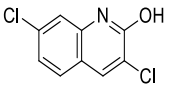
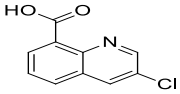
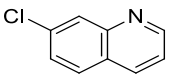
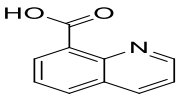
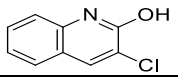


Fig. 14. The thermal degradation pathways of quinclorac at 54°C

3.5.2. Acidic and alkaline quinclorac degradation products and pathways

After 7 days of the forced acidic and alkaline degradation, neutralized samples were analyzed to identify the probable degradation pathways and major hydrolytic products using the GC/MS. **Table (9)** provides the identified degradation products with their structures and masses.

Table 9. The identified degradation products of quinclorac hydrolysis in acidic and alkaline solutions.

Product	Common name	RT(min)	Structure	m/z
P_1	2-hydroxyquinoline	10.559		145.1
P_2	3,7-dichloroquinoline	14.993		197.0
P_3	7-chloroquinolin-3-ol	20.498		179.0
P_4	3,7-dichloroquinolin-2-ol	23.988		213.0
P_5	3-chloroquinoline-8-carboxylic acid	27.736		207.6
P_6	7-chloroquinoline	28.462		161.9
P_7	Quinoline-8-carboxylic acid	29.041		173.1
P_8	3-chloroquinolin-2-ol	30.706		179.0

The forced acidic and alkaline hydrolytic pathways of quinclorac depicted in **Fig. 15.** Generally, this involves decarboxylation, dechlorination, hydroxylation, and substitution of chlorine with a hydroxyl group with the upholding of the integrity of both fused pyridine and benzene rings.

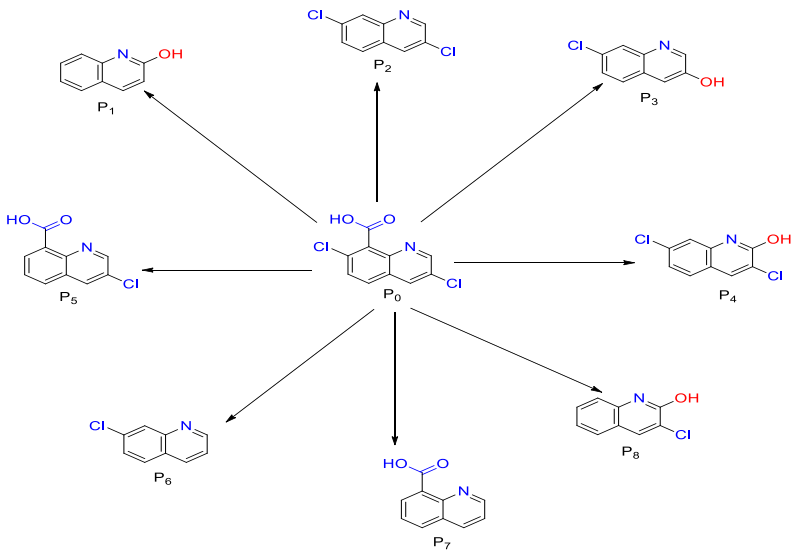


Fig. 15. The forced acidic and alkaline hydrolytic pathway for quinclorac.

3.6. Determination of quinclorac dissipation in soil sample

The physical and chemical parameters of typical Egyptian soil were evaluated prior to the investigation of quinclorac degradation in soil at the Soil, Water, and Environment Research Institute (SWERI) in Giza, Egypt. **Table (10)** shows that the soil was clay-loam with a low organic matter %. Furthermore, the pH of the research soil was alkaline below 9. The results in **Table (11)** demonstrate that the active ingredient within Queen 75% WG was reduced by 7.33% after 14 days of exposure to sunlight and climate conditions**.**

3.6.1. The kinetics of quinclorac dissipation in soil

As in the previous degradation procedures, the dissipation of quinclorac in clay-loam soil was found to follow the first order kinetics and was concentration-dependent. The plot of ln [C] versus time (days) yielded a straight line with an R^2 = 0.98316 and a slope of (-k) (**Fig. 16**).

Table 10. Chemical, mechanical and physical properties of soil used in the quinclorac dissipation study.

Chemical properties				
Organic matter %	1.92			
Soluble cations (cmolc kg^{-1} soil)	K^+	Na^+	Mg^{2+}	Ca^{2+}
	0.62	13.55	5.50	9.50
Soluble anions (cmolc kg^{-1} soil)	SO_4^{2-}	Cl^-	HCO_3^-	CO_3^{2-}
	9.47	18.50	1.00	---
Available macro-elements (mg/kg soil)	N	K	P	
	69	183	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^{-1})		pH (1:2.5- soil: water)	
62.99	2.91		8.59	

Table 11. Dissipation of quinclorac in clay-loam soil.

Periods (days)	Conc. of Quinclorac (µg/mL)	Degradation Rate %
0	99.24	0
1	98.88	0.36
3	97.59	1.66
5	95.98	3.28
7	94.86	4.41
14	91.97	7.33

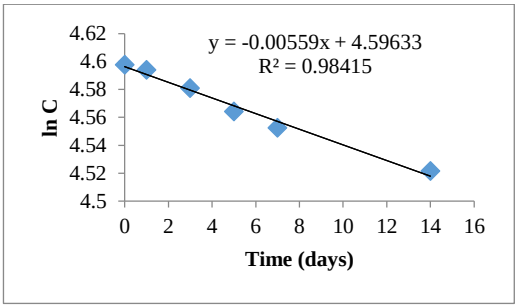


Fig. 16. A plot of ln C vs. time for the photolysis of quinclorac in clay-loam soil.

The half-life ($t_{1/2}$) of quinclorac degradation in Egyptian clay-loam soil was calculated to be 124.0 days, based on the data in **Table (12).**

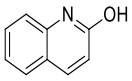
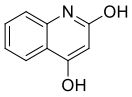
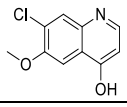
Table 12. Kinetic parameters of quinclorac photolysis in clay-loam soil.

Linear regression equation	R^2 values	K value (day^{-1})	$t_{1/2}$ (day)
$y = 5.59\times10^{-3}+4.59633$	0.98415	5.59×10^{-3}	124.0

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

A soil sample was investigated using GC/MS after a study of the photolysis of quinclorac in clay-loam soil to determine the degradation pathway and the major degradation products using Wiley and NIST mass spectral databases. The identified degradation products, structure and masses are provided in **Table (13).** The degradation pathway of quinclorac photolysis in clay-loam soil in **Fig (16)** can be explained as follows. 2-hydroxyquinoline (**P_1**) and 2,4-dihydroxyquinoline (**P_2**) were formed by quinclorac dechlorination, losses of carboxylic group and hydrolexation. The formation of 4-hydroxy-6-methoxy-7-chloroquinoline (**P_3**) is a result of the loss of chloride atom at position 3 as well as the carboxylic group, hydrolexation at position 4 and binding of OCH_3 at position 6. This product may be formed as a result of microorganism's activity in soil.

Table 13. The identified degradation products of quinclorac formulation after photolysis in clay soil.

product	Compound	RT (min)	Structure	m/z
P_1	2-Hydroxyquinoline	14.255		144.9
P_2	2,4-dihydroxyquinoline	13.185		161.0
P_3	4-hydroxy-6-methoxy-7-chloroquinoline	16.710		208.9

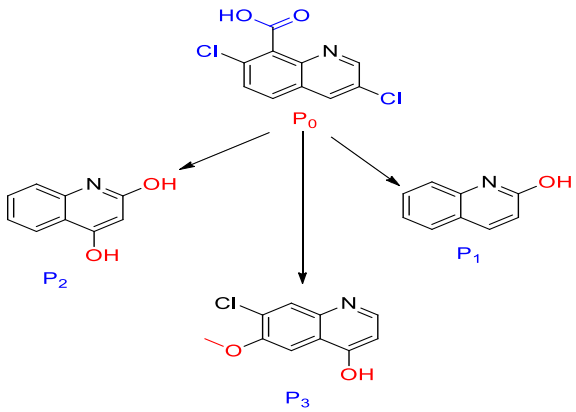


Fig. 16. The photolysis degradation pathway of quinclorac in clay soil.

4. Discussion

According to FAO/WHO (2010), the loss in average active ingredient content after storage for 12, 8, 6, and 2 weeks at 35, 40, 45, and 54°C, respectively, should not exceed 5% that of the initial amount before storage. Thus, storage of quinclorac under these conditions complied with FAO specifications at 35, 40, and 45°C after more 14 weeks however it was less than 12 weeks at 54°C.

The results are consistent with those of Pinna and Pusino (2012) who found that the reduced reactivity of quinclorac relative to quinmerac was caused by the electron withdrawing action of two chlorine atoms. As well, Lizarraga *et al*. (2005) indicated the strong electron-withdrawing groups in position 6 of the quinoline ring made the molecule more stable to counter the electron-withdrawing effect that the electronic delocalization within the π-orbitals of the aromatic ring. This provided for an extra intermolecular interaction resulting in an improvement of physical stability with aromaticity. When halogens (compounds with higher polarity and stronger dipole-dipole interactions) are present, this increases the molecule stability.

The obtained results indicate that the pH value, acid concentration, and exposure time in an acidic medium had an impact on quinclorac hydrolysis. As well, it was observed that the hydrolysis rate of quinclorac increased as the pH value decreased i.e. as the HCl concentration increased with the exposure time and vice versa. Roberts *et al*. (1999) found that quinclorac was stable to hydrolytic degradation between pH 3-9, however, it was degraded in natural water (pH 8) when exposed to UV radiation (254 nm) or natural sunlight. The current findings agree the findings of Roberts et al. (1999) as they indicate that as quinclorac degraded at pH=2. This amounted to a loss of 6.6% which increased to 25.55 % at pH=0. With the current results, it may be speculated that this % loss may also increase with the increase of time. Overall, the current results are consistent with Serafini (2001) who observed that quinclorac is not prone to hydrolysis at pH 5, 7 and 9. As well, FAO (2002) stated that the half life time of quinclorac was more than 30 day at 25 ºC in pH 5, 7 and 9.

The current results indicate that the alkaline hydrolysis of quinclorac reached a maximum in 1.0 N NaOH relative to 0.1 N and 0.01 N NaOH. Quinclorac was reported to be weakly acidic, and at solution pH levels higher than 7.0, it was susceptible to alkaline hydrolysis. The obtained results are in accordance with Huang *et al.* (2021) who found that quinclorac dissociates readily in alkaline conditions and is inhibited in acidic conditions. Mendoza *et al*. (2015) predicted that an electrophilic attack on quinclorac might cause a dechlorination, while a nucleophilic attack might lead to a decarboxylation and a free radical attack would cause a hydrogen substitution on the quinoline ring. Carboxyl groups are often deprotonated in an aqueous environment at pH ≥7, and they may lose an H^+ to become negatively charged. As a result, the reactivity of the deprotonated (anionic) form of quinclorac has the more reactive sites, namely: 3C, 7C and 7C for electrophilic, nucleophilic and free radical attacks, respectively. These findings show that an electrophilic assault on 3C will result in decarboxylation, whereas nucleophilic and free radical attacks on 7C may result in hydrogen substitution. As well, they predicted that decarboxylation may occur through an electrophilic attack while nucleophilic and free radical attacks may attack the hydrogens' of the ring.

Adesina (2022) stated that quinoline and isoquinoline are more reactive to nucleophiles in the pyridine ring particularly at the locations α and γ to the nitrogen. Overall, Deer and Beard (2001) stated that the degradation of the pesticide caused by alkaline hydrolysis may be controlled by water alkalinity, pesticide susceptibility, the duration of the pesticide's contact with water, and the temperature of the mixture.

According to the FAO (2002), the calculated average active ingredient content should not be less than 95% of the calculated average content found prior to storage. From the $t_{0.95}$, the shelf-life ($t_{0.95}$) of quinclorac in Queen 75% WG after storage at different temperatures was determined. The data demonstrated that shelf-life of quinclorac after storage at different temperatures conformed to the time period recommended by FAO/WHO. Quinclorac may therefore be more stable under thermal circumstances and may not be affected by high temperatures or prolonged exposure as the rate of degradation was extremely slow.

The data demonstrate that quinclorac's shelf life and half-life were impacted by the acidic medium. Notably, the shelf life and half-life of quinclorac in 1N HCl were reduced to 1/4 that of its shelf life and half-life in 0.01N HCl. Russell *et al*. (2002) reported that the rate of degradation in the spray water can be accelerated by both acidity and solubilization.

Green and Hale (2005) reported that weak acid herbicides' solubility and ionic state are controlled by the pH of the spray mixture, which in turn affects their uptake and biological activity. When the

herbicide's solubility limits absorption, increasing pH can increase solubility and improve the activity if the spray water pH is below the pKa of the herbicide. Thus, weak acids become anionic if the pH is raised over the pKa value, which makes it more difficult to pierce the lipophilic cuticle, the negatively charged membrane, and the cell wall. Transforming weak acids into the neutral or unionized form by lowering the pH below the pKa facilitates its lipophilic and negatively charged barriers penetration. Other herbicide characteristics such as chemical stability, volatility, and chemical compatibility are also influenced by pH. As a result, the manufacturers modify the pH of their adjuvant and herbicide compositions to create a balance among the various affecting factors.

Overall, the degradation of the parent compound (quinclorac) produced lower molecular weight molecules containing electron-drawing groups or atoms such as -COOH and -Cl, which increased the toxicity of the degradation products. Dong *et al*. (2023) investigated the structure-activity relationship and discovered that halogen elements and electron-withdrawn groups on the benzene ring improved its activity. Yang *et al.* (2018) stated that quinclorac residuals and converted products were deemed hazardous to aquatic animals, vegetation, and microbes. According to Liu *et al*. (2022), electron withdrawing groups improve the efficacy of biological activity.Their results were based on a study of the degradation of aryloxyphenoxypropionate herbicides containing phenoxypyridine, which is repeatedly substituted by electron withdrawing groups such as F, Cl, Br, NO_2, CN, and CF_3; with component Y as the connecting arm (**Fig. 17)**.

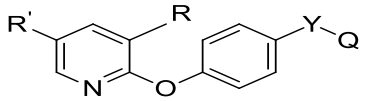


Fig. 17. General structure of phenoxypyridine.

In conclusion, the kinetics of quinclorac degradation followed first order kinetics model which was dependent on its initial concentration. Overall, degradation of the parent chemical (quinclorac) produced lower molecular weight molecules containing electron-drawing groups or atoms such as COOH and Cl, which increased the toxicity of the degradation products. During thermal degradation, 2 by-products were formed which may be attributed to dechlorination and decarboxylation while the quinolone ring remained stable. The same stability of quinolone ring was observed under forced acidic and alkaline solution. Degradation products formed under forced hydrolysis were a result of decarboxylation, dechlorination, hydroxylation, and substitution of chlorine with a hydroxyl group.

The obtained results clearly showed that quinclorac was degraded slowly in Egyptian clay-loam soil and that are consistent with PMRA (2016). They reported that quinclorac degraded slowly in soil and it does not undergo photo transformation with half-life 162 days. In the absence of photo-sensitizers (humic acids, natural oxidants and formulants), quinclorac is a persistent chemical in both terrestrial and aquatic environments. Pinna and Pusino (2012) indicated that quinclorac was unreactive under both UV light and simulated sunlight due to the electron withdrawing effect of two chlorine atoms that was responsible for its lower reactivity.

Lym (2016) studied quinclorac dissipation in four soils from the Northern Great Plains and found that the average DT_{50} across all moisture and temperature regimes for the Fargo clay (7% OM) and Svea-Barnesloam soils was 42 and 43 days, respectively, as opposed to an average of 59 and 72 days for the Glendive-Havre clay (1.2% OM) and Lamoure sandy loam (2.6% OM), respectively. Soil pH was not a reliable indicator of quinclorac half-life because Fargo-clay and Svea-Barnes loam, the two soils with the shortest average half-lives, had pH values of 7.2 and 5.7, respectively. Dissipation generally increased with soil moisture content, but in low OM soils, moisture had less of an effect and these are in agreement with the current findings as the Egyptian clay-loam soil has a low organic matter 1.92% and higher saturation percentage (62.99%) therefore the dissipation of quinclorac decreased.

Quinclorac was reported to be persistent according to Greenhalgh *et al.* (1980) and Pinna and Pusino (2012). However, Greenhalgh et al. (1980) classified the persistence of herbicides in the soil into three groups: persistent with half-life more than 90 days, moderately persistent with half-life from 20 to 90 days and not-persistent with half-life less than 20 days. The persistence of quinclorac in soil leads to the higher the risk of environment contamination as affected the growth and development of crops planted after application.

Hill *et al*. (1998) found that quinclorac had a half-life of 48 weeks in the Lethbridge clay loam with low organic matter (1.2%). The current results are in line with APVMA (2005), which stated that quinclorac has half-lives in laboratory soil that are longer than six months as a result of microbial metabolism and

photo-degradation. However, two metabolites, namely: 2-hydroxyquinclorac and quinclorac methyl ester, were discovered at low levels (20% of applied concentration). As well, quinclorac was resistant to hydrolysis, to photolysis in sterile water, as well as to aerobic and anaerobic metabolism (Pinna and Pusino, 2012). As a result, it is not included in Annex I of EC Directive 91/414 (Council of the European Communities, 1991). However, Non-European countries continue to employ quinclorac for rice harvests (Norsworthy *et al*., 2010).

USEPA/OPP (2007) stated that quinclorac is resistant to both aerobic and anaerobic biodegradation in soil. A main degradates -3-chloro-8-quinoline carboxylic acid- was found to be detectable to 55.7% using radioactivity after 6 months and 30.8% after 12 months. A half-life of 141 days was reported for photolysis on soil surfaces. ECHA (2018) reported that the Biodegradation of quinclorac was <10% in 28 days.

5. Conclusion:

In this research, the forced thermal and hydrolytic (acid and alkaline) degradation of quinclorac in its commercial formulation Queen 75% WG were investigated. The results indicate that the degradation rate of quinclorac significantly declined (5.57%) after 14 weeks of storage at 54°C. During the same time period, however, the reduction was modest, ranging between 1.5- 3% at 35, 40, and 45°C, respectively. As well, the shelf life of quinclorac after storage at different temperatures was consistent with the time period recommended by FAO/WHO. The acidic hydrolysis of quinclorac improved the shelf-life and half-life to 5.40 and 72.96 days, respectively, which is almost four times that of 1.0 N HCl. However, in alkaline conditions, the shelf-life and half-life of quinclorac were lowered to 1.02 and 13.73 days, respectively. Increasing the alkaline concentration to 1.0 N NaOH further reduced these results to 0.44 and 5.95 days, respectively. Generally, the kinetics of quinclorac degradation followed a first-order model that was reliant on its initial concentration. Furthermore, the half-life of quinclorac dissipation was determined to be 124 days in local clay-loam soil (with organic matter of 1.92% and a greater saturation percentage of 62.99%), and hence it is considered a persistent herbicide. The degradation products of quinclorac were identified by GC/MS and may be attributed to decarboxylation, dechlorination, hydroxylation, and the substitution of chlorine with a hydroxyl group.

6. Conflicts of interest

"There are no conflicts to declare".

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