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RESEARCH ARTICLE

Chemical Degradation of Nicosulfuron: Insights into Forced Acidic and Alkaline Hydrolysis and Its Photolysis Behavior in Egyptian Clay-Loam Soil

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Abstract

The fate of nicosulfuron in herbicide formulation (4% OD) under forced acidic and forced alkaline hydrolysis in HCl and NaOH as well as its photolysis in Egyptian clay soil samples was investigated in this study. The results indicated that nicosulfuron's shelf life and half-life were affected by an acidic medium with the herbicide half-life and shelf life being longer in HCl concentrations (0.01 N- 1.0 N). On the other hand, the shelf-life and half-life in 0.01N NaOH decreased to 1/5 of its values in 1.0 N NaOH. The kinetics of nicosulfuron degradation was found to follow the first-order model which depended upon its initial concentration. Furthermore, nicosulfuron dissipation in Egyptian clay-loam soil (pH 8.59) was 27.67 days. The mechanism of nicosulfuron degradation in forced acidic and alkaline conditions as well as in soil photolysis was elucidated and was found to be caused by the initial cleave of the urea moiety. The major degradation products of nicosulfuron in the soil and the forced acidic degradation were identified to be 2-(aminosulfonyl)-N,N-dimethylnicotinamide and 2-amino-4,6-dimethoxypyrimidine in the forced acidic degradation, which were not evident in the forced alkaline condition. In the soil, a contraction reaction occurs, similar to what occurs in forced alkaline conditions.

Keywords: Degradation products; Dissipation; Half-life; Hydrolysis; Shelf-life; Herbicide formulation

1. Introduction

Sulfonylurea herbicides were first discovered by DuPont in 1975 (Beyer, 1986). Sulfonylureas are a class of organic compounds consisting of a sulfonyl group bonded to a nitrogen atom of an ureylene group a dehydrogenated derivative of urea. Structurally, sulfonylureas are comprised of an aryl ring, a sulfonylurea bridge, and a heterocycle containing nitrogen atoms (Willian, 1992) (Fig. 1). These compounds have been widely used both in medicine and agriculture. In agriculture, sulfonylureas are used as herbicides that have the function to abrupt the plant biosynthesis of certain amino acids. Generally, sulfonylureas show higher activity per unit of active ingredient than the majority of other herbicides, which makes them effective at low rates (4 to 32 g ai/ha).

Nicosulfuron is N-sulfonylurea (2-(carbamoylsulfamoyl)-N,N-dimethylpyridine-3-carboxamide substituted by a 4,6-dimethoxypyrimidin-2-yl group at the amino nitrogen) (Fig. 2) which is widely used in Egypt. Nicosulfuron is used as a post-emergence alternative in forage maize to control a variety of annual grasses weeds, broad- leaved weeds, and perennial grass weeds such as *Sorghum halepense* and *Agropyron repens*. It is a contact-acting chemical that attacks acetolactate synthetase (ALS), the enzyme needed for biosynthesis of the amino acids such as

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isoleucine, leucine, and valine within the plant to interrupt its production (FMC-Agro, 2023). In this effect, nicosulfuron application may result in weed eradication within 20 – 25 days.

In 1989, Haga *et al*. synthesized nicosulfuron from 2-chloronicotinic acid via a multi-stage process using 2-aminosulfonyl-N,N-dimethylnicotinamide as per the scheme shown in (Fig. 3).

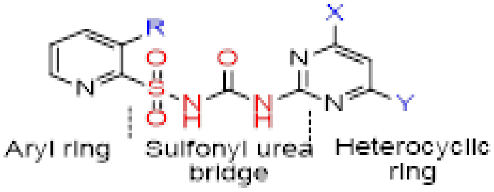


Figure 1. General structure of Sulfonyl urea.

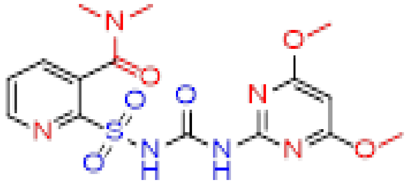


Figure 2. Chemical structure of nicosulfuron

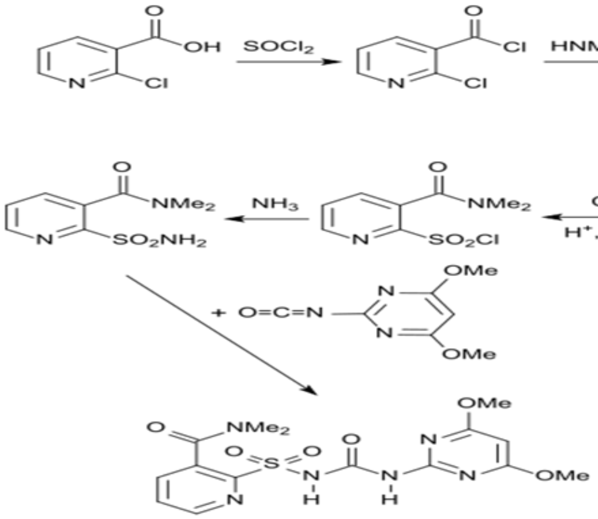


Figure 3 . Synthesis of nicosulfuron according to Haga *et al*. (1989).

Nicosulfuron was synthesized according to Unger (1996) from 2-mercapto nicotinic acid by its reaction with methanol, acetic acid, tert-butylamine, N,N-dimethyl amino dimethyl aluminum, and trifluoroacetic acid The final product was added to phosgene and 2-amino-4,6-dimethoxypyrimidine to about nicosulfuron (Fig. 4).

Generally, Pesticides' fate in the environment is determined by both their physicochemical properties and environmental conditions. These may include pesticide solubility, volatility, and soil mobility (Raj and Krishnan, 2023). Also, pesticide degradation in water and soil was reported to be influenced by the nature of soil and water, pH, temperature, soil water content, soil organic matter content, and soil type (Bromilow *et al*., 1999).

Hydrolysis of sulfosulfuron under different pH conditions was studied by (Saha and Kulshrestha, 2002). Sulfosulfuron was reported to decompose rapidly in acidic (pH 4.0) and sluggishly in neutral pH and alkaline conditions (pH 9.2). Factors affecting sulfosulfuron stability were also investigated. It was found that sulfosulfuron was unstable at 10°C in the organic solvents such as acetonitrile after 10 days and degraded within five months. The same effect was noted for temperatures over 40°C. The herbicide was susceptible to alkaline and acid hydrolysis with $t_{1/2}$ of 9.3 and 13.9 days, respectively. Degradation was stipulated to occur through contraction and rearrangement in alkaline conditions, but trough the breakdown of the urea bridge in an acidic condition.

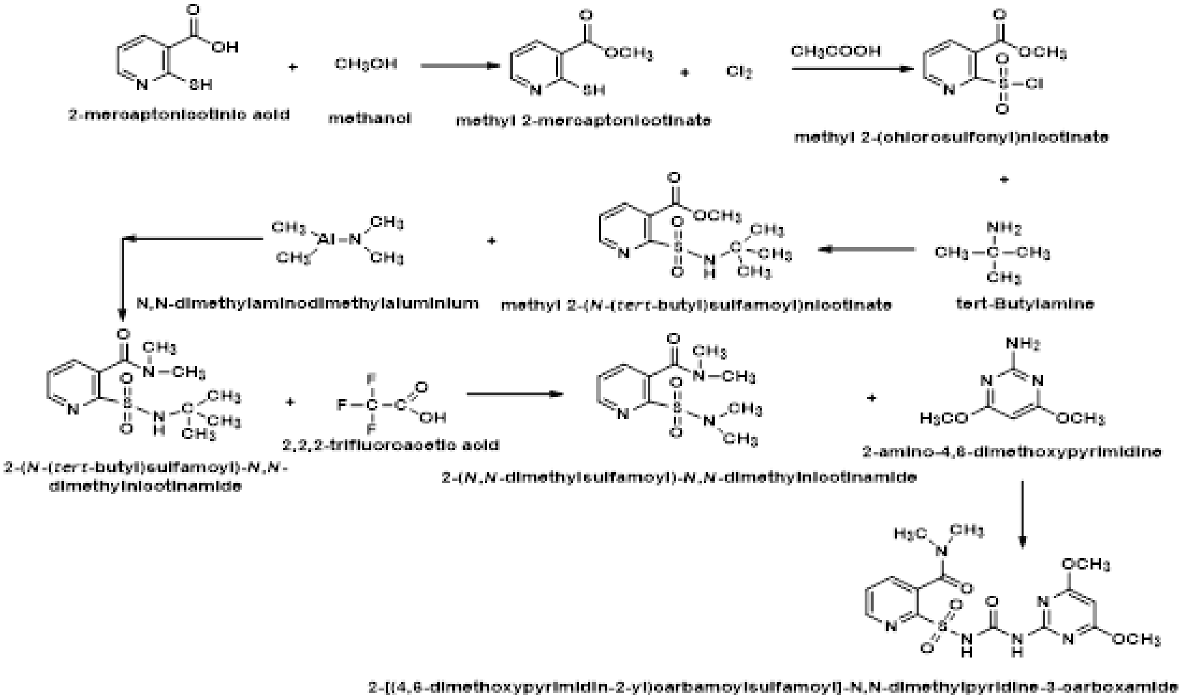


Figure 4. Synthesis of Nicosulfuron according to Unger (1996).

Azimsulfuron's deterioration in aqueous solutions at various pH levels was examined by Boschin *et al.* (2007). HPLC results showed that the hydrolysis rate was pH dependent as well it increased significantly under acidic conditions compared to neutral or mildly basic conditions.

The dynamics of nicosulfuron dissipation and half-life in various soil water combinations, as well as the influence of soil water content on nicosulfuron dissipation, were studied by Jia *et al*. (2014). HPLC aided with a UV detector (HPLC-UV) was used to determine the residues of nicosulfuron after extraction from soil samples using acetonitrile and phosphate buffer (1:1; v/v %) as mobile phase. The method was linear at the concentration range of 0.25 to 4 mg/L ($R^2 = 0.999$). The recovery in the fortified experiment was 91%–106%, with a relative standard deviation (RSD) of 5.4%–9.5% at fortified levels of 0.05, 0.25, and 1.25 mg/kg. The limit of quantification (LOQ) for the method was 0.04 mg/kg, and the limit of detection (LOD) was 0.012 mg/kg. The half-life time of nicosulfuron was not significantly affected by soil moisture content when it was less than 50%. With a water content of more than 50%, the half-life first increased and then declined. This resulted in the maximum rate of nicosulfuron dissipation in soil between 60% and 90% water content.

Nicosulfuron residual persistence was investigated by Ahmadi *et al.* (2017) in maize field soil following the application rates of 80 and 160 (ai)/ha at 28 days after sowing to suppress weeds. Using the HPLC-DAD system, the presence of residues in the subsurface soil demonstrated a quick mobility of nicosulfuron from the top to lower layers. After 60 days, there were no residues after 80 ai/ha application. With variable doses and soil depths, the analysis of nicosulfuron revealed that its half-life ranged from 14 to 20 days.

Although nicosulfuron is applied to crops in small doses, it still poses a threat to the environment with its strong solubility and low volatility. Moreover, herbicides are chemically and photochemically stable in mild conditions and do accumulate in soil. This accumulation may manifest itself through the food chain to reach humans. On the other hand, they may affect beneficial microbial communities in the environment.

Hence, the purpose of this research is to study the fate of nicosulfuron under forced acidic and alkaline hydrolysis as well as its photolysis in Egyptian clay soil. This work will evaluate the shelf life and half-life times under these conditions and identify its' degradation products by GC/MS.

2. Materials and methods

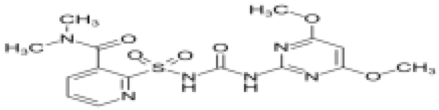
2.1. Materials

▪A certified reference standard of nicosulfuron (purity of 94.93%) was purchased from Dr. Ehrenstorfer^{TM} Gmbh (Augsburg, Germany). The chemical and physical properties of nicosulfuron are provided in Table (1).

▪Acetonitrile and methanol (HPLC grade) were purchased from Sigma-Aldrich.

▪QuEChERS (Quick Easy Cheap Effective Rugged Safe) extraction kits (4g $MgSO_4$, 1g NaCl, 1g sodium citrate tribasic dihydrate, and 0.5g sodium citrate dibasic sesquihydrate) and clean-up kit (25mg PSA sorbent and 150mg $MgSO_4$) were acquired from Sigma-Aldrich to determine nicosulfuron in soil sample.

Table 1. Chemical and physical properties of nicosulfuron.

ISO common name	Nicosulfuron	
IUPAC name	2-[(4,6-dimethoxypyrimidin-2-ylcarbamoyl)sulfamoyl]-N,N-dimethylnicotinamide. or 1-(4,6-dimethoxypyrimidin-2-yl)-3-(3-dimethylcarbamoyl-2-pyridylsulfonyl)urea.	
CA name	2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino] carbonyl]amino]sulfonyl]-N,N-dimethyl-3-pyridinecarboxamide	
Chemical class	Pyrimidinylsulfonylurea	
Pesticide group	Herbicide	
CAS Registry number	111991-09-4	
CIPAC number	709	
Structural formula		
Molecular formula	$C_{15}H_{18}N_6O_6S$	
Molecular weight	410.41 g/mol	
Melting point	145 - 170°C (98.4% pure nicosulfuron) accompanied by decomposition.140-161 °C (99-99.8%, nicosulfuron monohydrate form)	
	Solvent	g/L
Solubility in organic solvents at 20°C (99.8%)	n-Hexane	$\leq 2x10^{-5}$
	Toluene	$3 \times 10^{-2} - 8 \times 10^{-2}$
	Dichloromethane	21.3
	Acetone	8.9
	Ethylacetate	2.4
	isopropanol:	0.94
	Methanol	0.40

2.2. Methods

2.2.1. Calibration curve of nicosulfuron using HPLC

HPLC (Agilent Technologies 1260 infinity system) equipped with a thermostated column compartment, DAD detector, and four quaternary pumps (G1311B, G1316A, G1315D, and G1328C) and Agilent C18 (4.6mm ID x 150mm x 4µm) chromatographic column was used to carry out the chromatographic separation. A stock solution of standard nicosulfuron (400µg/mL) was prepared in acetonitrile and maintained at -18°C. Isocratic elution of nicosulfuron was done using a mobile phase consisting of water (+1% H_3PO_4), methanol, and acetonitrile (5:5:90, v/v/v %) at a flow rate of 1 mL/min with an injection volume of 5µL. Fig. 5 shows the HPLC chromatogram obtained for standard nicosulfuron (400µg/mL) detected at λ =205 nm with a retention time of 1.704 min. The calibration curve of nicosulfuron was prepared using concentrations of 10, 25, 50, 100, 150, 200, 250, 300, and 350µg/mL using the above separation conditions.

Figure 5. HPLC chromatogram of nicosulfuron standard (400µg/mL) at λ = 205 nm.

2.2.2. Forced hydrolytic degradation of nicosulfuron

Forced hydrolysis studies were conducted using acid and base aqueous media at room temperature to allow for chemical /pesticide breakdown as a result of its interaction with water media.

- **Acid hydrolysis studies**

10 mg of nicosulfuron were mixed with 2 mL of suitable concentration of HCl (0.01N, 0.10N, and 1.0 N) in 25 mL volumetric flasks and were left at room temperature for 1, 3, 5, and 7 days. After each period, the sample was neutralized with 2 mL of NaOH of an acid-equivalent concentration to prevent further degradation and the solution was diluted, and filtered through a 0.45µm nylon syringe filter before being analyzed.

- **Alkaline hydrolysis**

10 mg of nicosulfuron were mixed with 2 mL of suitable concentration of NaOH (0.01N, 0.10N, and 1.0N) in 25 mL volumetric flasks and were left at room temperature for 1, 3, 5, and 7 days. After each period, the sample was neutralized with 2mL of HCl of the base-equivalent concentration to prevent further degradation. The solution was diluted, and filtered through a 0.45µm nylon syringe filter before being analyzed.

2.2.3. Soil photolysis

10 g of soil sample was weighed and set in several Petri dishes. Each dish was spiked with 100 µg/mL of the pesticide formulation and the content was spread uniformly. The dishes were exposed to sunlight for 1, 3, 5, 7, 14 and 21 days. After each predestined period, the contents of each petri dish were transferred to a capped 50 mL centrifuge tube and mixed with 10 mL of acetonitrile. The contents were vortexed for one minute to ensure maximum sample-solvent interaction. QuEChERS extraction pouch kit was added, and the samples were vortexed again for 1 min. The extracts were centrifuged for 10 min at 4000 rpm and the supernatant layer was transferred to a tube containing a QuEChERS clean-up kit. The tube

content was vortexed for 1 min then centrifuged at 4000 rpm for 10 min. The obtained residue was filtered through a 0.45µm nylon syringe filter before analysis.

2.3. Kinetic studies

Following the identification of the reaction rate equation, the kinetics of nicosulfuron dissipation was determined. The constant degradation rates, half-life, and shelf life periods were estimated accordingly.

2.4. Identification of the degradation products

The degradation products of nicosulfuron were determined using GC-MS Agilent 7890 B, 5977 with an Agilent mass spectrometric detector, direct capillary interface, and fused silica capillary column (30m 0.025mm HP-5-0.25 micron -60 to 325/325°C). Samples were injected at a pulsed split mode with a split ratio of (10:1), a split flow of 10 mL/min, and a flow rate of 1 mL/min, with helium as the carrier gas. The injection volume was 1µL with a 4-minute solvent delay. The temperature was programmed to start at 50°C for 0.5 minutes, then raised to 190°C at a rate of 10°C/min with a 1 min hold time, then raised to 220°C at a rate of 10°C/min with a 1 min hold time and finally raised to 300°C at a rate of 10°C/min with a 2 min hold time at 300°C. The injector was set at a constant temperature of 280°C. The resulting fractions were identified using the NIST and Wiley mass spectral databases.

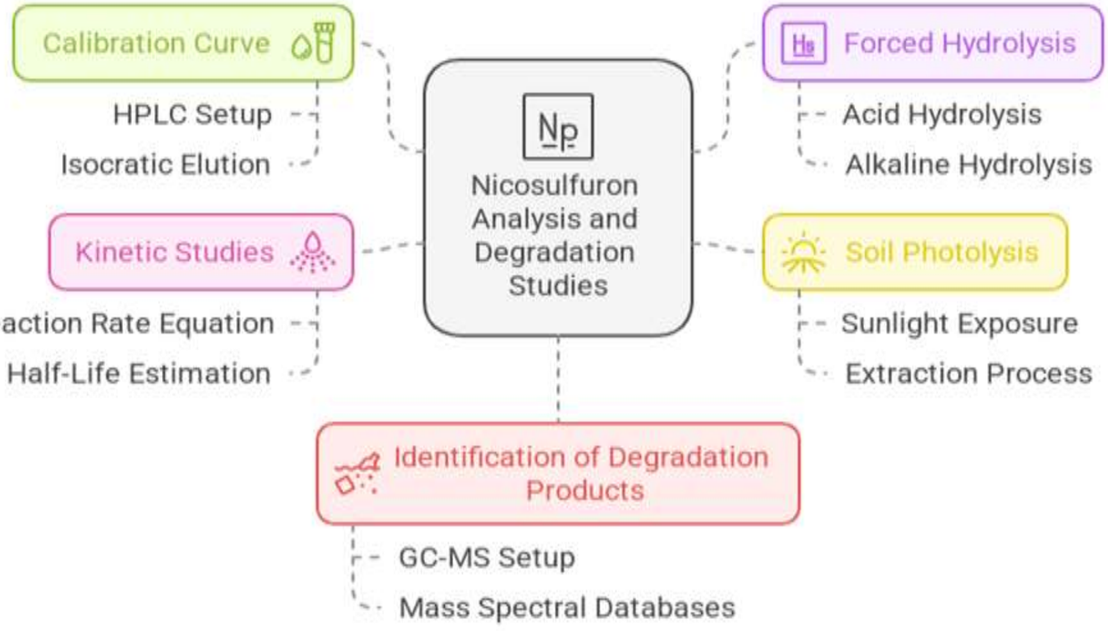


Figure 6. Flowchart for determining nicosulfuron and identifying its degradation products.

3. Results and discussion

3.1. Calibration curve for nicosulfuron standard.

The standard calibration curve for nicosulfuron obtained by HPLC at working concentrations of 10, 25, 50, 100, 150, 200, 250, 300 and 350 µg/mL is shown in Fig. 7. The plot was linear having a correlation coefficient (R^2) of 0.99745.

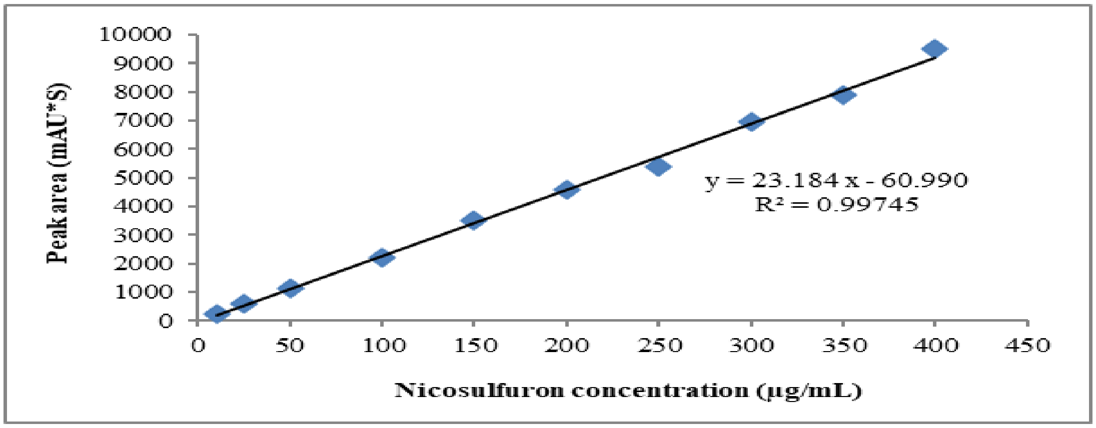


Figure 7. Standard Calibration curve for nicosulfuron using HPLC.

3.2. Forced hydrolytic degradation of nicosulfuron 4% OD

3.2.1. Effect of acid hydrolysis.

Mansour *et al.* (2018) reported a positive relationship between the length of storage periods and the degradation rate of pesticides under different environmental conditions. Table 2 shows that the concentration of nicosulfuron 4% OD exhibited 76.21% after 7 days due to hydrolysis in 1.0N HCl, compared to losses of 6.77% and 4.18% in 0.10N and 0.01N HCl over the same period.

Table 2. Nicosulfuron degradation rates in 0.01, 0.10, and 1.0 N HCl.

Concentration of reagent	Storage period (Days)	Conc. of Nicosulfuron(μg/mL)	Degradation rate (%)
0.01 N HCl (pH=2)	0	399.78	0.0
	1	397.02	0.69
	3	392.00	1.95
	5	387.89	2.97
	7	383.08	4.18
0.10 N HCl (pH=1)	0	399.78	0.0
	1	396.62	0.79
	3	390.31	2.37
	5	382.19	4.40
	7	372.73	6.77
1.0 N HCl (pH=0)	0	399.78	0.0
	1	355.54	11.07
	3	237.58	40.57
	5	170.90	57.25
	7	95.11	76.21

Notably, the hydrolysis of nicosulfuron increased in with the increase of HCl concentration and time. This indicates that the acid pH value, acid concentration, and exposure time in an acid medium all impacted nicosulfuron hydrolysis.

Feng *et al.* (2017) stated that sulfonylurea herbicides were unstable in an acidic environment due to their low isoelectric point. The current results are consistent with those of Sarmah *et al.* (2000), who reported that sulfonylurea dissipation was higher in acidic rather than in neutral or mildly basic conditions. As well, Saha and Kulshrestha (2002) studied the hydrolysis of sulfosulfuron under different pH values and found that sulfosulfuron decomposed less quickly in neutral pH but more quickly in acidic (pH 4.0) than in alkaline conditions (pH 9.2).

Boschin *et al*. (2007) studied azimsulfuron's deterioration in aqueous solutions at various pHs. They found that the hydrolysis rate was pH-dependent and increased significantly in acidic conditions compared to neutral or mildly basic conditions. Ruan *et al*. (2013) demonstrated that the pH value altered the decomposition rates of sulfonylurea herbicides and that acidic pH aided to the degradation process. Overall, the results are in agreement with those of Zhao *et al*. (2015), who claimed that nicosulfuron might be partially destroyed through chemical hydrolysis in natural environments, particularly those with an acidic pH.

3.2.2. Effect of alkaline hydrolysis

The results in Table 3 show that the concentration of nicosulfuron 4% OD exhibited a loss of 13.81% after 7 days of hydrolysis in 1.0 N NaOH, compared to 5.44% and 3.10% in 0.10 and 0.01N NaOH over the same period.

Table 3. The alkaline hydrolysis of nicosulfuron in 0.01, 0.10 and 1.0 N NaOH.

Concentration of reagent	Storage period (Days)	Conc. of Nicosulfuron(μg/mL)	Degradation rate (%)
0.01 N NaOH (pH=12, pOH=2)	0	399.78	0
	1	397.52	0.57
	3	393.50	1.57
	5	389.98	2.45
	7	387.40	3.10
0.10 N NaOH (pH=13, pOH=1)	0	399.78	0
	1	395.70	1.02
	3	389.55	2.56
	5	382.39	4.35
	7	378.05	5.44
1.0 N NaOH (pH=14, pOH=0)	0	399.78	0
	1	391.74	2.01
	3	372.67	6.78
	5	356.60	10.80
	7	344.56	13.81

The results clearly showed that the degradation rate of nicosulfuron in alkaline solutions decreased as pH approached the neutralization point. This is consistent with Leposhkin *et al.* (2013) who reported that nicosulfuron was hydrolytically stable at pH 7 and 9 in water, as well as at a temperature of 25°C. However, at pH 5, nicosulfuron had a half-life of 18 days. Benzi *et al.* (2011) found that nicosulfuron degrades slowly and can remain in neutral and alkaline environments for a long time.

Mansour *et al.* (2024) found that flonicamid hydrolysis was enhanced in strongly alkaline media with the OH^- ion targeting the molecule's terminal O and N atoms in the side chain. In general, hydrolysis rate increased as the pH increased resulting in a shorter chemical breakdown period.

Xiuying *et al*. (2012) found that the degradation of monosulfuron-ester occured more quickly in acid buffers and slowly in alkali buffers. Feng *et al*. (2017) also demonstrated that at pH levels greater than 7.0, the rate of nicosulfuron decomposition steadily decreased as the pH values increased.

Overall, the obtained results are consistent with those of Sarmah *et al.* (2000) who reported that sulfonylurea dissipation was usually higher in acidic conditions than in neutral or mildly basic conditions. Saha and Kulshrestha (2002) also found that sulfosulfuron decomposed more quickly in acidic (pH 4.0) than in alkaline conditions (pH 9.2).

3.3. Kinetics of the forced degradation of nicosulfuron

3.3.1. Acid hydrolysis of nicosulfuron

The nicosulfuron acid hydrolysis in 0.01, 0.10, and 1.0 N HCl is plotted as ln C vs. time (Figures 8-10). The calculated kinetic parameters are provided in Table 4. The plot of (ln C) vs. time yielded a straight line with a slope of the plots was (-k), which represents the degradation constant in (day^{-1}).

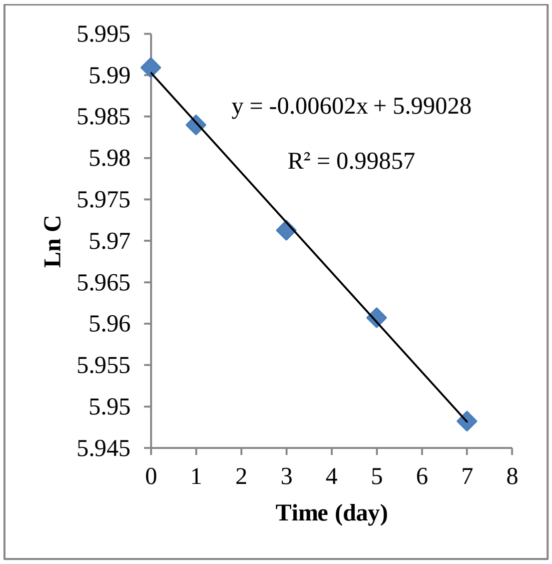


Figure 8. Ln. C vs. time for the acidic degradation of nicosulfuron in 0.01 N HCl.

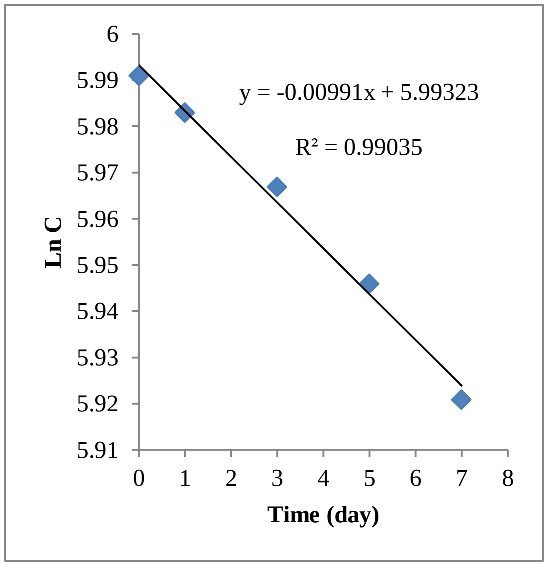


Figure 9. Ln. C vs. time for the acidic degradation of nicosulfuron in 0.10 N HCl.

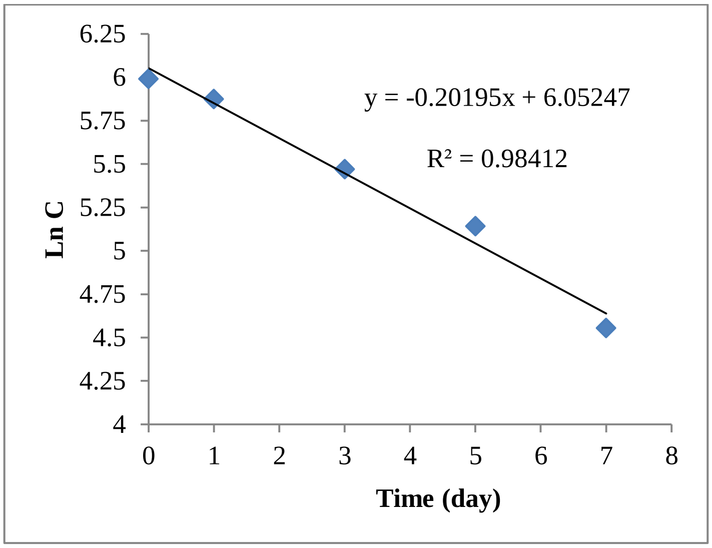


Figure 10. Ln. C vs. time for the acidic degradation of nicosulfuron in 1.0 N HCl.

Overall, the data in Table 4 demonstrated that nicosulfuron's shelf life and half-life were impacted by the acidic medium. In 0.01N HCl, nicosulfuron hydrolysis had a longer half-life and shelf life than in 0.10N HCl, which in turn had a longer half-life than in 1.0N HCl.

Table 4. Degradation kinetic parameters of nicosulfuron 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 = -0.00602x + 5.99028	0.99857	6.02×10^{-3}	8.52	115.14
0.10 N	y = -0.00991x + 5.99323	0.99035	9.91×10^{-3}	5.18	69.94
1.00 N	y = -0.20195x + 6.05247	0.98412	20.20×10^{-2}	0.25	3.43

According to Mansour *et al*. (2023), pH values influenced the herbicide properties including chemical stability, volatility and chemical compatibility. As a result, manufacturers adjust the pH of their adjuvant and herbicide formulations to achieve a balance with the numerous influencing factors.

3.3.2. Alkaline hydrolysis of nicosulfuron

The nicosulfuron alkaline hydrolysis in 0.01, 0.10, and 1.0N NaOH is plotted as ln C vs. time (Figures 11-13). The calculated kinetic parameters are provided in Table 5. The plot yielded a straight line indicating that alkaline hydrolysis of nicosulfuron followed first-order kinetics. The slope of the plots was (-k), which represents the degradation constant in (day^{-1}).

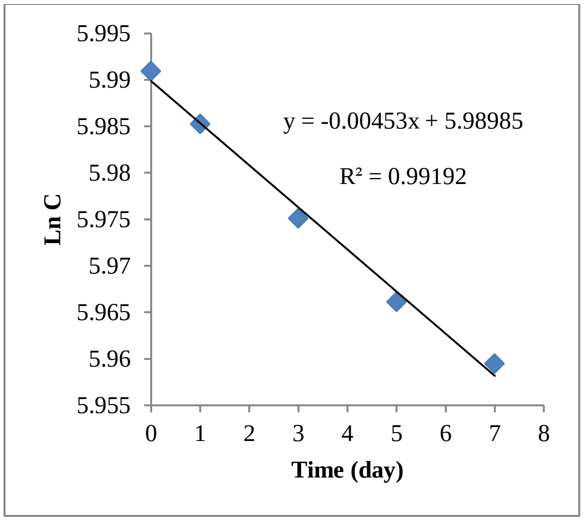


Figure 11. A plot of ln C vs. time for the alkaline degradation of nicosulfuron in 0.01 N NaOH

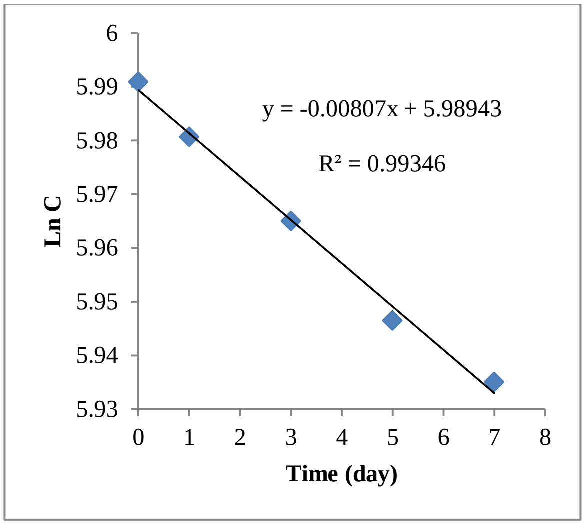


Figure 12. A plot of ln C vs. time for the alkaline degradation of nicosulfuron in 0.1 N NaOH

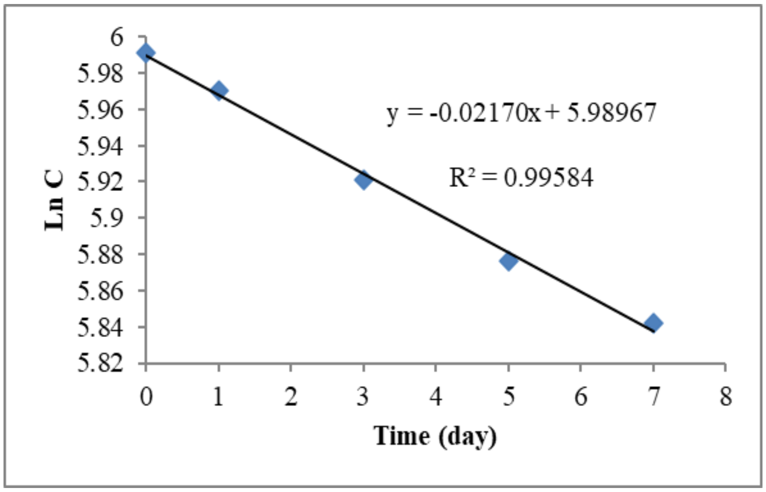


Figure 13. A plot of ln C vs. time for the alkaline degradation of nicosulfuron in 1.0 N NaOH

The data in Table (5) showed that the shelf life and half-life of nicosulfuron in 1.0 N NaOH decreased to approximately 1/5 of its shelf life and half-life in 0.01N NaOH.

Table 5. Degradation kinetic parameters of nicosulfuron in alkaline solutions.

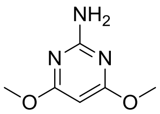
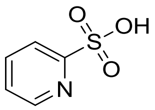
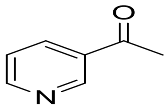
Conc. of NaOH	Linear regression equation	R^2 coefficient	K (day^{-1})	Shelf life $t_{0.95}$ (day)	Half-life $t_{1/2}$ (day)
0.01 N	y = -0.00453x + 5.98985	0.99192	4.53×10^{-3}	11.32	153.01
0.10 N	y = -0.00807x + 5.98943	0.99346	8.07×10^{-3}	6.36	85.89
1.00 N	y = -0.02170x + 5.98967	0.99584	21.70×10^{-3}	2.36	31.94

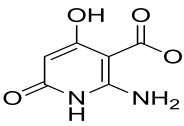
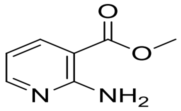
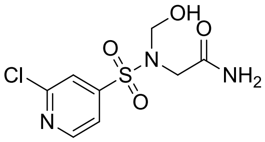
3.4. Identification of nicosulfuron degradation products using GC/MS

3.4.1. Acid nicosulfuron degradation products and pathways

The degradation products of nicosulfuron in acid media were analyzed using GC/MS to identify the probable degradation pathways and major hydrolytic products. Table (6) provides the identified degradation products from nicosulfuron.

Table 6. The identified degradation products of nicosulfuron hydrolysis in acidic solutions.

Product	Compound	RT (min)	Structure	m/z
P_1	2-Amino-4,6-dimethoxypyrimidine	12.498		154.9
P_2	2-Pyridinesulfonic acid	16.973		159.0
P_3	3-Acetylpyridine	24.663		121.1

P_4	2-Amino-4-hydroxy-6-oxo-1,6-dihydro-pyridine-3-carboxylic acid methyl ester	26.872		184.0
P_5	Methyl 2-aminonicotinate	27.936		152.1
P_6	2-(2-chloro-N-(hydroxymethyl)pyridine-4-sulfonamido)acetamide	28.308		280.8

The proposed mechanism for the forced acid hydrolysis of nicosulfuron in Fig. (14) which may be explained as follows.

- The cleavage of C-N bond on the sulfonylurea bridge in nicosulfuron (**p_0**) is to form 2-amino-4,6-dimethoxypyrimidine **(P_1)**.
- Cleavage of S-N bond and hydrolexation to form 2-pyridinesulfonic acid **(P_2)** after losing N,N-dimethyl formamide.

3-acetyl pyridine **(P_3)** is formed due to the loss of dimethyl amine and the cleaving of the bond between the pyridine ring and sulfamoyl groups.

- 2-Amino-4-hydroxy-6-oxo-1,6-dihydro-pyridine-3-carboxylic acid methyl ester **(P_4)** may be formed from hydroxylation at position 4 and dehydration at position 6 in the pyridine ring after the binding of the methoxy group to acetyl pyridine and the binding of amine to the pyridine ring at position 2.
- (**P_5**) Methyl 2-amino nicotinate is formed from the binding of the methoxy group to acetyl pyridine and the binding of amine to the pyridine ring at position 2.

(P_6) was formed due to the reaction between sulfonamide with acetamide and the methoxy group at position 4 in the pyridine ring and chlorination at position 2.

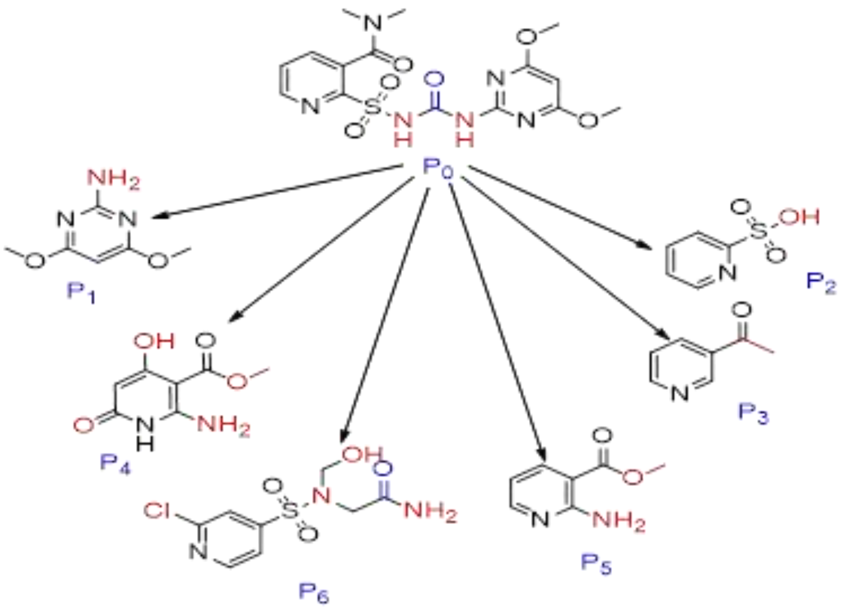


Figure 14. The forced acidic hydrolytic pathway of nicosulfuron.

3.4.2. Alkaline degradation of nicosulfuron: products and pathways

The degradation products of nicosulfuron in alkaline media were analyzed using GC/MS to identify the probable degradation pathways and major hydrolytic products. Table (7) provides the identified degradation products.

Fig. (15) show the proposed mechanism of the alkaline degradation of nicosulfuron which may be explained as follows:

a- Sulfur dioxide (**P_1**) was liberated as a result of cleaving of the C-S bond and S-N bond.

b- The methylation and hydrolexation processes in urea produced 1,3-bis(hydroxymethyl)urea (**P_2**).

c- N-acetyl-N-methylacetamide (**P_3**) was produced by the interaction of N-methyl acetamide with methanol.

d- N,N-dimethylhydroxylamine (**P_4**) was formed due to the cleavage of the N-C in the acetyl group and the hydroxelation of the amine.

e- The product 2,4-dimethyl pyridine (**P_5**) was generated by cleaving the C-S link between the pyridine ring and N-carbamoylsulfonic amide and losing formamide, followed by methyl binding at positions 2 and 4 in the pyridine ring.

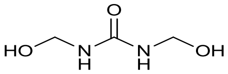
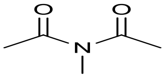
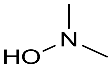
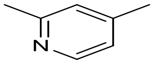
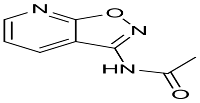
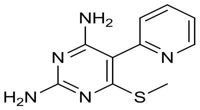
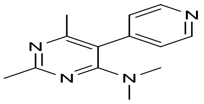
f- N-(isoxazolo[5,4-b]pyridin-3-yl)acetamide (**P_6**) was formed by the cyclization reaction of the molecule by the development of a "bridge" bond between the nitrogen atom linked to the oxygen atom and the carbon atom of the carbonylic group in the pyridine ring.

g- 6-(methylthio)-5-(pyridin-2-yl)pyrimidine-2,4-diamine (**P_7**) was formed by contraction of pyridine and pyrimidine rings and binding of methyl sulfide at position 6 and amino group at position 2 and 4 in pyrimidine.

The product N,N,2,6-tetramethyl-5-(pyridin-4-yl)pyrimidin-4-amine (**P_8**) was a result of the contraction of the pyridine and pyrimide rings after the loss of N-carbamoylsulfonic amide and N,N-dimethyl formamide, followed by the binding of dimethylamine at position 4 in the pyrimidine ring.

Table 7. The identified degradation products of nicosulfuron hydrolysis in alkaline solutions

Product	**Compound**	**RT (min)**	**Structure**	**m/z**
P_1	Sulfur dioxide	5.374	O=S=O	63.8

P_2	1,3-bis(hydroxymethyl)urea	7.194		120.1
P_3	N-acetyl-N-methylacetamide	14.049		114.9
P_4	N,N-dimethylhydroxylamine	15.497		61.1
P_5	2,4-dimethyl pyridine	18.541		107.0
P_6	N-(isoxazolo[5,4-b]pyridin-3-yl)acetamide	18.609		177.9
P_7	6-(methylthio)-5-(pyridin-2-yl)pyrimidine-2,4-diamine	22.254		233.1
P_8	N,N,2,6-tetramethyl-5-(pyridin-4-yl)pyrimidin-4-amine	23.112		227.9

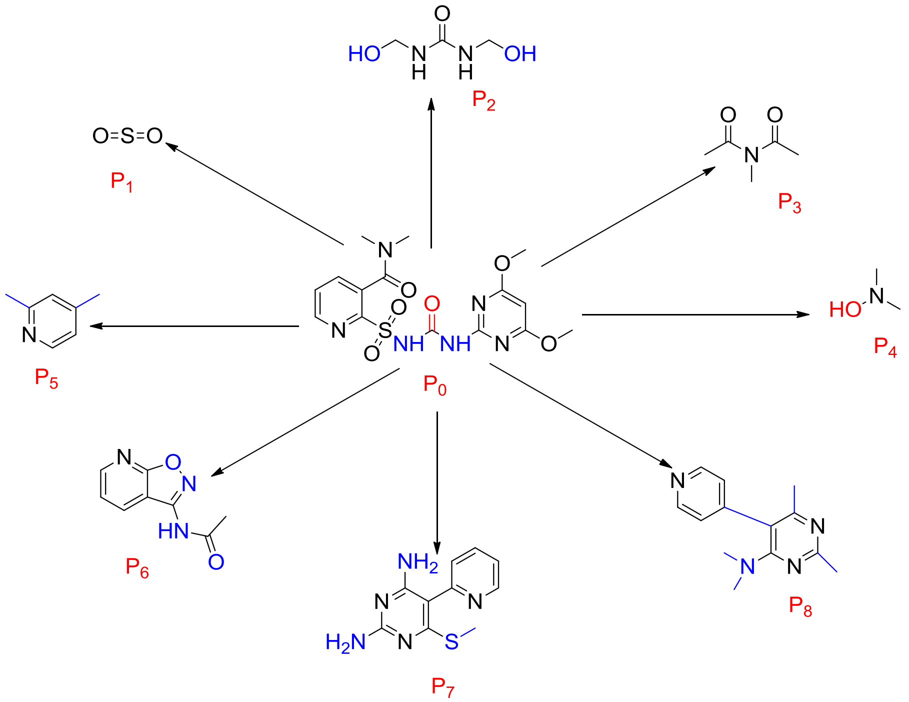


Figure 15. The forced alkaline hydrolytic pathway of nicosulfuron.

The results of nicosulfuron hydrolysis are consistent with those of Mansour *et al*. (2024) who observed that during acidic as well as alkaline degradation, flonicamid exhibited hydration and hydroxylation of its side chain through excess H^+ and OH^- ions in the solution, facilitating its breakdown to fewer moieties. Furthermore, the presence of abundant H^+ in acidic hydrolysis environments favored the replacement of pyridine ring H with Cl at the C2 and C3 positions.

3.5. Determination of nicosulfuron dissipation in soil sample

The chemical, mechanical, and physical characteristics of the soil used in the study determined at the Soil, Water and Environment Research Institute (SWERI) in Giza, Egypt, are shown in Table (8).

Table 8. Chemical, mechanical and physical properties of soil used in the nicosulfuron dissipation study.

Chemical properties				
Organic matter %	1.92			
Soluble cations	K^+	Na^+	Mg^{2+}	Ca^{2+}
(meq./L)	0.62	13.55	5.50	9.50
Soluble anions	SO_4^{2-}	Cl^-	HCO_3^-	CO_3^{2-}
(meq./L)	9.47	18.50	1.00	---
Available macro-elements	N	K	P	
(mg/Kg soil)	69.00	183.00	8.34	
Available micro-elements	Cu	Fe	Mn	Zn
(mg/Kg soil)	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	

The results in Table (9) and Fig. (16) demonstrate that during 14 days and at ambient conditions, the active ingredient of nicosulfuron was reduced by 29.39%. The degradation of nicosulfuron in clay soil was slow which may be attributed to the soil alkaline pH.

Table 9. Dissipation of nicosulfuron in clay-loam soil

Exposure Periods (days)	Conc. of Nicosulfuron (μg/mL)	Decomp. Rate %
0	97.25	0
1	95.89	1.40
3	90.84	6.59
5	86.19	11.37
7	82.96	14.69
14	68.67	29.39

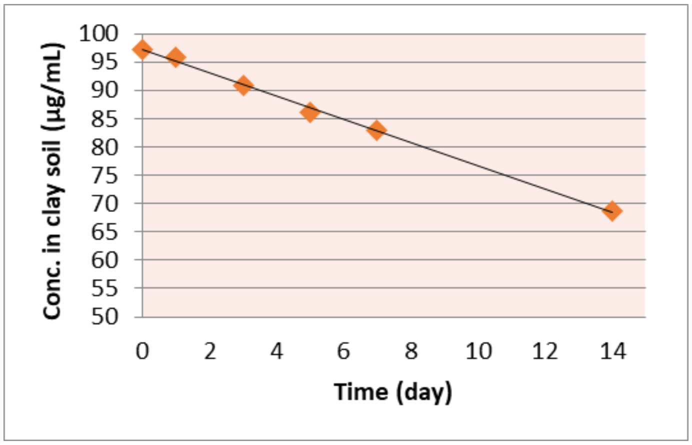


Figure 16. Dissipation of nicosulfuron 4% OD in clay-loam soil.

Chemical hydrolysis and microbiological degradation may occur in clay-loam soil causing the break of nicosulfuron. As well, since the pH of the soil was alkaline, the rate of degradation and the hydrolysis was pH-dependent similar to forced alkaline degradation. The obtained results are consistent with those of Ostojić *et al*. (2009) who evaluated nicosulfuron degradation in three soil samples and found that acidic soil degraded nicosulfuron more quickly than neutral or weakly basic soil. Chand *et al*. (2022) reported that flucetosulfuron decomposition in soil was accelerated by acidic pH and soil microbial activity.

The lower dissipation of nicosulfuron in clay-loam soil may depend upon nicosulfuron properties, pH-dependent, and the adsorption of the chemical to soil particles. This is in agreement with MacBean (2010) findings reporting that the (pka) of nicosulfuron was 4.60, which means that it was weakly acid. Kah and Brown (2006) reported that weak acid dissociated to produce protons and exits in both neutral and anionic form according to the following equation:

$[HA]+[H_2O] \rightleftharpoons [A^-]+[H_3O^+]$, $Ka=[H_3O^+]\cdot[A^-]/[HA]$, where $[H_3O^+]$, $[A^-]$, and $[HA]$ are the concentrations of hydronium ion (or proton), anionic species, and neutral species, respectively.

In addition, as pKa= −log Ka and pH= -log $[H_3O^+]$, the ratio of $[HA]/[A^-]=10^{(pKa-pH)}$ becomes a function of the pH and shows the increasing dominance of the anion at higher pH**.** The pH value of the study soil was 8.59, and hence the anion form of nicosulfuron increased. This is consistent with Doucette (2000) who stated that anions do not adhere to soils with organic carbon and clay any more strongly than their neutral equivalents, therefore the dissipation of nicosulfuron becomes low.

The current results are in line with Wei *et al.* (2006) who reported that the adsorption coefficient (K_f) values increased as organic matter (OM) and clay content increased; however, they were reduced as soil pH increased. In the current study, the soil sample had lower organic matter and a higher pH value, therefore the adsorption of nicosulfuron to soil decreased

3.5.1. Kinetic study of nicosulfuron dissipation in soil

The kinetics of nicosulfuron dissipation in clay-loam soil followed a first-order kinetics model depending on the chemical's initial concentration. ln C was plotted versus time (days) provided a straight line with an R^2 coefficient of 0.99782 and a slope of (-k) (Fig. 17).

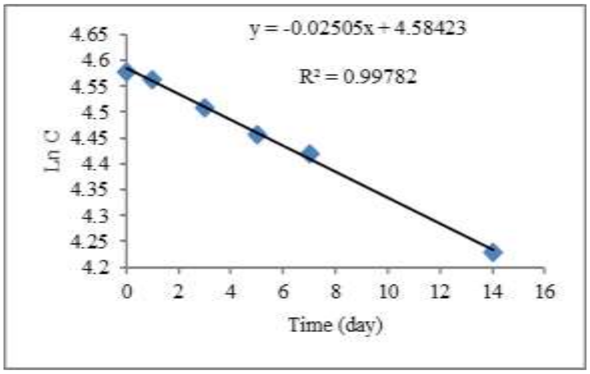


Figure 17. A plot of ln C vs. time for the photolysis of nicosulfuron in clay-loam soil.

Greenhalgh *et al.* (1980) classified herbicide persistence in soil into three groups: persistent ($t_{1/2}$ > 90 days), moderately persistent ($t_{1/2}$= 20-90 days), and not persistent (short-term) ($t_{1/2}$< 20 days). Based on the results in Table (10), nicosulfuron degradation half-life after application to clay-loam soil and exposure to sunlight was 27.67 days. Therefore, nicosulfuron may be considered moderately persistent in the Egyptian clay-loam soil. Jia *et al.* (2014) found that the half-life time of nicosulfuron was not significantly affected by soil moisture content when it was less than 50% and, with more than 50%, the half-life first increased and then declined. The study soil has a saturation percentage of 62.99% therefore the moisture content may have an impact on nicosulfuron dissipation and its half-life.

Table 10. Kinetic parameters of nicosulfuron photolysis in clay-loam soil

Pesticide	Linear regression equation	R^2 coefficient	K value (day^{-1})	$t_{1/2}$ (day)
Nicosulfuron 4% OD	y = -0.02505x + 4.58423	0.99782	25.05×10^{-3}	27.67

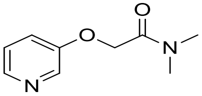
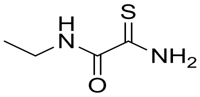
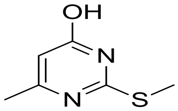
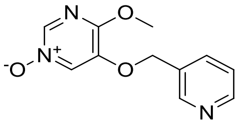
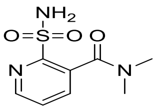
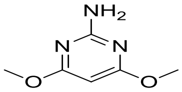
3.5.2. GC/MS identification of the degradation products of nicosulfuron in soil

Following the photolysis of nicosulfuron in soil, the residues were extracted from a soil sample and examined using GC/MS to identify the degradation products and provide a possible degradation pathway. The identified degradation products are provided in Table (11).

The photolysis degradation pathway of nicosulfuron in clay-loam soil provided in Fig.(18) can be explained as follows.

- The formatrion of N,N-dimethyl-2-(pyridin-3-yloxy)acetamide (**P_1**) as methoxy group interacts with the N,N-dimethyl acetamide at position 3 of the pyridine ring.
- The 2-amino-N-ethyl-2-thioxoacetamide (**P_2**) may be formed through the reaction between methanethioamide and N-ethyl acetamide.
- The product 6-methyl-2-(methylthio)pyrimidin-4-ol **(P_3)** may be a product of hydroxelation and the binding of methyl and methanethiol at positions (4, 6 and 2), respectively, in the pyrimidine ring.
- The product (**P_4**) 4-methoxy-5-(pyridin-3-ylmethoxy)pyrimidine1-oxide may be formed via the contraction reaction between 4-methoxy pyrimidine 1-oxide and the pyridine ring via the methoxy group at position 3 in pyridine. The bond C-N between carbon in pyrimidine and nitrogen in the urea portion is cleaved and pyrimidine is oxidized at the N to provide pyrimidine oxide, whereas the bond C-S between carbon in pyrimidine and sulfur is cleaved.
- The C-N bond of the sulfonylurea bridge in nicosulfuron (**P_0**) is cleaved to produce 2-(aminosulfonyl)-N,N-dimethylnicotinamide (**P_5**) and 2-amino-4,6-dimethoxypyrimidine (**p_6**), which are the major products.

Table 11. The identified degradation products of nicosulfuron photolysis in clay-loam soil.

Product	compound	RT (min)	Structure	m/z
P_1	N,N-dimethyl-2-(pyridin-3-yloxy)acetamide	8.722		179.9
P_2	2-amino-N-ethyl-2-thioxoacetamide	9.569		131.9
P_3	6-methyl-2-(methylthio)pyrimidin-4-ol	15.634		155.9
P_4	4-methoxy-5-(pyridin-3-ylmethoxy)pyrimidine 1-oxide	16.160		231.9
P_5	2-(aminosulfonyl)-N,N-dimethylnicotinamide	23.112		228.9
P_6	2-amino-4,6-dimethoxypyrimidine	15.634		154.9

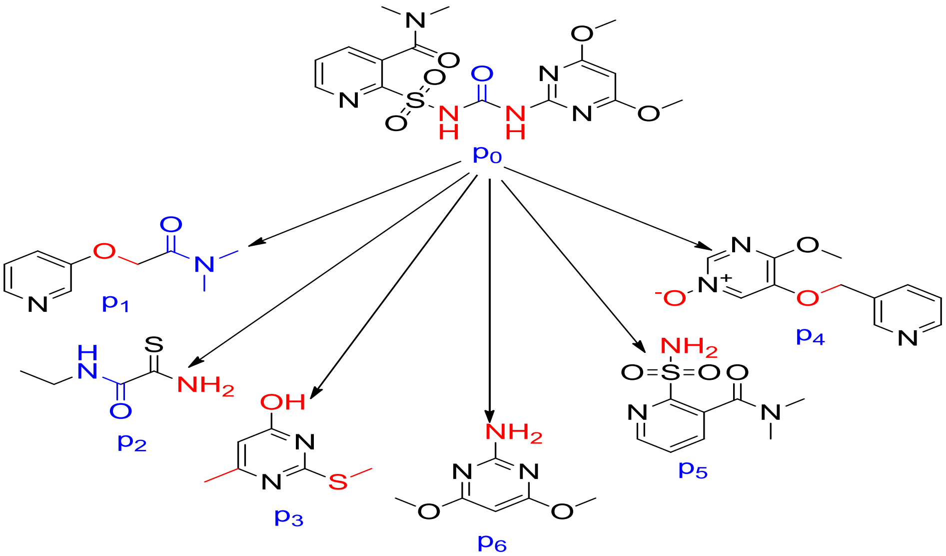


Figure 18. The photolysis degradation pathway of nicosulfuron in clay soil.

4. Conclusion

The kinetics of nicosulfuron degradation under different studied conditions followed the first-order model and was dependent upon its initial concentration. The forced acidic and alkaline conditions and soil photolysis were effective in cleaving the urea portion of nicosulfuron. The major degradation products of nicosulfuron in soil, which are 2-(aminosulfonyl)-N,N-dimethylnicotinamide and 2-amino-4,6-dimethoxypyrimidine similar to those identified in the forced acidic degradation, while in the forced alkaline condition these products disappeared. A contraction reaction occurs in the soil, similar to that occurs in the forced alkaline condition. The degradation of the parent compound (nicosulfuron) resulted in the formation of lower molecular weight compounds with electron-withdrawing groups such as sulfonyl (SO_2 and SO_2R), ammonium (NR), aminocarbonyl ($CONR_2$) and acyl groups (COR), which caused an increase in the toxicity of the degradation products.

Acknowledgments

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Conflicts of interest

"There are no conflicts to declare".

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