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# Thermal And Forced Hydrolytic Degradation Studies Of Flonicamid And Its Photolysis In Egyptian Clay-Loam Soil

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**Abstract**

The present study investigated the stability of Teppeki 50% WG (a flonicamid formulation) during forced thermal degradation at (35, 40, 45, and 54°C); forced acidic and alkaline hydrolysis in 1.0, 0.1, and 0.01N HCl and NaOH; and photolysis in clay-loam soil. The results showed that flonicamid active ingredient was significantly degraded (15.83 %) after storage at 54 °C after 14 weeks and its shelf-life decreased to 1/3 that of its shelf-life at 35°C. Acidic hydrolysis of flonicamid increased its shelf–life and half-life to 18.65 and 252.05 days in 1.0 N HCl which is almost 5 times that in 0.01 N HCl. Nonetheless, the shelf-–life and half-life of flonicamid in the alkaline media was reduced to 0.57 and 7.72 days and 0.07 and 0.95 days in 0.01N and 1.0 N NaOH, respectively. The half-life for flonicamid dissipation in clay-loam soil (pH 8.59) was 2.46 days. Generally, the kinetics of flonicamid degradation followed the first order model being dependent upon the initial concentration. During the thermal degradation and acidic and alkaline hydrolysis of flonicamid, the byproducts rendered indicated the cleavage and rearrangement of side chain however, they indicated that the pyridine ring remained stable. Nevertheless, the dissipation of flonicamid in soil was effective in the cleavage of the pyridine ring. This may be attributed to the macro and micro content available in soil tested which played a role in this molecule transformation.

*Keywords:* Type your keywords here, separated by semicolons ;

## 1. Introduction

Flonicamid – a nicotinamide derivative- is a novel class of insecticide with a distinct chemical structure (Fig. 1). Discovered in 1992, it was produced by Ishihara Sangyo Kaisha, Ltd. and was registered in Japan in 2006 under the trade name of Ulala DF. The IUPAC name of flonicamid is (N-cyanomethyl-4-(trifluoromethyl) nicotinamide). From its structure, this compound is considered a combination of an organofluorine, a pyridine-carboxamide, and a nitrile. Schirmer et al. [1] synthesized flonicamid through the reaction of trifluoromethylnicotinic acid with thionyl chloride and amino acetonitrile (Fig. 2). They also produced larger quantities of flonicamid using 1,3,5-tricyanomethylhexyhydro-1,3,5-triazine as the source of amino-acetonitrile.

Flonicamid is considered a systemic and activity selective insecticide that is widely used to control aphids and whiteflies on crops as well as thysanopterous bugs [2]. As well, it has a reduced toxicity against helpful arthropods to avert the emergence of pesticides' cross-resistance in insects [3-4]. This mode of action inhibits the feeding habit of aphids and not the nicotinic acetylcholine receptor.

Photo, chemical, and microbiological degradations of pesticides individually or combined may have an impact on their persistence. Nonetheless, a single pesticide may undergo all three phases of degradation during its decomposition.

As well, both the chemistry of the pesticide and its surrounding environment may affect the rate of its degradation. Other factors that affect the pesticide persistence may be by temperature, type of soil, water pH, microbial activity, its distribution between foliage and soil, and other media properties [5].

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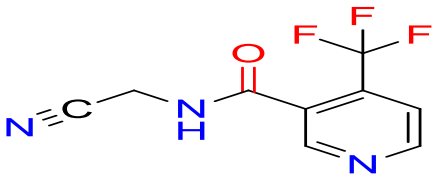


Fig. 1. Chemical structure of Flonicamid.

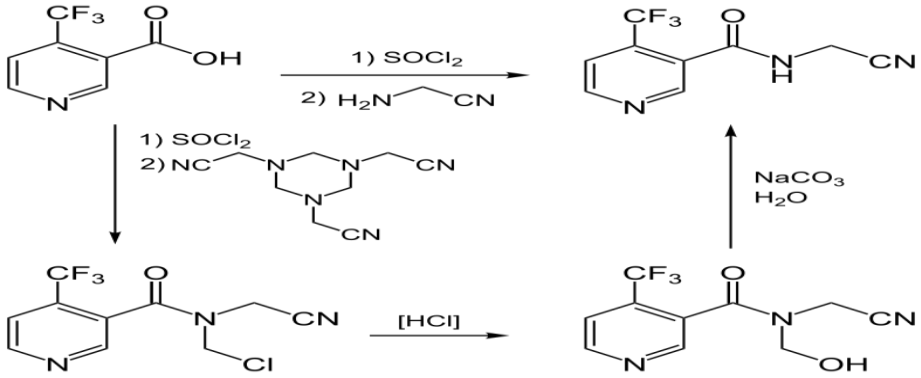
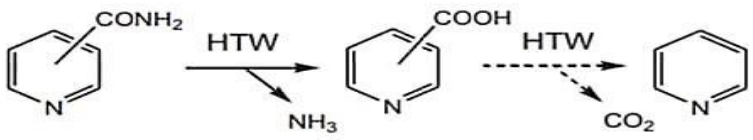


Fig. 2. Synthesis of flonicamid from 4-(Trifluoromethyl) nicotinic acid.

Ayare and Gogate [6] studied the impact of the pH range (1-6) on flonicamid degradation in aqueous media using ultra-sonication (100 W) at 30°C using an initial concentration of 75 ppm. In their work, the solution COD was considered the guiding parameter and an indicator of the pesticide degradation. Their results demonstrated that a maximum COD reduction of (39.23%) was achieved at pH 2. Using pH 6, the COD reduction was (20%) which was attributed to the decrease in solution hydroxyl radical content.

The effect of temperature on 2-pyridinecarboxamide hydrolysis in solution was studied by Fu et al. [7]. The experimental conditions applied were: temp: 220 °C, 8 MPa and an initial pesticide concentration 0.5 g/L. Their results indicated that ortho-pyridinecarboxamide and ortho-picolinic acid had lower hydrothermal stability at high temperatures. As well, they found that while 2-pyridinecarboxamide stability did decline over time, 2-picolinic acid and pyridine stability did increase. From these results, they proposed the following potential pathway for pyridinecarboxamide hydrolysis (Fig. 3).



HTW → High-temperature water.

Fig. 3. Pathway of pyridinecarboxamide hydrolysis.

Aizawa [8] examined the stability of aqueous [14C-3-pyridyl]-flonicamid] in sterilized buffer solutions at pH (4, 5, 7 and 9) and at different temperatures (25, 40 or 50°C) in the dark. The study revealed that flonicamid was stable within all pH ranges at 25°C. Moreover, he indicated that flonicamid had a half-life of 17 days at pH 9 and 40°C. After being irradiated with a xenon lamp (light intensity: 10-36 W/m2, λ: 290-800 nm) at 25°C, [14C]-Flonicamid was found to be stable in buffer solutions of pH 6 and 7 and in natural river water (pH 8) for up to 30 days. The major products of

flonicamid breakdown in aqueous were established to be the formation of an amide (2) and a carboxylic acid (3) as a result of the hydration/oxidation of the cyano-moiety. The hydrolytic breakdown process of flonicamid was provided in (Fig. 4).

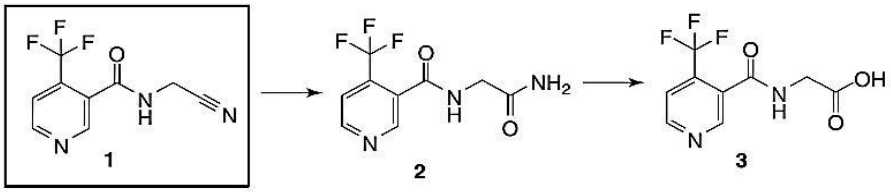



Fig.4. The degradation pathway of flonicamid during photolysis and hydrolysis.

Furthermore, photolysis and hydrolysis play significant roles on how the pesticides are to be dissipated during their application to the environment [9]. Neonicotinoid degradation in soils was reported to be dependent upon soil type (particularly texture and the concentration of organic matter), UV radiation (for surface degradation), moisture, temperature, and pH [10]. In addition, this rate of degradation was found to depend upon the geographic location. In other words, half-lives may become longer in middle and higher latitudes compared to the tropics due to fewer daylight hours, lower sunlight intensity, and cooler temperatures.

Moreover, flonicamid may readily and quickly undergo substantial microbe-mediated degradation in aerobic soil to produce either carbon dioxide or residues that were attached to the soil [11]. The $DT_{50}$ (dissipation time of 50%) values for flonicamid in a North American and three European soils were found to range from 0.7 to 1.8 days at 20°C and 2.4 days at 10°C. Similarly, the respective $DT_{90}$ (dissipation time of 90%) ranged from 2.3 to 6.0 days and 7.9 days. In rivers and surface waters, flonicamid had half-lives of 37.3 and 30.3 days, respectively. In addition, in water/ sediment systems of rivers and ponds, the $DT_{50}$ was found to be 43.6 and 35.7 days and the corresponding $DT_{90}$ was 144.8 and 118.7 d, respectively.

The persistence of flonicamid and its metabolites in soil and cabbages during harvest and their dissipation behaviors was examined by Wang et al. [12]. The half-lives of flonicamid alone and total residues (the sum of flonicamid and its metabolites) were 1.49-4.59 and 1.97-4.99 days in cabbage and 2.12-7.97 and 2.04-7.62 days in soil, respectively. As well, the dissipation kinetics of flonicamid itself and its total residues in cabbage and soil followed the first-order kinetic model. Their results indicated that maximum residues of total flonicamid in cabbage and soil were 0.070 and 0.054 mg/kg, respectively, when 50% flonicamid WG was sprayed once or twice within the permissible dose and 1.5-fold the recommended dose.

The purpose of this research is to investigate the forced thermal, hydrolytic (acidic and alkaline) degradation of flonicamid as well as the photolysis of flonicamid in clay-loam soil. Furthermore, the degradation products of this pesticide will be identified using GC/MS to elucidate the degradation pathways. Finally, the analytical data will be used for the quantification of shelf-life and half-life times of this pesticide under the applied experimental conditions.

## 2. Material and methods

2.1 Materials

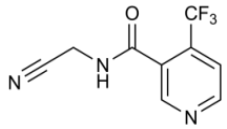
• Certified reference standard of flonicamid (purity of 99%) was purchased from Dr. Ehrenstorfer$^{TM}$ Gmbh (Augsburg, Germany).

• Flonicamid formulation used was Teppeki 50% WG that was readily available on the local Egyptian market. The chemical and physical properties of flonicamid are provided in Table (1).

•All organic solvents utilized (acetonitrile, methanol) were HPLC grade and were acquired from Sigma-Aldrich.

•QuEChERS extraction kits (Sigma-Aldrich) (4g $MgSO_4$, 1g NaCl, 1g sodium citrate tribasic dihydrate and 0.5g sodium citrate dibasic sesquihydrate) and QuEChERS clean-up kit (Sigma–Aldrich) (25 mg PSA sorbent + 150 mg $MgSO_4$) were utilized for the determination of flonicamid in soil samples.

Table (1): Chemical and physical properties of Flonicamid.

| | | |
|---|---|---|
| ISO common name | Flonicamid | |
| IUPAC name | N-cyanomethyl-4-(trifluoromethyl)nicotinamide | |
| CA name | N-(cyanomethyl)-4-(trifluoromethyl)-3-pyridinecarboxamide | |
| Chemical class | Pyridine carboxamide insecticides | |
| Pesticide group | Neonicotinoid insecticide | |
| CAS Registry number | 158062-67-0 | |
| CIPAC number | 763 | |
| Structural formula |  | |
| Molecular formula | $C_9H_6F_3N_3O$ | |
| Molecular weight | 229.16 g/mol | |
| Melting point | 157.5°C | |
| Solubility at 20°C in organic solvents | Solvent | g/L |
| | Acetone | 163.5 |
| | Ethyl Acetate | 34.2 |
| | Methanol | 104.3 |
| | Dichloromethane | 4.5 |
| | Toluene | 0.55 |
| | Hexane | 0.0002 |
| | n-Octanol | 3 |
| | Acetonitrile | 132.8 |
| | Isopropyl Alcohol | 18.7 |
| Solubility at 20°C in water | 5.2 g/L | |
| Mean Relative Density (20 ºC) | 1.54 g/mL | |
| Minimum purity of active | 960 g/Kg | |
| Flammability | Not highly flammable (98.7%) | |
| Mode of action | Systematic, selective, and long-term in nature. Modulator for a chordotonal organ. | |
| Formulation Name | Teppeki 50% WG | |

**2.2 Methods:**

**2.2.1. Calibration curve of flonicamid using HPLC**

A stock solution of standard flonicamid (400 µg/mL) was prepared in acetonitrile in a 50 mL volumetric flask and stored at -18°C. Flonicamid concentrations (10, 25, 50, 100, 200 and 300 µg/mL) were used to obtain the calibration plot for the pesticide using HPLC (Agilent Technologies 1260 Infinity System) with a quaternary pump (G 1311 B, G1316 A, G1315 D, and G1328 C), thermostatted column compartment and DAD detector at 205 nm. Chromatographic separation was carried out using Agilent C18 (4.6 mm ID x 150 mm x 4µm) analytical column. Isocratic elution was carried out using a mobile system comprised of water (+1% H3PO4): methanol: acetonitrile (5:5:90) at a flow rate of 1 mL/min and an injection volume of 5µL. The chromatogram for Flonicamid is shown in (Fig. 5) indicating a retention time of 1.547 min for this compound.

**2.2.2 Forced thermal and hydrolytic degradation of Flonicamid:**

**•Thermal Degradation studies.**

• Accelerated high temperature storage procedures were carried out according to CIPAC MT 46.1 [13]. About 20 g of the pesticide formulation was put in glass beakers.

The glass beakers were introduced into an electrical oven at following temperatures (35, 40, 45 and 54 ºC) in the dark.

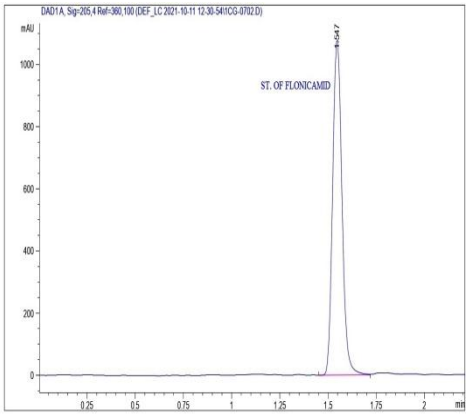



Fig. 5. The HPLC chromatogram of flonicamid standard (400µg/mL)

For each temperature, 14 beakers were used and the oven temperature was regulated in order to allow for the withdrawal of samples at the predetermined period of (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14 weeks) per temperature. After withdrawal, each individual sample was analyzed to identify 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 allows the monitoring the tested pesticide breakdown as a result of its interaction with water.

**•Acidic hydrolysis studies**

10 mg of flonicamid were mixed with 2 mL of each HCl concentration (0.01 N, 0.1 N, or 1.0 N) in 25 mL volumetric flasks. 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 analyzed.

**•Alkaline hydrolysis**

10 mg of flonicamid were mixed with 2 mL of suitable concentration of NaOH (0.01 N, 0.1 N, and 1.0 N) in 25 mL volumetric flasks. 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 analyzed.

**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 one minute to ensure 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 flonicamid 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 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 325ºC. 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.

## 3. Results and Discussion

### 3.1. Calibration curve for flonicamid standard.

The curve between flonicamid standard working concentrations of 10, 25, 50, 100, 200 and 300 µg/mL and measured peak area using HPLC is shown in (Fig. 6). The curve had a correlation coefficient ($R^2$) equal to 0.99682 indicating a linear relationship between the tested concentration range and measured peak area.

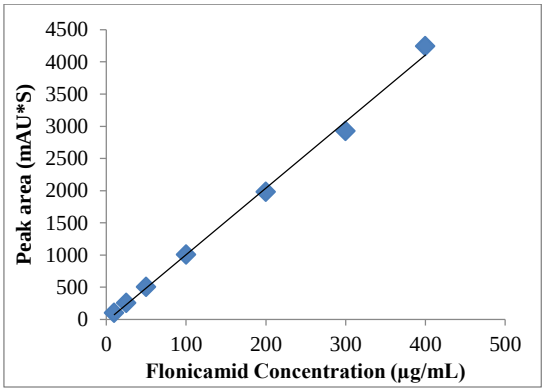



Fig. 6. Standard Calibration curve for flonicamid using HPLC.

### 3.2. Thermal conditions stability of active ingredient of Flonicamid in Teppeki 50% WG:

Table (2) shows the results obtained for the forced thermal degradation of the active ingredient of Teppeki 50% WG during the predefined thermal storage conditions. The results show that the active ingredient was significantly degraded (15.83%) during storage at 54 °C after 14 weeks. However, the reduction at 35, 40, and 45 °C was less ranging between 5- 10 % for the same period.

FAO/WHO [14] indicated that the average reduction in active ingredient of a pesticide during storage for 2, 6, 8, and 12 weeks at 35, 40, 45, and 54°C, respectively, should not exceed 5% of its average initial content. In this respect, storage of flonicamid for 14 weeks at 35 °C, 9 weeks at 40 °C, 8 weeks at 45 °C, and 4 weeks at 54 °C did comply with FAO specifications. However, these results indicate that thermal storage should be restricted to not more than 14, 9, 8, and 4 weeks at 35, 40, 45, and 54 °C, respectively.

Theodoridis [15] stated that C–F bond in pesticides is stronger than the C–H bond with its energy being 485 kJ $mol^{-1}$ compared to 416 kJ $mol^{-1}$, respectively. This bond strength may contribute to the increased oxidative and thermal stability of the molecule. As well, the high electronegativity of F compared to H (4.0 and 2.1) may contribute to the change in electronic properties of the molecule, the modification of its physical properties and chemical reactivity. Therefore, the noted stability of flonicamid at these elevated temperatures may be attributed to the C-F bonds attached to the benzene ring.

The obtained data indicate that the full degradation of flonicamid may require higher activation energy, which is consistent with the findings of Ring [16]. In this context, he stated that flonicamid must be kept at ambient temperature and not exposed to higher temperatures, with which the current findings agree. This precautionary measure may attribute to the extension of the pesticide shelf-life. This is in agreement with ECHA [17] which reported that flonicamid with a purity of 99.7% was stable for 36 months at 25 °C.

Fu et al. [7] examined the hydrolysis of 2-pyridinecarboxamide at 220 °C. Their data indicated that ortho-pyridinecarboxamide and ortho-picolinic acid had lower hydrothermal stability at higher temperatures. However, the hydrolysis of 2-pyridinecarboxamide declined with time and that of 2-picolinic acid and pyridine increased. These results are similar to the findings of the current study concerning the stability of flonicamid, which is a pyridine carboxamide.

Table (2): Effect of storage at 35, 40, 45 and 54 °C on the stability a.i. of Teppeki 50% 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 | 397.84 | 0 | 397.84 | 0 | 397.84 | 0 | 397.84 | 0 |
| 1 | 397.15 | 0.17 | 396.92 | 0.23 | 396.51 | 0.33 | 395.03 | 0.71 |
| 2 | 396.06 | 0.45 | 395.02 | 0.71 | 394.28 | 0.89 | 392.29 | 1.40 |
| 3 | 394.17 | 0.92 | 393.10 | 1.19 | 392.89 | 1.24 | 388.23 | 2.42 |
| 4 | 393.38 | 1.12 | 390.46 | 1.86 | 389.42 | 2.12 | 383.65 | 3.57 |
| 5 | 391.94 | 1.60 | 388.92 | 2.24 | 386.29 | 2.90 | 377.79 | 5.04 |
| 6 | 390.67 | 1.80 | 386.76 | 2.79 | 383.65 | 3.57 | 372.93 | 6.26 |
| 7 | 389.22 | 2.17 | 384.49 | 3.36 | 380.41 | 4.38 | 366.19 | 7.96 |
| 8 | 387.18 | 2.68 | 382.17 | 3.94 | 378.18 | 4.94 | 361.29 | 9.19 |
| 9 | 385.98 | 2.98 | 379.38 | 4.64 | 375.63 | 5.58 | 357.42 | 10.16 |
| 10 | 384.10 | 3.45 | 376.97 | 5.25 | 372.04 | 6.49 | 351.46 | 11.66 |
| 11 | 383.54 | 3.59 | 374.72 | 5.81 | 368.72 | 7.32 | 347.85 | 12.57 |
| 12 | 382.09 | 3.96 | 372.81 | 6.29 | 365.32 | 8.17 | 344.38 | 13.44 |
| 13 | 380.72 | 4.30 | 370.51 | 6.87 | 363.49 | 8.63 | 338.70 | 14.87 |
| 14 | 378.83 | 4.78 | 368.37 | 7.41 | 360.67 | 9.34 | 334.85 | 15.83 |

Table (3): Flonicamid degradation rates in 0.01, 0.1 and 1.0N HCl.

| Concentration of reagent | Storage period | Conc. of Flonicamid (µg/mL) | Degradation rate (%) |
|---|---|---|---|
| 0.01 N HCl (pH=2) | 0 | 397.84 | 0 |
| | 1 | 392.11 | 1.44 |
| | 3 | 380.78 | 4.27 |
| | 5 | 369.62 | 7.09 |
| | 7 | 363.14 | 8.72 |
| 0.1 N HCl (pH=1) | 0 | 397.84 | 0 |
| | 1 | 395.58 | 0.57 |
| | 3 | 392.83 | 1.26 |
| | 5 | 389.79 | 2.02 |
| | 7 | 385.13 | 3.19 |
| 1 N HCl (pH=0) | 0 | 397.84 | 0 |
| | 1 | 397.12 | 0.18 |
| | 3 | 394.55 | 0.83 |
| | 5 | 392.41 | 1.36 |
| | 7 | 390.20 | 1.92 |

Table (4): The alkaline hydrolysis of flonicamid in 0.01, 0.1 and 1.0 N NaOH.

| Concentration of reagent | Storage period | Conc. of Flonicamid (µg/mL) | Degradation rate (%) |
|---|---|---|---|
| 0.01 N NaOH (pOH= 2, pH=12) | 0 | 397.84 | 0 |
| | 1 | 371.45 | 6.63 |
| | 3 | 313.94 | 21.09 |
| | 5 | 259.24 | 34.84 |
| | 7 | 205.50 | 48.35 |
| 0.1 N NaOH (pOH= 1, pH=13) | 0 | 397.84 | 0 |
| | 1 | 271.61 | 31.73 |
| | 3 | 143.36 | 63.97 |
| | 5 | 17.89 | 95.50 |
| | 7 | 0 | 100 |
| 1 N NaOH (pOH= 0, pH=14) | 0 | 397.84 | 0 |
| | 1 | 219.57 | 44.81 |
| | 3 | 42.83 | 89.23 |
| | 5 | 0 | 100 |
| | 7 | 0 | 100 |

### 3.3. Forced hydrolytic (acidic and alkaline) degradation of flonicamid in (Teppeki 50% WG).

#### 3.3.1. Effect of acidic hydrolysis.

The data in Table (3) shows that after 7 days of acidic hydrolysis in 0.01 N HCl, the active ingredient in Teppeki 50% WG had an 8.72% loss. However, the loss in 0.1 N and 1.0 N HCl for the same duration was 3.19 % and 1.92 %, respectively.

The obtained results indicate that the pH, acid concentration, and exposure time in aqueous medium did have an impact on flonicamid hydrolysis. As well, it was observed that the hydrolysis rate of

flonicamid increased as the acidic medium pH value decreased i.e. the HCl concentration decreased. Subsequently, the stability of the chemical compound in concentrated acid solution may attributed to the $H^+$ protonation of the terminal O and N atoms thus stabilizing the side chain.

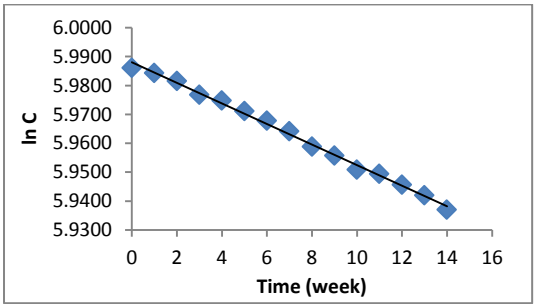



Fig. 7. A plot of ln C vs. time (weeks) for flonicamid degradation after 35°C storage

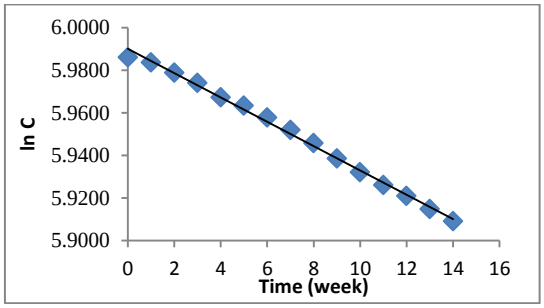



Fig. 8. A plot of ln C vs. time (weeks) for flonicamid degradation after 40°C storage.

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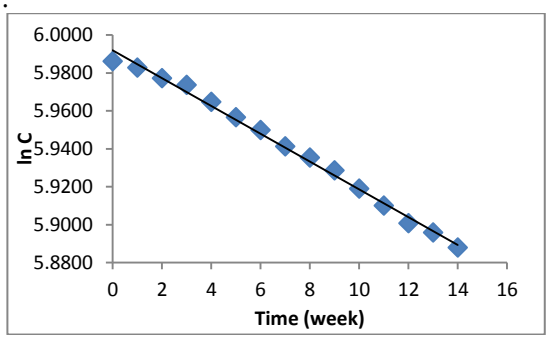



Fig. 9. A plot of ln C vs. time (weeks) for flonicamid degradation after 45°C storage.

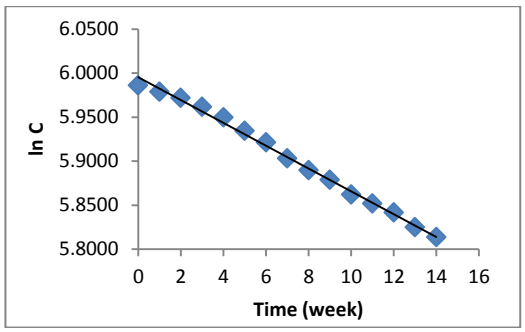



Fig. 10. A plot of ln C vs. time (weeks) for flonicamid degradation after 54°C storage.

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

| Pesticide formulation | **Temp** (°C) | Linear regression equation | $R^2$ | Degradation rate (K) ($week^{-1}$) | Shelf-life (week) |
|---|---|---|---|---|---|
| (Teppeki 50% WG) | 35 | $y = -3.35\times10^{-3}x+5.986$ | 0.99153 | $3.35\times10^{-3}$ | 15.31 |
| | 40 | $y = -5.30\times10^{-3}x+5.986$ | 0.98894 | $5.30\times10^{-3}$ | 9.68 |
| | 45 | $y = -6.72\times10^{-3}x+5.986$ | 0.98497 | $6.72\times10^{-3}$ | 7.63 |
| | 54 | $y = -1.192\times10^{-2}x+5.986$ | 0.98767 | $1.192\times10^{-2}$ | 4.30 |

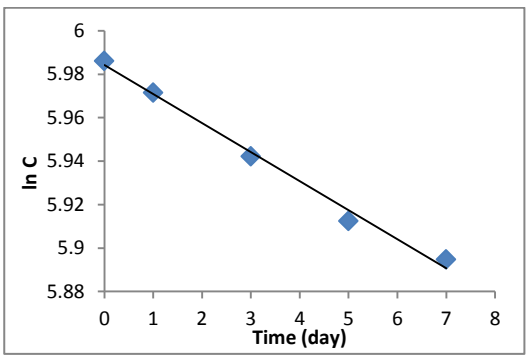



Fig. 11. A plot of ln C vs. time for the acidic degradation of flonicamid in 0.01 N HCl

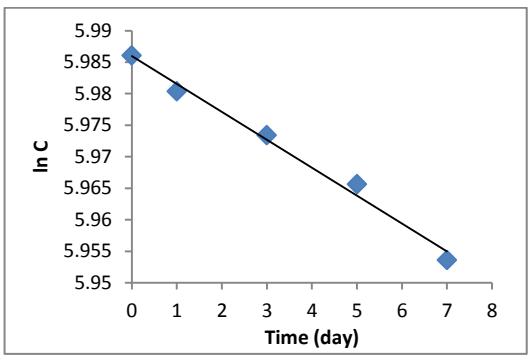



Fig. 12. A plot of ln C vs. time for the acidic degradation of flonicamid in 0.1 N HCl

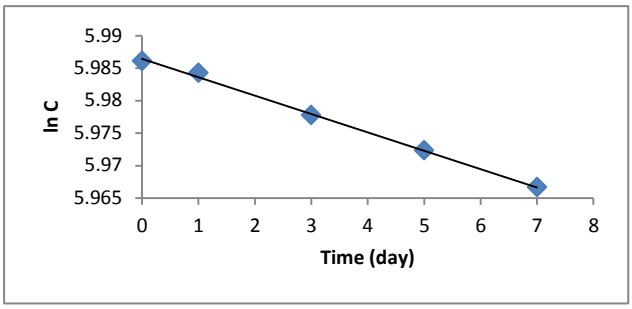



Fig. 13. A plot of ln C vs. time for the acidic degradation of flonicamid in 1.0 N HCl

Abdel-Ghany et al. [10] indicated that neonicotinoid degradation was dependent on moisture, temperature, and solution pH, with which the current findings agree. Moreover, the present results are in accordance with Aizawa [8] observations concerning the stability of [14C-3-pyridyl]-flonicamid in sterilized buffer solutions of pH 4, 5, 7 and 9 at 25, 40 or 50 °C in the dark.

Overall, the current results are in accordance with FAO [18] directive that stated that the active ingredient of flonicamid is stable at pH 4 and pH 5. Beer and Beard [19] indicated that organophosphate and carbamate insecticides were more susceptible to hydrolysis than chlorinated hydrocarbon insecticides. As well, they stated that lowering the pH of water to the optimum range of 4 to 7 was needed before mixing with the pesticide in order to avoid its rapid hydrolysis.

### 3.3.1. Effect of alkaline hydrolysis

The data in Table (4) shows that the alkaline hydrolysis of the active ingredient in Teppeki 50% WG after 7 days in 0.01 N NaOH reached 48.35% loss. Total loss of the pesticide's active ingredient was observed after 7 and 5 days in 0.1 N and 1.0 N NaOH, respectively.

From the above data, it is notable that the alkaline hydrolysis of flonicamid depended upon the increase in OH- in solution which aided the degradation of this chemical. As well, at highly alkaline pH, flonicamid hydrolysis was facilitated with the OH- ion attacking the terminal O and N atoms of the side chain of the molecule. Generally, the hydrolysis rate increased as the pH increased thus the compound degradation period was reduced accordingly.

The obtained results agreed with the findings of Ring [16] who indicated that flonicamid was stable at pH ranging from 4 to 7, with the compound degradation rate increasing as the pH exceeded 7.5.

In addition, the results are consistent with Aizawa [8] who examined the aqueous stability of [$^{14}$C-3-pyridyl]-flonicamid in pH 9 at 40 °C. He also predicted the half-life at this pH was 17 days. The primary breakdown of flonicamid referred to the formation of an amide and carboxylic acid which resulted from the hydration/oxidation of the cyano-moiety.

The current results of alkaline hydrolysis of flonicamid are consistent with those of Arfanis et al. [20]. They reported that thiamethoxam (a neonicotinoid) was completely degraded after 90 minutes when the pH medium changed from neutral to alkaline. As well, Aizawa [8] indicated that Flonicamid undergoes hydrolysis at the -CN and -$CONH_2$ groups. Overall, Deer and Beard [19] indicated that the pesticides' hydrolysis rate was rapid within the pH range of 8 to 9. As well, they stressed that for every pH point increase, the rate of hydrolysis was to increase by approximately 10 times. As well, they pointed out that the extent of degradation due alkaline hydrolysis may be controlled by water alkalinity, the susceptibility of the pesticide, the amount of time the pesticide is in contact with the water and the temperature of the mixture.

## 3.4. Kinetics of the forced degradation of flonicamid.

### 3.4.1. Thermal degradation of flonicamid

Plots of ln [C] of flonicamid vs. time (weeks) during storage at 35, 40, 45, and 54 °C are shown in (Fig. 7, 8, 9 and 10), respectively. The plots were linear indicating R2 values ranging between 0.98767 and 0.9943. The kinetic parameters calculated from these plots are provided in Table (5).

The shelf life (t0.95) of flonicamid in Teppeki 50% WG after storage at these temperatures indicated that the rate of flonicamid degradation depended upon the initial concentration following 1st order rate equation. As well, the rate increased gradually with the increase in storage temperature. Incidentally, the shelf-life obtained during storage at 54 °C was 1/3 that of the pesticide shelf-life at 35 °C.

Nonetheless, the shelf-lives of flonicamid after storage at these temperatures were consistent with the period of time specified by FAO/WHO. Mansour et al. [21] reported that there was a positive relationship between temperature, the intensity of light, length of storage periods, and the degradation rate of pesticides' active ingredients. As well, they advocated that in order to achieve best pesticides' stability storage has to be at lower temperatures, as high temperatures increased the chemical's degradation. This is in agreement with the current findings.

### 3.4.2. Acidic hydrolysis of flonicamid

Plots of ln C vs. time for the acidic hydrolysis of flonicamid in 0.01 N, 0.1 N and 1.0 N HCl are shown in Figures (11-13). The respective kinetic parameters are provided in Table (6). Generally, the plots indicate that the acidic pesticide hydrolysis followed the first order model and the slopes of the plots was equal to (-k) degradation constant in ($day^{-1}$).

Table (6):Degradation kinetic parameters of flonicamid in acidic solutions.

| Conc. Of HCl (N) | Linear regression equation | $R^2$ | K ($day^{-1}$) | Shelf-life $t_{0.95}$ (day) | Half-life $t_{1/2}$ (day) |
|---|---|---|---|---|---|
| 0.01 | $y = -1.372x10^{-2} x+5.986$ | 0.99064 | $1.372\times10^{-2}$ | 3.74 | 50.5 |
| 0.1 | $y = -4.44x10^{-3} x+5.986$ | 0.98919 | $4.44\times10^{-3}$ | 11.55 | 156.1 |
| 1.0 | $y = -2.75x10^{-3} x+5.986$ | 0.99657 | $2.75\times10^{-3}$ | 18.65 | 252.0 |

Overall, the data in Table (6) indicate that the shelf life and half-life of flonicamid hydrolysis in 0.01 N HCl were lower than those in 0.1 N HCl, which were lower than those in 1 N HCl, respectively.

The obtained results are in agreement with Walsh and Murray [22] who studied the rate of hydrolysis of similar substance labeled with 14C at the C-3 carbon in the pyridine ring as a function of pH and temperature. The study was conducted in buffered solutions at pH 5, 7 and 9 for 30 days at 25 $^0$ C and for 120 days at 50 $^0$ C in darkness. They observed that no hydrolysis was evident below pH 7 but only at elevated temperature. The main hydrolytic product was 4-trifluoromethylnicotinamide which was produced from the hydrolysis of the nitrile group to form an amide.

### 3.4.3. Alkaline hydrolysis of flonicamid

Plots of ln C vs. time for the alkaline hydrolysis of flonicamid in 0.01N, 0.1N and 1.0 N NaOH are shown in Fig (14, 15 and 16), respectively. The respective kinetic parameters are provided in Table (7). These plots were linear with an intercept equal to ln [$C_0$] and $R^2$ ranging from 0.09931 to 0.99759.

Overall, the data in Table (7) indicated that the shelf life and half-life of flonicamid during hydrolysis in 1.0N NaOH were lower than those for 0.1N NaOH and 0.01 N NaOH, respectively. Deer and Beard [19] indicated that it was important to know the pH of water used with a pesticide and the susceptibility of the pesticide to hydrolysis. As well, they recommended that only the small quantities were to be mixed with water in the shortest time possible and that the pH of the water should be adjusted to an optimum level before application.

## 3.5. Identification of flonicamid degradation products using GC/MS.

### 3.5.1. Thermal degradation products and pathways.

The thermal degradation products of Teppeki 50% WG after 14 weeks of storage at 54 °C were analyzed using GC/MS for analysis. The identified degradation products and their respective structures are provided in Table (8) using Wiley and NIST mass spectral data base.

Table (7): Degradation kinetic parameters of flonicamid 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 | $y=-8.98x10^{-2} x +5.986$ | 0.98985 | $8.98x10^{-2}$ | 0.57 | 7.72 |
| 0.1 N | y = - 0.644x +5.986 | 0.97503 | 0.64401 | 0.08 | 1.08 |
| 1 N | y = - 0.728x +5.986 | 0.99254 | 0.72808 | 0.07 | 0.95 |

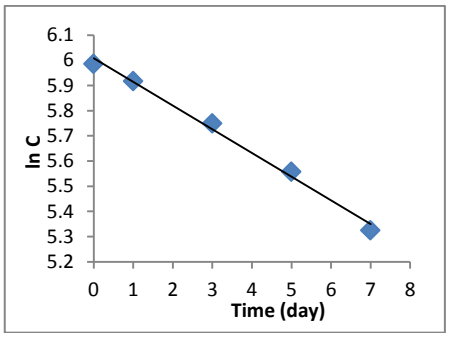



Fig. 14. A plot of ln C vs. time for the alkaline degradation of flonicamid in 0.01 N NaOH

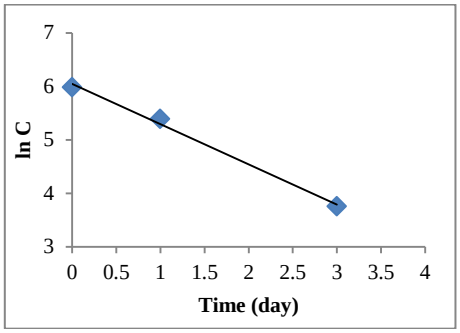



Fig. 16. A plot of ln C vs. time for the alkaline degradation of flonicamid in 1.0 N NaOH

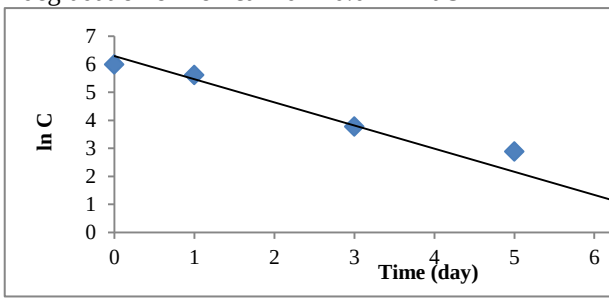
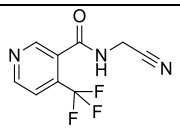
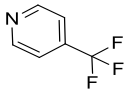
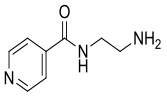
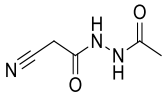
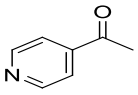



Fig. 15. A plot of ln C vs. time for the alkaline degradation of flonicamid in 0.1 N NaOH

Table (8):The identified thermal degradation products of flonicamid at 54°C using GC/MS

| Product | Compound | RT (min) | Structure | m/z |
|---|---|---|---|---|
| $P_0$ | Flonicamid | 15.23 |  | 229.2 |
| $P_1$ | 4(trifluoromethyl) pyridine | 19.71 |  | 147.0 |
| $P_2$ | N-(2-aminoethyl) isonicotinamide | 24.48 |  | 165.1 |
| $P_3$ | N'-acetyl-2-cyanoacetohydrazide | 11.70 |  | 141.1 |
| $P_4$ | 4-acetyl pyridine | 28.77 |  | 121.1 |

According to the obtained data, the thermal degradation pathways of flonicamid provided in Figure (17) may be explained as follows:

•**(P1)**: the cleavage of C-C bond between the carbon atoms of the formamide moiety and pyridine ring to form 4-(trifluoromethyl) pyridine.

•**(P2):** the formation of N-(2-aminoethyl) isonicotinamide through the loss of trifluoromethyl and the reduction of methylcyanide to ethylamine.

•**(P3)**: the formation of N'-acetyl-2-cyanoacetohydrazide due to the loss of 4-(trifluoromethyl) pyridine and the rearrangement of formamide and acetonitrile.

•**(P4)**: formation of 4-acetylpyridine formation through the loss of trifluoroamine and methylcyanide.

**3.5.2. Acidic flonicamid degradation products and pathways**

A neutralized acid degraded flonicamid sample was neutralized after 7 days for GC/MS analysis. The resulting degradation products were investigated by mass and structural formulae in order identify the possible degradation pathways and the main hydrolytic products. The identified degradation

formulae and their respective structure are provided in Table (9).

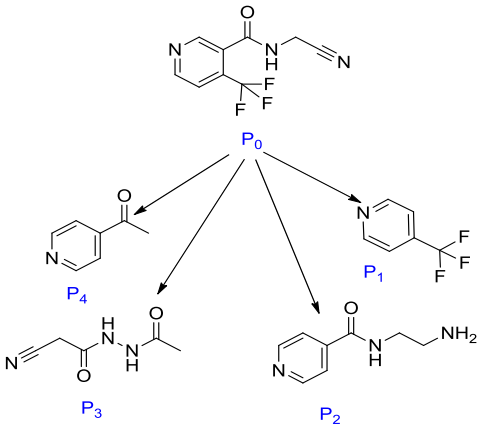



Fig.17. The thermal degradation pathways of flonicamid at 54°C

The forced acidic hydrolytic pathway of flonicamid in (Fig. 18) may be explained as follows.

- (**$P_1$**): the formation of a- pyridine-3-carboxamide may be attributed to the loss of trifluoromethyl and acetonitrile from the parent compound (**$P_0$**).
- (**$P_2$**): 2-cyano-N-(pyridin-3-ylmethyl) acetamide formation was a result of the rearrangement of cyanomethyl formamide in C- 3 in the pyridine ring.
- (**$P_3$**): the loss of hydrogen cyanide and trifluoromethyl from the parent compound and the binding of chlorine atoms at positions 5 and 6 in the pyridine ring have given rise to methyl 5, 6-dichloropyridine-3-carboxamide
- (**$P_4$**): 3-fluoro-4-(fluoromethyl)pyridin-2-ol (p4) was formed by the hydrolyzation at position 2 in the pyridine ring, the loss of a fluorine atom, and the binding of fluorine at position 3.
- (**$P_5$**): 2-(2-Cyano-ethylamino)-nicotinonitrile formation may be attributed to the binding of acetonitrile at position 3 and aminopropanenitrile at position 2 within the pyridine ring

### 3.5.3. Alkaline flonicamid degradation products and pathways.

A neutralized sample of forced flonicamid alkaline degradation was analyzed after 7 days with GC/MS to identify the possible degradation products and their structures. The potential pathways for the formation of these main hydrolytic products are provided in Table (10). The forced alkaline hydrolytic pathway of flonicamid depicted in Fig. (19) may be explained as follows:

The forced alkaline hydrolytic pathway of flonicamid is depicted in (Fig. 19):

- (**$P_1$**): The formation of pyridine, 5-ethenyl-2-methyl may be formed due to degradation of acetamide, cyanomethyl, and the loss of trifluoromethyl and the rearrangement of methyl groups.

Table (9): The identified degradation products of flonicamid hydrolysis in acidic solutions.

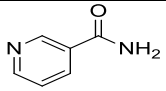
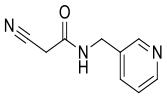
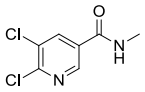
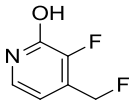
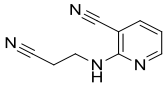
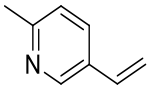
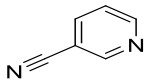
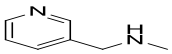
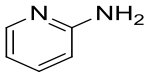
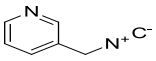
| Prod | Compound | RT (min) | Structure | m/z |
|---|---|---|---|---|
| $P_1$ | pyridine-3-carboxamide | 13.94 |  | 122.1 |
| $P_2$ | 2-cyano-N-(pyridin-3-ylmethyl) acetamide | 18.41 |  | 175.1 |
| $P_3$ | Methyl 5,6-dichloropyridine-3-carboxamide | 18.67 |  | 207.1 |
| $P_4$ | 3-fluoro-4-(fluoromethyl)pyridin-2-ol | 18.91 |  | 146.0 |
| $P_5$ | 2-(2-Cyano-ethylamino)-nicotinonitrile | 19.46 |  | 174.0 |

Table (10): The identified degradation products of flonicamid hydrolysis in alkaline solutions.

| Prod | Compound | RT (min) | Structure | m/z |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| $P_1$ | pyridine,5-ethenyl-2-methyl | 7.43 |  | 119.1 |
| $P_2$ | 3-Pyridinecarbonitrile | 13.25 |  | 105.1 |
| $P_3$ | N-methyl-3-pyridinemethylamine | 14.48 |  | 122.1 |
| $P_4$ | Pyridine-2-amine | 18.17 |  | 94.1 |
| $P_5$ | 3-(isocyanomethyl)pyridine | 18.76 |  | 132.0 |

• **(P2):**3-Pyridinecarbonitrile may be a result of the binding of acetonitrile to C in position 2.

•**(P3):** The formation on N-methyl-3-pyridinemethylamine is formed through the hydrolysis of acetamide to methane amine and the combination of the formed methyl group at position 3 of the pyridine ring.

•**(P4)** The Pyridine-2-amine formed is due to the hydrolysis of acetamide to amine and the loss of trifluoromethyl and cyanomethyl groups.

• Finally, **(P5)** 3-(isocyanomethyl) pyridine is formed due to loss of acetamide and trifluoromethyl from pyridine ring.

Overall, the degradation of the parent compound (flonicamid) resulted in lower molecular weight compounds containing electron-withdrawing groups or atoms such as ($CF_3$, -C≡N, Cl), which caused an increase in the toxicity of the degradation products. Dong et al [23] studied the structure-activity relationship and showed that the presence of halogen elements and electron withdrawal groups on the benzene ring was beneficial in improving the activity.

Liu et al. [24] indicated that electron withdrawing group increases the efficacy of biological activity. Their findings were based upon studying the degradation of the structure of aryloxyphenoxypropionate herbicides which contained phenoxypyridine, which is multiply substituted by electron withdrawing groups, such as F, Cl, Br, $NO_2$, CN, and $CF_3$; part Y is the linking arm (Fig. 20).

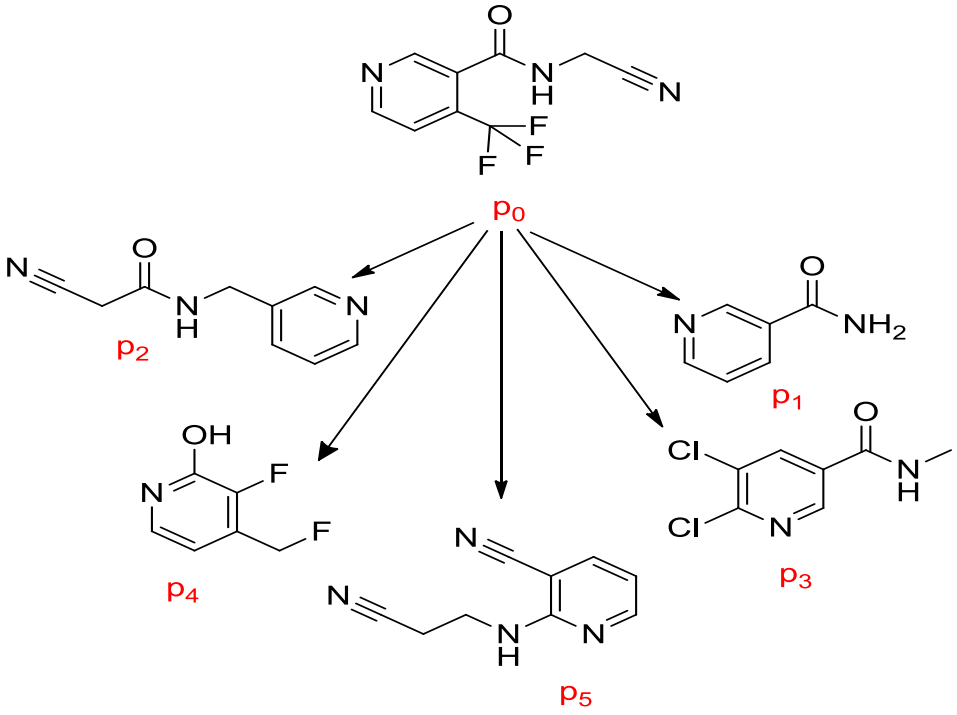



Fig. 18. The forced acidic hydrolytic pathway of flonicamid

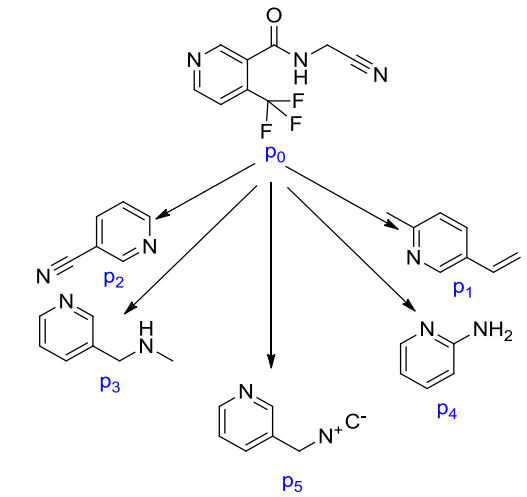



Fig.19. The forced alkaline hydrolytic pathway of flonicamid

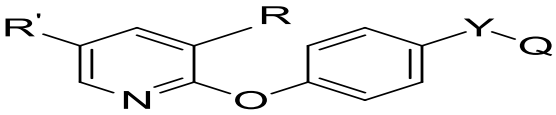



Fig.(20): General structure of phenoxypyridine

In conclusion, the kinetics of degradation of flonicamid followed the first order model being dependent upon its initial concentration. Overall, the degradation of the parent compound (flonicamid) resulted in lower molecular weight compounds containing electron-withdrawing groups or atoms. During the thermal degradation, the compound rendered 4 byproducts which may be attributed to the cleavage and rearrangement of side chain while the pyridine ring remained stable. The same stability of pyridine ring was observed during the acidic and alkaline hydrolysis of flonicamid. On the other hand, during the acidic and alkaline degradation, the molecule exhibited hydration and hydroxylation of the side chain via the excess H+ and OH- ions present in solution which facilitated its breakdown to smaller moieties. As well, the present of excess H+ in acidic hydrolysis media facilitated the substitution of pyridine ring H with Cl in C2 and C3 positions

### 3.6. Determination of flonicamid dissipation in soil sample.

Prior to the study of flonicamid degradation in soil, the physical and chemical characteristics of typical Egyptian soil were determined at the Soil, Water and Environment Research Institute (SWERI) in Giza, Egypt. Data in Table (11) indicate that the soil was clay-loam with low organic matter (1.92%). As well, the pH of the study soil was alkaline.

Table (11): Chemical, mechanical and physical properties of soil used in the Flonicamid dissipation study.

| **Chemical properties** | | | | |
|---|---|---|---|---|
| Organic matter % | | 1.92 | | |
| Soluble cations (meq./L) | $K^+$ | $Na^+$ | $Mg^{2+}$ | $Ca^{2+}$ |
| | 0.62 | 13.55 | 5.50 | 9.50 |
| Soluble anions (meq./L) | $SO_4^{2-}$ | $Cl^-$ | $HCO_3^-$ | $CO_3^{2-}$ |
| | 9.47 | 18.50 | 1.00 | --- |
| Available macro-elements (mg/Kg soil) | N | K | P | |
| | 138.00 | 183.00 | 8.34 | |
| Available micro-elements (mg/Kg soil) | Cu | Fe | Mn | Zn |
| | 0.046 | 0.876 | 0.342 | 0.152 |
| **Mechanical properties** | | | | |
| Soil texture | Clay % | | Silt % | Sand % |
| Clay | 89.52 | | 8.99 | 1.51 |
| **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 (12) demonstrated that during 5 days at ambient conditions, the active ingredient was reduced by 78.95% to reach a 100% loss after 7 days. This may be attributed to the soil alkaline pH and the exposure of soil to sunlight.

Table (12): Dissipation of flonicamid in clay-loam soil.

| Exposure Period (days) | Conc. of Flonicamid (µg/mL) | Decomp. Rate % |
|---|---|---|
| 0 | 97.08 | 0 |
| 1 | 83.78 | 13.70 |
| 3 | 50.82 | 47.65 |
| 5 | 20.44 | 78.95 |
| 7 | N.D. | 100 |
| 14 | N.D. | 100 |

N.D.: not detected

After pesticide application, light, temperature and precipitation played an important role in the dissipation of pesticides [12]. As well, the half-life and dissipation rate strongly depended upon the regional location, the lower the latitude. They also indicated that the half-life of flonicamid and its metabolites in soil was 2.12-7.97 days. Flonicamid significantly deteriorated in soil within the first two weeks of application due to evaporation and/or photodecomposition [25].

Flonicamid includes chromophores which absorb in UV-region at wavelengths >290 nm and hence were sensitive to direct photolysis by sunlight in the soil [24]. Organic matter such as manure may play a role in the degradation of flonicamid in soil. Yang et al. [26] indicated that role of microbial activity of A. faecalis CGMCC 17553 increased the degradation flonicamid in soil via hydrolysis and hydration of cyano-group insecticides. Varshavsky and Wu et al. [27-28] stated that amidases may be a major contributor towards the degradation of flonicamid in soil. Amidases catalyzes the hydrolysis of amides to their related carboxylic acid and ammonia, primarily by targeting the amide C-N bond. They concluded that Soil microbial activity and pesticide breakdown was largely linked to soil temperature. As well, Aizawa [8] indicated that the primary degradation pathway of flonicamid included the hydrolysis of cyano and carbamoyl moieties.

### 3.4.1. Kinetic study of flonicamid dissipation in soil

The kinetics of dissipation of flonicamid in clay-loam soil also followed first order kinetics similar to the previous degradation cases being dependent upon the initial concentration of the chemical. A plot of ln C versus time produced a straight line with an R2 coefficient of 0.94641 and a slope of (-k), where k is the degradation constant in day-1 (Fig. 21).

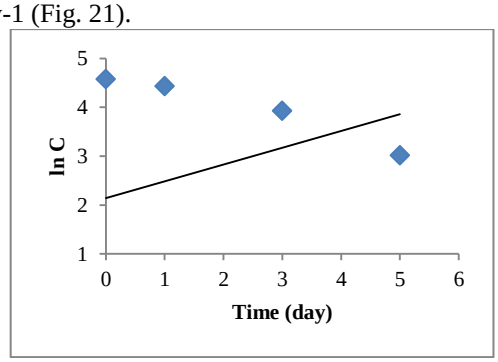



Fig. 21. A plot of ln C vs. time for the photolysis of flonicamid in clay-loam soil

The half-life of flonicamid degradation after application to clay-loam soil was found to be 2.46 days, (Table 13). The results are consistent with APVMA and Yang et al. [11-23] who illustrated that the active ingredient of flonicamid readily and quickly underwent microbial mediated destruction in aerobic soil. As well, it was reported that in cold weather, 50% dissipation times of flonicamid in North American and three European soils ranged between 0.7 to 1.8 days at 20°C.

Table (13): Kinetic parameters of flonicamid photolysis in clay-loam soil.

| Pesticide | Linear regression equation | $R^2$ coefficient | K value ($day^{-1}$) | $t_{1/2}$ (day) |
|---|---|---|---|---|
| Teppeki 50% WG | y = -0.28227x +4.57554 | 0.94641 | 0.28227 | 2.46 |

### 3.4.2. GC/MS identification of the degradation products of flonicamid in soil

A sample of the flonicamid containing soil was analyzed by GC/MS to identify the main degradation products and provide possible pathways for flonicamid degradation based upon Wiley and NIST mass spectral data bases. The identified degradation products, structure and masses are provided in Table (14).

The potential degradation pathway of flonicamid in clay-loam soil (Fig. 22) can be explained as follows.

•**(P1)** The formation of 4-(Trifluoromethyl)nicotinic acid may be a result of the hydrolysis of acetamide moiety.

•**(P2)** the hydrolysis of cyanomethyl and acetamide, facilitated the formation of 5-Nitro-4-(trifluoromethyl)pyridin-2-amine due to the replacement of cyanomethyl and acetamide by nitro groups at position 5, and amine at position 2 in the pyridine ring.

•**(P3)** The product 2-((trifluoromethyl) thio) acetonitrile formation in soil may be a result of the reaction of sulfur which is present in soil, with trifluoromethyl and acetonitrile.

•**(P4)** 2-Amino-4,6-dimethylnicotinamide, N'-acetyl may be due to hydrolysis of the acetonitrile group, loss of trifluoro, and rearrangement reactions of methyl groups at positions 4 and 6 in the pyridine ring.

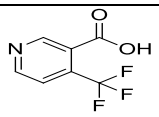
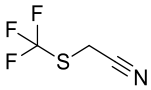
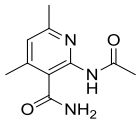
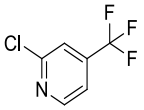
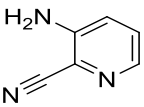
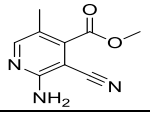
•**(P5)** The product 2-chloro-4-trifluoromethylpyridine was formed through the hydrolysis of cyanomethyl and acetamide and the binding of the chloride atom, which is present in soil with the pyridine ring at position 2.

•**(P6)** The formation of 3-amino-2-cyanopyridine was due to binding of cyano group to pyridine ring at position 2 and amine at position 3 after hydrolysis of acetamide and acetonitrile group at position 3 in the pyridine ring.

•(P7) The product 2-amino-3-cyano-5-methyl-isonicotinic acid methyl ester was formed as a result of binding of cyano group to pyridine ring at position 3 and amine at position 2 and methyl at position 5 after hydrolysis of acetamide to nicotinic acid and acetonitrile group at position 3 in the pyridine ring

.

Table (14): The identified degradation products of flonicamid photolysis in clay soil.

| Product | compound | RT (min) | Structure | m/z |
|---|---|---|---|---|
| **P1** | 4-(Trifluoromethyl)nicotinic acid | 16.09 |  | 191.0 |
| **P2** | 5-Nitro-4-(trifluoromethyl)pyridine -2-amine | 11.67 |  | 206.9 |
| **P3** | 2-((trifluoromethyl) thio)acetonitrile | 11.85 |  | 140.9 |
| **P4** | 2-Amino-4,6-dimethylnicotinamide, N'-acetyl | 18.56 |  | 206.8 |
| **P5** | 2-Chloro-4-trifluoromethylpyridine | 16.03 |  | 181.0 |
| **P6** | 3-Amino-2-cyanopyridine | 8.76 |  | 118.9 |
| **P7** | 2-Amino-3-cyano-5-methyl-isonicotinic acid methyl ester | 14.86 |  | 191.0 |

In comparison with the thermal and hydrolytic degradation of flonicamid, it was observed that dissipation of this chemical in soil effectively cleaved the pyridine ring. This may be attributed to the fact that macro and micro elements like S and Cl as well as the excess of N and P in soil tested played a role in this molecule transformation.

## 4. Conclusion:

In this study, the forced thermal and hydrolytic (acid and alkaline) degradation of flonicamid in its commercial formulation Teppeki 50% WG were

investigated. The results show that the active ingredient was significantly degraded (15.83%) during storage at 54°C after 14 weeks. However during the same period, the reduction at 35, 40, and 45°C was less ranging between 5- 10%, respectively.

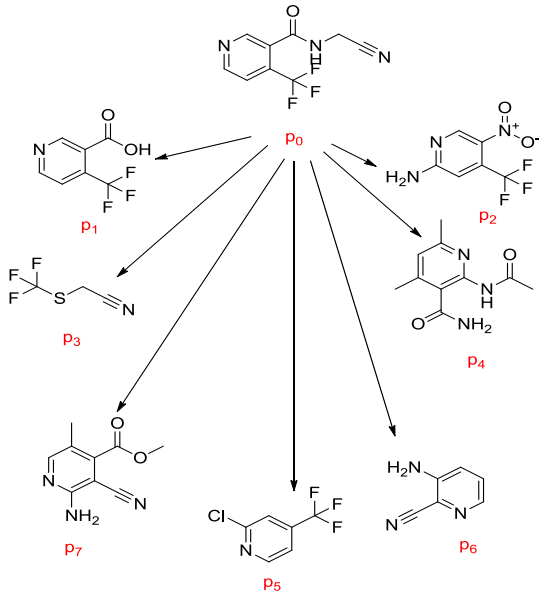



Fig. 22. The photolysis degradation pathway of flonicamid in clay-loam soil

Moreover, it was observed that the shelf-life during storage at 54°C was 1/3 that of its shelf- life during storage at 35°C. Acidic hydrolysis of flonicamid indicated that the shelf –life and half-life of the product increased in 1 N HCl to 18.65 and 252.05 days, respectively, which is almost 5 times that for 0.01 N HCl. On the other hand, the shelf –life and half-life in the alkaline hydrolysis of flonicamid process was reduced to 0.57 and 7.72 days, respectively. As well, increasing the alkaline content to 1 N NaOH further decreased these values to 0.07 and 0.95 days, respectively. Moreover, the half-life of flonicamid after application to local clay-loam soil (with pH 8.59) was found to be 2.46 days.

Generally, the kinetics of degradation of flonicamid followed the first order model being dependent upon its initial concentration. However, during the thermal degradation, the compound rendered 4 by-products which may be attributed to the cleavage and rearrangement of side chain while the pyridine ring remained stable. The stability of pyridine ring was observed during the acidic and alkaline hydrolysis of flonicamid. Essentially, during the acidic and alkaline degradation, the molecule exhibited hydration and hydroxylation of the side chain via the excess H+ and OH- ions in solution facilitated the breakdown of the parent molecule into smaller moieties. As well, the excess H+ in acidic hydrolysis media facilitated the substitution of pyridine ring H with Cl in C2 and C3 positions.

In comparison with the thermal and hydrolytic degradation by products, the dissipation of Flonicamid in soil effectively caused a cleavage of the pyridine ring. This may be attributed to the fact that macro and micro elements like S and Cl as well as the excess of N and P in soil tested played a role in this molecule transformation.

## 5. Conflicts of interest

"There are no conflicts to declare".

## 6. Acknowledgments

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