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Thermal Stability and Photolytic Degradation of Imazapic Herbicide in Technical and Soluble Concentrate Formulations

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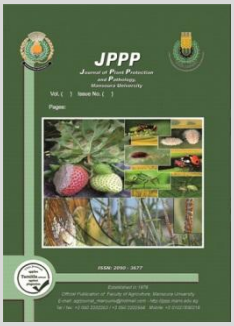

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ABSTRACT

This research analyzed the temperature and sunlight's impact on the stability and degradation kinetics of imazapic herbicide in its technical (TC) and soluble concentrate (SL) formulations, including identifying photodegradation intermediate products in the TC formulation. Samples were placed at 30, 45, and 54 °C for up to 336 hours and were directly exposed to sunlight for up to 144 hours. Degradation followed first-order kinetics; however, the SL formulation was more thermally stable than TC at all tested temperatures. The half-lives at 30°C were 577.5 hours for TC and 693 hours for SL, while at 54°C these values dropped to 65.38 hours for TC and 119.48 hours for SL. Photodegradation was much more pronounced, with half-lives of 15 hours for TC and 24.57 hours for SL. From imidazole ring breakup, GC-MS detected several photodegradation products that were formed mainly through decarbonylation and decarboxylation, for example: 4-*tert*-butyl-2-(3-hydroxy-5-methylpyridin-2-yl)-4-methyl-1*H*-imidazol-5(4*H*)-one, (*E*)-5-methyl-2-((3-methylbut-2-en-2-ylimino)methyl) nicotinic acid, and (*E*)-*N*-(1,2-dimethylprop-1-enyl)-1-(5-methyl-2-pyridyl)methanimine. These results promote the need for proper storage for imazapic formulations and suggest that specific components in the SL formulation counteracting thermal and photolytic degradation significantly improve stability.

Keywords: Imazapic, thermal degradation, photodegradation, GC-MS.

INTRODUCTION

Imazapic is one of the commonly used selective derived from the imidazolinone chemical family that targets weeds in cropped and uncropped areas. Due to its possible steady behavior and impact on ecosystems, the efficiency of the imazapic and its outcome has been times a question of interest. Environmental factors, particularly sunlight exposure and high temperatures entail high breakdown rates of imazapic and consequently high degradation product formation. Understanding these components is crucial to assessing its long-standing environmental behavior and the threats related to it. In Egypt, Imazapic is extensively used for controlling nutsedge species (*Cyperus spp*.), which pose serious problems in many crops, particularly peanuts. Imazapic acts as a selective systemic herbicide with marked activity on nutsedge. In Egypt, several registered commercial formulations of soluble concentrate imazapic are available at a concentration of 24%, with a recommended application rate of 100 milliliters per feddan (Egyptian acre) (APC, 2025). Imazapic contains pyridine with an elementary unit of imidazole leading to its stability in environmental conditions because of its chemical structure (Liu *et al.,* 2012). Imazapic is a post-emergence herbicide that is utilized for the selective removal of invasive grasses and specific broad-leaf plants in rangeland and agricultural land. Its effectiveness change depends on the rates of application, time of application, and the environment in which it is applied in the plant. Imazapic decreased the percentage cover of downy brome in rangeland communities but had similar effects on the establishment of seeded species (Morris *et al.,* 2009). Imazapic is an imidazolinone herbicide that passes through a degradation process under certain environmental conditions. It is also revealed that photolytic degradation is dependent on the pH level as the increasing of pH in the aqueous solutions enhances the rates of degradation (Norashikin *et al.,* 2017; Christiansen *et al.,* 2015). Based on the results, accelerated photodegradation occurs in solution than on soil with a half-live record of 85.56 days of photodegradation on the soil surface under sunlight (Norashikin *et al.,* 2017). The existence of natural organic material in solutions lowers photodegradation rates because of light shading impacts, in addition, imazapic degraded more quickly under 253.7 nm light than under 310 nm (Christiansen *et al.,* 2015). Photolysis leads to degradation imazapic, which produces several intermediates and is known to affect the environmental persistence of the herbicide; however, this study investigates the degradation in aqueous solutions where ultrahigh-resolution mass spectrometry identified multiple photoproducts derived from the transformation of the imidazole ring, and also elevated temperatures accelerate the breakdown of imazapic, and specifically the degradation rate was significantly increased at 40 °C (5.5×10^{-3} min^{-1}) compared to lower temperatures indicating that elevated temperatures will speed up the decomposition of the herbicide via higher rates of abiotic chemical reactions and microbial activity (Harir *et al.,* 2007). Imazapyr degradation rate is significantly enhanced at higher temperatures. As an example of such degradation, (Osajima *et al.,* 2008) demonstrated that rates of degradation increase spike 38% when the temperature is varied between 20°C and 50°C. Imazapic degradation is also influenced by soil factors: increasing temperature, soil pH, and moisture levels, and decreasing organic matter content causes the degradation rate to increase (Su *et al.,* 2019).

This study investigates the impact of varying temperature levels and sunlight exposure on the stability and degradation rate of imazapic in both its technical (TC) and soluble concentrate (SL) forms over different intervals by calculating half-lives. Additionally, the research seeks to identify certain photodegradation products of imazapic

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technical following direct sunlight exposure. The identification and quantification of imazapic and its degradation products were validated using high-performance liquid chromatography (HPLC) with external standard and gas chromatography-mass spectrometry (GC-MS).

MATERIALS AND METHODS

Chemicals

Imazapic PESTANAL®, an analytical standard, used in this study was purchased from Supelco® company and has a CAS registry number of [104098-48-8] and a purity of 98%. The technical 97% w/w imazapic used in the present study was obtained from Weifang Cynda Chemical Co., Ltd. – China while the imazapic 24% SL (w/v) formulation Sheto-Plus® is formulated in Egypt by Starchem Industrial Chemicals. The methanol used in this work was high-performance liquid chromatography for analysis grade, which was purchased from Merck. Imazapic chemical structure is described in Fig. 1 as follows:

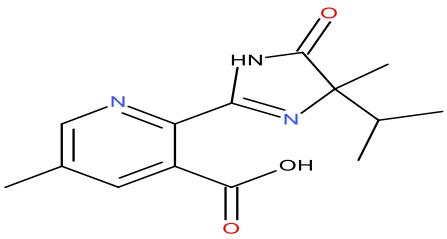


Fig. 1. Chemical structure of imazapic

Procedure

Imazapic technical 97% and imazapic formulation (Sheto-Plus® 24% SL (w/v)) were both prepared as stock solutions in methanol, with a concentration of 400 µg ml^{-1} each. The active ingredient is 400 micrograms per milliliter in one milliliter of methanol. After 1 milliliter of stock solution was added to Petri dishes and allowed to dry at room temperature, the dishes were subjected to the following conditions: first condition in a digital thermal oven at varying temperatures of 30, 45, and 54 ˚C for 1, 2, 4, 6, 12, 24, 48, 72, 96, 168 and 336 hours, second condition exposure to direct sunlight for 1, 2, 4, 6, 12, 24, 48, 72, and 96 hours. Quantitative methanol transfers were performed on all exposed and tested imazapic technical and formulation samples, and HPLC was used to assess the imazapic residue concentration.

Measurements

1. HPLC Determination

The protocol reported by (Christiansen *et al.,* 2015) was followed. The Agilent Technologies 1260 infinity II auto sampling system, which included a quaternary pump, column, and UV detector, was utilized to conduct high-performance liquid chromatography (HPLC) analyses. Phenomenex C_{18} chromatographic column with dimensions of 4.6 mm internal diameter, 250 mm length, and five µm was utilized to carry out the chromatographic separation. The ratio of acetonitrile to methanol to water for the mobile phase was 85:10:5= v/v/v, and the flow rate was 1 milliliter per minute. An ultraviolet (UV) detector with a wavelength of 235 nm was able to identify imazapic. The volume of the injection was five microliters. Under these circumstances, imazapic had a typical retention time of 2.832 minutes, and the standard for imazapic is depicted in Fig. 2. Excellent linearity was achieved within the range of 4-400 ng $µl^{-1}$ for the active ingredient, exhibiting a correlation coefficient of 0.99998, as illustrated in Fig. 3.

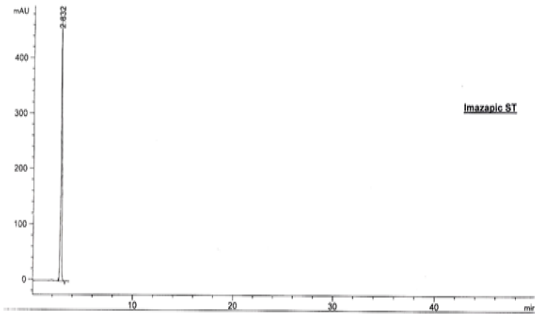
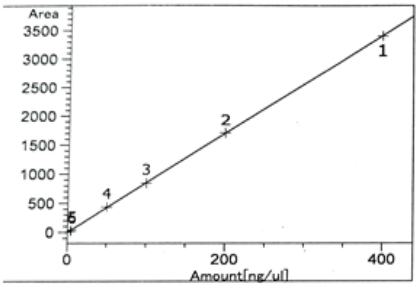


Fig. 2.Chromatogram of imazapic Standard

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Imazapic St at exp. RT: 2.832
VWD1 B, Wavelength=235 nm
Correlation:              0.99998
Residual Std. Dev.:       9.58708
Formula: y = mx + b
      m:        8.54017
      b:       -3.66283
      x: Amount[ng/ul]
      y: Area
```

Fig. 3. Standard calibration curve of imazapic using HPLC

2. GC-MS Conditions

A gas chromatograph (7890B) and a mass selective detector (5977A) from Agilent were used to carry out the analyses. The chromatographic system consisted of a 30 m x 0.25 mm I.D., fused silica capillary column (HP-5MS) film thickness of 0.25 µm and an interface. At a rate of approximately 1.0 ml/min, helium was introduced into the carrier gas pulsed split mode. The injection was a precise 1 µl volume. Gas chromatography temperature was ramped at 10 °C per minute from 50 °C for half a minute, then held at 190 °C for half a minute. An increase in heat rate to 10°C/min was then applied, starting at 300°C and keeping it there for 2 minutes. This analytical procedure was completed in 29.5 minutes. The injector was 280 °C. The Wiley Library of mass spectra was searched to index the mass spectra.

3. Kinetic study

According to (Harir *et al.,* 2007 and El-Dars *et al.,* 2023), the assumption of first-order kinetics in the concentration of herbicide allowed the calculation of the half-life of imazapic using the corresponding kinetic equation. We used the first-order rate equation to find the degradation rate constants and half-lives:

$$C_t = C_0 e^{-kt}$$

C_t is the pesticide concentration at time t, C_0 is the concentration at the start, and k is the degradation rate constant in (days-1). We calculated the k value by plotting the logarithm of concentration against time and using the k value to calculate the half-life ($t_{0.5}$) according to the following equation:

$$t_{0.5} = Ln\ (0.5)/k$$

RESULTS AND DISCUSSION

Thermal and photodegradation kinetics of imazapic formulations.

Imazapic was assessed in both technical (TC) and soluble (SL) formulations for thermal and photodegradation under varying temperature conditions as well as with direct sunlight exposure. Important mechanistic outlines can be drawn about the stability profiles and environmental degradation kinetics of this herbicide in relation to its storage, handling, and field application practices.

1. Thermal stability of imazapic at different temperatures

Technical Concentrate (TC) formulation

Table 1 and Fig. 4 show the experiment results, which confirm the thermal stability of imazapic in the technical concentrate (TC) formulation.

Table 1. Thermal stability of imazapic TC at different temperatures.

Exposure time (h)	30 °C		45 °C		54 °C	
	µg**	Loss %	µg	Loss %	µg	Loss %
0*	400 ±1	0	400 ±1	0	400 ±1	0
1	399.5 ±0.61	0.125	399.15 ±0.76	0.21	395.78 ±0.72	1.06
2	398.99 ±0.77	0.25	398.3 ±0.97	0.42	390.6 ±1.00	2.35
4	396.59 ±0.86	0.85	394.61 ±1.05	1.35	387.38 ±0.83	3.15
6	394.99 ±0.81	1.25	391.93 ±1.01	2.02	372.34 ±1.06	6.92
12	393.65 ±0.96	1.59	387.92 ±0.81	3.02	356.19 ±0.81	10.95
24	385.1 ±0.75	3.73	383.09 ±0.51	4.23	315.1 ±1.04	21.23
48	378.55 ±0.78	5.36	365.18 ±0.91	8.71	243.41 ±0.86	39.15
72	362.34 ±1.07	9.42	341.2 ±0.81	14.7	188.38 ±1.08	52.91
96	357.47 ±0.89	10.63	328.12 ±1.05	17.97	148.49 ±0.97	62.88
168	325.76 ±0.50	18.56	276.81 ±0.67	30.8	65.33 ±0.85	83.67
336	262.04 ±0.95	34.49	195.74 ±0.95	51.06	11.33 ±0.71	97.17
$t_{0.5}$ (h)***	577.5		330		65.38	

*: Samples were collected directly after the quantitative transfer (zero time)

: Each value represents an average of three replicates: mean or average and STDEV. $t_{0.5}$*: Half-life value

It was evaluated over a period of 336 hours and tested at three different temperatures: 30°C, 45°C, and 54°C. At 30°C, only 3.73% loss was measured after 24 hours, which would be gradual degradation, and a cumulative loss of 34.49% after 336 hours, indicating a half-life of 577.5 hours. At 45°C, the degradation was accelerated with 51.06% loss after 336 hours, giving a half-life of 330 hours. The most significant degradation occurred at 54°C, whereby at the end of the experiment, 97.17% of the active ingredient was degraded, yielding a half-life of only 65.38 hours. This pattern indicates that the imazapic TC is sensitive to increased temperatures, showing non-linear increased degradation rates with higher temperatures.

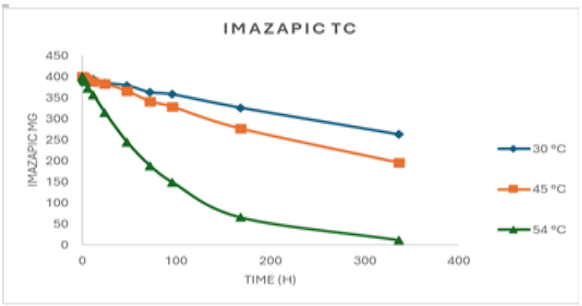


Fig. 4. Thermal degradation of imazapic TC

Soluble Concentrate (SL) formulation

The soluble concentrate (SL) formulation outperformed TC in thermal stability at all tested temperatures, which are displayed in Table 2 and Fig. 5.

Table 2. Thermal stability of imazapic SL at different temperatures.

Exposure time (h)	30 °C		45 °C		54 °C	
	µg**	Loss %	µg	Loss %	µg	Loss %
0*	400 ±1	0	400 ±1	0	400 ±1	0
1	399.6 ±0.19	0.1	399.38 ±0.83	0.16	397.67 ±0.57	0.58
2	399.21 ±0.64	0.2	398.77 ±0.56	0.31	395.36 ±0.96	1.16
4	397.42 ±0.56	0.65	395.54 ±1.03	1.12	390.77 ±0.59	2.31
6	395.64 ±0.70	1.09	394.32 ±0.33	1.42	384.23 ±0.55	3.94
12	393.28 ±0.81	1.68	391.67 ±0.92	2.08	375.94 ±0.42	6.02
24	387.62 ±0.95	3.1	382.47 ±0.68	4.38	337.71 ±0.27	15.57
48	385.47 ±0.73	3.63	377.46 ±0.76	5.64	307.26 ±0.60	23.19
72	374.53 ±0.64	6.37	360.96 ±0.75	9.76	267.75 ±0.62	33.06
96	365.79 ±0.70	8.55	341.95 ±0.64	14.51	225.4 ±0.83	43.65
168	335.81 ±0.60	16.05	315.7 ±0.43	21.08	156.03 ±1.04	60.99
336	286.98 ±0.80	28.26	238.24 ±0.37	40.44	56.27 ±0.66	85.93
$t_{0.5}$ (h)***	693		462		119.48	

*: Samples were collected directly after the quantitative transfer (zero time)

: Each value represents an average of three replicates: mean or average and STDEV. $t_{0.5}$*: Half-life value

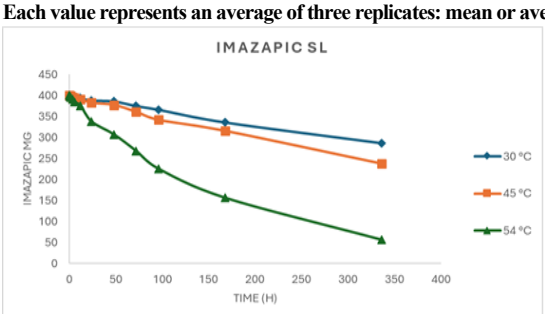


Fig. 5. Thermal degradation of imazapic SL

At 30°C, SL only suffered 28.26% degradation in 336 hours, corresponding to a half-life of 693 hours. Degradation increased to 40.44% at 45°C after the same duration, with a half-life of 462 hours. At 54°C, 85.93% degradation resulted in a half-life of 119.48 hours. The longer half-lives associated with SL indicate protective impacts of formulation additives against thermal degradation, likely through stabilization of the active ingredient or diminished molecular collisions involving the reacting molecules.

Stability comparison between the different formulations

As described in the previous sub-chapter, the Imazapic degradation in both TC and SL formulations at 30, 45, and 54 °C was evaluated using first-order kinetics based on the linear relationship between the logarithm of remaining concentration versus time, as shown in Figs. 6 and 7.

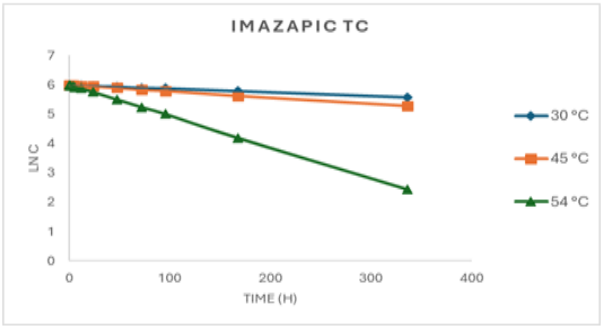


Fig. 6. First-order rate plot of thermal degradation for imazapic TC

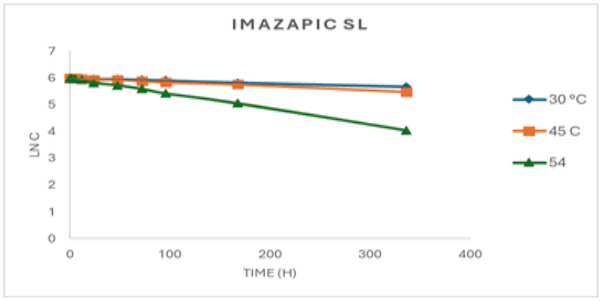


Fig. 7. First-order rate plot of thermal degradation for imazapic SL

Both formulations showed a considerable increase in degradation with higher temperatures, but the change was more significant for the TC formulation. After 336 hours (14 days) at 54 °C, the TC formulation lost 97.17% of the Imazapic, and the SL formulation lost 85.93%. The observed considerable differences in the degradation rate between the two formulations at high temperatures demonstrate the formulation compositional impact on the stability of herbicides during adverse storage conditions.

Remarkably, the difference between the stability of SL and TC increases further with temperature. As an example, the ratio of half-life for SL and TC at 30 °C is about 1.2 (693/577.5), but at 54 °C, this ratio has increased to about 1.8 (119.48/65.38). This indicates that the protective factors of the SL formulation are more pronounced at higher temperatures, possibly because higher temperatures limit solvents' molecular mobility or reduce exposure to degradative factors. These differences can be explained by the compositional components of the SL preparation, which seem to offer some shielding against thermal and photolytic degradation. The concentrated soluble formulation usually has surfactants, stabilizers, or other formulation ingredients that protect the active substance from direct exposure to factors that lead to its degradation or change the matrix around the active molecule.

Our results corroborate with (Su *et al.,* 2019) who noted that the environmental factors have an impact on the thermal degradation of imazapic. Increased temperatures enhance the rate of imazapic degradation; also, (Harir *et al.,* 2007) reported that imazapic degradation rates were much higher at 40°C compared to 25°C and 30°C, suggesting some form of seasonal temperature-dependent variation in the risk of pesticide accumulation.

1. Photodegradation from imazapic direct sunlight exposure

Compared to heat exposure, the effect of direct sunlight on imazapic accelerated degradation nearly twofold for both formulations. As highlighted in Table 3 and illustrated in Fig. 8, the half-life of the TC formulation under direct sunlight was heavily diminished to 15 hours. In contrast, the SL formulation showed a slightly longer half-life of 24.57 hours after 96 hours of continuous sunlight exposure. This remarkable photosensitivity indicates that imazapic is subject to swift photolytic degradation, likely via photochemical pathways including direct photolysis and indirect photodegradation by reactive oxygen species.

Table 3. Photodegradation of Imazapic TC and SL upon exposure to sunlight light

Exposure time (h)	TC		SL	
	µg**	Loss %	µg	Loss %
0*	400 ±1	0	400 ±1	0
1	380.05 ±0.63	4.99	388.95 ±0.35	2.76
2	361.1 ±0.80	9.73	380.21 ±0.94	4.95
4	325.98 ±0.71	18.51	355.61 ±0.83	11.1
6	291.28 ±0.44	27.18	332.13 ±0.55	16.97
12	219.5 ±0.81	45.13	280.83 ±1.10	29.79
24	117.18 ±0.68	70.71	210.25 ±0.88	47.44
48	34.33 ±0.79	91.42	101.29 ±0.90	74.68
72	10.06 ±0.96	97.49	57.25 ±0.97	85.69
96	6.23 ±0.76	98.44	25.19 ±0.82	93.7
$t_{0.5}$ (h)***	15		24.57	

*: Samples were collected directly after the quantitative transfer (zero time)

: Each value represents an average of three replicates: mean or average and STDEV. $t_{0.5}$*: Half-life value

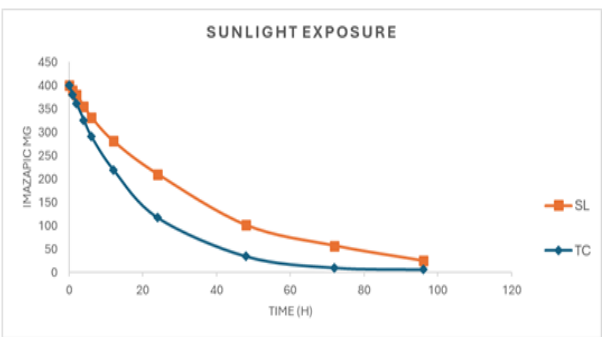


Fig. 8. Photodegradation of Imazapic TC and SL.

The degradation trend under the sunlight revealed that with 24-hour exposure time, the TC formulation lost 70.71% of its initial concentration, whereas the SL formulation was reduced by 47.44%. At 72 hours, TC formulation was almost entirely degraded (97.49% loss), while SL formulation retained roughly 14.31% of the initial concentration. This difference in photostability suggests that SL formulation provides some degree of protective photodegradation, perhaps due to some light-absorbing or radical-scavenging matrix ingredients.

Like thermal degradation, the photodegradation of both formulations also obeyed first-order kinetics as shown

in Fig. 9, albeit with much greater rate constants at all investigated temperatures. This suggests that the efficacy of imazapic treatment may depend on timing and environmental factors. The significant photodegradation rate indicates that many photochemical processes are likely to occur, including direct photolysis of the imidazolinone ring, photo-oxidation events, and/or the photochemical generation of reactive intermediates. The slight advantage of the SL formulation in terms of photostability might be due to the light scattering effects of the components that reduce light access to the active component while in solution. This difference in formulation is attributed to components of SLs, such as auxiliary additives, surfactants, or even antioxidants, stabilizing the active substance. SL structure could mitigate photon penetration by forming physical shields or micelles that encapsulate imazapic molecules. However, this protection accounts for the photostability difference, evidencing the SL formulation's longer half-life under sunlight (24.57 h versus 15 h for TC).

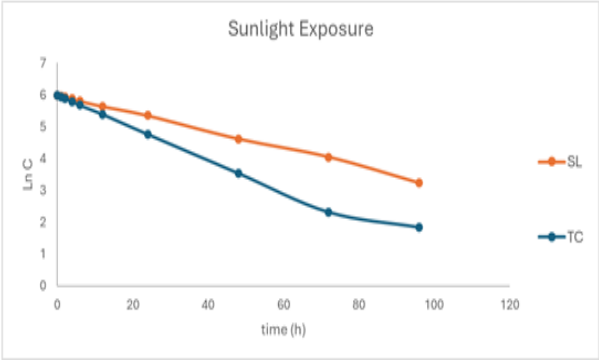


Fig. 9. First-order rate plot of the photodegradation for imazapic TC and SL

In the formulation of pesticides, surfactants and auxiliary additives are essential because they improve stability and effectiveness. They may increase biological activity by changing the spray droplet dynamics and improving the uptake and translocation of the active constituents (Katagi, 2008). Certain surfactants can also shield pesticides from undergoing photodegradation, thus markedly increasing their half-life. Regardless, the selection of surfactants remains essential because some may act to increase photodegradation (Johnson & Dureja, 2002).

The protective effects of the formulation are temperature dependent, with SL exhibiting more stability benefits at intermediate temperatures (30-45°C). Still, less pronounced protective effects at severe heat (54°C) suggest that protective additives may increase or decrease photolytic degradation than thermal degradation of SL formulations. Their SL formulation makes photostable field operations possible by absorbing UV radiation and stabilizing the molecules simultaneously. On the other hand, TC formulation doesn't contain any surfactants or auxiliary additives to protect them from the effects of sunlight exposure or heat, so TC formulations must be stored indoors and protected from heat and direct sunlight due to their usage in SL manufacturing.

The results obtained are compatible with several investigators (Norashikin *et al.,* 2017, Christiansen *et al.,* 2015, and Harir *et al.,* 2007). They reported that photodegradation of imazapic is significantly influenced and become faster by environmental factors such as pH, light wavelength, exposure to direct sunlight and differences in temperatures, also photolysis leads to degradation imazapic, which produces multiple photoproducts derived from the transformation of the imidazole ring, and also elevated temperatures accelerate the breakdown of imazapic.

3. Identification of the photodegradation products of imazapic TC by GC-MS

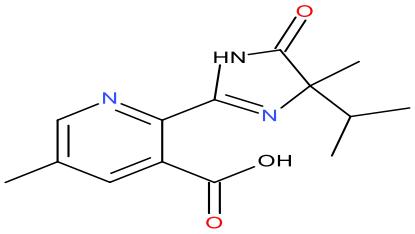
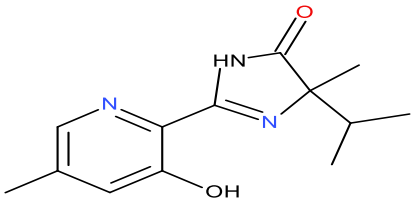
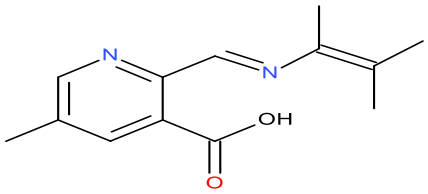
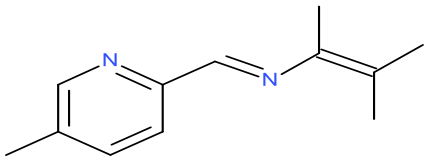
Imazapic TC was photodegraded under the sun to mimic conditions typical in agriculture. Analyzed results showed that imazapic could be photolytically transformed using direct sunlight, which correlates with other studies on imidazolinone herbicides. The photoproducts of imazapic were identified and characterized along with imazapic using gas chromatography-mass spectrometry (GC-MS). Many photodegradation products were found and characterized according to their retention times and mass spectra. Mass spectral analysis made it possible to suggest structures for the most important primary photodegradation products. The structural transformation of imazapic seems to be mainly in the procedures on the imidazole ring, which is in agreement with other works that studied photolytic pathways of imazapic through ultrahigh resolution mass spectrometry.

Characteristic ions at m/z 275, 249 [M^++2], 232, and 190 [M^++2] corresponded to the molecular ions of imazapic, 4-*tert*-butyl-2-(3-hydroxy-5-methylpyridin-2-yl)-4-methyl-1*H*-imidazol-5(4*H*)-one, (*E*)-5-methyl-2-((3-methylbut-2-en-2-ylimino)methyl) nicotinic acid, and (*E*)-*N*-(1,2-dimethylprop-1-enyl)-1-(5-methyl-2-pyridyl)methanimine. However, Table 4 indicates the identification of the photodegradation products of imazapic TC by GC-MS.

By examining the chemical structure of imazapic, it is observed that imazapic has carboxylic acid group that is easy to break by photolysis via decarbonylation process to give 4-*tert*-butyl-2- (3-hydroxy-5-methylpyridin-2-yl)- 4-methyl- 1 *H*-imidazol - 5(4*H*)-one m/z, 249 [M^++2]. The photolytic transformation of imazapic predominantly involves the breakdown of the imidazole moiety, which is the functional group responsible for its herbicidal activity to obtain (*E*)-5-methyl-2-((3-methylbut-2-en-2-ylimino)methyl) nicotinic acid m/z, 232, followed by another transformation via decarboxylation process to give (*E*)-*N*-(1,2-dimethylprop-1-enyl)-1-(5-methyl-2-pyridyl)methanimine m/z, 190 [M^++2]. Based on the result, it can be concluded that photodegradation minimizes the biological potency of the compound's activity in systems under solar radiation. Regarding the pathways that lead to the photodegradation of imazapic, we agreed with earlier studies focusing on imidazolinone herbicides (Christiansen *et al.,* 2015; Harir *et al.,* 2007). They reported that imazapic degraded by photolysis to several photoproducts via decarbonylation, cleavage of the imidazole ring leading to the formation of pyridine derivatives, and the decarboxylation process.

Fig. 10 elucidates the above reactions by illustrating the potential photodegradation pathways of imazapic TC.

Table 4. Identification of the photodegradation products of imazapic TC by GC-MS

Structure	RT(min)	Characteristic ions (m/z)
	22.82	$[M]^+$ =275,257,231,214,188,163,145,119,92 imazapic
	18.81	$[M]^+$ =249 $[M^+$+2],231,216,188,160,146,119,92 4-*tert*-butyl-2-(3-hydroxy-5-methylpyridin-2-yl)-4-methyl-1*H*-imidazol-5(4*H*)-one
	18.16	$[M]^+$ =232, 216, 188,160,119,92 (*E*)-5-methyl-2-((3-methylbut-2-en-2-ylimino)methyl) nicotinic acid
	17.32	$[M]^+$ =190 $[M^+$+2], 161,135,120,93 (*E*)-*N*-(1,2-dimethylprop-1-enyl)-1-(5-methyl-2-pyridyl)methanimine

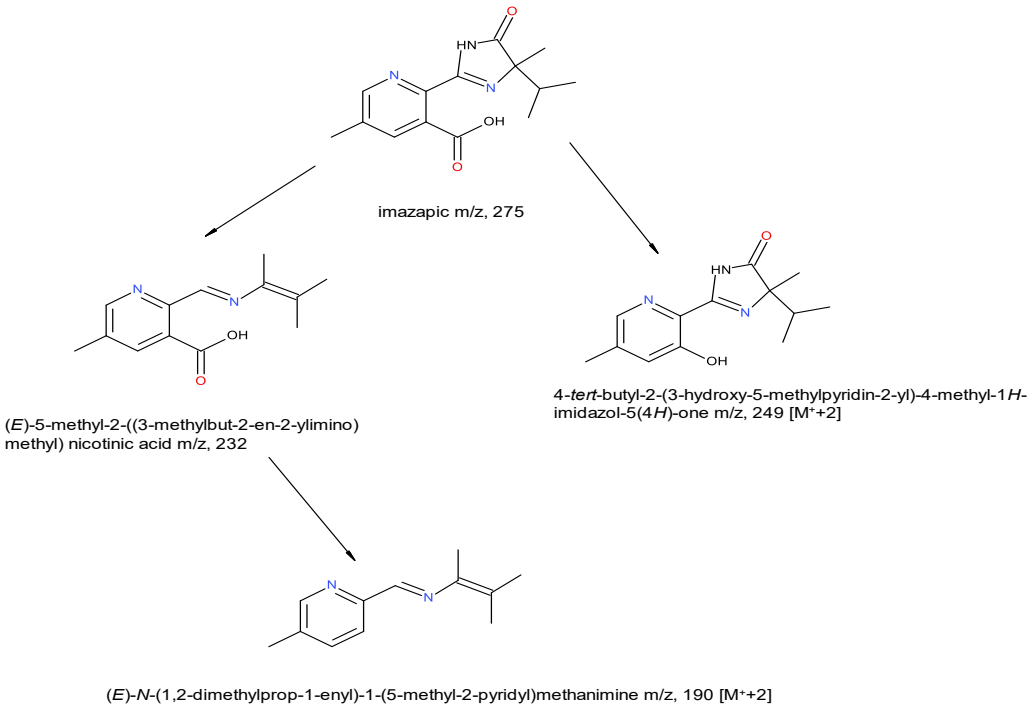


Fig. 10. The possible photodegradation pathways of imazapic TC

CONCLUSION

The study investigated the thermal and photolytic stability of the imazapic herbicide in its technical (TC) and soluble concentrate (SL) formulations. As the temperature increased from 30°C to 45°C and then to 54°C, the difference in stability between SL and TC narrowed, with SL consistently surpassing TC in stability at all tested temperatures. The half-life ratio of SL to TC increased from 1.2 at 30°C to 1.8 at 54°C. Both formulations, especially TC,

were photodegraded substantially more than thermally degraded. The half-lives of TC and SL were 15 and 24.57, respectively, when they were exposed to sunlight. With 72 hours of direct sunlight, TC lost 97.49% of its concentration while SL lost 85.69%. This illustrates how formulation additives effectively reduce thermal and photodegradation for the SL formulation. Gas Chromatography-Mass Spectrometry (GC-MS) studies show that the principal paths of photolytic destruction involve breaking the imidazole ring through decarbonylation and decarboxylation pathways. These findings are crucial concerning the storage, handling, and application of imazapic, demonstrating that design focus needs to enhance stability under such environmental conditions. Further research needs to be done to develop strategies to improve the stability of imazapic under severe environmental conditions, analyze the impact degradation products would have on the environment, and identify potential ecological consequences.

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الثبات الحرارى والتحطم الضوئى لمبيد الحشائش إيمازابيك في الصورة الخام والمركزة القابلة للذوبان

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الملخص

حللت هذه الدراسة تأثير درجة الحرارة وأشعة الشمس على استقرار وسرعة تحطم مبيد الأعشاب إيمازابيك في صورته الخام (TC) وصورتة المجهزة المركزه القابلة للذوبان (SL)، بما في ذلك تحديد نواتج التحطم الناتجة عن التحلل الضوئي للخام TC. تم وضع العينات عند درجات حرارة ٣٠ و٤٥ و٥٤ درجة مئوية لمدة تصل إلى ٣٣٦ ساعة، وتم تعريضها مباشرة لأشعة الشمس لمدة تصل إلى ١٤٤ ساعة. يتبع التحلل كينتيك من الدرجة الأولى؛ ومع ذلك، كانت صورة SL أكثر استقرارًا حراريًا من TC عند جميع درجات الحرارة المختبرة. كانت فترة نصف العمر عند ٣٠ درجة مئوية ٥٧٧,٥ ساعة للخام TC و٦٩٣ ساعة للصورة SL، بينما عند ٥٤ درجة مئوية انخفضت هذه القيم إلى ٦٥,٣٨ ساعة للخام TC و١١٩,٤٨ ساعة للصورة SL. كان التحلل الضوئي أكثر وضوحًا، حيث كانت فترة نصف العمر ١٥ ساعة للخام TC و٢٤,٥٧ ساعة للصورة SL. من خلال كسر حلقة الإيميدازول، تم الكشف عن عدة منتجات تحلل ضوئي باستخدام تقنية الكروماتوغرافيا الغازية - مطياف الكتلة (GC-MS) التي تشكلت أساسًا من خلال إزالة الكربونيل وإزالة الكربوكسيل، على سبيل المثال:-2-(3-hydroxy-5-methylpyridin-2-yl)-4-*tert*-butyl-2-(*E*)-*N*-(1,2-dimethylprop-1-enyl)-1-(5-(*E*)-5-methyl-2-((3-methylbut-2-en-2-ylimino)methyl) nicotinic acid-yl)-4-methyl-1*H*-imidazol-5(4*H*)-one methyl-2-pyridyl)methanimine تعزز هذه النتائج الحاجة إلى التخزين المناسب لصور إيمازابيك وتقترح أن مركبات معينة فى تركيب صورة SL هى التي تقاوم التحلل الحراري والضوئي وتحسن الاستقرار بشكل كبير.