OPEN ACCESS

Kashf Journal of Multidisciplinary Research
Vol: 02 - Issue 08 (2025)
P-ISSN: 3007-1992 E-ISSN: 3007-200X
https://kjmr.com.pk

PHOTOCATALYTIC DEGRADATION OF IMIDACLOPRID PESTICIDE USING UV LIGHT, H_2O_2, HNO_3, AND TIO_2 IN AGRICULTURAL SAMPLES FROM SUKKUR AND SHIKARPUR, PAKISTAN

[1]Sanaullah Ansari*, [2]Mushtaque Ali Jakhrani

[1, 2]Institute of Chemistry, Shah Abdul Latif University, Khairpur, Sindh, Pakistan

****Corresponding author:*** sanaullah.ansari@salu.edu.pk

DOI Url: https://doi.org/10.71146/kjmr585

Article Info

Abstract

The extensive use of pesticides in agriculture has raised significant environmental concerns due to their adverse effects and persistence on ecosystems and human health. Imidacloprid, a widely used neonicotinoid insecticide, is frequently detected in soil, water, and food commodities, particularly in intensively farmed regions. This study investigates the photocatalytic degradation of imidacloprid under laboratory conditions using ultraviolet (UV) radiation alone and in combination with H_2O_2, HNO_3, and TiO_2 catalysts. Standard solutions (10–50 ppm) were used, and field samples collected from the agricultural districts of Sukkur and Shikarpur, Pakistan, were subjected to photolytic, photo-oxidative, and photocatalytic treatments. UV-Vis spectroscopy was employed to monitor degradation, while GC-MS analysis confirmed the fragmentation of imidacloprid into less toxic by-products such as 6-chloronicotinic acid, desnitro-imidacloprid, and formyl guanidine. Among all treatments, UV/TiO_2 and UV/HNO_3 exhibited the highest efficiency in pesticide degradation compared to UV alone. The findings demonstrate that photocatalytic processes can significantly accelerate the degradation of persistent pesticides in contaminated agricultural environments. This study provides valuable insights into the application of advanced oxidation processes (AOPs) for sustainable pesticide remediation strategies in developing agricultural regions.

Keywords:

Imidacloprid, Photocatalysis, UV Degradation, Pesticide Residues, Advanced Oxidation Processes, GC-MS.

1. Introduction

The growing demand for agricultural productivity has resulted in the extensive use of pesticides, particularly in developing countries where pest infestations significantly affect most of the crop yields. While pesticides such as imidacloprid are effective against a broad range of insects, their excessive and indiscriminate use contributes to bioaccumulation and environmental contamination (Tudi et al., 2021). Imidacloprid, a neonicotinoid pesticide, has gained global attention due to its high-water solubility, persistence in water and soil, and potential ecological hazards, making it a pesticide of global concern (Kumar, Kaur, Sud, Saini, & Bansal, 2023).

Modern agriculture depends heavily on pesticides, and these chemicals can leave behind harmful residues that pose a risk to people and ecosystems. Imidacloprid is a neonicotinoid insecticide and is popularly known for its heavy use in vegetable farming in Pakistan, especially in the Sukkur and Shikarpur regions. The combination of high agricultural pesticide use, coupled with the region's warm climate, increases the risk of pesticide residues in water and soil. The development of effective degradation techniques, such as photocatalysis, involving UV radiation with catalysts like titanium dioxide (TiO_2), provides sustainable options for mitigating pesticide pollution. This study aims to evaluate the photocatalytic degradation efficiency of Imidacloprid under varying operational parameters.

In Pakistan, agriculture is fundamental for the economy, and the use of pesticides is prominent in the agricultural regions of Sukkur and Shikarpur. The widespread application of neonicotinoids poses significant health and ecological challenges, particularly for non-target species like pollinators and aquatic organisms. There is growing concern in the literature regarding the need for effective policies to reduce the neonicotinoid pollution of agricultural soils and water in Pakistan (Zhang et al., 2023).

Advanced oxidation processes, and particularly photocatalysis, give promising outcomes for the effective removal of pesticides. Their effectiveness is based on the formation of very active hydroxyl radicals, which oxidize complicated organic molecules to simpler and less harmful materials (Khader et al., 2024). Pesticide and other recalcitrant pollutants' photocatalytic degradation can be achieved through UV light, TiO_2, and oxidants like H_2O_2 and HNO_3 (El Sharkawy, Shawky, Elshypany, & Selim, 2023).

This study aims to evaluate the effectiveness of photocatalytic degradation of imidacloprid in field-collected vegetable samples from Sukkur and Shikarpur. The study evaluates UV alone, UV + H_2O_2, UV + HNO_3 (photo-oxidative), and UV + TiO_2 (photocatalytic) to assess the difference in treatment approaches. The results are expected to enhance the effectiveness of localized policies tailored to agricultural needs.

2. Materials and Methods

2.1. Chemicals

The standard of imidacloprid was obtained from a well-known American chemical industry, Med Chem Express (MCE), NJ, USA. Solvents and reagents used during the study were analytical-grade which including hydrogen peroxide, nitric acid, and titanium dioxide, which were purchased from a reputable company, Merck, Germany. The Field samples were collected from the agricultural areas in the Sukkur and Shikarpur districts of Pakistan.

2.2. Study Area

The study was conducted in the regions of Sukkur and Shikarpur districts (Figure 1), which are one of the major agricultural zones in Pakistan. These areas heavily depend upon pesticide use in vegetable farming, raising concerns regarding residues produced by pesticides in water and soil. Due to the conditions of climate, accumulation of pesticides, irrigation practices, and intensive agriculture pose significant risks to both the environment and human health. Investigation of the photocatalytic degradation of imidacloprid in these regions is essential for the development of effective and locally adapted remediation strategies.

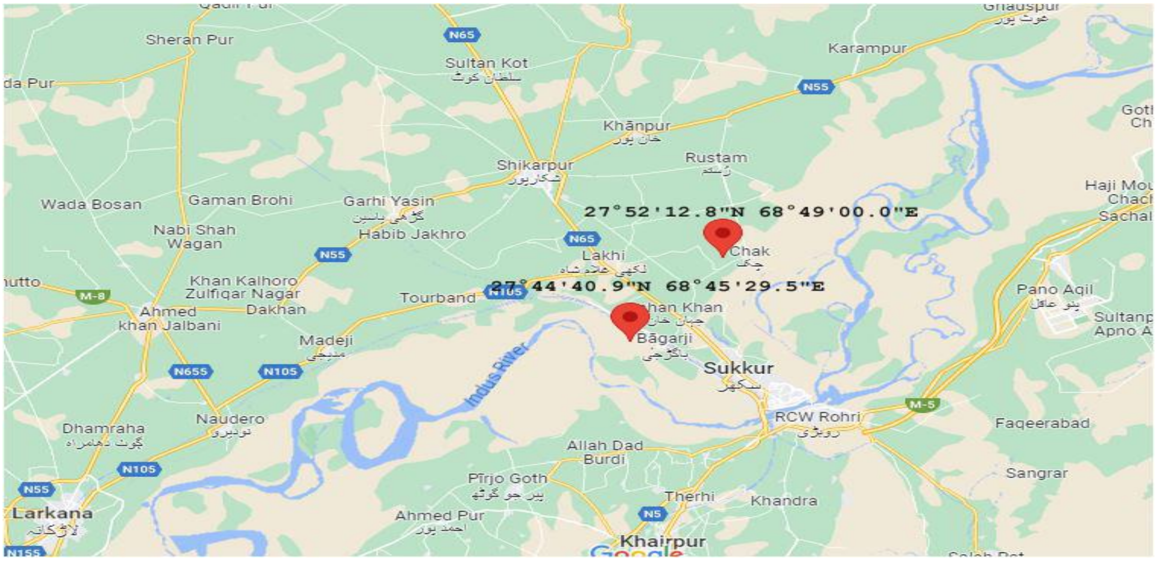


Fig. 1 Map of the Sampling sites

2.3. Preparation of Standards and Sample

Standard imidacloprid solutions with concentrations of 10, 20, 30, 40, and 50 ppm were prepared by dissolving 0.01 g, 0.02 g, 0.03 g, 0.04 g, and 0.05 g, respectively, in deionized water to make a final volume of 1000 mL. These standards were used for optimization experiments with 125 W UV lamps. Experimental treatments included pesticide concentrations of 10–50 ppm, combined with different doses of oxidants/catalysts: 0.2, 0.4, 0.6, and 0.8 mL of 30% H_2O_2; 0.2, 0.4, 0.6, and 0.8 mL of 65% HNO_3; and 0.2, 0.4, 0.6, and 0.8 g of TiO_2.

Field samples (Brinjal and Lady-finger) were collected before and after one day of pesticide spraying from vegetable fields in Sukkur and Shikarpur districts. Distinct sampling zones were identified, and samples were collected using clean containers, gloves, and zip-lock bags to prevent contamination. Sampling points were selected randomly to ensure representativeness. Samples were collected in triplicate from each site to calculate mean values. Each sample was properly coded and essential details were recorded, including date and location, and stored under cooled conditions during transport to the laboratory. All laboratory analyses were performed following established safety protocols, including the use of protective clothing, gloves, and masks (Iqbal, Maqbool, Perveez, Farooq, & Rafique Asi, 2009).

2.4. Extraction of Pesticide Residues from Vegetables

Vegetable samples were chopped into small pieces, homogenized to obtain a uniform mixture, and weighed. A 1:1 mixture of methanol and acetone was added to the homogenate in a beaker and stirred for 30 minutes for extraction of pesticide residues. The mixture was then centrifuged to separate the solid plant portion from the solvent (containing pesticides). The supernatants were filtered through research grade filter paper, and the concentration of extract was achieved through rotary evaporator.

The concentrated extract was characterized with a UV-Visible spectrophotometer for quantification of imidacloprid residues. Calibration curves (Figure 2) were established using imidacloprid standards. Degradation studies were then conducted following a developed method (Ansari & Jakhrani, 2022).

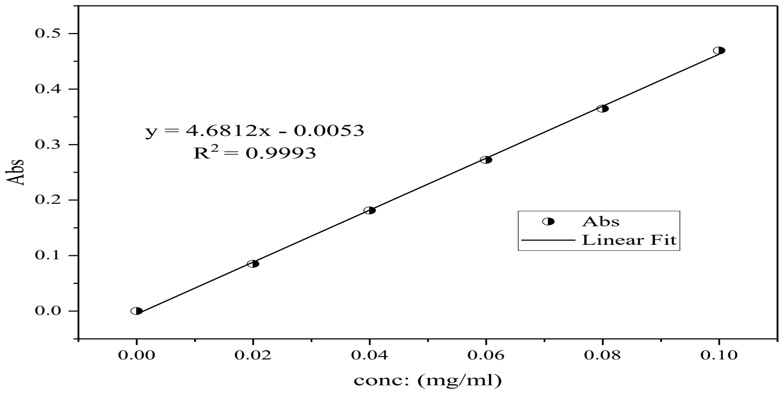


Fig. 2 Calibration of the pesticide Imidacloprid

2.5. Degradation Experiments

A laboratory-scale reactor (1 L glass vessel) was used to evaluate the effectiveness of UV light, with and without TiO_2, H_2O_2, and HNO_3, on imidacloprid degradation in aqueous solutions. Ultraviolet radiation was provided by a low-pressure mercury lamp (125 W), placed at the center of the reactor within a protective quartz tube to enhance photocatalytic action (Yari, Seidmohammadi, Khazaei, Bhatnagar, & Leili, 2019).

Four treatment processes were tested:

- UV (125 W) photolysis
- UV (125 W) + H_2O_2 photo-oxidation
- UV (125 W) + HNO_3 photo-oxidation
- UV (125 W) + TiO_2 photocatalysis

These treatments were compared to assess the influence of different oxidants and catalysts on degradation efficiency.

2.6. Characterization

2.6.1. UV-Visible Spectrophotometry

Degradation of imidacloprid was monitored at different time intervals (1, 2, 3 hours, etc.) using a UV-Vis spectrophotometer. Measurements were taken in 1 × 1 cm quartz cuvettes, with ultrapure water as the reference. Spectra were recorded in the range 200–400 nm, and 20 nm/min (scanning rate) using UV software Win-Lab. Initial absorption maxima were recorded before treatment, and subsequent measurements tracked changes in absorption to determine degradation efficiency (Safni, Jumiaty, & Aziz, 2021).

2.6.2. GC-MS Spectrometry

Further identification of degradation products was carried out using GC-MS (Shimadzu). A moderately polar capillary column (5% phenyl-methyl polysiloxane) was used (30 m length, 0.25 µm film thickness, and 0.25 mm internal diameter). Helium gas served as the carrier gas with a flow rate of 1.0 mL/min. The starting temperature of the program was 50°C, ramped at 10–20°C/min, and held for 10 minutes at 300°C. Injections (1 µL) were made in split-less mode at a temperature of 250°C. The MS operated with a scan speed of 476 with a scan range of 50–1500 m/z. Compound identification was performed using NIST pesticide-specific libraries (Sani, Bakar, Rahman, & Abas, 2020).

3. Results and Discussion

3.1 UV-Vis Spectrophotometric Analysis

Figure 3a shows the Lambda max of Imidacloprid 20 ppm Standard at 295 nm, while Figures 3b, c, d, and e illustrate the absorbance spectra changes of Imidacloprid field samples over degradation time. The decline in absorbance at 295 nm confirmed the degradation process under different photocatalytic treatments.

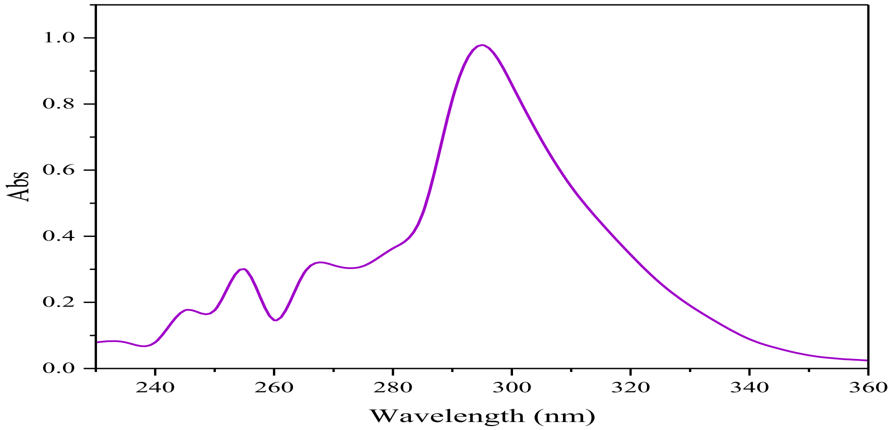


Fig. 3a Lambda max of pesticide Imidacloprid (20 ppm) at 295 nm

3.2 Photocatalytic Degradation Efficiency

Among all tested conditions, the combination of a 125 W UV lamp with TiO_2 and HNO_3 demonstrated the highest degradation rates, due to enhanced generation of reactive oxygen species, facilitating pesticide breakdown. Comparative analysis indicated the ranking of degradation efficacy as: UV + TiO_2 > UV + HNO_3 > UV + H_2O_2 > UV alone (Figures 3b, c, d, and e).

The results of this study reveal that imidacloprid degradation was strongly influenced by the applied treatment method. Photolysis using UV light alone achieved only moderate degradation, consistent with previous reports highlighting the limited efficiency of UV irradiation due to the stability of imidacloprid's molecular structure. However, when combined with oxidants or catalysts, the degradation rate significantly increased.

The UV/H_2O_2 system exhibited enhanced degradation due to the generation of hydroxyl radicals through H_2O_2 photolysis. Similarly, UV/HNO_3 provided oxidative conditions; its efficiency was comparatively higher. The UV/TiO_2 photocatalytic system demonstrated the highest degradation efficiency, in line with previous studies on TiO_2-mediated photocatalysis of neonicotinoids. The synergistic effect of UV light and TiO_2 facilitated electron-hole pair formation, producing reactive oxygen species that accelerated pesticide breakdown.

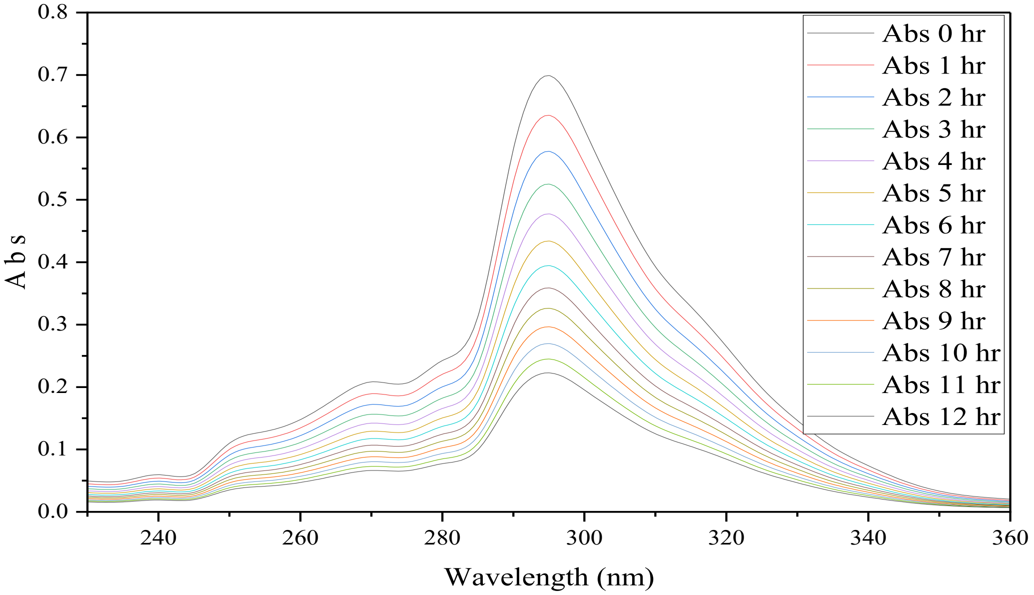


Fig. 3b Field Samples of Imidacloprid pesticide degraded with 125 W UV alone at 295 nm

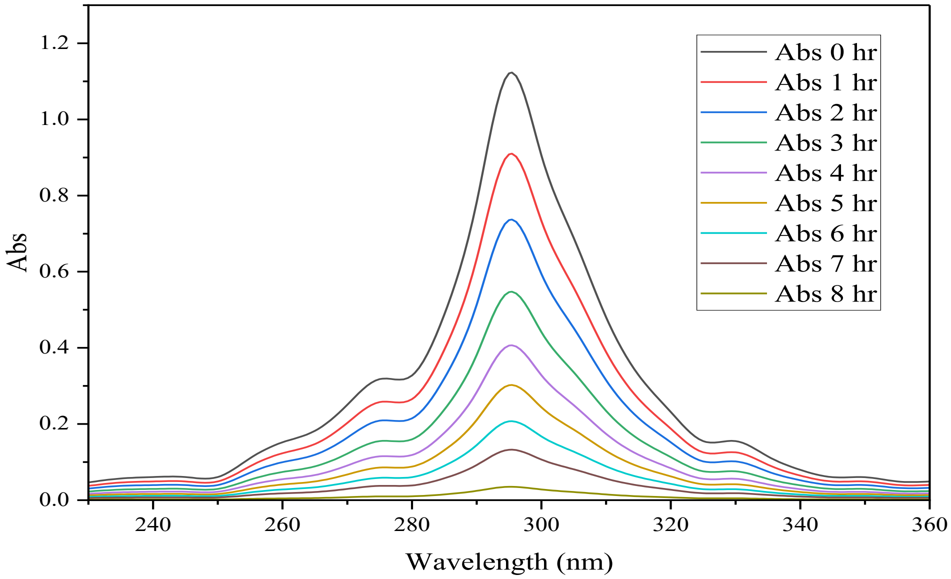


Fig. 3c Field Samples of Imidacloprid pesticide degraded with 125 W UV/H_2O_2 at 295 nm

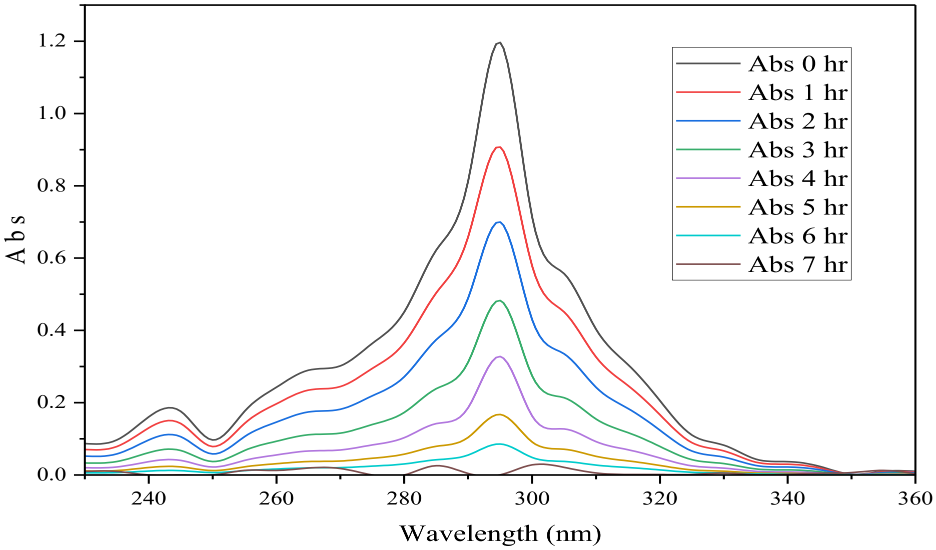


Fig. 3d Field Samples of Imidacloprid pesticide degraded with 125 W UV/HNO_3 at 295 nm

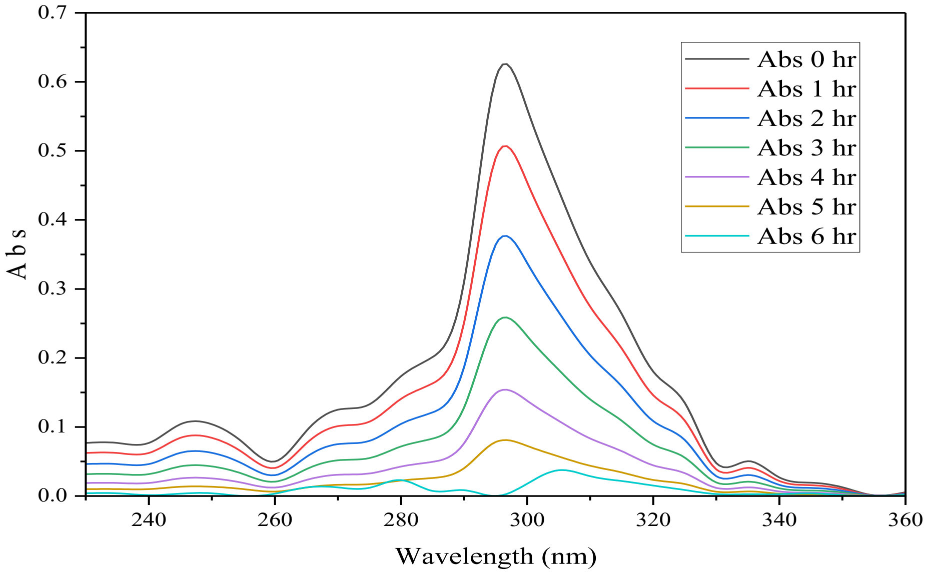


Fig. 3e Field Samples of Imidacloprid pesticide degraded with 125 W UV/TiO_2 at 295 nm

3.3 GC-MS Identification of Degradation Products

Figures 4a and 4b show the GC and MS spectra of imidacloprid before degradation. Mass spectra and GC-MS chromatograms of treated samples revealed distinct degradation patterns depending on the applied process. Under UV irradiation alone, degradation products such as 6-chloronicotinic acid, desnitro-imidacloprid, oxalyl chloride, and a small fraction of undegraded imidacloprid were detected (Figures 5a–5e). Treatment with UV light and H_2O_2 produced formyl guanidine, 2-chloronicotinic acid, desnitro-imidacloprid, imidazolidine, along with minor amounts of undegraded imidacloprid (Figures 6a–6f). Similarly, UV combined with HNO_3 yielded nitrosoguanidine, formyl guanidine, 6-chloronicotinic acid, and imidazolidine (Figures 7a–7e). In contrast, UV irradiation with TiO_2 generated nitroguanidine, hydroxyproline, and 6-chloronicotinic acid as the major products (Figures 8a–8d). These degradation products were confirmed by their molecular weights and fragmentation patterns. Collectively, the findings indicate that imidacloprid undergoes breakdown into less toxic intermediates through a stepwise degradation pathway involving hydroxylation, de-chlorination, and cleavage of the nitroguanidine moiety. Although these intermediates are less persistent than the parent compound, additional mineralization studies are required to confirm complete detoxification.

Importantly, field samples from Sukkur and Shikarpur showed similar degradation trends to laboratory standards, indicating the practical applicability of these AOPs in real agricultural settings. This highlights the potential of photocatalytic treatments as cost-effective and environmentally friendly solutions for mitigating pesticide contamination in developing countries.

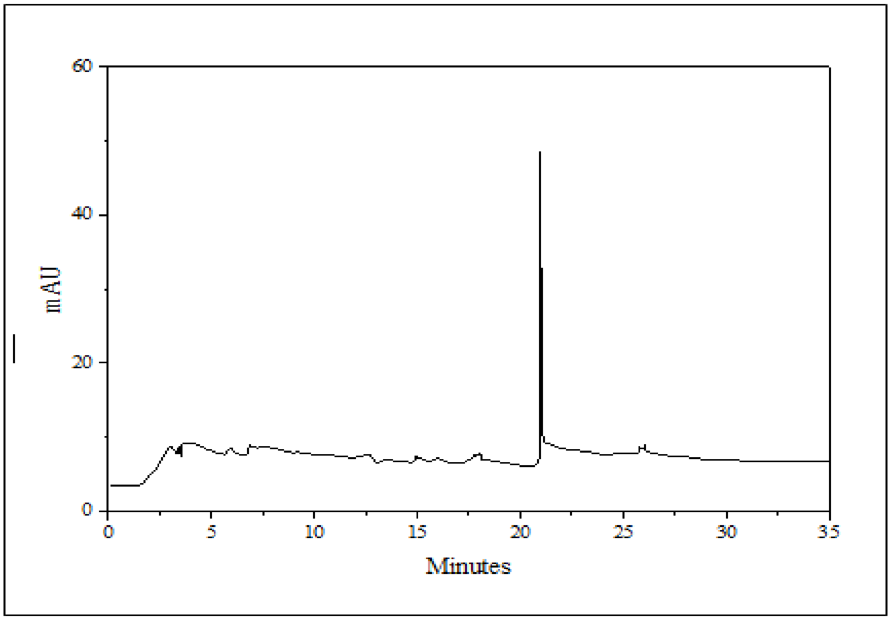
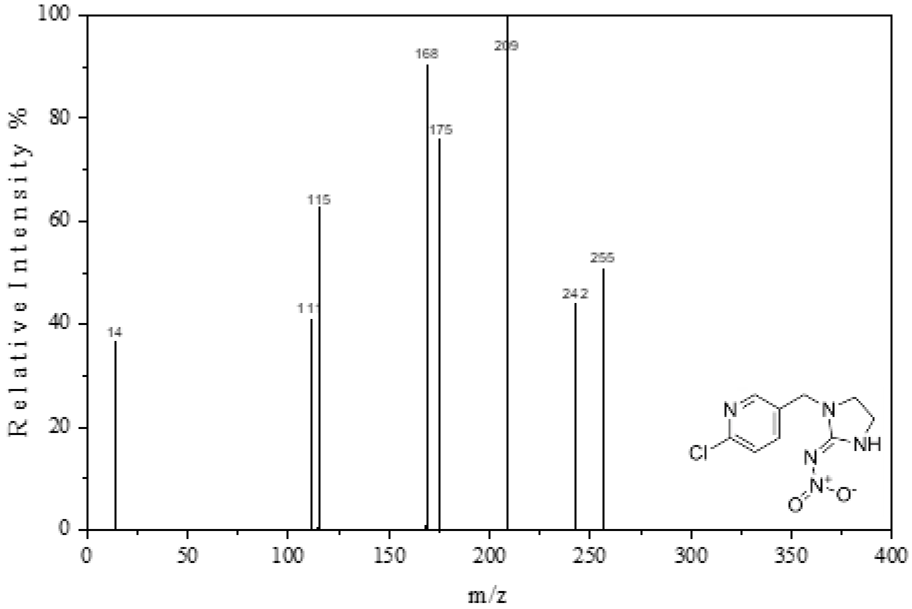


Fig. 4a GC chromatogram of Imidacloprid before process of degradation



Imidacloprid

255.5 g/mol

$C_9H_{10}ClN_5O_2$

Fig. 4b MS spectrum of Imidacloprid before process of degradation

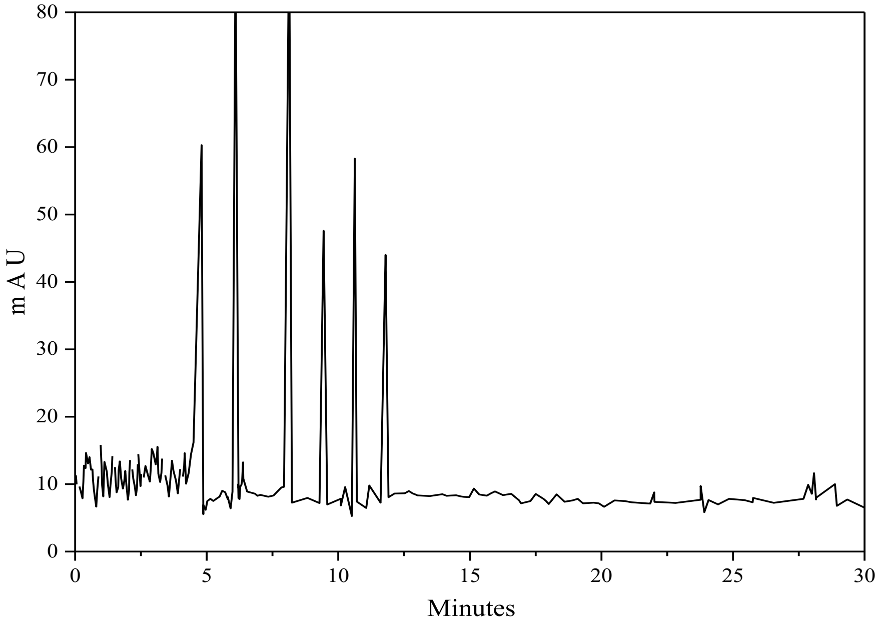
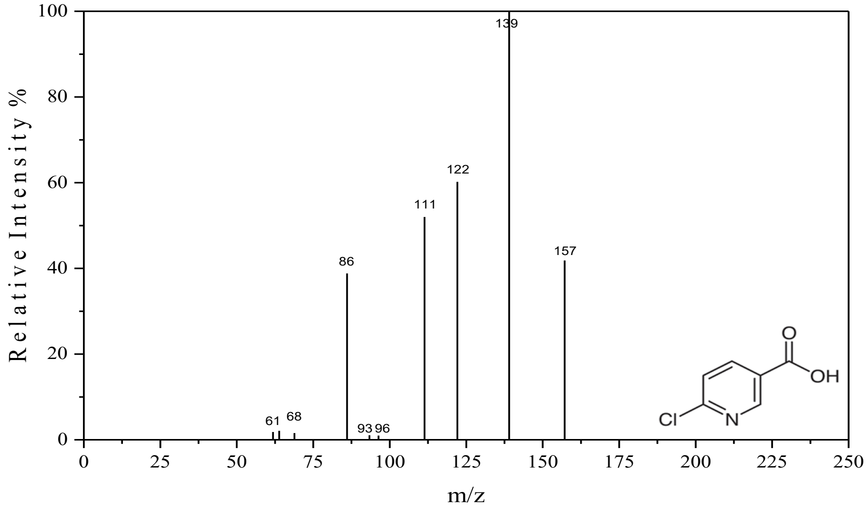


Fig. 5a GC chromatogram of degraded Imidacloprid Field Samples with 125 W UV alone

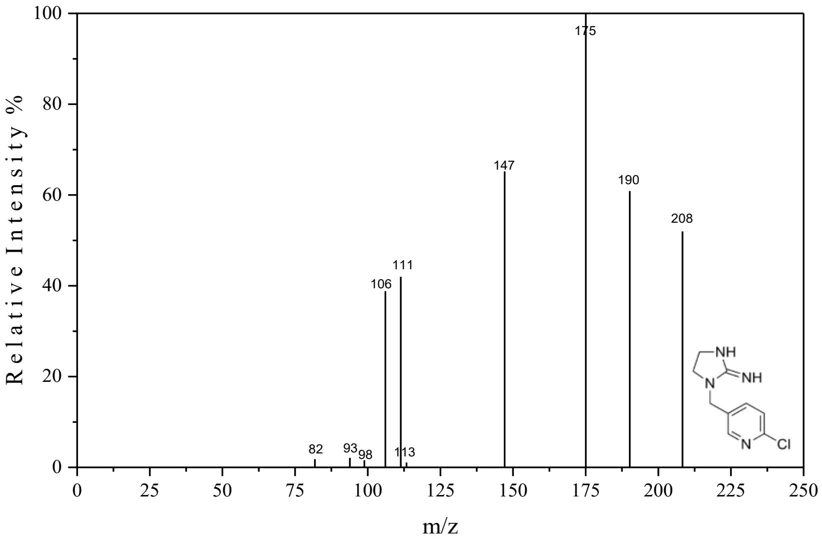


6-chloronicotinic acid

157.5 g/mol

$C_6H_4ClNO_2$

Fig. 5b MS spectrum-1 of degraded Imidacloprid Field Samples with 125 W UV

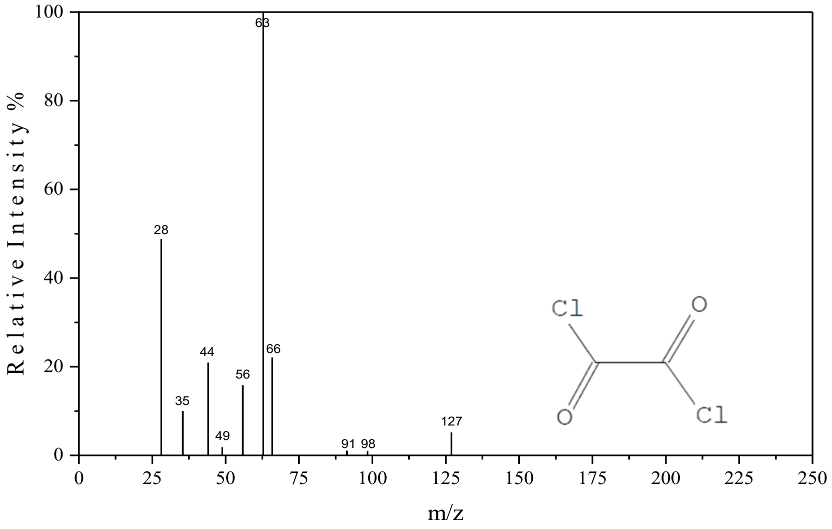


Desnitro-imidacloprid

208.5 g/mol

$C_9H_9ClN_4$

Fig. 5c MS spectrum-2 of degraded Imidacloprid Field Samples with 125 W UV

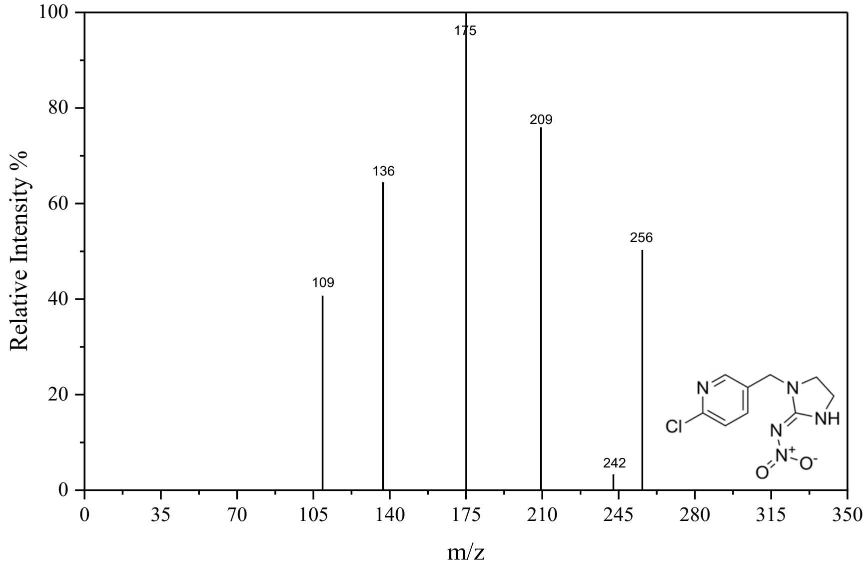


Oxalyl Chloride

127 g/mol

$C_2Cl_2O_2$

Fig. 5d MS spectrum-3 of degraded Imidacloprid Field Samples with 125 W UV



Imidacloprid $_{\text{(undegraded)}}$

255.5 g/mol

$C_9H_{10}ClN_5O_2$

Fig. 5e MS spectrum-4 of degraded Imidacloprid Field Samples with 125 W UV

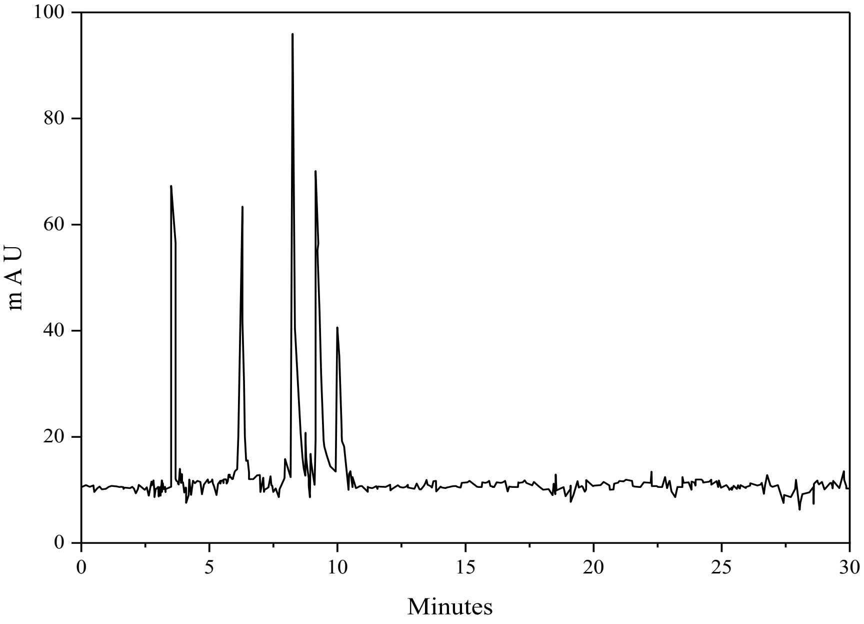
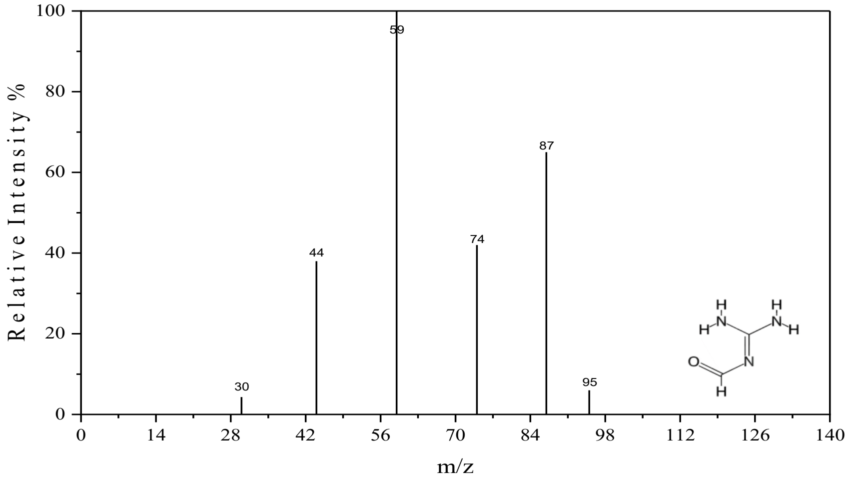


Fig. 6a GC chromatogram of degraded Imidacloprid Field Samples with 125 W UV/H_2O_2

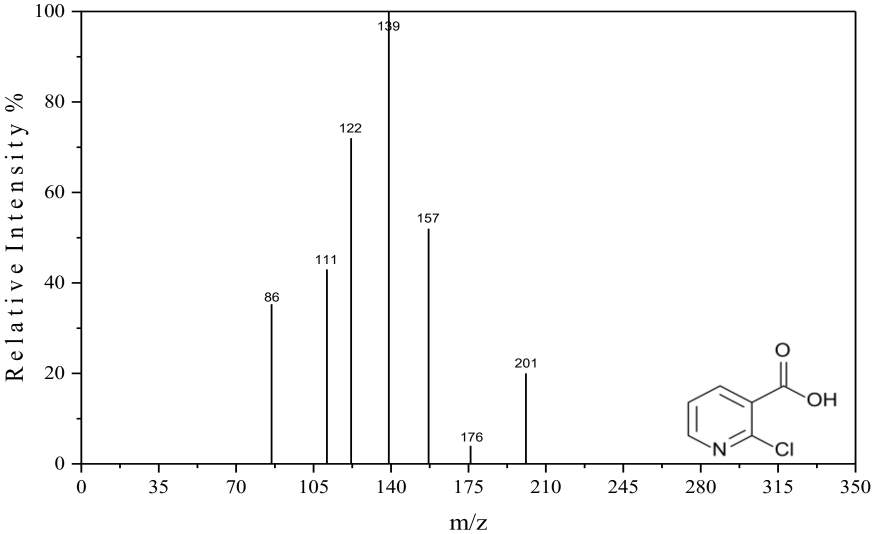


Formyl guanidine

87 g/mol

$C_2H_5N_3O$

Fig. 6b MS spectrum-1 of degraded Imidacloprid Field Samples with 125 W UV/H_2O_2

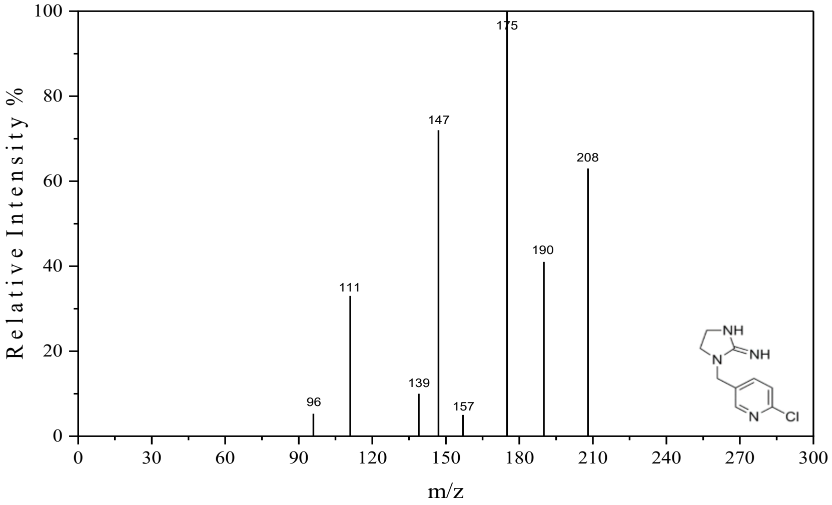


2-chloronicotinic acid

157.5 g/mol

$C_6H_4ClNO_2$

Fig. 6c MS spectrum-2 of degraded Imidacloprid Field Samples with 125W UV/H_2O_2

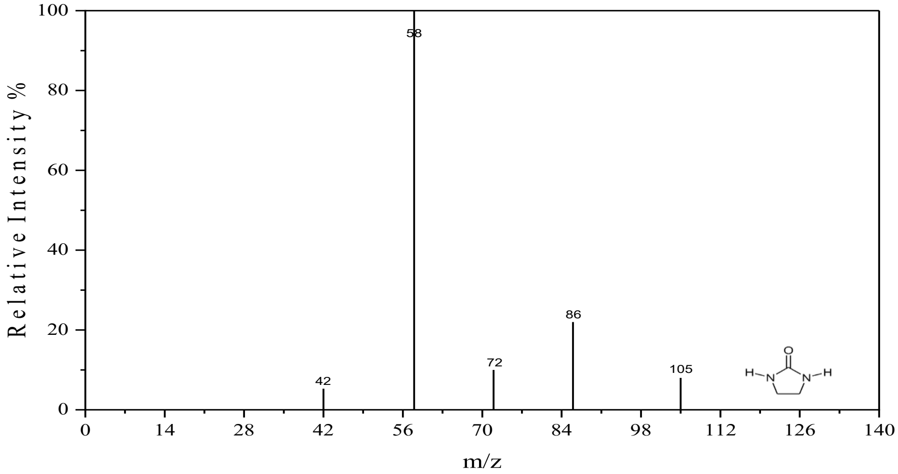


Desnitro-imidacloprid

208.5 g/mol

$C_9H_9ClN_4$

Fig. 6d MS spectrum-3 of degraded Imidacloprid Field Samples with 125 W UV/H_2O_2

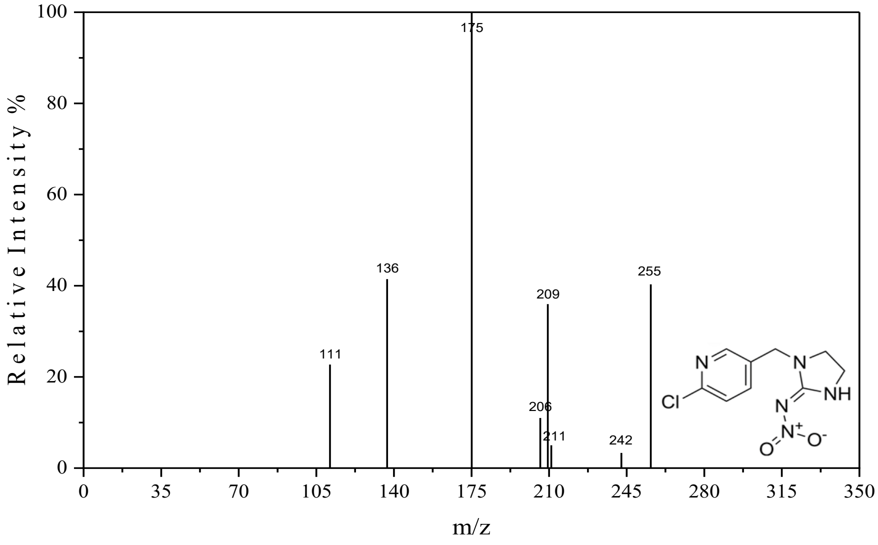


Imidazolidine

72 g/mol

$C_3H_8N_2$

Fig. 6e MS spectrum-4 of degraded Imidacloprid Field Samples with 125 W UV/H_2O_2



Imidacloprid (undegraded)

255.5 g/mol

$C_9H_{10}ClN_5O_2$

Fig. 6f MS spectrum-5 of degraded Imidacloprid Field Samples with 125 W UV/H_2O_2

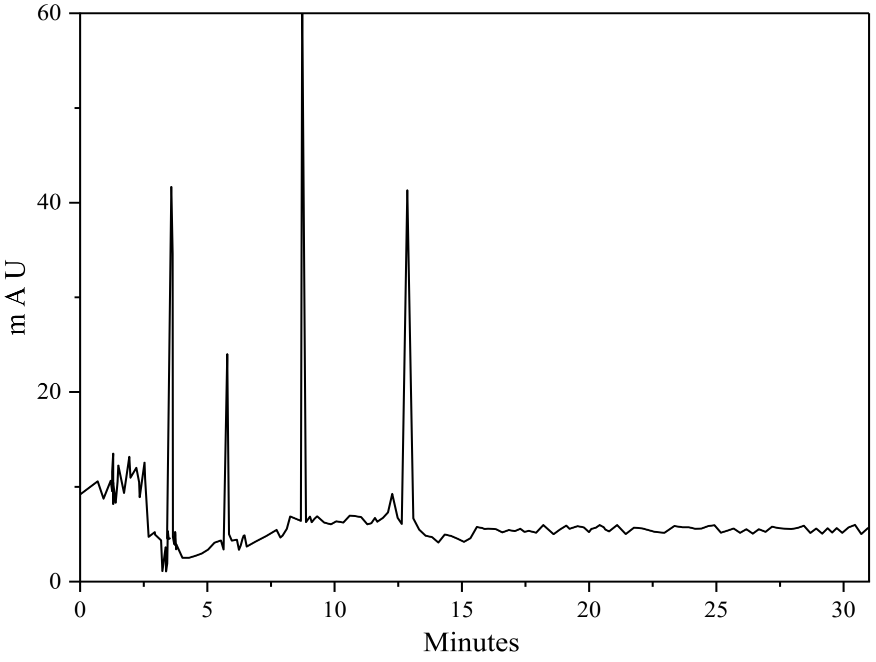
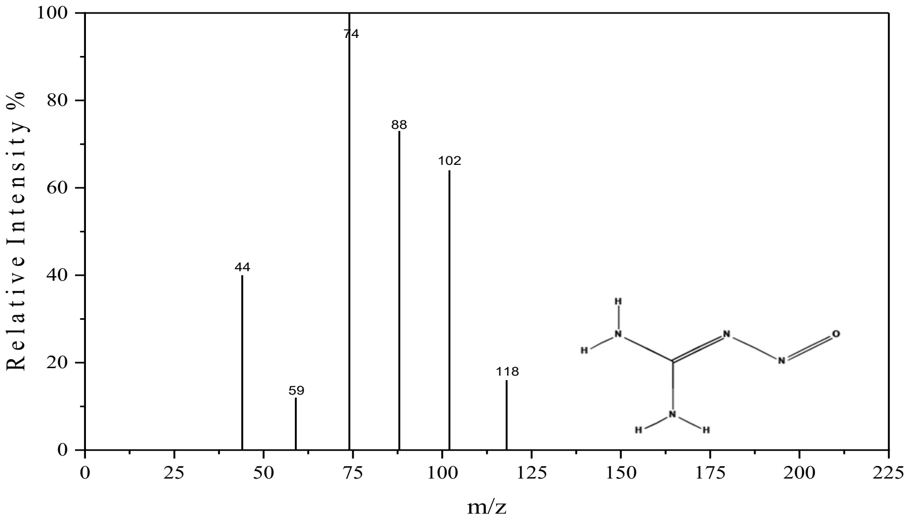


Fig. 7a GC chromatogram of degraded Imidacloprid Field Samples with 125 W UV/HNO_3

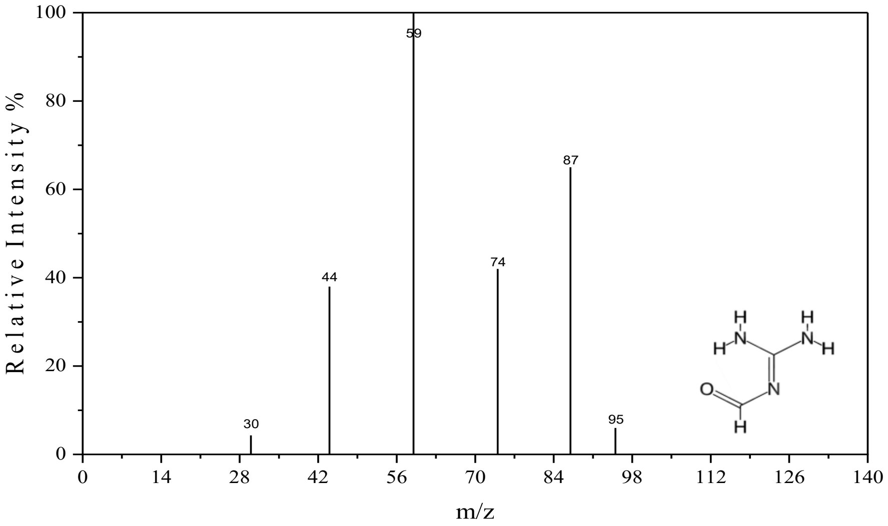


Nitrosoguanidine

88 g/mol

CH_4N_4O

Fig. 7b MS spectrum-1 of degraded Imidacloprid Field Samples with 125 W UV/HNO₃

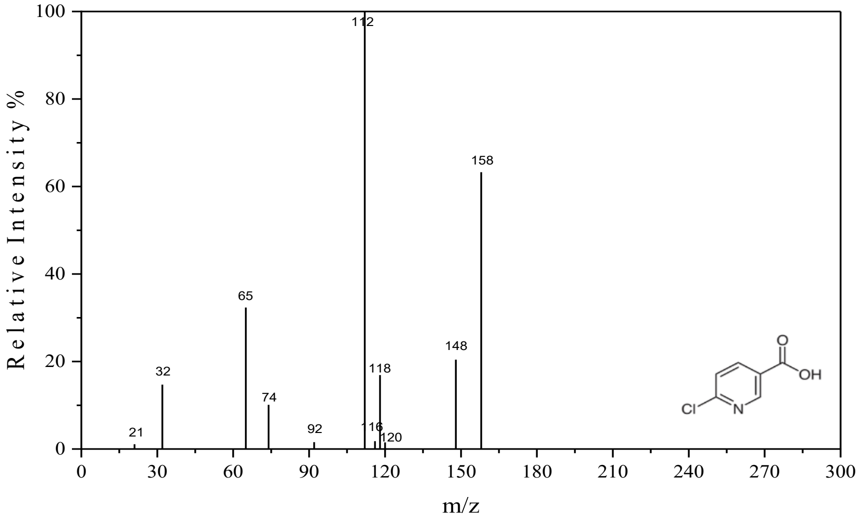


Formyl guanidine

87 g/mol

$C_2H_5N_3O$

Fig. 7c MS spectrum-2 of degraded Imidacloprid Field Samples with 125 W UV/HNO₃

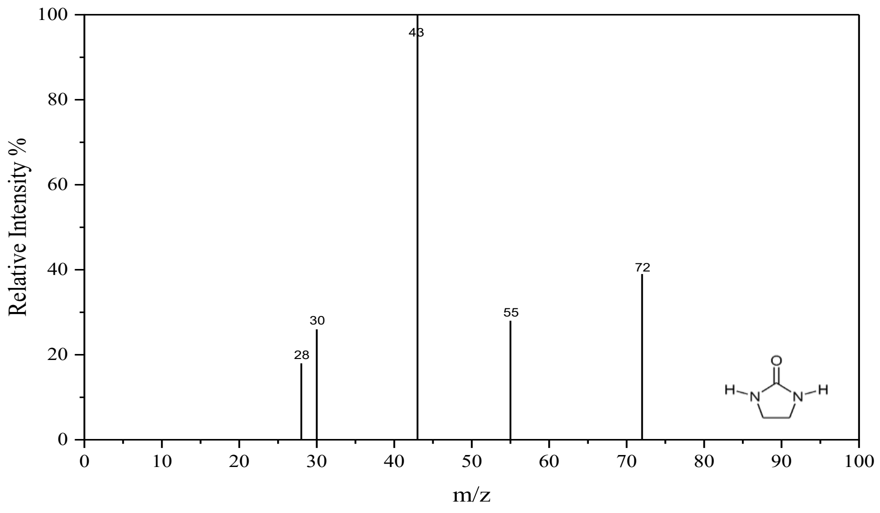


6-chloronicotinic acid

157.5 g/mol

$C_6H_4ClNO_2$

Fig. 7d MS spectrum-3 of degraded Imidacloprid Field Samples with 125 W UV/HNO_3



Imidazolidine

72 g/mol

$C_3H_8N_2$

Fig. 7e MS spectrum-4 of degraded Imidacloprid Field Samples with 125 W UV/HNO_3

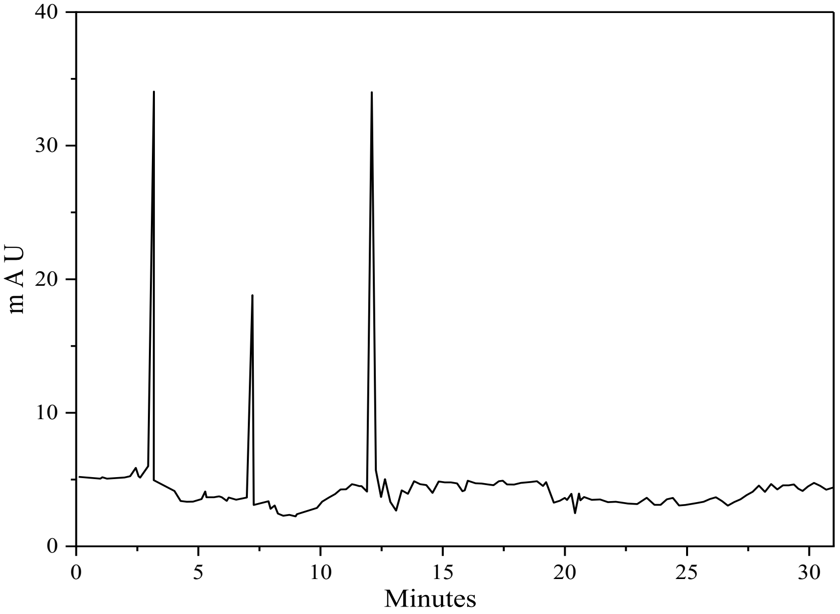
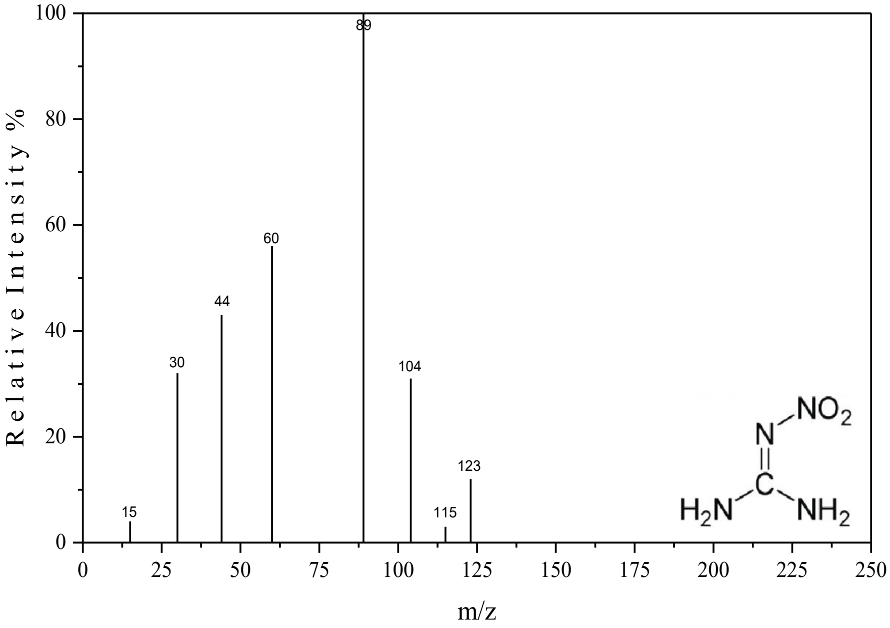


Fig. 8a GC chromatogram of degraded Imidacloprid Field Samples with 125 W UV/TiO_2

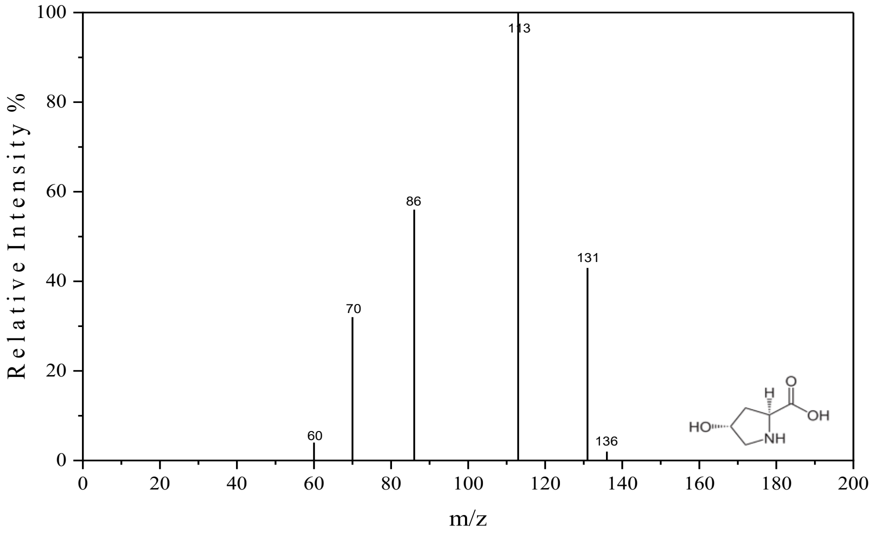


Nitroguanidine

104 g/mol

$CH_4N_4O_2$

Fig. 8b MS spectrum-1 of degraded Imidacloprid Field Samples with 125 W UV/TiO_2

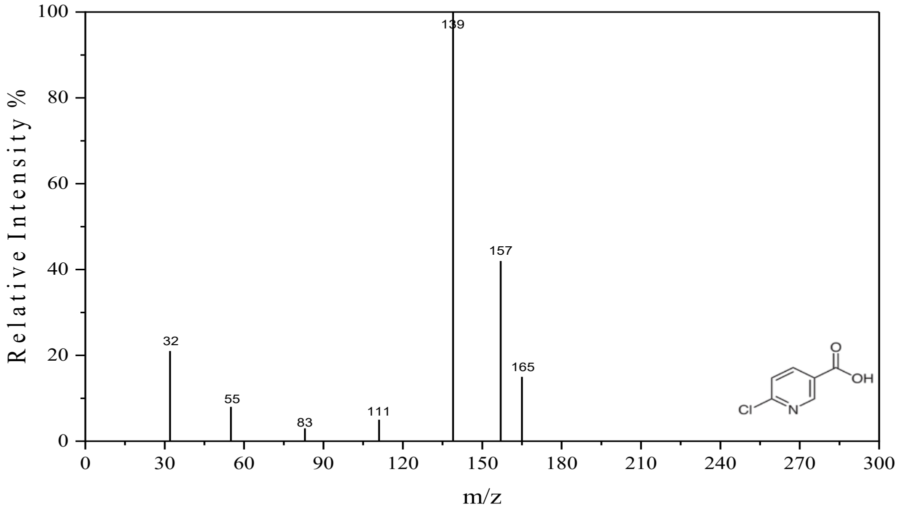


Hydroxyproline

131 g/mol

$C_5H_9NO_3$

Fig. 8c MS spectrum-2 of degraded Imidacloprid Field Samples with 125 W UV/TiO₂



6-chloronicotinic acid

157.5 g/mol

$C_6H_4ClNO_2$

Fig. 8d MS spectrum-3 of degraded Imidacloprid Field Samples with 125 W UV/TiO_2

4. Conclusion

This study successfully demonstrates that photocatalytic degradation using UV light in combination with TiO_2 and HNO_3 is highly effective in breaking down imidacloprid residues in agricultural samples. The degradation pathways identified through UV-Vis and GC-MS analyses confirm the conversion of imidacloprid into less harmful intermediates. Among the tested methods, the UV/TiO_2 system showed the highest efficiency, underscoring its potential as a practical remediation approach for pesticide-contaminated water and soils.

Given the high reliance on pesticides in regions like Sukkur and Shikarpur, implementing advanced oxidation processes could significantly reduce environmental and health risks associated with pesticide residues. Future research should focus on scaling up the process, evaluating mineralization efficiency, and assessing the long-term ecological impacts of photocatalytic treatments.

Competing Interests

The authors have no competing interests.

References

Ansari, S., & Jakhrani, M. A. (2022). Scholar: PHOTOCATALYTIC DEGRADATION OF EMAMECTIN BENZOAT AND IMIDACLOPRID PESTICIDES USED IN DIFFERENT VEGETABLES AND ITS IMPACT ON ENVIRONMENT. doi:10.13140/RG.2.2.18206.00324

El Sharkawy, H. M., Shawky, A. M., Elshypany, R., & Selim, H. (2023). Efficient photocatalytic degradation of organic pollutants over TiO(2) nanoparticles modified with nitrogen and MoS(2) under visible light irradiation. Sci Rep, 13(1), 8845. doi:10.1038/s41598-023-35265-7

Iqbal, M. F., Maqbool, U., Perveez, I., Farooq, M., & Rafique Asi, M. (2009). Monitoring of insecticide residues in brinjal collected from market of Noshera Virkan, Pakistan. Journal of Animal and Plant Sciences, 19.

Khader, E. H., Muslim, S. A., Saady, N. M. C., Ali, N. S., Salih, I. K., Mohammed, T. J., . . . Zendehboudi, S. (2024). Recent advances in photocatalytic advanced oxidation processes for organic compound degradation: A review. Desalination and Water Treatment, 318, 100384. doi: https://doi.org/10.1016/j.dwt.2024.100384

Kumar, J., Kaur, P., Sud, D., Saini, A., & Bansal, P. (2023). Persistence, sorption, and forced degradation of imidacloprid in environmental matrix. Mater. Today, 78, 849-857. doi:10.1016/j.matpr.2022.11.502

Safni, S., Jumiaty, H., & Aziz, H. (2021). Degradation of imidacloprid residue on red tomatoes (Solanum lycopersicum) by Advanced Oxidation Processes and analysis using spectrophotometer and HPLC. J. Kim. Val., 7(2), 150-157. doi:10.15408/jkv.v7i2.21630

Sani, M. S. A., Bakar, J., Rahman, R. A., & Abas, F. (2020). Effects of coated capillary column, derivatization, and temperature programming on the identification of Carica papaya seed extract composition using GC/MS analysis. J. Anal. Test., 4(1), 23-34. doi:10.1007/s41664-020-00118-z

Tudi, M., Daniel Ruan, H., Wang, L., Lyu, J., Sadler, R., Connell, D., . . . Phung, D. T. (2021). Agriculture Development, Pesticide Application and Its Impact on the Environment. Int J Environ Res Public Health, 18(3). doi:10.3390/ijerph18031112

Yari, K., Seidmohammadi, A., Khazaei, M., Bhatnagar, A., & Leili, M. (2019). A comparative study for the removal of imidacloprid insecticide from water by chemical-less UVC, UVC/TiO2 and UVC/ZnO processes. J. Environ. Health Sci. Eng., 17(1), 337-351. doi:10.1007/s40201-019-00352-3

Zhang, X., Huang, Y., Chen, W.-J., Wu, S., Lei, Q., Zhou, Z., . . . Chen, S. (2023). Environmental occurrence, toxicity concerns, and biodegradation of neonicotinoid insecticides. Environmental Research, 218, 114953. doi: https://doi.org/10.1016/j.envres.2022.114953