Advances in Research

Volume 25, Issue 4, Page 30-39, 2024; Article no.AIR.116563
ISSN: 2348-0394, NLM ID: 101666096

Studies on the Persistence of Pyraclostrobin 10% CS in Acidic, Neutral and Basic Waters by Validated HPLC-DAD Method

Joga Simhachalam [a] and Gandham Hima Bindu [a*]

[a] Department of Engineering Chemistry, AUCE (A), Andhra University, Visakhapatnam-530003, Andhra Pradesh, India.

Authors' contributions

This work was carried out in collaboration between both authors. Bothl authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AIR/2024/v25i41078

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/116563

Original Research Article

Received: 26/02/2024
Accepted: 01/05/2024
Published: 06/05/2024

ABSTRACT

This paper presents a method for the determination of pyraclostrobin 10% CS, a fungicide used in agriculture, in water samples with different pH values. The method is based on high-performance liquid chromatography with diode array detection (HPLC-DAD) and uses a reversed-phase column and a gradient elution. The method was validated according to the SANCO guidelines and showed good linearity, accuracy, precision, sensitivity and selectivity. The method was applied to study the persistence of pyraclostrobin 10% CS in acidic, neutral and basic water under laboratory conditions. The results showed that pyraclostrobin 10% CS was degraded rapidly in basic water with a half-life of less than ten days. The degradation products were identified by HPLC. The study involved exposing water samples to direct sunlight until the end of the experiment. The water samples had different pH levels: acidic (4.0), neutral (7.0) and basic (9.0). The water samples also contained Pyraclostrobin, a fungicide. The researchers collected aliquots of the water samples at various time

**Corresponding author: E-mail: himabinduauce@gmail.com;*

intervals: 0, 1, 5, 10, 15, 20 and 30 days. The analysis continued until the Pyraclostrobin residues were below the detection limit. The DT50 can vary significantly depending on environmental conditions, such as pH levels.
At pH 4, pH 7, and pH 9, the reported DT50 ranges between 6 to 8.1 days, indicating a moderate rate of degradation or dissipation in these conditions. These values suggest that the substance is relatively stable across a range of acidic to basic conditions, with only slight variations in the degradation rate.

Keywords: Pyraclostrobin 10% CS; HPLC-DAD; SANCO; method validation; acidic water; basic water; neutral water.

1. INTRODUCTION

Pyraclostrobin is a fungicide from the strobilurin class that inhibits mitochondrial respiration in fungus [1]. This chemical molecule inhibits electron transmission within the respiratory chain of fungal cells, disrupting important biological processes and eventually terminating fungal development [2]. It is especially efficient against a variety of crop-damaging fungi, including Botrytis cinerea and Alternaria alternata, which can cause substantial harm to plants such as strawberries, raspberries, and pistachio [3]. Despite its efficiency, there is concern that resistance will evolve in fungal populations, particularly as a result of cytochrome b gene alterations. Pyraclostrobin is widely utilised in agriculture throughout the United States, particularly in locations such as the Upper Midwest. However, it should be handled with caution because to its toxicity and potential irritating effects on the eyes and skin [4]. It is also worth noting that, while pyraclostrobin does not accumulate considerably in food, it is not regarded highly biodegradable, raising worries about its environmental impact, notably its ability to bioaccumulate in aquatic creatures. The balance between the benefits of pyraclostrobin for crop protection and its environmental and health concerns is a subject of continuous research and regulation [5].

Pesticide persistence in water is a difficult topic that is regulated by a variety of factors, including water pH. Pesticides react differently in acidic, neutral, and basic waters according to their chemical qualities [6]. Pesticide stability is generally affected by the pH of the water, with some pesticides hydrolyzing more rapidly in alkaline circumstances, particularly between pH 8 and 9. For example, for every unit increase in pH, some pesticides' hydrolysis rate can increase tenfold [7]. This is crucial since both surface and groundwater supplies often have inherent alkalinity that creates pH levels between 7-9.

Pesticides' environmental fate, including persistence and mobility, is controlled by their chemical structure as well as the environmental conditions in which they are used. Soil conditions, pesticide properties, hydraulic loads, and crop management practises all influence whether pesticides reach groundwater or surface water [8]. The chemical stability and physical properties of pesticides, such as half-life, soil sorption coefficient, water solubility, and vapour pressure, are critical in determining their environmental fate. In addition, metrics such as the Groundwater Ubiquity Score (GUS) and the Henry's Law constant are utilised to forecast pesticide environmental behavior [9]. Pesticide persistence in plants and soils is determined by both the pesticide's properties and environmental conditions such as temperature, precipitation, and air movement. Pesticide persistence is also influenced by plant and soil features such as species, crop type, organic matter content, and microbial population [10]. It is vital to highlight that the goal is to apply pesticides that are particular and last only as long as necessary to manage pests, without causing undue harm to non-target creatures or the environment [11]. Understanding the durability of pesticides in various pH waters is critical for making informed pesticide selections and maintaining water quality. As research progresses, it is hoped that more sustainable and environmentally friendly pest management strategies will be created, considering the intricate interactions between pesticides and the ecosystems they enter [12].

The study offers a method for measuring pyraclostrobin 10% CS, an agricultural fungicide, in water samples with varied pH values utilizing high-performance liquid chromatography with diode array detection (HPLC-DAD). The method was validated and shown excellent linearity, accuracy, precision, sensitivity, and selectivity.

The results showed that pyraclostrobin was stable in acidic and neutral water for up to 28 days, but deteriorated rapidly in basic water.

2. MATERIALS AND METHODS

Preparation of Acidic water (pH 4.0): pH 4.0 buffer solution was prepared by adding 8.0251 g of potassium dihydrogen phosphate in water and diluted to 1000 mL. The pH was adjusted to 4.0 using potassium dihydrogen phosphate.

Preparation of Neutral water (pH 7.0): pH 7.0 buffer solution was prepared by adding 6.3045 g of disodium hydrogen ortho phosphate and 5g of potassium dihydrogen phosphate by dissolving in water and diluted to 1 litre. The pH of the buffer was adjusted with disodium hydrogen ortho phosphate and potassium dihydrogen phosphate.

Preparation of Basic water (pH 9.0): pH 9.0 buffer solution was prepared by adding 12.5002 g of boric acid & 15g potassium chloride by dissolving in water and diluted to 1 litre. The pH was adjusted to 9.0 using sodium hydroxide**.**

Chromatographic Conditions: The instrument is a Agilent HPLC 1100 Series, a DAD detector, and a EZ chrom software system. It uses a column called Phenomenex C18 (250 mm x 4.6 mm x 5 µ), a mobile phase of acetonitrile, 0.1% O-phosphoric acid ratio (80: 20 v/v), with a 220 nm wavelength, 1.0 ml/min flow rate, and 5.2 minutes retention time.

2.1 Method Validation

Specificity Test: Following solutions were injected in specificity test

- Diluent Blank (Methanol)
- Mobile Phase-D (0.1 % Orthophosphoric acid solution in water)
- Mobile phase-B (Acetonitrile)
- Prepared RO Water
- Reference Item Solution in Prepared pH-4 buffer solution (Accuracy Solution-LOQ Level)
- Reference Item Solution in Prepared pH-7 buffer solution (Accuracy Solution-LOQ Level)
- Reference Item Solution in Prepared pH-9 buffer solution (Accuracy Solution-LOQ Level)
- Reference Item Solution (1.00 mg/L-Linearity-3 solution)
- Preparation of Test Item Solution

Accurately weighed 10.12 mg of test item (10 %) into 10 mL volumetric flask. Contents were dissolved in about 5 mL of methanol by sonication and make upto mark with the same diluent. From the prepared solution, an aliquot of 0.100 mL solution was diluted to 10 mL with methanol. The solution concentration is 1.000 mg/L. The same solution was injected as test item solution in specificity test.

Detector linearity test: Accurately 10.19 mg of reference item (99.5%) was weighed into 10 mL volumetric flask. Contents were dissolved in about 5 mL of methanol and make upto mark with the same. The stock solution concentration was 1013.91 mg/L. The linearity stock solutions were diluted in following way.

All the linearity solutions were analyzed by High Pressure Liquid Chromatography A linear curve was plotted for the concentration of standard versus observed peak area and the correlation coefficient was determined.

Recovery and Repeatability: Accuracy was performed at two fortification levels (0.05 µg/mL and 0.5 µg/mL).

Table 1. Detector linearity solutions

Standard Stock Solution Concentration (µg/mL)	Aliquot of stock taken (mL)	Made up to Volume (mL)	Concentration of solution prepared (µg/mL)	Solution ID
1013.91	0.987	10	100.07	Linearity-6
1013.91	0.494	10	50.09	Linearity-5
1013.91	0.100	10	10.14	Linearity-4
10.14	1.000	10	1.01	Linearity-3
1.01	0.5	10	0.05	Linearity-2
1.01	0.15	10	0.015	Linearity-1

2.2 In pH-4 Buffer

0.05 mg/L fortification level: Accurately pipetted out 0.500 mL of 0.99 µg/mL reference item solution was taken into five different 10 mL of volumetric flasks and made to the mark with pre-saturated n-octanol, then sonicated for 5 minutes for homogenization. Samples were prepared in five replicates LOQ Level (R1, R5).

0.5 mg/L fortification level: Accurately pipetted out 0.500 mL of 9.85 mg/L specificity test item solution was taken into five different 10 mL of volumetric flasks and made to the mark with n-octanol, then sonicated for 5 minutes for homogenization. Samples were prepared in five replicates (R1, R5).

Note: Linearity -3 Standard was used for Accuracy test.

2.3 In pH-7 Buffer

0.05 mg/L fortification level: Accurately pipetted out 0.500 mL of 0.99 µg/mL reference item solution was taken into five different 10 mL of volumetric flasks and made to the mark with pre-saturated n-octanol, then sonicated for 5 minutes for homogenization. Samples were prepared in five replicates LOQ Level (R1, R5).

0.5 mg/L fortification level: Accurately pipetted out 0.500 mL of 9.85 mg/L specificity test item solution was taken into five different 10 mL of volumetric flasks and made to the mark with n-octanol, then sonicated for 5 minutes for homogenization. Samples were prepared in five replicates (R1,.R5).

Note: Linearity -3 Standard was used for Accuracy test.

2.4 In pH-7 Buffer

0.05 mg/L fortification level: Accurately pipetted out 0.500 mL of 0.99 µg/mL reference item solution was taken into five different 10 mL of volumetric flasks and made to the mark with pre-saturated n-octanol, then sonicated for 5 minutes for homogenization. Samples were prepared in five replicates LOQ Level (R1, R5).

0.5 mg/L fortification level: Accurately pipetted out 0.500 mL of 9.85 mg/L specificity test item solution was taken into five different 10 mL of volumetric flasks and made to the mark with n-octanol, then sonicated for 5 minutes for homogenization. Samples were prepared in five replicates (R1,.R5).
Note: Linearity -3 Standard was used for Accuracy test.

2.5 Limit of Quantification

The lowest validated level with sufficient recovery is defined as the limit of quantification (LOQ). The LOQ was determined using 5 injections of 0.05 mg/L fortification level recovery samples. Low level recovery solutions were used for LOQ.

2.6 Limit of Detection

The limit of detection (LOD) is defined as the lowest detectable concentration of an analytic in a sample. It was expressed as lowest calibration Standard in linearity test. Limit of detection was established by dividing the concentration of the LOQ with 3.3 values.

2.7 Method of Fortification

Required quantity of the test item was fortified in water samples (pH 4.0, pH 7.0 and pH 9.0) to get the uniform concentrations.
T_1– Pyraclostrobin 10 % CS @ 1 µg/mL active
T2– Pyraclostrobin 10 % CS @ 2 µg/mL active

2.8 Sample Storage Condition

The test samples prepared in different buffer solutions were stored directly under sunlight in transparent glass bottles.

2.9 Sample Preparation

During each sampling occasion, water samples were mixed thoroughly and sub sampled 50ml using a pipette.

2.10 Half-Lives

The degradation rate expressed as the concentration (µg/mL) in the buffer solution as Permethrin technical was estimated from fitting the data to the following equation [13,14].

$$K_{obs} = \frac{2.303}{t} \log_{10} \frac{C0}{Ct}$$

$$T1/2 = 0.693 / K_{obs}$$

Where,

Kobs is the rate constant.

A linear regression analysis of log10 (C) versus time derives an equation whose slope = -k. The half-life (t1/2) is therefore calculated as 0.693/Kobs.

3. RESULTS AND DISCUSSION

3.1 Method Validation

Specificity: The analytical method was found to be specific. There was no interference observed at the retention time of the pyraclostrobin peak.

Linearity: The analytical method was found to be linear in the range 0.015 mg/L to 100.07 mg/L with Correlation co-efficient (r) =1.0000, Slope = 23.38 and Intercept = 1.91. The Results are presented in Table 2 and linearity curve presented in Fig. 1.

3.2 Recovery and Repeatability

Multiple recovery control samples (n=2) at each of 2 fortification levels equivalent to 0.05 mg/L and 0.5 mg/L for both buffers and octanol phase. pyraclostrobin in the final solution were assayed using HPLC.

For pH-4 buffer, the overall assay accuracy of 88.91% recovery and a precision of 1.25 % RSD indicated an acceptable method of analysis at LOQ Level. The overall assay accuracy of 92.23% recovery and precision RSD of 1.15% indicated an acceptable method of analysis in high concentration.

Table 2. Detector linearity test

Concentration (mg/L)	Area
100.07	1811141
50.09	900587
10.14	199652
1.01	19854
0.05	987
0.015	298
Slope	18044.03
Intercept	3432.49
CC	1.0000

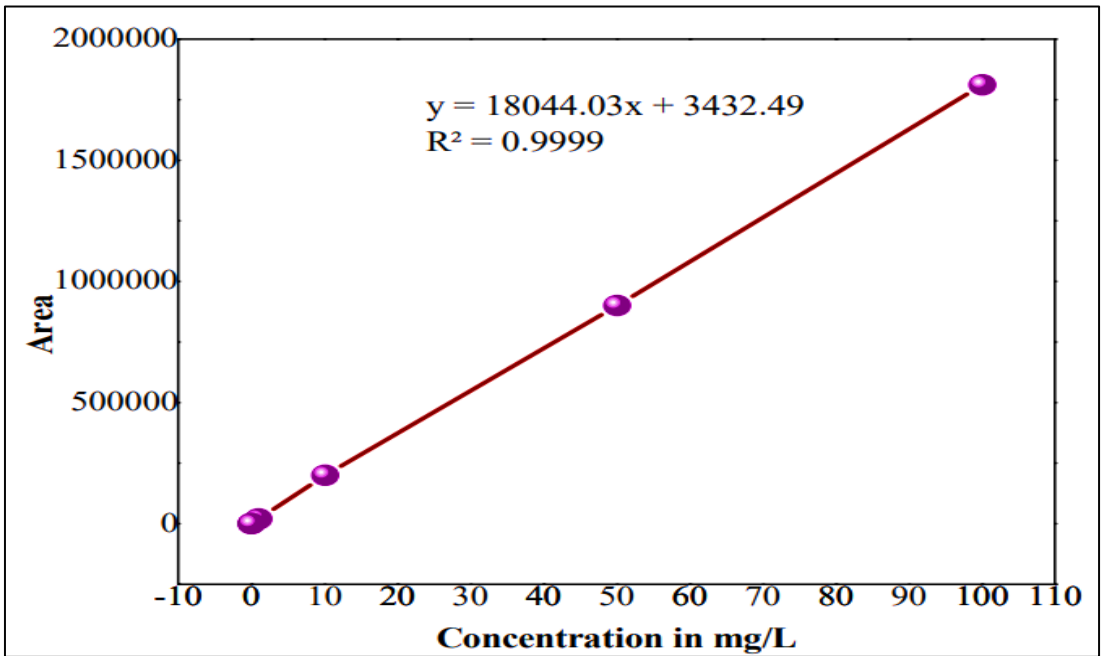

Fig. 1. Graph of detector linearity test

For pH-7 buffer, the overall assay accuracy of 89.11 % recovery & precision RSD of 1.35% at LOQ level and 90.74 % recovery & precision RSD of 1.46 % at LOQ x 10 level. For pH-9 buffer, the overall assay accuracy of 88.67 % recovery & precision RSD of 1.52 % at LOQ level and 90.06% recovery & precision RSD of 1.71 % at LOQ x 10 level.

3.3 Limit of Quantitation (LOQ)

Limit of Quantitation (LOQ) was established to be 0.05 mg/L from the lower level recovery test in three buffers.

3.4 Limit of Detection (LOD)

Limit of Detection (LOD) was established to be 0.015 mg/L and that was lowest limit of calibration curve.

3.5 Persistence Details

Acidic water: The initial concentration of pyraclostrobin in acidic water on 0 day was 0.977 mg/L and 1.889 mg/L at T1and T2 dosages respectively, which on the 1st day had dissipated to 0.549 mg/L and 0.902 mg/L in T1 and T2 dosages. On the 5th day, the residue levels were at 0.359 mg/L in (T1) and 0.706 mg/L in (T2), on the 10th day it was found to be 0.295 mg/L in (T1) and 526 mg/L in (T2). By 15th day the residues were found to be 0.196 mg/L in (T1) and 0.428 mg/L in (T2) and on 20th day it was 0.133 mg/L in (T1) and 0.217 mg/L in (T2). Complete dissipation of residues of pyraclostrobin to below determination level in both the tested dosages was observed on the 30th day. The regression analysis results of pyraclostrobin in acidic water presented in Table 3 and Dissipation curve of pyraclostrobin in acidic water presented in Fig. 2**.**

Neutral Water: The initial concentration of pyraclostrobin in acidic water on 0 day was 0.985 mg/L and 1.893 mg/L at T1and T2 dosages respectively, which on the 1st day had dissipated to 0.521 mg/L and 1.006 mg/L in T1 and T2 dosages. On the 5th day, the residue levels were at 0.322 mg/L in (T1) and 0.615 mg/L in (T2), on the 10th day it was found to be 0.285 mg/L in (T1) and 516 mg/L in (T2). By 15th day the residues were found to be 0.184 mg/L in (T1) and 0.391 mg/L in (T2) and on 20th day it was 0.129 mg/L in (T1) and 0.241 mg/L in (T2). Complete dissipation of residues. of pyraclostrobin to below determination level in both the tested dosages was observed on the 30th day. The regression analysis results of pyraclostrobin in acidic water presented in Table 4 and Dissipation curve of pyraclostrobin in acidic water presented in Fig. 3.

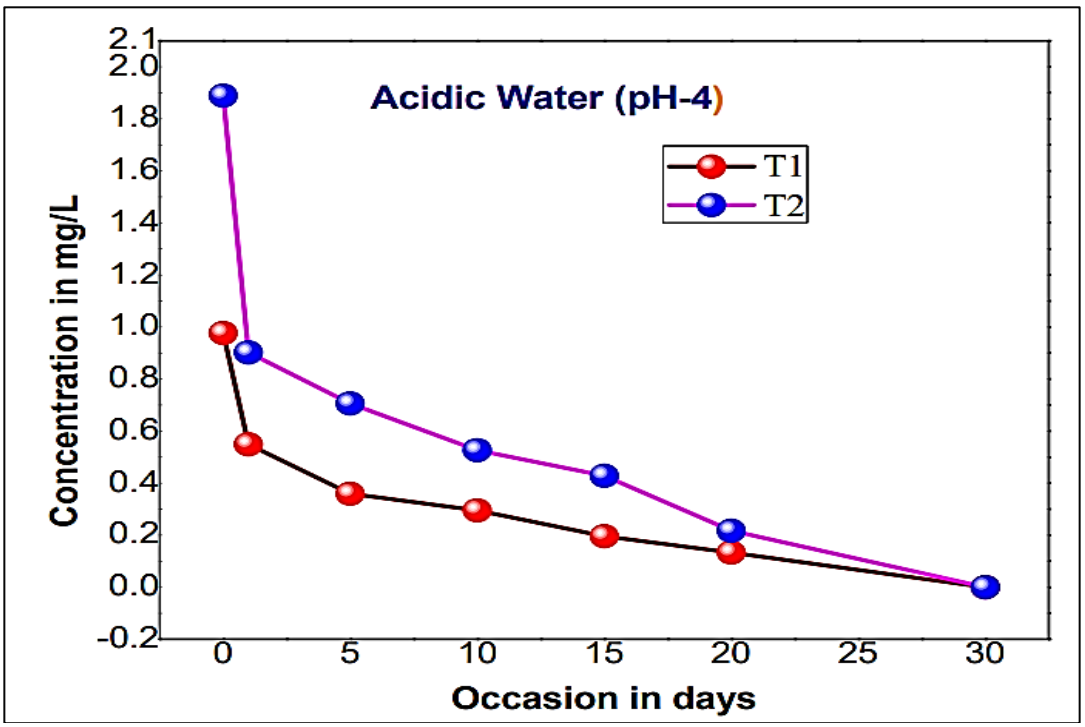

Fig. 2. Dissipation curve of pyraclostrobin in acidic water

Table 3. The regression analysis results of pyraclostrobin in acidic water

Occasion in days	T1 Concentration in mg/L.	Concentration In Log(10) T1	T2 Concentration in mg/L.	Con. In Log(10) T2	Regression Parameters	T1	T2
0	0.977	-0.010	1.889	0.276	**Slope**	-0.037	-0.038
1	0.549	-0.260	0.902	-0.045	**Half life (DT50)**	8.05	8.01
5	0.359	-0.445	0.706	-0.151	**Intercept**	0.154	0.114
10	0.295	-0.530	0.526	-0.279	**CCC**	0.961	0.944
15	0.196	-0.708	0.428	-0.369			
20	0.133	-0.876	0.217	-0.664			
30	BDL	0.000	BDL	0.000			

Table 4. The regression analysis results of pyraclostrobin in Neutral water

Occasion in days	T1 Concentration in mg/L.	Concentration In Log(10) T1	T2 Concentration in mg/L.	Con. In Log(10) T2	Regression Parameters	T1	T2
0	0.985	-0.007	1.893	0.277	**Slope**	-0.038	-0.037
1	0.521	-0.283	1.006	0.003	**Half life (DT50)**	8.02	8.08
5	0.322	-0.492	0.615	-0.211	**Intercept**	-0.173	0.109
10	0.285	-0.545	0.516	-0.287	**CCC**	-0.947	-0.944
15	0.184	-0.735	0.391	-0.408			
20	0.129	-0.889	0.241	-0.618			
30	BDL	0.000	BDL	0.000			

Table 5. The regression analysis results of pyraclostrobin in Basic water

Occasion in days	T1 Concentration in mg/L.	Concentration In Log(10) T1	T2 Concentration in mg/L.	Con. In Log(10) T2	Regression Parameters	T1	T2
0	0.952	-0.021	1.869	0.272	**Slope**	-0.046	-0.046
1	0.596	-0.225	1.009	0.004	**Half life (DT50)**	6.53	6.60
5	0.402	-0.396	0.836	-0.078	**Intercept**	-0.125	0.150
10	0.241	-0.618	0.431	-0.366	**CCC**	-0.986	-0.979
15	0.142	-0.848	0.305	-0.516			
20	0.101	-0.996	0.182	-0.740			
30	0.000	0.000	BDL	0.000			

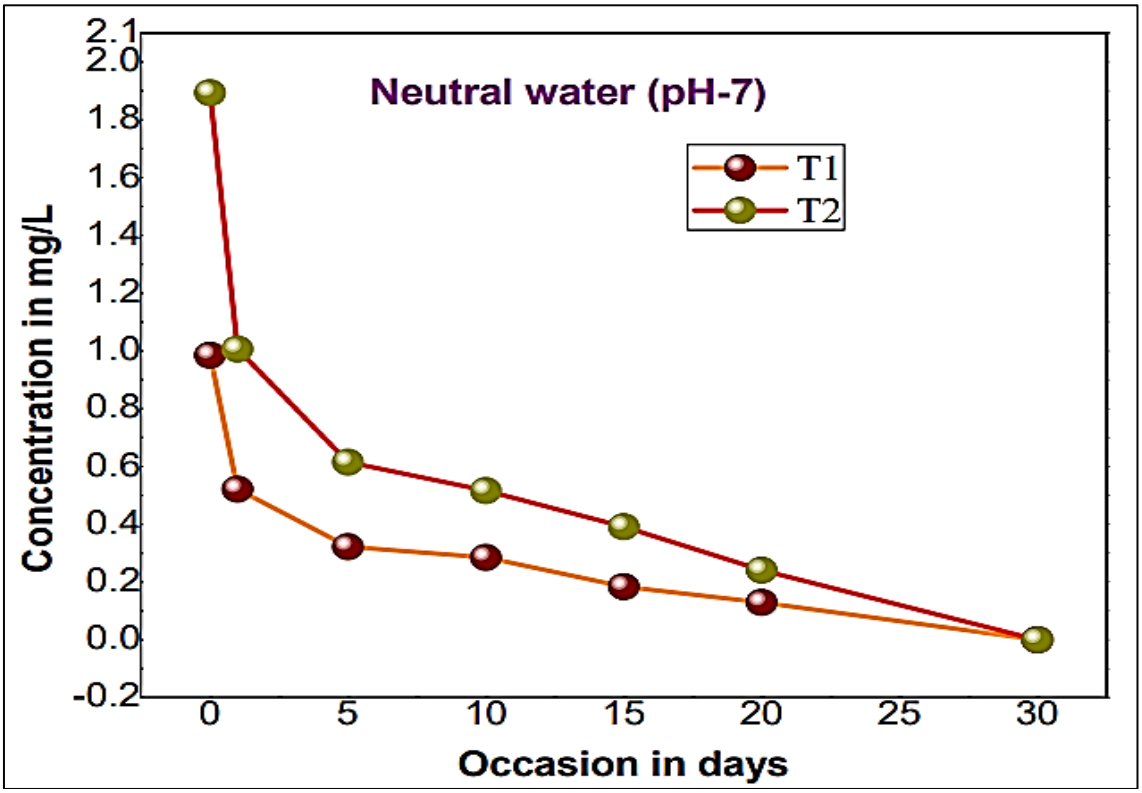

Fig. 3. Dissipation curve of pyraclostrobin in Neutral water

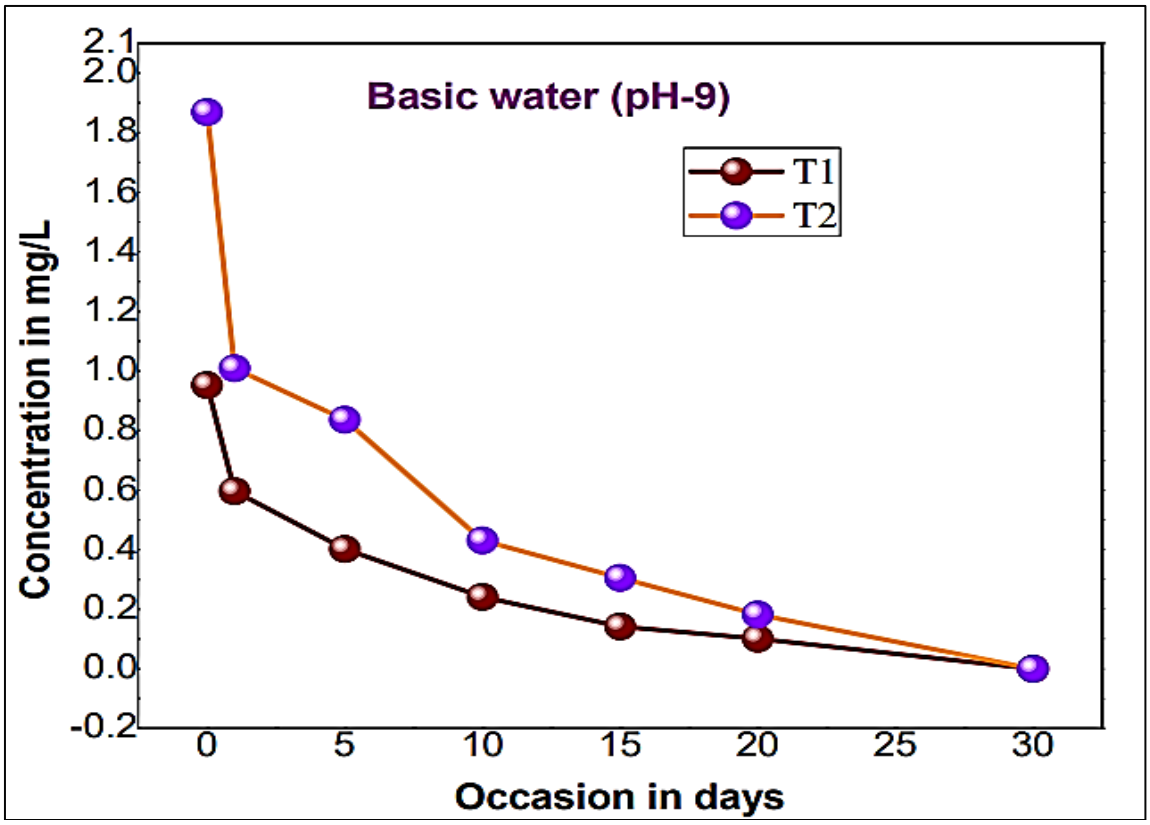

Fig. 4. Dissipation curve of pyraclostrobin in Neutral water

Basic Water: The initial concentration of pyraclostrobin in acidic water on 0 day was 0.985 mg/L and 1.893 mg/L at T1and T2 dosages respectively, which on the 1st day had dissipated to 0.521 mg/L and 1.006 mg/L in T1 and T2 dosages. On the 5th day, the residue levels were at 0.322 mg/L in (T1) and 0.615 mg/L in (T2), on the 10th day it was found to be 0.285 mg/L in (T1) and 516 mg/L in (T2). By 15th day the residues were found to be 0.184 mg/L in (T1) and 0.391 mg/L in (T2) and on 20th day it was 0.129 mg/L in (T1) and 0.241 mg/L in (T2). Complete dissipation of residues. of pyraclostrobin to below determination level in both the tested dosages was observed on the 30th day. The regression analysis results of pyraclostrobin in acidic water presented in Table 5 and Dissipation curve of pyraclostrobin in acidic water presented in Fig. 4.

4. CONCLUSIONS

The study under consideration highlights significant advances in agricultural chemistry, particularly in the analysis and monitoring of fungicides in environmental samples. The use of high-performance liquid chromatography with diode array detection (HPLC-DAD) to quantify pyraclostrobin, a fungicide, demonstrates the method's reliability in terms of linearity, accuracy, precision, sensitivity, and selectivity. The rapid degradation of pyraclostrobin in basic water environments, as evidenced by a half-life of less than ten days, is an important discovery. It indicates that the fungicide's persistence in such conditions is limited, which may have implications for environmental safety and agricultural practice planning. This type of research is important in ensuring that the use of agrochemicals does not harm water quality, and it provides valuable data for regulatory bodies to assess the environmental impact of these substances.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Yang M, Zhang J, Zhang J, Rashid M, Zhong G, Liu J, The control effect of fungicide pyraclostrobin against freckle disease of banana and its residue dynamics under field conditions, J. Environ. Sci. Heal. - Part B Pestic. Food Contam. Agric. Wastes. 2018;53:615–621. Available:https://doi.org/10.1080/03601234.2018.1473974
2. Dominguez AN, Emmert GE, Gil DM, Álvarez RMS, Experimental and theoretical vibrational study of the fungicide pyraclostrobin, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 2021;259. Available:https://doi.org/10.1016/j.saa.2021.119888
3. Joshi J, Sharma S, Guruprasad KN, Foliar application of pyraclostrobin fungicide enhances the growth, rhizobial-nodule formation and nitrogenase activity in soybean (var. JS-335), Pestic. Biochem. Physiol. 2014;114:61–66. Available:https://doi.org/10.1016/j.pestbp.2014.07.002
4. Avenot H, Morgan DP, Michailides TJ, Resistance to pyraclostrobin, boscalid and multiple resistance to Pristine® (pyraclostrobin + boscalid) fungicide in *Alternaria alternata* causing alternaria late blight of pistachios in California, Plant Pathol. 2008;57:135–140. Available:https://doi.org/10.1111/j.1365-3059.2007.01701.x.
5. Yan Z, Cai G, Jin Z, Fu Y, Ma J, Li M, Han W, Wu Y, Determination of pyraclostrobin residue in wax gourd and its dietary risk assessment, Food Sci. Technol. 2023;43:1–6. Available:https://doi.org/10.1590/fst.110622
6. Li H, Yang S, Li T, Li X, Huang X, Gao Y, Li B, Lin J, Mu W, Determination of pyraclostrobin dynamic residual distribution in tilapia tissues by UPLC-MS/MS under acute toxicity conditions, Ecotoxicol. Environ. Saf. 2020;206: 111182. Available:https://doi.org/10.1016/j.ecoenv.2020.111182
7. Fulcher JM, Wayment DG, White PM, Webber CL, Pyraclostrobin wash-off from sugarcane leaves and aerobic dissipation in agricultural soil, J. Agric. Food Chem. 2014;62:2141–2146. Available:https://doi.org/10.1021/jf405506p.
8. Shen H, Yuan H, Liang J, Zhou X, Ge P, Liu Y, Gao T, Yang K, Yang D, Degradation of pyraclostrobin in water using a novel hybrid gas–liquid phase discharge reactor, Water (Switzerland). 2023;15. Available:https://doi.org/10.3390/w15081562

9. Han L, Wu Q, Wu X, Dissipation and residues of pyraclostrobin in *Rosa roxburghii* and soil under filed conditions, Foods. 2022;11:1–11. Available:https://doi.org/10.3390/foods11050669
10. Parlakidis P, Adamidis G, Alexoudis C, Pythoglou P, Papadopoulos S, Vryzas Z, Adjuvant Effects on Pyraclostrobin and Boscalid Residues, Systemic Movement, and Dietary Risk in garlic under field conditions, Agric. 2023;13. Available:https://doi.org/10.3390/agriculture13081636
11. Sad N, Dissipation rate of boscalid and pyraclostrobin fungicide in. 2020;509–514.
12. Patel DK, Swami BL, Rajawat TL, Development and validation of stability indicating ultra Performance Liquid Chromatography method for simultaneous Quantification of Thiophante-methyl, fipronil and pyraclostrobin in pesticide formulation, Int. J. Sci. Res. Sci. Technol. 2018;5:1308–1317.
13. Alam Mir W. Rao, Tentu Nageswara. Prashanthi, Yarasani. Sridhar, V. Application of silica nanoparticles in the determination of herbicides in environmental water samples using liquid chromatography-mass spectroscopy, Current Nanoscience. 2020;16: 748-756.
14. Tentu Nageswara Rao, Mani Panagal, Botsa Parvatamma, Nanoremediation of dimethomorph in water samples using magnesium aluminate nanoparticles, Environmental Technology & Innovation. 2020;20:101176.

© Copyright (2024): Author(s). The licensee is the journal publisher. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/116563