**Photo Catalytic Applications Of Ferrous Doped Titanium Dioxide Nanoparticles In Dissipation Kinetics Of Tricyclazole Fungicide Residues In Different pH Waters Under Direct Sun Light**

Tentu. Nageswara Rao¹, T. Benarji Patrudu*², M. V. Basaveswara Rao¹
Karri Apparao¹ and N. Krishna Rao¹

¹Department of Chemistry, Krishna University, Machilipatnam, Andhra Pradesh, India.
²Department of Chemistry, GITAM University, Hyderabad, Telangana, India.

**Abstract:** Studied the dissipation behavior of tricyclazole under direct sunlight using Fe doped TiO2 nanoparticles (FeTiO2) as catalyst. FeTiO2 nanoparticles are synthesized and characterized by scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDX) and Fourier transform Infrared Spectroscopy (FT-IR). The photocatalytic studies were conducted by the 1 litre of milli-Q water; pH 4.0, 7.0 and 9.0 buffer were spiked with 1 mL of 1000 mg/L stock solution of tricyclazole 75 % WP to get 1µg/mL concentration of pesticide active in water. Three sets of such samples in triplicates were prepared and sonicated for 10 minutes to get homogeneous concentration of pesticide active in water and labeled as S1, S2, and S3. Two sets of samples (S1 and S2) were added FeTiO2 nanoparticles to get 0.06g/L content of photocatalyst. S1 and S3 sets of samples were exposed to sun light. S2 set of samples were kept in an oven at 40°C in dark. The milli-Q water spiked with stock solution of pesticide and without addition of FeTiO2 nanoparticles (S3) were also exposed to sun light for the measurement of photolytic degradation of pesticide in water. The FeTiO2 added Milli-Q water without spiking of pesticides (S4) were also maintained as untreated control for the identification of absence of pesticide. The collected samples were quantified using a validated HPLC-UV method. Kinetic parameters such as rate constant (k), DT50 and DT90 were calculated using the dissipation data of tricyclazole.

**Keywords:** Fe doped TiO2, Tricyclazole, HPLC-UV, SEM, TEM, DT50 and DT90.

I. **Introduction**

Tricyclazole (five-methyl-1, 2, four-triazolo[3,4-b]benzothiazole) is a completely unique fungicide for control of Pyricularia oryzae on rice. Tricyclazole is systemic in rice and could control rice blast disorder in any degree of plant improvement with the aid of a selection of software methods. Tricyclazole protects flowers from contamination by using P. oryzae by using preventing penetration of the epidermis with the aid of the fungus. The compound acts by way of inhibiting melanization inside the appressorium, as a result causing a loss of rigidity within the appressorial wall. Tricyclazole has no apparent effect on spore germination even though sporulation is reduced. Tricyclazole is not curative however is defensive in its activity. In the recent years the use of heterogeneous photo catalyst nano Fe doped TiO2 (FeTiO2) in the degradation and mineralization of herbicide, insecticide, N-heterocyclic compounds, saturated fatty acids, different organic dyes in water and gaseous pollutant in air using UV and visible-light has gained wide attention due to its low cost preparation, low toxicity, high stability and effectiveness than TiO2 [5] When FeTiO2 nanoparticles are subjected to UV, VIS or solar light, it gains energy from light and promote electrons (e-) from the valence band (VB) of TiO2 to the conduction band (CB) leaving a positive hole (h+). Fe in FeTiO2 trap electrons (e-) and positive holes (h+) from TiO2 since the energy levels of Fe2+/Fe3+ lies close to that of Ti3+/Ti4+, and reduce the recombination of photo-generated electron and hole pair in TiO2 and enhance the availability of electrons (e-) and positive holes (h+) in FeTiO2. These electrons (e-) and positive holes (h+) are involving in the degradation of organic molecules by oxidation / reduction process [6, 7, 8]. Destroying of Escherichia coli bacteria in water have been achieved completely within an hour by deposited Escherichia coli bacteria in water on FeTiO2 thin film and irradiating it in visible radiation [9, 10] based on the information present study was conducted to investigate the dissipation behavior of tricyclazole in three different buffers using FeTiO2 as catalyst under natural climatic conditions in solar light.

II. **Materials And Methods**

Reference analytical standard of tricyclazole (purity 97.5%), Titanium tetrachloride and Iron nitrate were obtained from Sigma Aldrich. The test item tricyclazole 75% Wettable powders (WP) was purchased from local market. Acetonitrile, Water HPLC grade, orthophosphoric acid Sodium hydroxide LR grade, Potassium chloride GR grade, Boric acid GR grade, Potassium biphthalate GR grade, Hydrochloric acid AR grade and
Potassium phosphate AR grade were obtained from the Merck India limited. Distilled water was purified by using the Milli-Q Plus apparatus (Millipore, Bedford, MA, USA).

2.1. Preparation of FeTiO$_3$ nanoparticles

TiO$_2$ nanoparticles were prepared by the drop wise addition of 5 mL of TiCl$_4$ (sigma Aldrich) in 100 mL distilled water containing 0.2 M HCl (AR Grade Purity-36.6) at 5°C ± 0.5°C and ultrasonicated for 1 hour at 82°C and kept for 18 hours at 82°C in a thermostat controlled oven (TiCl$_4$ + 2H$_2$O $\rightarrow$ TiO$_2$ + 4HCl). The obtained white precipitate was washed with distilled water ten times by using refrigerated centrifuge and finally washed with methanol. The methanol was then decanted and the precipitate (TiO$_2$ nanoparticles) was dried at 120°C for 4 hours. A 100 mL boiling solution of Iron nitrate (sigma Aldrich) was added drop wise to the boiling distilled water containing 2 g of TiO$_2$ nanoparticles. The solution was sonicated at 100°C about 30 min, according to the following chemical equation:

$$\text{TiO}_2(\text{aqua}) + \text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O(aqua)} \rightarrow \text{Fe}^{2+}-\text{TiO}_2$$

The obtained brown colour FeTiO$_2$ nanoparticles were washed with distilled water six times by using refrigerated centrifuge and finally washed with methanol. The FeTiO$_2$ nanoparticles dried at 120°C for 4 hours after decanted the methanol.

2.2. Standard stock solution

The stock solution of reference standard was prepared by weighing about 10 mg of tricyclazole of known purity into a 10 mL volumetric flask using an analytical balance having accuracy of 0.01 mg. The content of each flask was dissolved using HPLC grade acetonitrile and made up to the mark.

2.3. Sample stock solution

Accurately 132.77 mg of test item (purity 75.32%) of tricyclazole was taken into a 100 mL volumetric flask. The content was dissolved in 5 mL of acetonitrile, sonicated and made up to the mark with the acetonitrile. The concentration was 1000 mg/L solution. The stock sample solution was used for preparation of dose samples in different aqua’s buffers.

2.4. Acidic Buffer

The buffer solution of pH 4.0 was prepared by dissolving 4.0 g of disodium hydrogen orthophosphate in 1.0 L milli-Q water and the pH was adjusted to 4.0 using 1.0 mole/L hydrochloric acid solution.

2.5. Neutral Buffer

The buffer solution of pH 7.0 was prepared by dissolving 4.0 g of potassium dihydrogen orthophosphate in 1.0 L milli-Q water and the pH was adjusted to 7.0 using 1.0 mole/L sodium hydroxide solution.

2.6. Basic Buffer

The buffer solution of pH 9.0 was prepared by dissolving 1.25 g of boric acid and in 1.0 L milli-Q water and the pH was adjusted to 7.0 using 1.0 mole/L sodium hydroxide solution.

2.7. Photo catalytic studies

The photocatalytic studies were carried out in a borosil glass bottle under sunlight at GITAM University, Hyderabad. To the one litre of milli-Q water, pH 4.0, 7.0 and 9.0 buffer were spiked with 1 mL of 1000 mg/L stock solution of pesticide formulation to get 1µg/mL concentration of pesticide active in water (each pesticide was spiked into separate one litre glass bottle). Three sets of such samples in triplicates were prepared and sonicated for 10 minutes to get homogeneous concentration of pesticide active in water and labelled as S1, S2, and S3. Two sets of samples (S1 and S2) were added FeTiO$_2$ nanoparticles to get 0.06g/L content of photocatalyst (optimum amount). The sample suspension of FeTiO$_2$ were sonicated in the dark for 10 min before exposure to the sunlight, to get even disperse of FeTiO$_2$ particles in water and attain adsorption equilibrium. S1 and S3 sets of samples were exposed to sunlight from morning 8 am to evening 5 pm in the month of February. S2 set of samples were kept in an oven at 40°C in dark. The unexposed to sunlight samples (S2) were maintained for the measurement of nonphotocatalytic degradation of pesticide active in water. Milli-Q water spiked with stock solution of pesticide and without addition of FeTiO$_2$ nanoparticles (S3) were also exposed to sunlight for the measurement of photolytic degradation of pesticide in water. The FeTiO$_2$ added Milli-Q water without spiking of pesticides (S4) were also maintained as untreated control for the identification of absence of pesticides. The day temperature during the exposure period of soil samples under sunlight varied from 28 to 45°C. The intensity of the sunlight and temperature were measured during the exposure time using LUX meter.

2.8. Sampling data

Water samples were collected from the bottle at different depth on different occasion after exposure under sun light (0, 5, 9, 15, 18, 20, 27 and 36 hours for photocatalytic experiment. The collected water sample was centrifuged and filtered thoroughly 0.2 µ filter and analyzed in HPLC.

2.9. Chromatographic separation parameters

The HPLC-UV system used, consisted Shimadzu high performance liquid chromatography with LC-20AT pump and SPD-20A interfaced with LC solution software, equipped with a reversed phase Column

DOI: 10.9790/2402-100601109115 www.iosrjournals.org 110 | Page
Phenomenex C18 (25 cm x 4.6 mm i.d X 5µm particle size.), oven temperature was maintained at 40°C. The injected sample volume was 20µL. Mobile Phases A and B was Acetonitrile and 0.1% orthophosphoric acid in HPLC water (75:25 (v/v)). The flow-rate used was kept at 0.7 mL/min with a detector wavelength at 235 nm. The external standard method of Calibration was used for this analysis.

2.10. Method validation
Method validation ensures analysis credibility. Recovery studies were conducted by fortifying three different concentrations of each fungicide at 0.03, 0.15 and 0.3 µg/g levels in four different buffers. Three replicates determinations were made at each concentration level along with two control. Based on the recovery study the limit of quantification was established. Linearity was determined by different known concentrations (0.01, 0.05, 0.1, 0.5, 1.0 and 2.0 µg/mL) which were prepared by diluting the stock solution. The Limit of Detection (LOD, µg/mL) was determined as the lowest concentration giving a response of 3 times the baseline noise defined from the analysis of control sample. The Limit of Quantification (LOQ, µg/mL) was determined as the lowest concentration of a given fungicide giving a response of 10 times the baseline noise.

III. Results And Discussion

3.1. Description of FeTiO₂ nanoparticles
The scanning electron microscope (SEM) images of FeTiO₂ nanoparticles and Scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDX) for the quantitative determination and elemental composition of Fe/Ti ratio presented in Fig. 1 and Fig. 2 indicates the Fe content was 0.5 % and Ti, O and Fe are the elemental compositions and the size of the particle was observed to be 20-24 nm. The Fourier transform Infrared Spectroscopy was showed peaks at (652 –551 cm⁻¹), (1632 cm⁻¹) and (2235 cm⁻¹) indicated for molecular water, Ti-O and Ti-O-Fe stretching vibration band respectively and presented in Fig. 3.

3.2. Specificity
Specificity was confirmed by injecting the Mobile phase solvents i.e., Acetonitrile and 0.1% Orthophosphoric acid, HPLC water, sample solution standard solution and buffer controls (acidic, neutral, basic) There were no matrix peaks in the chromatograms to interfere with the analysis of fungicide residues shown in Fig. 4, Fig. 5 and Fig. 6. Furthermore, the retention time of tricyclazole was constant at 4.3 ± 0.2 min.

3.3. Linearity
Different known concentrations of tricyclazole (0.01, 0.05, 0.1, 0.5, 1.0 and 2.0 µg/mL) were prepared into a different 10 mL volumetric flasks by diluting the stock solution. These standard solutions were directly injected into a HPLC. A calibration curve has been plotted for concentration of the standards injected versus area observed and the linearity of method was evaluated by analyzing six standard concentration solutions. The details were presented in Table 1. The peak areas obtained from different concentrations of standards were used to calculate linear regression equation. This was Y=15771X + 1.3059 with correlation coefficient of 0.9998 respectively. A calibration curve is showed in Fig. 7.

3.4. Recovery
The methods were observed in precision with a acceptable range < 20 % of RSD when injected 10 x LOQ recovery sample five times consecutively into the HPLC. The statistical parameters such as standard deviation (SD) and percentage of relative standard deviation (% RSD) were presented in Table 2. The method had an acceptable recovery range (70 - 110 %) for fungicide in four different soil. The Limit of Quantification (LOQ) was established as 0.03 mg/L from 10:1 peak to noise height ratio. The statistical parameters for recovery such as mean recovery percentage, standard deviation (SD), percentage of relative standard deviation (% RSD) and Horwitz Limit are presented in Table 2. The formula for calculation residue and statistical parameters are presented below the equivation

\[
\text{Residue content (µg/mL)} = \frac{A \times C}{D}
\]

where,

\[A\] - Peak area of active content in sample (µV*sec)
\[C\] - Concentration of the standard solution µg/mL
\[D\] - Peak area of active content in standarde solution (µV*sec)

Recovered residue x 100

\[\text{Recovery \%} = \frac{\text{Fortified concentration}}{\text{Standard deviation \times 100}}\]
% RSD = \text{Mean} - \text{Horwitz Limit} = 2^{1+0.5 \times \log C} \times 0.67 \\
where, \ C \text{ – Concentration}

3.5. Photo catalytic decontamination of pesticide in water

On 0 hour analysis of tricyclazole fortified water showed that the residue of tricyclazole as 1.01 µg/L, 1.03 µg/L, 0.99 µg/L, and 1.02 µg/L, for milli-Q water, pH 4, pH 7 and pH 9 buffer water with 0.06 g/L load of catalyst respectively. The residues of tricyclazole dissipated to 0.33 µg/L, 0.31 µg/L on 18th h for milli-Q water, pH 7, for pH 4 and pH 9 dissipated to 0.21 µg/L, 0.33 µg/L on 9th h. On 27th h the tricyclazole concentration degraded to near the LOQ level for milli-Q water and pH 7, and got complete degradation on 36th h but pH 4 and pH 7 buffer water got complete degradation on 20th h.

The summarized results for photocatalytic studies are presented in Table 3 and Figure 8. The data clearly demonstrate that the decontamination of pesticide follows pseudo-first-order kinetics in FeTiO2 loaded water (S1) when calculated residues values with time by using below the first order kinetic formula (OECD 111). The absence of pesticide residues in S4 were observed because of no pesticide were applied and no degradation of fungicide in S2 were observed due to inactivation of the FeTiO2 in the absence of light. DT50 and DT90 values were calculated using the following formulas

\[ DT50 = \ln 2 / (k) \text{ and } DT90 = \ln 10 / (k) \]

Where, ‘k’ is slope of the curve obtained from the dissipation data.

The calculated DT50 and DT90 values are presented in Table 4. The rate constant value was calculated by linear regression equation from the first order rate equation.

\[ K = \ln \frac{a}{a-x} / dt \]

Where, dt is the time interval between t1 and t2 and a, x are the concentration of pesticides at times t1 and t2 respectively. A plot of concentration of the residues and rate with the R2 indicates first order kinetics in dissipation of fungicide. The, DT90 of tricyclazole calculated by regression analysis from the dissipation data. Results clearly indicate that the rate constant was high when the FeTiO2 was present in water than in absence of water and no degradation of pesticide in S2 set of water which were kept in dark. The decontamination was fast when studied under sunlight in presence of FeTiO2 in water due to the formation of electron (e-) and positive hole (h+) in TiO2 when it absorbed energy from sun light and the availability of electrons (e-) and the positive holes (h+) pairs which were contributing the simultaneous oxidation and reduction of pesticide in soil were enhanced by Fe in FeTiO2. This was confirmed by the no degradation of pesticide in water samples when store in dark. Absence of pesticide residues were also observed in water spiked (S4) water samples because of no pesticide was applied.

IV. Conclusion

The FeTiO2 nanoparticles were observed to be excellent decontaminating catalyst for tricyclazole in different water samples. In the absence of catalyst the compound persists several days. The mobile phase Acetonitrile and 0.1% orthophosphoric acid in HPLC water showed good separation and resolution and the analysis time required for the chromatographic determination of three different type of buffers is very short (around 15 min for a chromatographic run).

Satisfactory validation parameters such as linearity, recovery, precision and LOQ and DT 50 values were established by following South African National Civic Organization (SANCO) and Environmental Protection Agency (EPA) guidelines. Therefore, the proposed analytical procedure and dissipation data could be useful for regular monitoring, residue labs and research scholars to determine the tricyclazole residues in different commodities (crop, water and soil samples).

Acknowledgement

The authors are thankful to the Dr. K Raghur Babu, Professor, Department of Engineering Chemistry, Andhra University, Visakhapatnam for providing necessary facility to conduct the Laboratory experiment.

References


DOI: 10.9790/2402-100601109115 www.iosrjournals.org 112 | Page
Photo Catalytic Applications Of Ferrous Doped Titanium Dioxide Nanoparticles In Dissipation

**Fig. 4.** Representative Chromatogram of tricyclazole test item in acidic water - 5th hour

![Chromatogram of tricyclazole test item in acidic water - 5th hour](image)

**Fig. 5.** Representative Chromatogram of tricyclazole test item in neutral water - 9th hour

![Chromatogram of tricyclazole test item in neutral water - 9th hour](image)

**Fig. 6.** Representative Chromatogram of tricyclazole test item in basic water - 5th hour

![Chromatogram of tricyclazole test item in basic water - 5th hour](image)

**Fig. 7.** Representative Calibration curve of tricyclazole standard

![Calibration curve of tricyclazole](image)

Calibration curve of tricyclazole

- $y = 15771x + 1.3059$
- $R^2 = 0.9998$
- Tricyclazole
Photo Catalytic Applications Of Ferrous Doped Titanium Dioxide Nanoparticles In Dissipation

**Fig. 8.** Graph representing the dissipation curve of photocatalytic decontamination of tricyclazole in water under direct sunlight

![Graph representing the dissipation curve of photocatalytic decontamination of tricyclazole in water under direct sunlight](image)

**Table 1.** Calibration details – tricyclazole

<table>
<thead>
<tr>
<th>Concentration in (mg/L)</th>
<th>Peak area of tricyclazole (µv-sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>31425</td>
</tr>
<tr>
<td>1</td>
<td>15964</td>
</tr>
<tr>
<td>0.5</td>
<td>8029</td>
</tr>
<tr>
<td>0.1</td>
<td>1337</td>
</tr>
<tr>
<td>0.05</td>
<td>779</td>
</tr>
<tr>
<td>0.01</td>
<td>197</td>
</tr>
</tbody>
</table>

**Table 2.** Precision details – tricyclazole

<table>
<thead>
<tr>
<th>Statistical Parameters</th>
<th>Compound Name</th>
<th>Tricyclazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td></td>
<td>99</td>
</tr>
<tr>
<td>SD</td>
<td></td>
<td>1.25</td>
</tr>
<tr>
<td>% RSD</td>
<td></td>
<td>1.33</td>
</tr>
</tbody>
</table>

**Table 3.** Dissipation data for photocatalytic decontamination of tricyclazole in water under direct sunlight

<table>
<thead>
<tr>
<th>Tricyclazole</th>
<th>Occasion (hours)</th>
<th>Residues (µg/mL)</th>
<th>pH 8.0 (µv-sec)</th>
<th>Occasion (hours)</th>
<th>Residues (µg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Milli-Q Water</td>
<td>1.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.68</td>
<td>0.64</td>
<td>5</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>0.33</td>
<td>0.31</td>
<td>9</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>0.09</td>
<td>0.08</td>
<td>15</td>
<td>BDL</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>BDL</td>
<td>BDL</td>
<td>20</td>
<td>BDL</td>
</tr>
</tbody>
</table>

**Table 4.** Kinetic parameters for photocatalytic decontamination of tricyclazole in water under direct sunlight

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th>Water</th>
<th>pH 4.0</th>
<th>pH 7.0</th>
<th>pH 9.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricyclazole</td>
<td></td>
<td>3.97</td>
<td>7.46</td>
<td>4.26</td>
</tr>
<tr>
<td>DT50 (h)</td>
<td>7.79</td>
<td>13.20</td>
<td>24.78</td>
<td>14.14</td>
</tr>
<tr>
<td>DT90 (h)</td>
<td>25.88</td>
<td>174.4</td>
<td>92.9</td>
<td>162.9</td>
</tr>
<tr>
<td>k (1 x 10⁻³ h⁻¹)</td>
<td>89.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

DOI: 10.9790/2402-100601109115  www.iosrjournals.org  115 | Page