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DECONTAMINATION OF TETRACONAZOLE FUNGICIDE RESIDUES IN WATER SAMPLES USING $FeTiO_2$ NANOPARTICLES

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ABSTRACT

Decontamination of tetraconazole underneath direct daylight using Fe doped TiO_2 nanoparticles ($FeTiO_2$) as catalyst. $FeTiO_2$ nanoparticles are synthesized and characterised via scanning electron microscopy (SEM) blended with electricity Dispersive X-ray analysis (EDX) and FT-IR. The photocatalytic studies were conducted via the 1 litre of milli-Q water, pH 4.0, 7.0 and 9.0 buffer have been fortified with 1 mL of 1000 mg/L stock solution of tetraconazole 100 g/L EC to get 1 µg/mL awareness of pesticide animated in water. Three sets of such samples in triplicates were organized and sonicated for 10 minutes to get homogeneous concentration of pesticide active in water and categorized as S1, S2, and S3. Two units of samples (S1 and S2) have been introduced $FeTiO_2$ nanoparticles to get 0.06 g/L content material of photocatalyst. S1 and S3 units of samples were exposed to solar light. S2 set of samples have been kept in an oven at 40°C in dark. The milli-Q water spiked with stock answer of pesticide and without addition of $FeTiO_2$ nanoparticles (S3) were also exposed to sun mild for the size of photolytic degradation of pesticide in water. The $FeTiO_2$ added milli-Q water without spiking of pesticides (S4) was additionally maintained as untreated control for the identification of absence of pesticide. The amassed samples had been quantified using a validated HPLC-UV approach. Kinetic parameters including rate constant (k), DT50 and DT90 had been calculated the use of the dissipation details of tetraconazole.

Key words: Fe doped TiO_2, Tetraconazole, HPLC-UV, SEM, TEM, DT50 and DT90.

INTRODUCTION

The fungicide group, demethylation inhibitors (DMI), which include the triazole fungicides, was introduced in the mid-Nineteen Seventies. Triazoles include severa contributors, of which numerous are classified or are inside the technique of being categorized for use on area vegetation in Iowa--cyproconazole, flusilazole, flutriafol,

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metconazole, myclobutanil, propiconazole, prothioconazole, tebuconazole, and tetraconazole. Triazoles are used on many exclusive kinds of vegetation in Iowa such as field crops, fruit trees, small fruit, vegetables, and turf.[1,2] Those fungicides are fantastically powerful against many extraordinary fungal diseases, specifically powdery mildews, rusts, and many leaf-spotting fungi.[3] Tetraconazole is a huge spectrum fungicide possessing protecting, curative, and eradicant properties. It belongs to the triazoles chemical group and it is part of the SBI (Sterol Biosynthesis Inhibitors) institution, acting via inhibiting the meta-bolic pathway leading to fungal sterol production. It acts at the vegetative form of fungi blocking off the increase of the pathogen my-celium, each outdoor and within the handled plant.[4] The product suggests a very excessive and long lasting endotherapic interest. within the recent years using heterogeneous image catalyst nano Fe doped TiO_2 ($FeTiO_2$) in the degradation and mineralization of herbicide, insecticide, N-heterocyclic compounds, saturated fatty acids, extraordinary organic dyes in water and gaseous pollutant in air using UV and seen-light has received wide interest due to its low price practise, low toxicity, excessive balance and effectiveness than TiO_2[5] whilst $FeTiO_2$ nanoparticles are subjected to UV, VIS or solar mild, it gains power from light and sell electrons (e^-) from the valence band (VB) of TiO_2 to the conduction band (CB) leaving a advantageous hollow (h^+). Fe in $FeTiO_2$ lure electrons (e^-) and nice holes (h^+) from TiO_2 for the reason that electricity stages of Fe^{2+}/Fe^{3+} lies near that of Ti^{3+}/Ti^{4+}, and reduce the recombination of image-generated electron and hollow pair in TiO_2 and decorate the provision of electrons (e^-) and high quality holes (h^+) in $FeTiO_2$.[6] Those electrons (e^-) a[n]d fine holes (h^+) are regarding within the degradation of natural molecules by oxidation/reduction procedure.[7-9] Destroying of Escherichia coli microorganism in water were done completely within an hour with the aid of deposited Escherichia coli bacteria in water on $FeTiO_2$ thin movie and irradiating it in visible radiation,[10,11] eleven primarily based at the information gift have a look at turned into carried out to analyze the dissipation behavior of tetraconazole in three exclusive buffers the usage of $FeTiO_2$ as catalyst below natural climatic conditions in solar light.

EXPERIMENTAL

Materials and methods

Reference analytical standard of tetraconazole (purity 10.41%), Titanium tetrachloride and iron nitrate were obtained from Sigma Aldrich. The test item tetraconazole10.4% EC 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).

Preparation of $FeTiO_2$ nanoparticles

The 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 hr at 82°C and kept for 18 hrs at 82°C in a thermostat controlled oven ($TiCl_4 + 2\ H_2O \rightarrow TiO_2 + 4\ HCl$). 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 hrs. A 100 mL boiling solution of Iron nitrate (Sigma Aldrich) was added dropwise 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:

$$TiO_2\,(aqua) + Fe\,(NO_3)_3 \cdot 9H_2O\,(aqua) \rightarrow Fe\text{–}TiO_2$$

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 hrs after decanted the methanol.

Standard stock solution

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

Sample stock solution

Accurately 960.63 mg of test item (purity 10.41%) of tetraconazole 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.

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.

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.

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.

Photocatalytic 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 1 µg/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 mins 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 0.06 g/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 sun light 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 sun light 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 sun light 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.

Sampling data

Water samples were collected from the bottle at different depth on different occasion after exposure under sun light (0, 3, 6, 9, 12, 18, 27 and 36 hrs for photocatalytic experiment. The collected water sample was centrifuged and filtered thoroughly 0.2 µ filter and analyzed in HPLC.

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 Phenomenex C18 (25 cm x 4.6 mm i.d X 5 µm

particle size.), oven temperature was maintained at 30°C. The injected sample volume was 20 µL. Mobile Phases A and B was Acetonitrile and 0.1% orthophosphoric acid in HPLC water (65:35 (v/v)). The flow- rate used was kept at 1.0 mL/min with a detector wavelength at 220 nm. The external standard method of Calibration was used for this analysis.

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.

RESULTS AND DISCUSSION

Description of $FeTiO_2$ nanoparticles

The scanning electron microscope (SEM) images of $FeTiO_2$ 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. It 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.

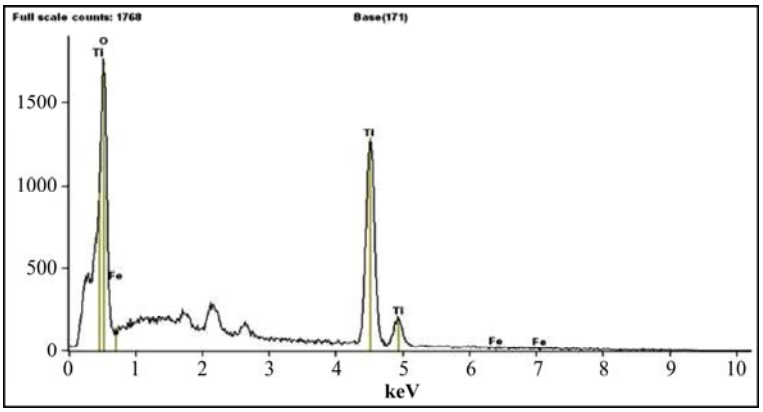

Fig. 1: EDX analysis of $FeTiO_2$ nanoparticles

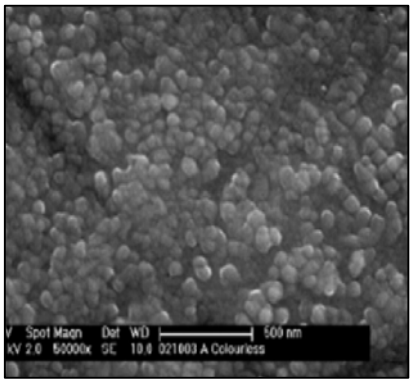

Fig. 2: SEM Image of $FeTiO_2$ nanoparticles

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.

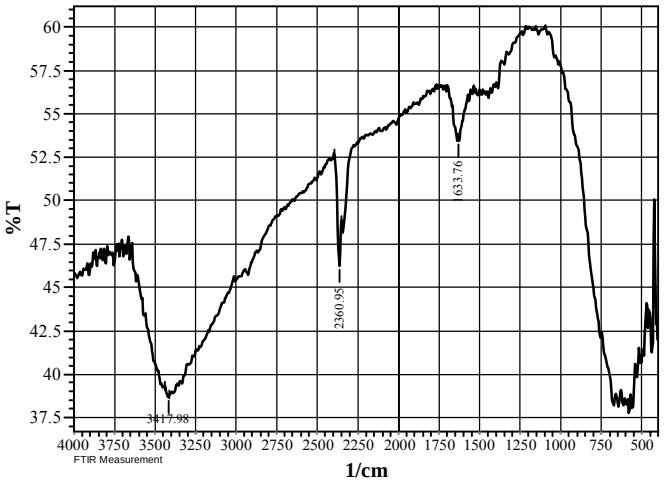

Fig. 3: FT-IR Spectra of $FeTiO_2$ nanoparticles

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 tetraconazolewas constant at 6.1 ± 0.2 min.

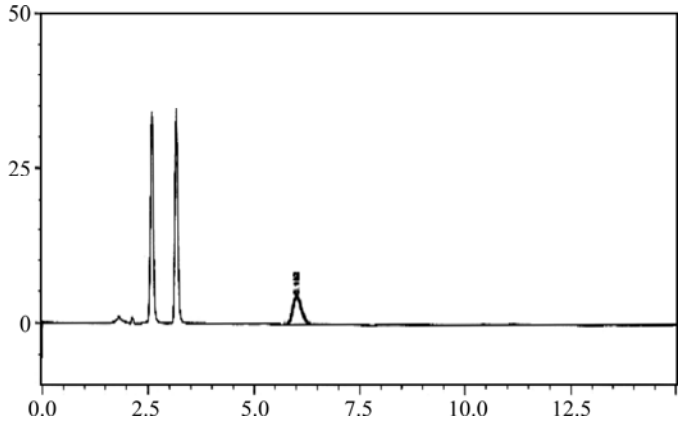

Fig. 4: Representative chromatogram of tetraconazole test item in acidic water- 3rd hr

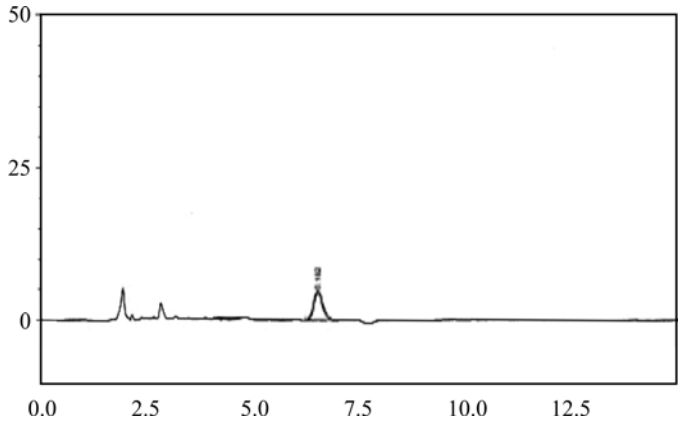

Fig. 5: Representative chromatogram of tetraconazole test item in neutral water -9th hr

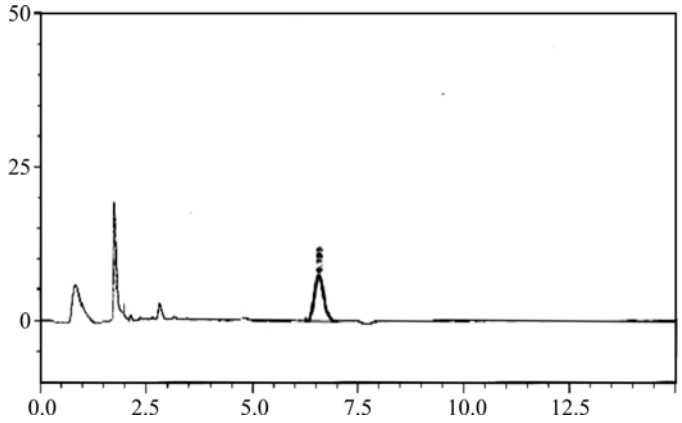

Fig. 6: Representative chromatogram of tetraconazole test item in basic water - 9th hr

Linearity

Different known concentrations of tetraconazole (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=11778X + 1.2976 with correlation coefficient of 0.9999, respectively. A calibration curve is showed in Fig.7.

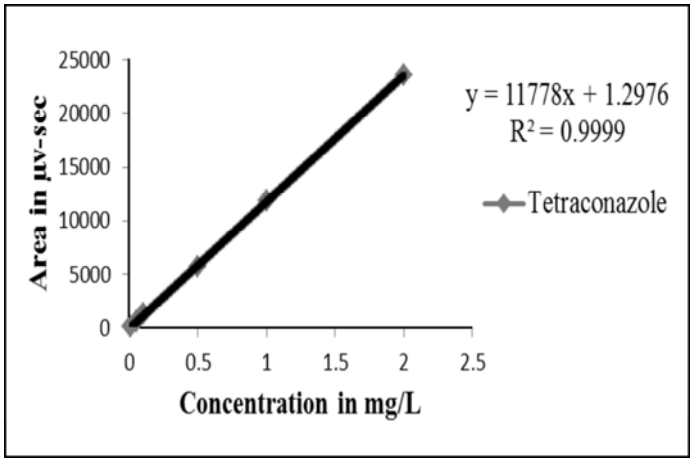

Fig. 7: Representative calibration curve of tetraconazole standard

Table 1: Calibration details –tetraconazole

Concentration in (mg/L)	Peak area of tetraconazole (µv-sec)
2	23551
1	11880
0.5	5695
0.1	1284
0.05	558
0.01	147

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.

Table 2: Precision details Tetraconazole

Statistical parameters	Compound name
	Tetraconazole
Precision	
Mean	98
SD	1.31
% RSD	1.54
Recovery	
Mean	99
SD	1.54
% RSD	1.62

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

$$\text{Residue content } (\mu g/mL) = \frac{A \times C}{D}$$

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)

$$\text{Recovery \%} = \frac{\text{Recovered residue x 100}}{\text{Fortified concentration}}$$

$$\% \text{ RSD} = \frac{\text{Standard deviation x } 100}{\text{Mean}}$$

Horwitz Limit = $2^{-(1-0.5 \times \log C)} \times 0.67$

where, C – Concentration

Photocatalytic decontamination of pesticide in water

On 0 hour analysis of tetraconazole fortified water showed that the residue of tetraconazole as 1.03 µg/L, 1.01 µg/L, 1.02 µg/L, and 0.97 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 tetraconazole dissipated to 0.34 µg/L, 0.35 µg/L, 0.43 µg/L, on 18th h for milli-Q water, pH 4, and pH 7 with 0.06 g/L load of catalyst, respectively. On 27th h the tetraconazole concentration degraded to near the LOQ level for milli-Q water, pH 4, pH 7 and got complete degradation on 36th h but pH 9 buffer water got complete degradation on 12th h.

The summarized results for photocatalytic studies are presented in Table 3 and Fig. 8. The data clearly demonstrate that the decontamination of pesticide follows pseudo-first-order kinetics in $FeTiO_2$ 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 $FeTiO_2$ in the absence of light.DT50 and DT90 values were calculated using the following formulas

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

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.

$$K = \ln a/a\text{-}x/dt$$

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 tetraconazole calculated by regression analysis from the dissipation data.

Table 3: Dissipation data for photocatalytic decontamination of tetraconazole in water under direct sunlight

Tetraconazole					
Occasion (hrs)	**Residues (µg/mL)**		**Occasion (hrs)**	**Residues (µg/mL)**	
	Milli-Q water	**pH 7.0**		**pH 4.0**	**pH 9.0**
0	1.01	1.03	0	0.99	1.02
9	0.68	0.64	5	0.49	0.62
18	0.33	0.31	9	0.21	0.33
27	0.09	0.08	15	BDL	0.09
36	BDL	BDL	20	BDL	BDL

Table 4: Kinetic parameters for photocatalytic decontamination of tetraconazole in water under direct sunlight

Tetraconazole					
Occasion (hrs)	**Residues (µg/mL)**			**Occasion (hrs)**	**Residues (µg/mL)**
	Milli-Q Water	**pH 7.0**	**pH 9.0**		**pH 4.0**
0	1.03	1.01	1.02	0	0.97
9	0.62	0.59	0.69	3	0.58
18	0.34	0.35	0.43	6	0.29
27	0.11	0.09	0.17	9	0.09
36	BDL	BDL	0.05	12	BDL

Results clearly indicate that the rate constant was high when the $FeTiO_2$ 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 $FeTiO_2$ in water due to the formation of electrons (e^-) and positive hole (h^+) in TiO_2 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 $FeTiO_2$. 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.

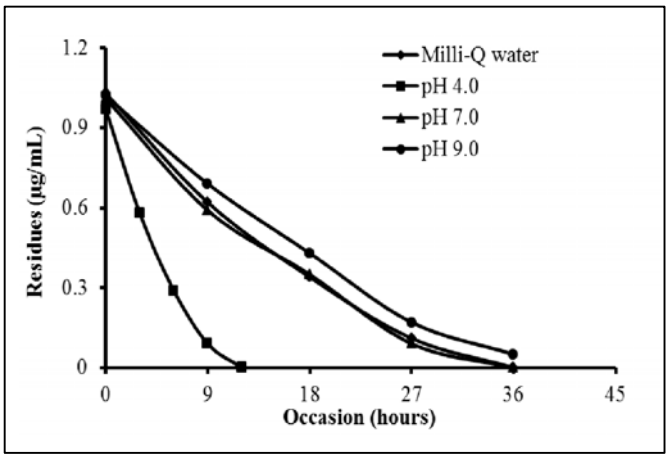

Fig. 8: Graph representing the dissipation curve of photocatalytic decontamination of tetraconazole in water under direct sunlight

CONCLUSION

The $FeTiO_2$ nanoparticles had been determined to be excellent decontaminating catalyst for tetraconazole in individual water samples. In the absence of catalyst the compound persists many days. The moble phase Acetonitrile and 0.1% orthophosphoric acid in HPLC water confirmed good separation and determination and the evaluation time required for the chromatographic determination of 3 distinct kind of buffers could be very quick (around 15 min for a chromatographic run).

Satisfactory validation parameters including linearity, recuperation, precision and LOQ and DT 50 values have been mounted by means of following South African National Civic Organization (SANCO) and Environmental Protection Agency (EPA) guidelines. Therefore, the proposed analytical method and dissipation information can be useful for regular monitoring, residue labs and studies students to determine the tetraconazole residues in different commodities (crop, water and soil samples).

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