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Photocatalytic degradation kinetics of pesticide residues in different pH waters using metal-doped metal oxide nanoparticles

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Abstract

We report the dissipation behavior of pyrazosulfuron-ethyl under direct sunlight using iron-doped titanium dioxide nanoparticles ($FeTiO_2$) as a catalyst. The test was carried out by reinforcement three varying aqueous pH solutions with pH~4.0,7.0 and 9.0 to make the homogeneous concentrations of T0 – untreated control, T1 – pyrazosulfuron-ethyl 70% WG @ 1 mg/L of pH water and T2 – pyrazosulfuron-ethyl 70% WG @ 2 mg/L of pH water. The fortified test samples were exposed to sunlight. The sampling occasions were 0, 1, 5, 10, 24, 48, 72 and 96th hours for all three different aqueous solutions having pH ~ 4.0 (acidic water), 7.0 (neutral water) and 9.0 (basic water). The acquired samples were quantified using validated high-pressure liquid chromatography with UV detection technique. The pyrazosulfuron-ethyl half-life (DT50) was calculated from the dissipation results by regression equation. The $FeTiO_2$ nanoparticles were determined to be a wonderful decontaminating catalyst for pyrazosulfuron-ethyl in various water samples.

Keywords
Fe doped TiO_2*, Pyrazosulfuron-ethyl, HPLC-UV, FT-IR, Herbicide, SEM*

Introduction

Sulfonylurea herbicides are a moderately new class of aggravates whose herbicidal action was found in the mid-1970s (Klaffenbach et al., 1993; Zhan et al., 2004). They are broadly used everywhere in the globe for controlling weeds in a few harvests, e.g., rice, wheat, maize, grain, sugar beet, and tomato. Their fast and great acknowledgment was because of the high viability at low application rates (10-15 g/ha) and low intensity and ceaseless mammalian toxicities (Zheng et al., 2008). The pyrazosulfuron-ethyl is a foundational sulfonylurea herbicide for control of different yearly and perpetual wide leaved weeds and sedges in the rice field (Wang et al., 2012; Wanget et al., 2013; Naveen et al., 2012). It is utilized as a pre or post new herbicide and was observed to be compelling at low portion rates. What's more, in view of its physical and synthetic properties, it tends to be given in the three noteworthy plans utilized in paddy rice culture in Japan, to be specific granular definition, suspension concentrate and large detailing. Besides, it demonstrates an abnormal state of security for warm-blooded animals, winged animals and amphibian living beings (Mukherjee et al., 2006; Singh et al., 2012; Yang et al., 2013). In latest years, the use of heterogeneous photocatalyst iron doped titanium dioxide nanoparticles (FeTiO2) in the degradation and mineralization of herbicide, insecticide, N-heterocyclic compounds, saturated fatty acids, various organic dyes in water and gaseous pollutants in air using UV and visible light has achieved broad publicity owing to its low-cost preparing, low toxicity, excellent stability and effectiveness than TiO_2 (Ghorai et al., 2015). Since the energy levels of Fe^{2+} and Fe^{3+} ions are closer to that of Ti^{3+} and Ti^{4+} ions, the iron (Fe) in $FeTiO_2$ trap electrons (e^-) and positive holes (h^+) from TiO_2 decreases the

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recombination of the photographed electron and gap pair in TiO_2 and improves the accessibility of electrons (e-) and positive gaps (h+) in $FeTiO_2$. These electrons (e-) and positive holes (h+) are involved in the degradation of organic molecules by oxidation/reduction process (Carey et al., 1976; Joung et al., 2006; Sun et al., 2006). The destruction of Escherichia coli organisms in water was accomplished in an hour by depositing Escherichia coli microorganisms in the water on FeTiO2 thin film and illuminating it in distinctive radiation (Zhang et al., 2000; Ruzmanova et al., 2013). With this motivation, we placed a lot of effort into investigating the dissipation activity of pyrazosulfuron-ethyl in three different pH waters using FeTiO2 nanoparticles as a catalyst in UV-Visible solar light under natural climate circumstances.

Materials and methods

The analytical reagent grades of pyrazosulfuron- ethyl (purity 99.8%), titanium tetrachloride ($TiCl_4$) and iron nitrate were obtained from Sigma Aldrich. The test item pyrazosulfuron- ethyl 70% wettable granule (WG) was purchased from the local market. Acetonitrile, water (HPLC grade), orthophosphoric acid (analytical reagent grade), sodium hydroxide (laboratory reagent grade), potassium chloride (guaranteed reagent grade), boric acid (guaranteed reagent grade), potassium biphthalate (guaranteed reagent grade), hydrochloric acid (HCl, analytical reagent grade) and potassium phosphate (KH_2PO_4, analytical reagent grade) were purchased from the Merck India limited. Distilled water was obtained by using the Milli-Q Plus device.

Preparation of $FeTiO_2$ nanoparticles

The TiO_2 nanoparticles were prepared by adding 5 ml of TiCl4 in 100 ml of distilled water containing 0.2 M HCl at 5 ° C ± 1 ° C for 1 hour at 85° C and kept in a thermostat-controlled oven for 18 hours at 85° C. The acquired white precipitate was tidied ten times with distilled water using a cooled centrifuge and furthermore washed with methanol. The methanol was then decanted and the precipitate was dehydrated for 4 hours at 120 °C to achieve the TiO_2 nanoparticles. After this, a 100 ml boiling a solution of iron nitrate was added dropwise to the 2% of aqueous TiO2 solution. The solution was sonicated at 100 °C for 30 minutes to achieve the brown color precipitate. The brown precipitate obtained was tidied six times with distilled water using a refrigerated centrifuge and furthermore washed with methanol. Again, methanol was dehydrated and the precipitate was dehydrated at 120 ° C for 4 hours to achieve the $FeTiO_2$ nanoparticles. The overall basic reaction for the formation of TiO_2 and $FeTiO_2$ nanoparticles can be expressed as follows:

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl \qquad [1]$$

$$TiO_2\,(Aqua.) + Fe(NO_3)_3{\cdot}9H_2O\,(Aqua.) \rightarrow FeTiO_2 \qquad [2]$$

Preparation of pyrazosulfuron-ethyl standard stock solution

Accurately 10.08 mg of the pyrazosulfuron-ethyl reference standard (purity, 99.8 %) was weighed into 20 ml volumetric flask; 10 ml of acetonitrile was added and sonicated to dissolve the content and made sufficient with the same dissolvable. The concentration of the solution was 503.0 mg/l and stored in a freezer at the temperature of -18 °C. The stock reference standard solution was used for up to 3 months. The suitable concentrations of working standards were prepared by the stock solution by diluting with acetonitrile, immediately prior to sample preparation.

Preparation of pyrazosulfuron-ethyl sample stock solution

Accurately 28.51 mg of test item (purity 70.15%) of pyrazosulfuron- ethyl was taken into a 20 ml volumetric flask, 5 ml of acetonitrile is added in a same volumetric flask, sonicated and made sufficient with the acetonitrile. The obtained concentration of the solution was 1000 mg/l. This solution of the stock sample was utilized for the preparation of dose samples (T1 and T2) in distinct aqueous buffers.

Preparation of acidic (pH ~ 4.0), neutral (pH ~ 7.0) and basic (pH ~ 9.0) water

The 8 g of KH_2PO_4 was dissolved in 1000 ml of distilled water for the preparation of acidic water. The pH of the buffer was changed in accordance with 4.0 with the same. For preparing the neutral water 6.3 g of disodium hydrogen orthophosphate and 5 g of KH_2PO_4 was dissolved in 1000 ml of deionized water. The pH of the buffer was changed in accordance with 7.0 with the same. On the other hand, basic water as prepared by dissolving the 12.5 g of boric acid and 15 g KCl in 1000 ml of deionized water. The pH was adjusted to 9.0 using 0.1M NaOH solution.

Chromatographic separation parameters

The Shimadzu high-performance liquid chromatography system was used with LC- 20ATvp pump with LC solution software, equipped with a reversed phase column eclipse X terra-C8 (150 mm x 4.6 mm i.d x 3.5µm particle size). The oven temperature was maintained at 30°C and the injected sample volume was 20µl. The ACN and 0.1% orthophosphoric acid [55:45 (v/v)] were two mobile phases A and B, respectively. The flow rate utilized was kept at 0.9 ml/min with detection of wavelength at 254 nm.

Name of the buffers	**Acidic, Neutral and Basic**
Replications	Three
Method of fortification	T0 (Untreated control) The 60 mg of $FeTiO_2$ nanoparticles mixed into respective buffer solution and before exposure to sunlight, the suspension samples of $FeTiO_2$ were sonicated in dark for the duration of 10 min to achieve homogeneous disperse of $FeTiO_2$ nanoparticles in water and attain adsorption equilibrium. T1 (1 mg/l level) The 1.0 ml of test item stock solution was spiked into one liter of each buffer solutions and added 60 mg of $FeTiO_2$ nanoparticles. Before exposure to sunlight, the suspension samples of $FeTiO_2$ was sonicated in dark for the duration of 10 min to achieve homogeneous disperse of $FeTiO_2$ nanoparticles in water and attain adsorption equilibrium. T2 (2 mg/l level) The 2.0 ml of test item stock solution was spiked into one liter of each buffer solutions and added 60 mg of $FeTiO_2$ nanoparticles. Before exposure to sunlight, the suspension samples of $FeTiO_2$ was sonicated in dark for the duration of 10 min to achieve homogeneous disperse of $FeTiO_2$ nanoparticles in water and attain adsorption equilibrium.

Table 1. Pyrazosulfuron-ethyl sample and $FeTiO_2$ nanoparticles application data in different pH waters

Sample exposure	Under direct sunlight	
Sample preparation	During each sampling occasion, water samples were mixed thoroughly and subsampled 10 ml using a pipette.	
Occasion (Hours)	0, 1, 5, 10, 24, 48, 72, 96 (pH ~ 4.0, 7.0 and 9.0)	
Location	Visakhapatnam: Latitude – 17.700^0, Longitude- 83.250^0	
Laboratory condition	Temperature	
	Minimum	Maximum
	20.7 °C	25. 8 °C

Table 2. Sampling data of different pH waters

Method validation

The method validation ensures the analysis reliability. In this study, the validated parameters recovery, linearity and limits of Quantification (LOQ) and Limits of Detection (LOD) were considered. The accuracy of the method used was determined by the recovery tests, using samples fortified at concentration levels of 0.05 and 0.5 µg/ml. The linearity was determined by different concentrations (0.05, 0.1, 0.5, 1.0, 2.0, and 5.0 µg/ml) which were prepared by diluting the stock solution. The LOD (mg/l) was determined as the lowest concentration of analyte giving a performance of thrice the baseline noise definite from the analysis of the control sample. The LOQ (mg/l) was determined as the lowest concentration of analyte given herbicide giving a response often times the baseline noise.

Results and discussion

Description of $FeTiO_2$ nanoparticles

The morphology of the $FeTiO_2$ nanoparticles was analyzed by field-emission scanning electron microscopy TESCAN; MIRA II LMH microscope as shown in Figure1. The average particle size was estimated using the slope-intercept method and was found to 22 nm. Also, an inhomogeneous particle size distribution was observed. The elemental composition of $FeTiO_2$ nanoparticles was evaluated by energy dispersive X-ray spectrometry (EDS) with an operating voltage of 15.0 kV within the energy range of 0.0-10.0 keV. Figure 2 showed the elemental composition of the nanoparticles determined by EDS. Only oxygen (O), iron (Fe) and Titanium (Ti) signals have been detected which

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confirms that the nanoparticles are primarily $FeTiO_2$.

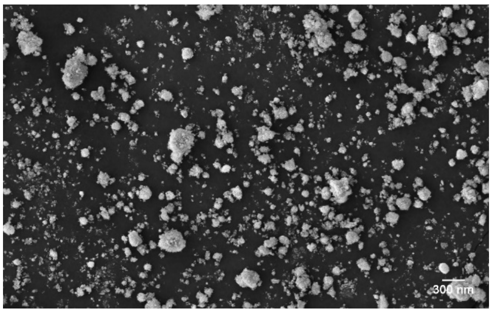


Figure 1. Field-emission scanning electron micrograph of $FeTiO_2$ nanoparticles

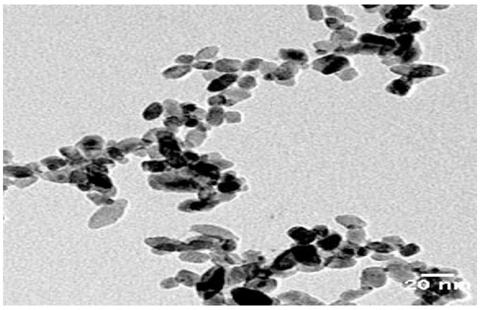
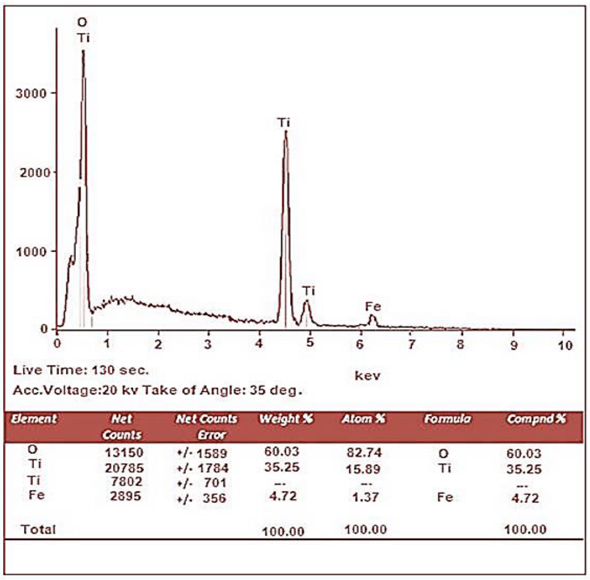


Figure 2. HRTEM of $FeTiO_2$ nanoparticles

The Fourier transmission infrared spectrum of the $FeTiO_2$ nanoparticles (as pellets in KBr) was observed with the help of a Fourier transmission infrared spectrometer in the range of 4000.0-400.0 cm^{-1} at ambient temperature as shown in Figure 3. The FT-IR spectra showed main absorption bands near (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.



Element	Net Counts	Net Counts Error	Weight %	Atom %	Formula	Compnd %
O	13150	+/- 1589	60.03	82.74	O	60.03
Ti	20785	+/- 1784	35.25	15.89	Ti	35.25
Ti	7802	+/- 701	---	---		---
Fe	2895	+/- 356	4.72	1.37	Fe	4.72
Total			100.00	100.00		100.00

Figure 3. EDS spectrum of $FeTiO_2$ nanoparticles

The phase purity of the $FeTiO_2$ nanoparticles was determined using by X-ray diffraction technique at room temperature using a Phillips X'pert MPD 3040 with CuKα radiations (λ = 1.5406.0 Å) operated at a voltage of 40.0-kilovolt and current of 30.0 milli angstroms. In Figure 4 the XRD patterns of $FeTiO_2$ nanoparticles show that the single phase sample was obtained. The peaks at diffraction angles of 25.46°, 37.35°, 38.18°, 38.94°, 48.41°, 54.24°, and 55.46°, related to the planes, (101), (004), (200), (105), (211), (204), (116), (220), and (215), respectively of anatase TiO_2 crystal, indicating that the sample consists of anatase as a unique phase, which is well matched with the JCPDS card NO. 460513. It is notable that no diffraction peak accredited to iron oxide can be found in the XRD pattern (Fig. 5), suggesting that the iron ions (Fe^{3+}) don't exist as a single phase however as a replacement part of Ti^{4+} ions into the crystal lattice of TiO_2. This is because the radius of Fe^{3+} is very similar to that of Ti^{4+}.

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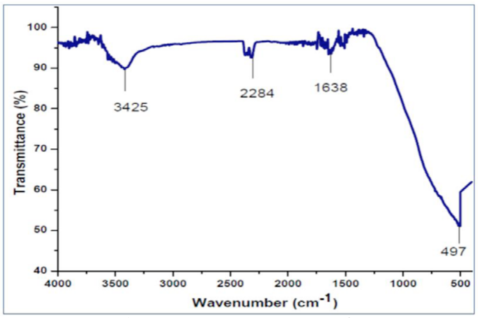

Figure 4. The FT-IR spectrum of $FeTiO_2$ nanoparticles

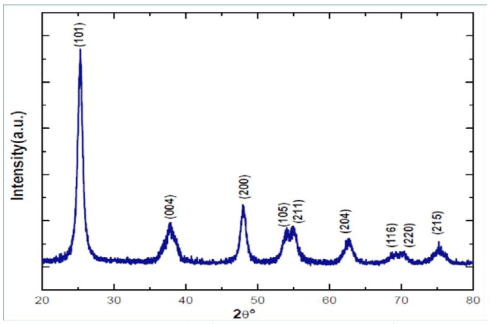

Figure 5. X-ray diffraction pattern of $FeTiO_2$ nanoparticles

Method Specificity. Specificity of the method was checked by injecting acetonitrile, pyrazosulfuron-ethyl reference standard and sample solutions and sample fortified 3 different water solutions. From the analysis it was found that none of the peaks interfered. Representative chromatograms of specifity are presented in Figures 6a, 6b, 6c.

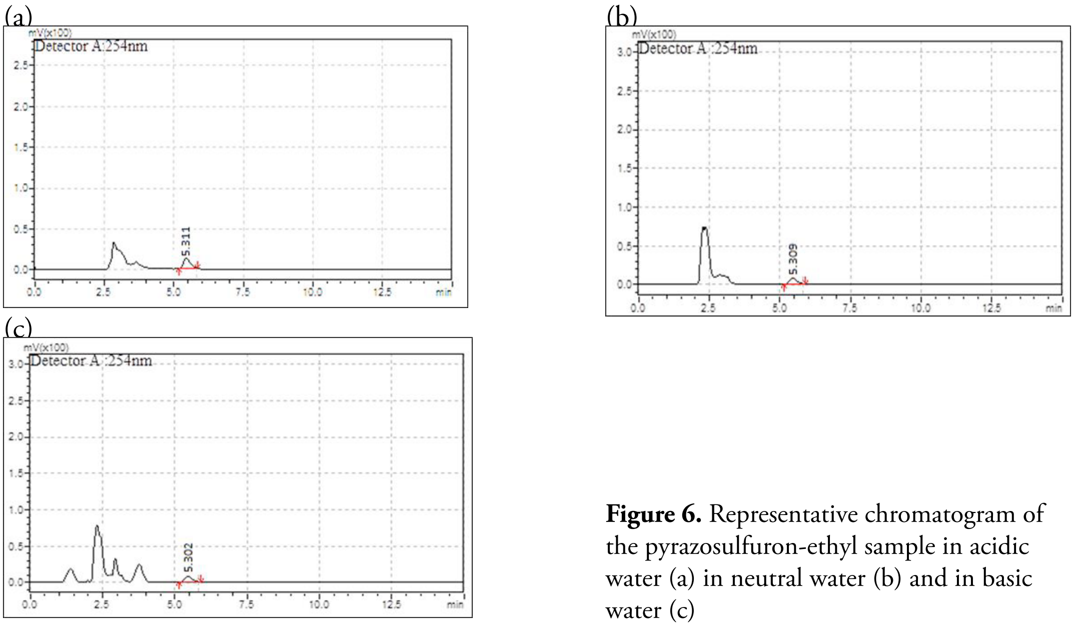

Figure 6. Representative chromatogram of the pyrazosulfuron-ethyl sample in acidic water (a) in neutral water (b) and in basic water (c)

Linearity. Different known concentrations of herbicide (0.05, 0.1, 0.5, 1.0, 2.0 and 5.0 µg/ml) were prepared into a varying 10 mL volumetric flasks by diluting the stock solution. The dilution details were provided in table 3.

Stock solution concentration (µg/mL)	The volume is taken from the stock solution (mL)	Finally makeup volume (mL)	Obtained concentration (µg/mL)
503.00	1.988	10	100
100	0.500	10	5
100	0.200	10	2
100	0.100	10	1
5	1.000	10	0.5
5	0.200	10	0.1
1	0.500	10	0.05

Table 3. Serial dilutions for linearity standard solutions

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A linearity curve was drawn for standard concentrations and these areas. The linearity of the method checked out by analyzing six standard concentration solutions. The linear regression equation was calculated using different standard concentrations with respective areas. This was Y=37038X – 194.69 with a regression coefficient of 0.9999 respectively. A calibration curve is shown in Figure 7.

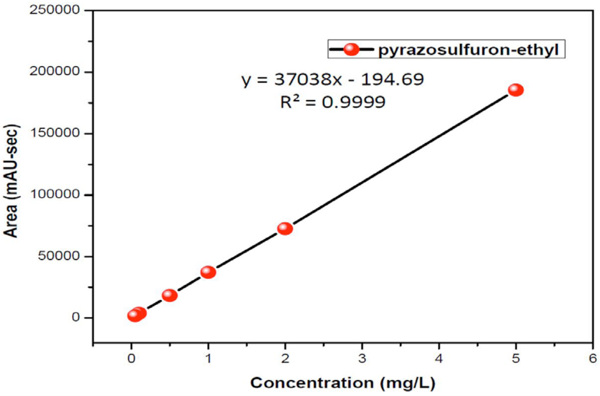

Figure 7. Representative calibration curve of pyrazosulfuron-ethyl standard

Recovery. Recovery studies in acidic, neutral and basic water were conducted by fortifying different concentrations of standard solutions (0.05 and 0.5 mg/L) of pyrazosulfuron-ethyl. The mean percent recovery for pyrazosulfuron-ethyl in acidic, neutral and basic water was 89.23±1.36; 87.58±1.51and 86±1.71 at 0.05 mg/L fortification level, 93±1.64; 91±1.1.18and 90±1.86 at 0. 5 mg/L fortification level.

Limits of Quantification (LOQ) and Limits of Detection (LOD). The LOQ was evaluated to be 0.05 mg/l. The limit of quantification was defined as the minimum fortification level estimated at which acceptable average recoveries (84-94%, RSD<2%) were achieved. This limit of quantification also reflects the spiked level at which an analyte peak was consistently generated at approximately ten times the baseline noise in the chromatogram. The LOD was determined to be 0.02 mg/l, at a level of about thrice the background of control injection over the retention time of the peak of interest.

Photocatalytic dissipation details

Acidic water. The initial concentration of pyrazosulfuron- ethyl in acidic water (0th hour) was 0.991 mg/l and 1.986 mg/l in T1and T2 dosages respectively, which on 5th hour dissipated to 0.872 mg/l and 1.605 mg/l. The 10th hour samples showed the residues 0.652 mg/l (T1) and 1.312 mg/l (T2), 24th hour samples showed 0.411 mg/l (T1) and 0.820 mg/l (T2), 48th hour samples showed 0.102 mg/l (T1) and 0.206 mg/l in (T2), 72th hour samples showed 0.057 mg/l (T1) and 0.119 mg/l (T2). A complete dissipation of residues to below detectable level (BDL) was observed on the 96th hour in both the tested sample dosages (T1) and (T2).

Neutral water. The initial concentration of pyrazosulfuron- ethyl in acidic water (0th hour) was 0.973 mg/l and 1.976 mg/l in T1and T2 dosages respectively, which on 5th hour dissipated to 0.826 mg/l and 1.582 mg/l. The 10th hour samples showed the residues 0.592 mg/l (T1) and 1.215 mg/l (T2), 24th hour samples showed 0.369 mg/l (T1) and 0.779 mg/l (T2), 48th hour samples showed 0.094 mg/l (T1) and 0.197 mg/l in (T2), 72th hour samples showed 0.054 mg/l (T1) and 0.109 mg/l (T2). A complete dissipation of residues to below detectable level (BDL) was observed on the 96th hour in both the tested sample dosages (T1) and (T2).

Basic water. The initial concentration of pyrazosulfuron- ethyl in acidic water (0th hour) was 0.964 mg/l and 1.882 mg/l in T1and T2 dosages respectively, which on 5th hour dissipated to 0.815 mg/l and 1.584 mg/l. The 10th hour samples showed the residues 0.559 mg/l (T1) and 0.903 mg/l (T2), 24th hour samples showed 0.214 mg/l (T1) and 0.526 mg/l (T2), 48th hour samples showed 0.072 mg/l (T1) and 0.167 mg/l in (T2), 72th hour samples showed 0.053 mg/l (T1) and 0.094 mg/l (T2). A complete dissipation of residues to below detectable level (BDL) was observed on the 96th hour in both the tested sample dosages (T1) and (T2).

The dissipation curve was plotted between the sampling occasions and a concentration of the analyte is shown in Figure 8.

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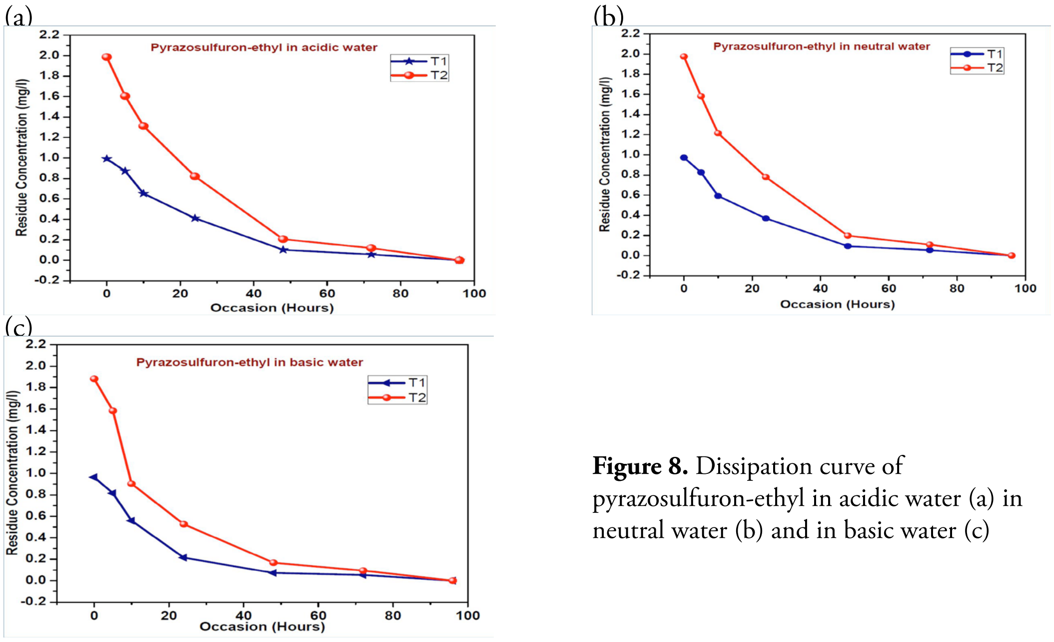

Figure 8. Dissipation curve of pyrazosulfuron-ethyl in acidic water (a) in neutral water (b) and in basic water (c)

The DT50 (time required to degrade 50% of residues i.e. half-life) value was calculated using the following formula:

$$DT50 = \frac{\ln(2)}{K} \qquad [3]$$

where K is the slope of the curve occurred from the dissipation data. The rate constant was determined by linear regression equation utilizing the first order rate equation [4]

$$K = \frac{\ln\left(\frac{a}{-b}\right)}{dt} \qquad [4]$$

where, *a* and *b* are the concentration of pyrazosulfuron-ethyl at time t_1 and t_2, respectively, and dt stands for a time interval between t_1 and t_2. A plot (Fig. 7) of concentration of the residues and rate with the $R^2=1$ indicates first-order kinetics in the dissipation of herbicide. The DT50 of pyrazosulfuron-ethyl evaluated by regression analysis of the dissipation data. The calculated DT 50 values are presented in table 4; it shows slight variation with different water samples (acidic, neutral and basic).

Water samples	Parameters	Dosages	
		T1	T2
(a) Acidic water	Regression équation	Y = 0.005– 0.018* X	Y = 0.293–0.018* X
	Half-life (Hours)	16.5	16.9
	Correlation coefficient	-0.992	0.991
(b) Neutral water	Regression équation	Y = -0.023– 0.018* X	Y = 0.282 – 0.018 * X
	Half-life (Hours)	16.4	16.6
	Correlation coefficient	-991	-0.992
(c) Basic water	Regression équation	Y = -0.078– 019* X	Y = 0.215–0.215* X
	Half-life (Hours)	16.1	16.3
	Correlation coefficient	-0.972	-0.987

Table 4. *Pegression analysis – Acidic water (a), neutral water (b), basic water (c) for Pyrazosulfuron-ethyl*

Conclusions

The $FeTiO_2$ nanoparticles ware observed as excellent decontaminating catalyst for removal of pyrazosulfuron-ethyl in different water samples. In absence of catalyst, the compound dissipated several days. Influence of this catalyst we reduced pesticides toxicity in an environment as well as reduced the toxic impact to human and animals.

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