Applications of Zinc Oxide Nanorods as Photocatalyst for the Decontamination of Imidacloprid and Spirotetramat Residues in Water

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Abstract: Zinc oxide nanorods having the size 100 to 250 nm and 1 to 2 μm length were prepared by reacting zinc acetate with triethanolamine. The structure of the nanorods was confirmed by scanning electron microscope analysis. Photocatalytic activity of zinc oxide nanorods on the new class of ketoenole and chloronicotinyl insecticides spirotetramat and imidacloprid was investigated. The decontamination effect of catalyst on the residues of spirotetramat and imidacloprid in water was studied at three different buffer solutions (4.0, 7.0 and 9.0). The catalytic reaction was measured under direct sunlight at two different concentration levels and the optimum concentration of catalyst required for the decontamination was also established by varying the amount of catalyst from 0.02 to 0.2 g/L. Residues are quantified by a high performance liquid chromatography UV method (HPLC-UV) and calculated the DT 50 and DT 90 from the dissipation data. The rate of the reaction showed first order kinetics in water. The addition of zinc oxide nanorods induced the photocatalytic reaction contributing significantly to the rapid dissipation of residues. Complete mineralization of the residues was confirmed by liquid chromatography electrospray tandem mass spectrometry (LC-ESI-MS/MS). The method has the limit of quantification 0.1 μg/L in water.

Keywords: Zinc oxide nanorods, Photocatalysis, Spirotetramat, Imidacloprid, LC-ESI-MS/MS.

INTRODUCTION

Pesticides are widely used in agriculture to bring down the pest infestations in the field eventually contributing to the problem of environmental contamination. Presence of agrochemical residues in water reservoirs and other environmental strata leads to environmental contamination and poses risk to the living organisms. Bayer Crop Science (India) introduced the spirotetramat (*cis*-3-(2, 5-dimethylphenyl)-8-methoxy-2-oxo-1-azaspiro [4.5] dec-3-en-4-yl ethyl carbonate; ketoenole insecticide) and Imidacloprid (1-[(6-chloro-3-pyridyl)-methyl] - 2-nitroimidazolidin; chloronicotinyl insecticide) as combinational insecticides (480 SC formulation) for the control of broad spectrum of sucking pests in agriculture.

The literature shows different methods for the determination of imidacloprid residues in environmental samples with lower than the CODEX (maximum residue) limit [1]. Several reports are published for the determination of residues of imdacloprid in water and other environmental substrates including the application of titania as photocatalytic agent for the decontamination of residues. Photocatalytic degradation of imidacloprid in water was studied with heterogeneous catalysis TiO₂ and homogeneous catalysis (by Photo-Fenton) under direct sunlight and UV irradiation [2-8]. The semiconductor oxides (TiO₂ and ZnO) are found to be most effective in photocatalytic degradation of residue of organophosphorus pesticide in water [9]. Degradation of neonicotinoid insecticides using oxidation process, effect of ozone on TiO_2 photocatalysis [10], the catalytic activity of TiO_2 on imidacloprid and other environmental contaminants [11-15] are widely reported by different researchers. Typically heat treated kerolites are also used for the decontamination of residues of imidacloprid in water and reported the influence of temperature on the degradation [16]. A comparative study between zinc oxide nanoparticle and its nano-crystalline particles in degradation of methylene blue in water under the influence of UV rays shows relatively high photocatalytic degradation capacity of ZnO nanoparticles than the ZnO nano crystallines [17]. The zero valent metals with ultrasonic irradiation showed good potential in degradation of thimethoxam and imidacloprid residues in water [18]. To meet the requirement of very low detection levels of imidacloprid and other pollutants, several methods including liquid chromatography UV detection and the tandem mass spectrometry detections are reported [19-22].

However the data pertaining to the fate of spirotetramat and its residues in water and the information on the application of zinc oxide nanorods as catalyst is scarce. In view of the paucity of information, present study was conducted with an objective to establish the photocatalytic activity of zinc oxide nanorods in decontamination of residues of imidacloprid, spirotetramat in water. The effect of zinc oxide nanorods in photocatalysis as a reaction enhancer in degradation of residues was studied and the data has been confirmed by LC-ESI-MS/MS analysis.

MATERIALS AND METHODS

Materials

Reference analytical standards of spirotetramat purity 99.4%, metabolite enol purity 99.4% and imidacloprid purity

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98.6%, the suspension concentration (SC) formulation of combinational insecticide were supplied by Bayer crop science limited, India. A composite solution of spirotetramat and imidacloprid reference standards was prepared by mixing aliquots of stock solution. From the stock solution prepared a series of calibration solutions by further dilution. Distilled water was purified by passing through the Milli-Q Plus apparatus (Millipore, Bedford, MA, USA). Acetonitrile HPLC gradient grade was obtained from Merck India limited. Zinc acetate and Triethanolamine supplied by Merck India limited are used in the preparation of nanorods. The other chemicals used are analytical grade reagents.

Analysis of Spirotetramat and Imidacloprid Residues

A Shimadzu prominence High Performance Liquid Chromatograph equipped with a UV detector was used for the quantification of residues of imidacloprid, spirotetramat and its metabolite enol. The detector wavelength 230 nm was used for the quantification of residues. The stationary phase Phenomenex C18 of 4.6 mm i.d. and 250 mm length was used for the separation of insecticides. The mobile phase used for the elution was a mixture of 400 ml of acetonitrile and 600 ml of 0.04 % formic acid in Milli q water, the flow rate was programmed between 1.5 to 2.0 ml per minute, the injection volume was 20 µl. The insecticides imidacloprid, metabolite enol and spirotetramat are eluted at 3.6 minutes; 5.8 minutes and 19.5 minutes retention times respectively.

For the confirmation purpose a High Capacity Ion Trap (HCT plus) LC-MS/MS System supplied by Bruker Daltonik GmbH was used. Drying gas and the nebulizing gas nitrogen was generated from the pressurized air using a Nitrox UHPLCMS nitrogen generator. The nebuliser gas flow was fixed to 10 L/min. For operations in MS/MS mode, helium was used as collision gas was with a pressure of 4×10^{-4} milli bar. A capillary voltage of 3.5 kV was used in positive ionization mode. The interface temperature was set to 360 °C. The scan range was 50 - 450 m/Z. Agilent 1200 HPLC system with Xterra MS C18 column (5 µm particle size, 4.6 mm i.d. x 150 mm length), gradient elution of 0.4 ml per minute having 0.1% formic acid in acetonitrile as mobile phase A and 0.1% formic acid in milli q water as mobile phase B, the flow programmed from 5% to 95% of mobile phase A were used for the separation of spirotetramat, metabolite enol and imidacloprid. The injection volume used for the analysis was 10 µl.

Preparation of Zinc Oxide Nanorods

The Zinc oxide nanorods are prepared using the method described [23]. The process involves the ultrasonic irradiation of 50 mL of aqueous solution containing 0.05 M of zinc acetate and 0.05 M of triethanolamine, at 80°C for two hours. The resulting product was washed several times with de-ionized water followed by methanol. Filtered and dried at 200°C in air for 2 hours. The structural morphology of the particle was done by scanning electron microscope and presented in Fig. (**1**). The particles are found to be rod shaped with 100 to 250 nm dia and 1 to 2 µm length.

Photocatalysis

The photocatalysis of spirotetramat and imidacloprid insecticides in water was studied by spiking two different concentrations of combinational insecticide formulation (480 SC) containing spirotetramat 12% and imidacloprid 36% at 1.0 and 2.0 mg/L of the product. The study was conducted in Milli q water and in three different buffers of pH 4.0, 7.0 and 9.0. Three replicate spiking solutions were prepared at each fortification level along with control samples for comparison. Two sets of spiked concentrations are prepared for the studies. To one set of samples the catalyst (Zinc oxide nanorods) was added and the other set was studied without the addition of catalyst. Exposed all the samples under direct sunlight every day for a period of 11 hours and monitored the catalytic activity by collecting and analysing the aliquots of the water sample on different predetermined intervals. The day temperature of the water samples during the period varied between 27 to 44 °C. The intensity of the sunlight light was measured during the exposure. This was presented graphically in Fig. (**2**). On each sampling occasion, filtered aliquot of the collected sample using 0.2 µ membrane filter and collected the filtrates in to amber coloured vials. All the samples were stored in dark at <4°C before subjecting to HPLC analysis. The samples fortified with Zinc oxide were
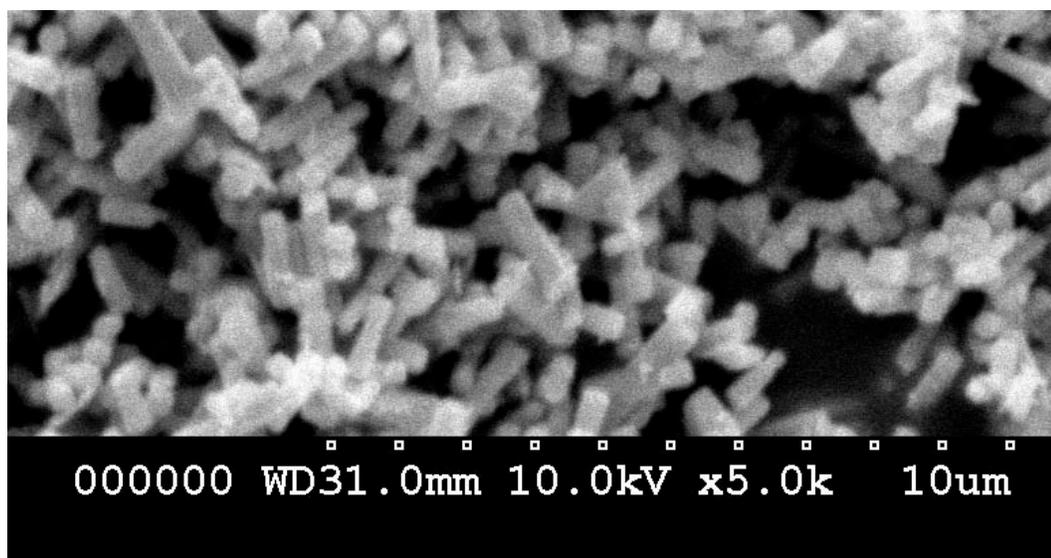

Fig. (1). Scanning Electron Microscope Image of Zinc oxide nano rods (100-250 nm).
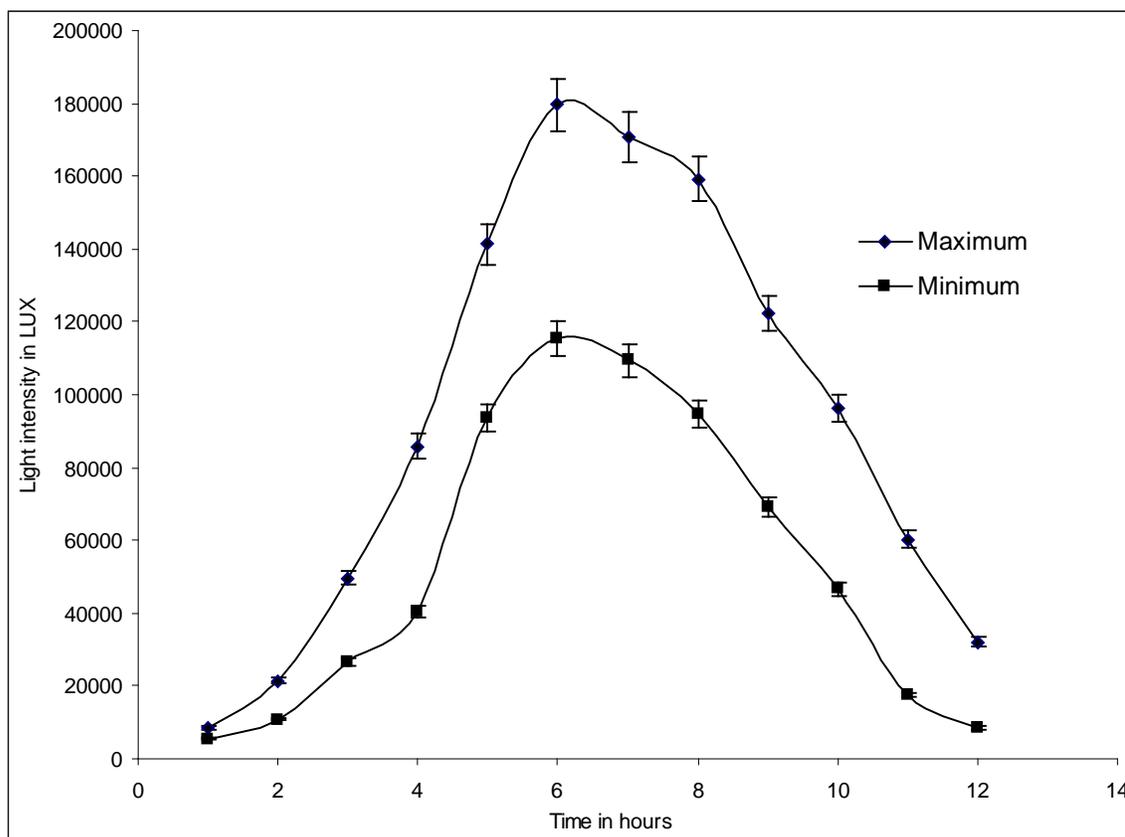
Fig. (2). Intensity of light during the study period.

centrifuged using Beckman cooling centrifuge at 10000 rotations per minute for 3 minutes at 2°C. Transferred the supernent and stored in dark at <4°C until analysis to avoid further degradation of residues.

The effect of adsorption of insecticides 0.1 mg/L on the catalyst was checked by the addition 0.07 g/L of catalyst in water. The sample was kept stirring continuously for a period of 3 hours in dark without aeration. The water samples in duplicate were collected every hour during this time period and analysed for the residues.

Recovery and Limit of Detection

Recovery studies were conducted by fortifying two different concentrations of spirotetramat and imidacloprid (0.2 - 0.02 mg/L). The limit of quantification (LOQ) was established based on the recovery study and signal to noise ratio with minimum of 10:1. The linearity of the method was studied over the concentration range 5.0 - 0.01 mg/L by using HPLC-UV method.

Confirmation of Residues by LC-ESI-MS/MS

The samples were analyzed by LC-ESI-MS/MS detection. A high capacity ion trap MS/MS with dioctapole was used for the confirmation of residues in electro spray ionization mode. The insecticide imidacloprid got eluted at 8.0 minute and showed a molecular ion peak at m/Z 256.2 and the fragment ions appeared at 208.6; 174.6; 127.6. The spirotetramat and its metabolite enol are eluted at 11.1 and 9.2 minutes respectively. Spirotetramat showed a molecular ion peak at m/Z 374.2 and the prominent fragment ions at m/Z 329.9; 301.9;

269.8; 252.7 and 215.7. The metabolite enol has the molecular ion peak at m/Z 302 and the fragment ion peaks at m/Z 269.8; 252.7; 215.7. The method has the limit of quantification 0.1 µg/L. The complete mineralization of residues was confirmed by analysing the sample by LC-ESI-MS/MS.

RESULTS AND DISCUSSION

The photolysis data of imidacloprid and spirotetramat insecticide in aqueous media at different pH levels under the influence of direct sun light without the catalyst was presented in Tables **1** and **2**. The study showed that the compounds degraded to below detectable levels within 20 days in milli q water. In acidic water (pH 4.0) and in neutral water (pH 7.0) the degradation was within 10 days. Degradation of imidacloprid is further rapid in basic water (pH 9.0) and the residues went down the detectable level within 7 days. The spirotetramat residue was rapidly degraded within 5 hours in basic water.

Adsorption of Insecticides on the Catalyst

The adsorption of insecticides on the catalyst was tested by quantifying the presence of residues in water hourly in sequence after the addition of catalyst. The results showed no significant adsorption of residues by zinc oxide nanorods when tested for a period of three hours with constant stirring in dark. Recovery studies in water and different buffers were conducted with 0.07 g/L level of zinc oxide catalyst in dark. The recovery in Milli q water was found to be in the range 88 to 94% for spirotetramat, 88 to 96% for metabolite enol and 89 to 93% for imidacloprid. Recovery in acidic water

Table 1. Photolysis of Imidacloprid and Spirotetramat Under Direct Sun Light in Milli q, Acidic and Neutral Water (without Catalyst)

Tested Dose	Imidacloprid		Spirotetramat	
	0.36 mg/L	0.72 mg/L	0.12 mg/L	0.24 mg/L
Sampling Occasions Days	Dissipation of Residues in Milli Q Water (mg/L)			
0	0.32	0.62	0.12	0.24
1	0.3	0.61	0.1	0.21
3	0.26	0.54	0.08	0.19
5	0.19	0.44	0.05	0.14
7	0.14	0.31	0.03	0.1
10	0.09	0.19	<LOQ	0.05
15	0.04	0.08	<LOQ	<LOQ
20	<LOQ	<LOQ	<LOQ	<LOQ
Dissipation of Residues in Acidic Water (mg/L)				
0	0.33	0.69	0.13	0.24
1	0.31	0.63	0.11	0.22
3	0.3	0.58	0.1	0.21
5	0.23	0.49	0.07	0.16
7	0.17	0.36	0.06	0.12
10	0.12	0.24	0.03	0.06
15	0.05	0.11	<LOQ	<LOQ
20	<LOQ	<LOQ	<LOQ	<LOQ
Dissipation of Residues in Neutral Water (mg/L)				
0	0.13	0.24	0.35	0.7
1	0.12	0.22	0.31	0.62
3	0.05	0.1	0.11	0.17
5	<LOQ	<LOQ	0.08	0.12
7	<LOQ	<LOQ	<LOQ	0.04
10	<LOQ	<LOQ	<LOQ	<LOQ

Table 2. Photolysis of Imidacloprid and Spirotetramat Under Direct Sun Light in Basic Water

Dissipation of Residues in Basic Water (mg/L)		
Occasion in Hours	Spirotetramat	
	0.12 mg/L	0.24 mg/L
0	0.13	0.23
0.5	0.1	0.21
1	0.08	0.19
3	0.04	0.09
5	<LOQ	<LOQ
Occasion in Days	Imidacloprid	
	0.36 mg/L	0.72 mg/L
0	0.34	0.71
1	0.2	0.42
3	0.11	0.2
5	<LOQ	<LOQ

compound was found rapid at this level under the influence of zinc oxide catalyst. Further experiments were conducted at this concentration level. The photocatalysis of insecticides in presence of zinc oxide nanorods under the influence of direct sun light and different buffer solutions were presented in Table **3**.

The DT 50 and DT 90 values calculated from the dissipation data of insecticides are presented in Table **4**. From the study it was observed that the reaction process was influenced by the changes in pH. With lower pH, the reaction observed is slow and with increase in pH the dissipation is rapid. When compared with imidaclorid the dissipation of spirotetramat is more rapid in basic solution. Further it was observed that the aeration of solutions after the addition of Zinc oxide nano catalyst enhanced the degradation of insecticide in water. The influence of the aeration in decontamination of residues in water was presented in Fig. (**3**).

The rate constant k [24] was calculated from the dissipation of imidacloprid and spirotetramat with time using the following equation

$$K = \ln C_1/C_2/\Delta t$$

where Δt is the time interval between t_1 and t_2 and C_1, C_2 are the concentration of pesticides at times t_1 and t_2 respectively. The higher coefficient of correlation ($R^2 = 1.000$) for the least square indicates that the first order kinetics in dissipation of both the insecticides in water. The rate constant k was calculated from the first order rate equation and summarised in Table **5**.

The rate constant of imidacloprid in direct photolysis reaction (without the catalyst) at the studied concentrations (0.36 and 0.72 mg/L) are 0.025, 0.035 in milli q water;

was between 89 to 92% for spirotetramat, 94 to 98% for enol and 92 to 95% for imidacloprid. The recovery percentage in neutral water was 85 to 92%, 89 to 93%, 86 to 94% for spirotetramat, metabolite enol and imidacloprid respectively. The recovery percentage for spirotetramat, enol and imidacloprid are 83 to 93%, and 89 to 97% respectively in basic water.

Influence of Catalyst and the pH of the Buffer Solutions

To identify the nominal concentration of catalyst required for the rapid degradation of the insecticides the amount of zinc oxide nanorods added to the aqueous solution was varied from 0.02 g to 0.2 g/L level. The increase in amount of catalyst enhanced the degradation and attained equilibrium at a concentration level 0.07 g/L. The dissipation of the

Table 3.   Photocatalysis of Imidacloprid and Spirotetramat Under Direct Sun Light in Presence of Zinc Oxide Nanorods as Catalyst - Dissipation in Water at Different pH Levels

Tested Dose	Imidacloprid		Spirotetramat		Tested Dose	Imidacloprid		Spirotetramat	
	0.36 mg/L	0.72 mg/L	0.12 mg/L	0.24 mg/L		0.36 mg/L	0.72 mg/L	0.12 mg/L	0.24 mg/L
Sampling Occasions (Hours)	Residues in Milli Q Water (mg/L)				Sampling Occasions (Hours)	Residues in Neutral Water (mg/L)			
0	0.31	0.59	0.13	0.25	0	0.27	0.56	0.13	0.23
1	0.29	0.57	0.11	0.21	1	0.25	0.52	0.1	0.2
3	0.26	0.53	0.09	0.17	3	0.23	0.47	0.08	0.17
5	0.22	0.46	0.07	0.15	5	0.2	0.39	0.05	0.12
7	0.18	0.37	0.05	0.09	7	0.16	0.3	0.03	0.08
10	0.14	0.24	0.03	0.06	10	0.12	0.25	<LOQ	0.04
20	0.08	0.17	<LOQ	<LOQ	20	0.06	0.14	<LOQ	<LOQ
30	0.03	0.08	<LOQ	<LOQ	30	<LOQ	0.06	<LOQ	<LOQ
60	<LOQ	<LOQ	<LOQ	<LOQ	60	<LOQ	<LOQ	<LOQ	<LOQ
	Residues in Acidic Water (mg/L)					Residues in Basic Water (mg/L)			
0	0.29	0.59	0.12	0.25	0	0.26	0.53	0.11	0.24
1	0.28	0.57	0.1	0.23	0.5	0.24	0.51	0.08	0.13
3	0.26	0.54	0.08	0.2	1	0.23	0.48	0.03	0.06
5	0.23	0.45	0.06	0.18	2	0.21	0.42	<LOQ	<LOQ
7	0.19	0.38	0.03	0.14	3	0.18	0.38	<LOQ	<LOQ
10	0.16	0.29	<LOQ	0.1	5	0.16	0.3	<LOQ	<LOQ
20	0.09	0.19	<LOQ	<LOQ	7	0.09	0.23	<LOQ	<LOQ
30	0.03	0.09	<LOQ	<LOQ	10	0.03	0.14	<LOQ	<LOQ
60	<LOQ	<LOQ	<LOQ	<LOQ	15	<LOQ	<LOQ	<LOQ	<LOQ

Table 4.   DT 50 and DT 90 Value of Imidacloprid and Spirotetramat in Water at Different pH Conditions with and without Zinc Oxide Nano Catalyst

Insecticide	DT 50 and DT 90 in Days (Without Catalyst)							
	Milli Q Water		pH 4.0		pH 7.0		pH 9.0	
	DT 50	DT 90	DT 50	DT 90	DT 50	DT 90	DT 50	DT 90
Imidacloprid	4.9 ± 0.1	16.3 ± 0.2	5.6 ± 0.2	18.5 ± 0.4	2.2 ± 0.2	7.2 ± 0.3	1.8 ± 0.1	6.0 ± 0.3
Spirotetramat	4.6 ± 0.1	15.3 ± 0.2	6.1 ± 0.2	20.4 ± 0.6	2.3 ± 0.2	7.5 ± 0.3	1.9 ± 0.2*	6.6 ± 0.6*
	DT 50 and DT 90 in Hours							
	With Zinc Oxide nano catalyst @ 0.07 g/L							
Imidacloprid	10.1 ± 0.2	33.5 ± 0.5	11.5 ± 0.1	38.3 ± 0.5	9.2 ± 0.2	30.5 ± 0.7	4.0 ± 0.2	16.4 ± 0.3
Spirotetramat	5.0 ± 0.2	16.7 ± 0.6	5.5 ± 0.5	19.4 ± 0.7	3.7 ± 0.3	12.1 ± 0.7	0.5 ± 0.1	1.7 ± 0.2

* DT 50 and DT 90 value in hours.

0.024, 0.033 in acidic water, 0.056, 0.057 in neutral water and 0.021 in basic water sample. The rate constant values increased significantly with the addition of catalyst. The rate constant values calculated for imidacloprid in presence of catalyst are 0.54, 0.68 in milli q water and in acidified water sample, 0.53, 0.62 in neutral water and 0.68, 0.8 in basic water.
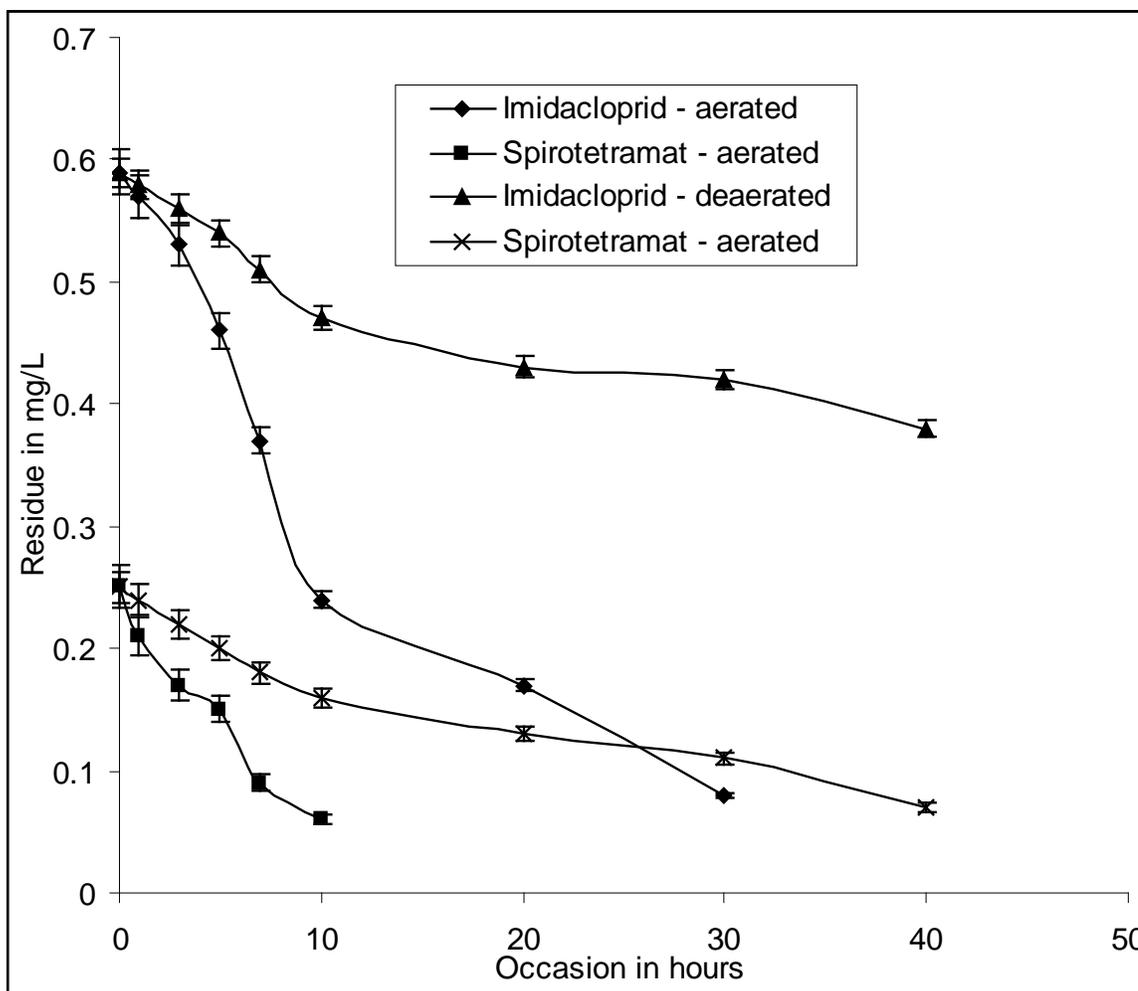
Fig. (3). Influence of aeration in degradation of residues in water.

Table 5.   Rate Constant of Imidacloprid and Spirotetramat in Water at Different pH Conditions with and without Zinc Oxide Nano Catalyst

| Dosage in mg/L | Substrate | Rate constant | | Dosage in mg/L | | |
| | | Spirotetramat | | | Imidacloprid | |
		Without Catalyst	With Catalyst		Without Catalyst	With Catalyst
0.12	Milli Q water	0.024	0.5	0.36	0.025	0.54
0.24		0.008	0.17	0.72	0.035	0.54
0.12	pH 4.0 Buffer	0.022	0.59	0.36	0.024	0.68
0.24		0.009	0.21	0.72	0.033	0.68
0.12	pH 7.0 buffer	0.062	0.48	0.36	0.056	0.53
0.24		0.053	0.54	0.72	0.057	0.62
0.12	pH 9.0 buffer	1.337	1.46	0.36	0.021	0.68
0.24		0.699	0.77	0.72	0.021	0.8

The rate constant values calculated for spirotetramat under the influence of direct sun light (without the catalyst) are; milli q water - 0.024, 0.008; acidic water - 0.022, 0.009; neutral water - 0.062, 0.053 and basic water 1.337, 0.699 at the tested concentrations 0.12 and 0.24 mg/L respectively. The rate constant values of photocatlytic reaction in presence of catalyst are; milli q water - 0.50, 0.17; acidic water - 0.59, 0.21; neutral water - 0.48, 0.54 and basic water -1.46, 0.77. This clearly indicates that zinc oxide nano rods enhanced the photocatalytic degradation of imidacloprid and spirotetramat.

During the photolysis study, formation of metabolite of spirotetramat (enol form) was identified by HPLC-MS-MS detection. In the catalytic reaction of the metabolite enol formation was observed within three hours after the application and the residues are at 0.03 mg/L. The fifth hour sample showed 0.06 mg/L (milli q water) and 0.07 mg/L (acidic water and neutral water). The levels of residues of metabolite were 0.05 mg/L in milli q water, 0.06 mg/L in acidic water and neutral water on 7th hour. Residues degraded to 0.03 mg/L by 20th hour. Complete dissipation of residues was observed by 30th hour. The basic water showed 0.03 to 0.04 mg/L metabolite 30 minutes after starting experiment probably due to the rapid hydrolysis of spirotetramat. The metabolite reached maximum concentration 0.07 mg/L by second

hours and subsequently degraded to 0.04 mg/L level by 20th hour and 0.03 mg/L level by 30th hour. Complete dissipation of the metabolite was observed by 40th hour. The formation of metabolite and residues of parent molecules are confirmed by LC-ESI-MS/MS. The total ion chromatogram for the residues in standard, on 3rd day sample and after complete mineralization of the residues in water samples are presented in Fig. (**4**), observed that the presence of metabolite enol on the third day sample. Further the residues were degraded to below detectable level in presence of zinc oxide catalyst. The confirmation spectra for residues and metabolite and its fragmentation patterns are presented in Fig. (**5**).
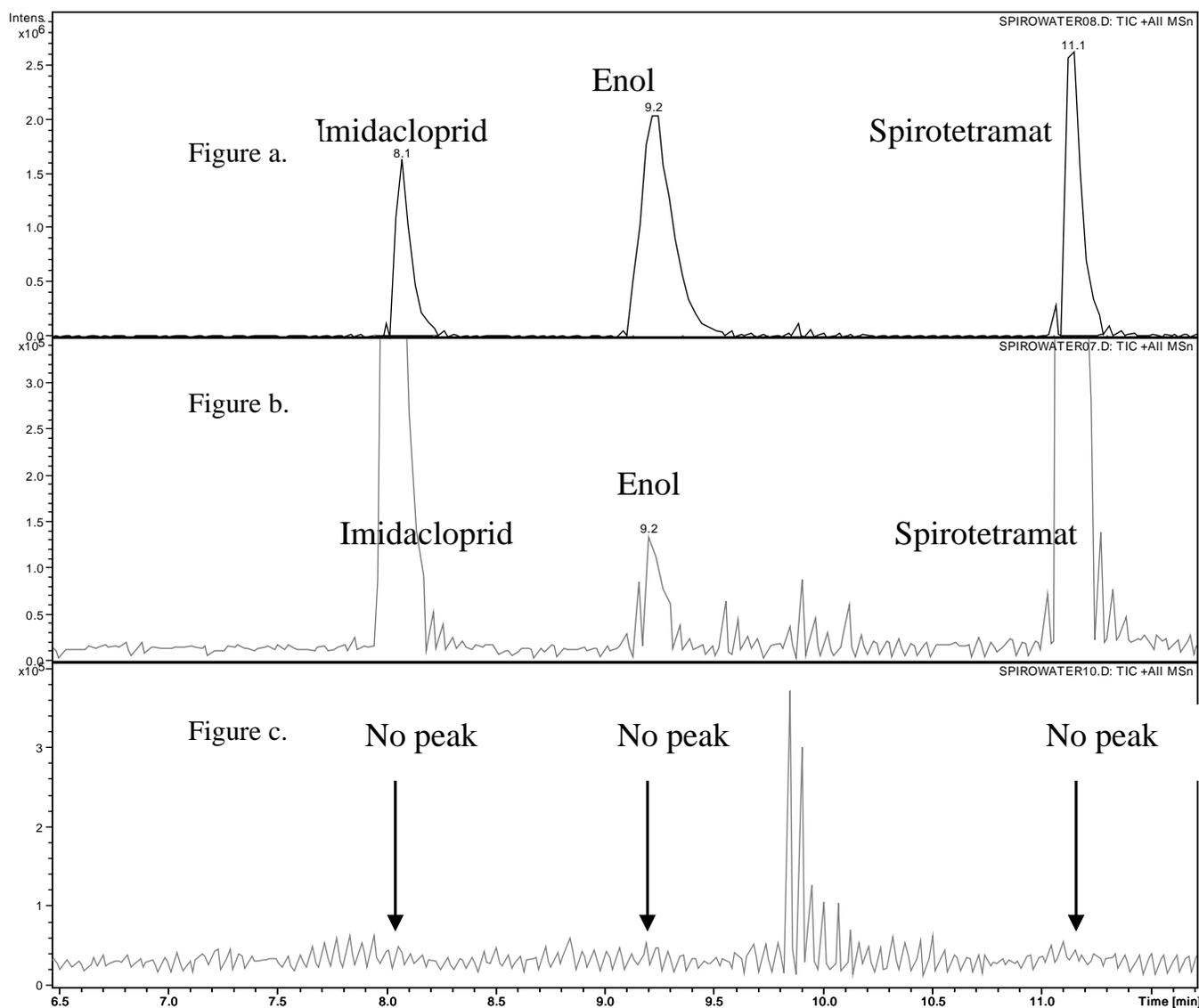
a.   Standard mixture containing imidacloprid, spirotetramat and enol at 0.1 mg/L

b.   Third hour sample showing the formation of metabolite in milli q water sample

c.   Milli q water sample after complete degradation of residues

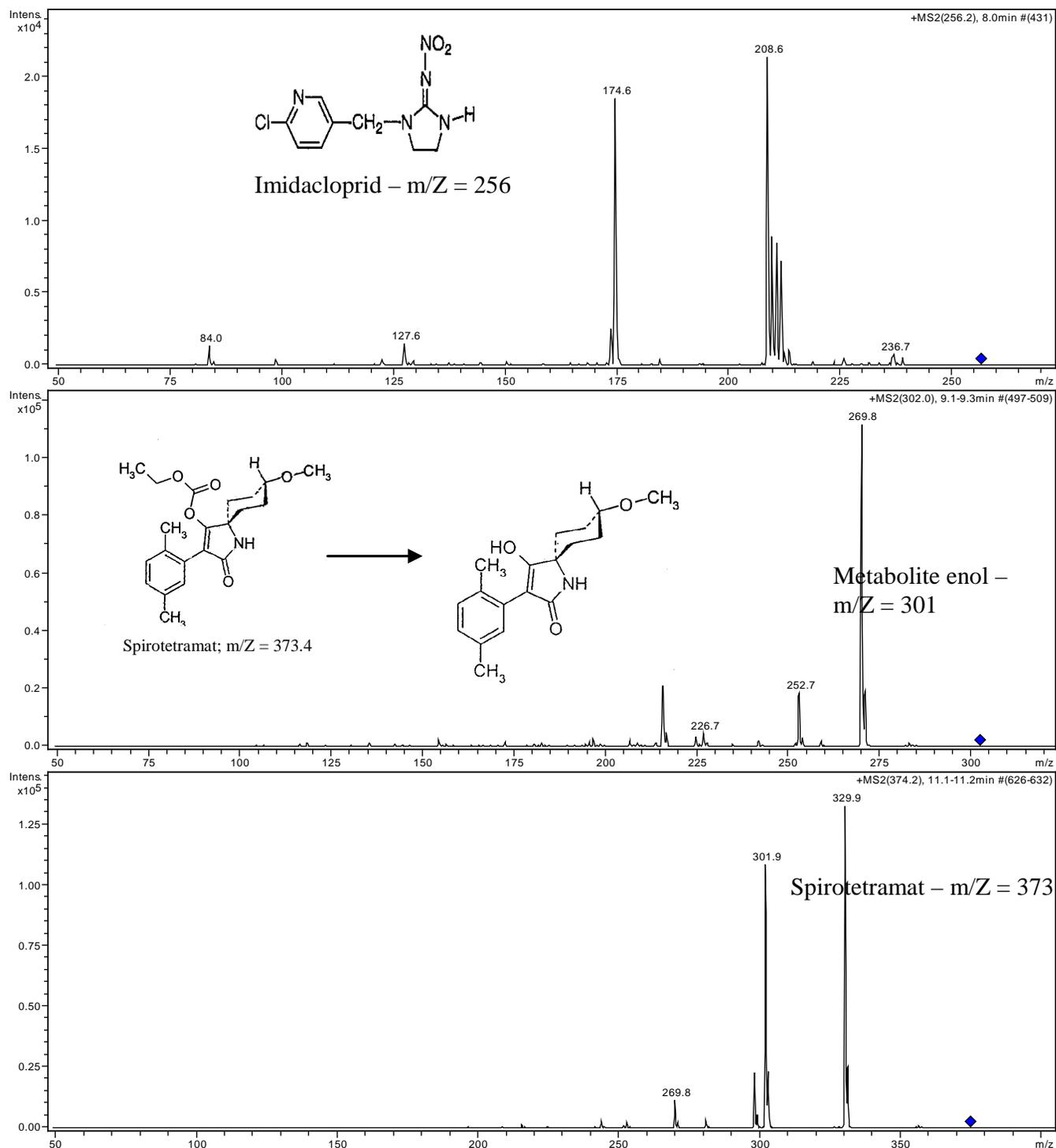**Fig. (4).** Electrospray tandem mass spectrometry - Total ion chromatogram of standard and sample.

Fig. (5). Mass spectra of imidacloprid, metabolite enol and spirotetramat by LC-ESI-MS/MS.

CONCLUSIONS

The photocatalytic degradation of residues of spirotetramat and imidacloprid clearly indicates that the sunlight photolysis was influenced by the addition of the zinc oxide nanorods as catalysts. The catalysis reaction proceeded rapidly degrading the molecules very fast. This was further enhanced with the increase in pH of the aqueous solutions. The basic pH contributed significantly degrading the residues

very rapidly. Metabolites of spirotetramat (enol form) was identified and quantified by LC-ESI-MS/MS detection. The commercially available zinc oxide was also tried by several researchers in decontamination process.

Few pesticides such as 2, 4-D and Monocrotophos are tried for this purpose. However when compared the present findings with the published data it is very clear that the zinc oxide nano rods functions as a more effective catalyst in the

decontamination process. Thus the greater photocatalytic activity of zinc oxide nano rods can be attributed due to their well defined nano particles size facilitating the easy transformation of energy.

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