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Applications of Zinc Oxide Nanorods in Decontamination of Azoxystrobin Residues in Different p^H Waters

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Original Research Article

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Abstract: Zinc oxide nanorods having the size 100 to 250 nm diameter and 1 to 2 µm length was synthesized by reaction with zinc acetate and triethanolamine. The synthesized nanoparticles are characterized by Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) X-Ray Diffraction (XRD) and Fourier Transform Infra Red spectroscopy (FTIR). The photo-catalytic activity of zinc oxide nanorods on pesticide azoxystrobin residues in water was investigated. The decontamination of the pesticide residues was studied in Milli-Q water, p^H 4, p^H 7 and p^H 9 water solutions under sunlight in natural climatic conditions. Kinetic parameters such as rate constant (k), DT_{50} and DT_{90} were calculated using the dissipation data of all pesticides. The degradation order was p^H 4 < Milli-Q water < p^H 7 < p^H 9 for azoxystrobin. The optimum concentration of catalyst required for the rapid decontamination of pesticide residues in water was established by varying the amount of catalyst in the range of 0.02 to 0.1 g/L. The optimum concentration of catalyst was 0.06 g/L. The effective concentration of humic acid required for the rapid decontamination of pesticide residues in water was established by varying the amount of humic acid in the range of 5 to 20 mg/L. The effective concentration of humic acid was 15 mg/L for azoxystrobin. The effect of cations, anions and surfactant on the decontamination of pesticide in water were carried out by adding 10^{-2} mole/L concentrations of cations (Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}), anions (SO_4^{2-}, Cl^-,ClO_4^-, CO_3^- and HCO_3^-) and surfactant (CTAB, SDS and Brij-35). There was no effect except Cu^{2+} was observed.

Keywords: azoxystrobin; Zincoxide; Photocatalyst; Decontamination, DT50 and DT90

INTRODUCTION

Photo-catalysis is being widely used in industry for the effective decontamination of large quantities of effluents and other wastages to protect environment and human health. In recent years researchers identified nanoparticles having different physical and chemical properties as catalysts when compared with their conventional material due to availability of large surface area. Nano sized TiO_2 dominates the inorganic UV absorption phenomena for the photo-catalytic decontamination of organic pollutants. The nano-sized ZnO is also used in similar applications at smaller volumes. The ZnO nanoparticles are known to promote the reactions in presence of light and have the potential to accelerate the degradation rate due to photo-assisted oxidative mineralization of pesticides to carbon dioxide and water when exposed to UV irradiation/sunlight. The photo-catalysis of ZnO was effective in decontamination of residues of organic pollutants in water due to absorption of large spectrum of solar light and more light quanta when comparing TiO_2. The photo-catalytic activity of ZnO [1] can be explained from the fact that when photons of a certain wavelength are incident upon its surface, electrons are promoted from the valance band and transferred to conductance band; this leaves positive holes in valance band, which reacts with hydroxylated surface to produce $OH^{\cdot}$ radicals, which are the most potent oxidizing agents.

Literature survey revealed that ZnO is found equally or more effective photo-catalyst in decontamination of environmental pollutant than TiO_2. Gold coated ZnO nanorods are also exhibited higher activity than TiO_2 in decontamination of Rhodamine A. Flat plate reactor ZnO as photo catalyst under UV irradiation is used (Burbano et al., 2008) for the decontamination of 2, 4 - D. Anandan reported La doped ZnO has higher catalytic activity for the degradation of monocrotophos in aqueous solution. The degradation of methomyl in water under UV radiation using TiO_2 and ZnO as photo-catalysts, phenolic compounds [2] Iodosulfuron [3] 2, 4 D in aqueous solution in presence of oxidizing agent are reported.

Photo-catalytic degradation of sulfonylurea urea herbicides in water with ZnO catalyst [4], 4-Chlorophenol decontamination in presence of different anions and cations are studied by UV induced photo-catalytic degradation. The degradation of methylene blue in water under the influence of UV rays shows ZnO nanoparticles are better than its nano crystalline form [5]. The photo-catalytic activity of TiO_2 and ZnO are reported for the decontamination of polychlorinated dibenzo-p-dioxins [6], isothiazolin-3-ones phosphomidon in water [7].

The presence of decatungstate effect of activated carbon adsorption in decontamination [8] is also reported. The residues and breakdown products of azoxystrobin due to photo-catalysis are identified and confirmed the photo-products using LC-MS/MS. The degradation of sulfonylurea herbicides thifensulfuron methyl, chlrosulfuron [9] and azoxystrobin by light induced photo-degradation [10] are studied in aqueous suspension.

Several researchers studied the decontamination of azoxystrobin and other persistent pollutants in water using semiconductor photo catalysts. However, the data pertaining to the application of ZnO as catalyst in decontamination of azoxystrobin in water is scarce. In view of paucity of information, the present study is conducted with an objective to establish the conditions for photo-catalytic activity of ZnO nanorods in the decontamination of residues of azoxystrobin in water and the factors influencing degradation rates.

EXPERIMENTAL

Synthesis and characterization of ZnO nanorods

The ZnO was prepared using the method described by Rongguo et al., The procedure involves ultrasonic irradiation of 0.05 M zinc acetate and 0.05 M triethanolamine aqueous solutions at 80°C for two hours. The resulting precipitate washed several times with de-ionized water, methanol, centrifuged at 10000 rpm, dried at 200°C in air for 2 hours and at 400°C for 6 hours.

The scanning electron microscope (SEM) and FTIR data of ZnO nano rods were presented in Figure. 1 and Figure. 2 respectively. The size of ZnO nanorods was 50 to 200 nm dia., and 0.5 to 1 µm length. From XRD analysis the size was calculated using “Debye scherrer” equation

$$D = \frac{0.9\,\lambda}{\beta \cos\theta}$$

Where, D is the average crystalline size, λ the X – ray wavelength, β the angular line width at half maximum intensity, θ Bragg’s angle.

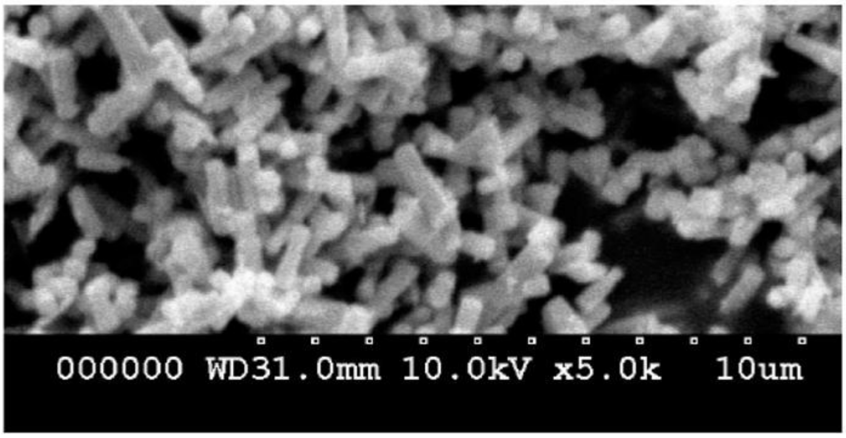
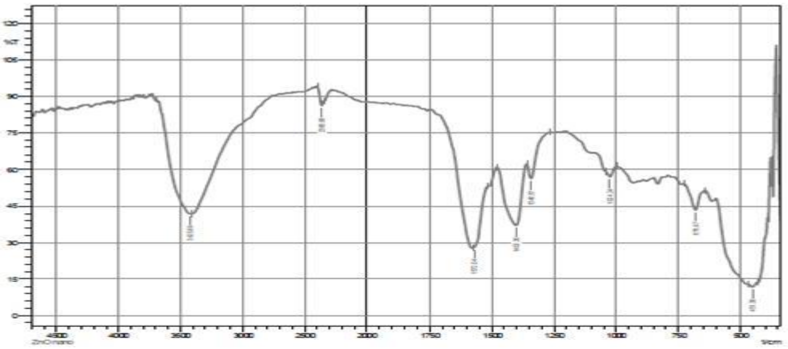


Fig-1: Scanning Electron Microscope Image of Zinc oxide nanorods



Wave number CM^{-1}	Intensity
451.36	11.6
678.97	43.4
1024.24	57.1
1340.57	56.4
1402.30	37.1
1572.04	28.0
2360.95	86.1
3425.69	41.9

Fig-2: FTIR spectra of Zinc oxide nanorods

Validation

HPLC-UV separation parameters

The residue concentrations were quantified by using HPLC-UV system, consisted shimadzu high performance liquid chromatography with LC- 20AT pump and SPD-20A interfaced with LC solution software, equipped with a reversed phase C18 analytical column of 250 mm x 4.6 mm and particle size 5 µm (Phenomenex) and the Column temperature was maintained at 30°C. The injected sample volume was 10µL. Mobile Phases A and B was acetonitrile and formic acid in milli-Q water (70:30 (v/v)). The flow-rate used was kept at 1.0 mL/min. A detector wavelength was 235 nm.

Calibration, Recovery, repeatability and limit of quantification

Linearity was studied by analyzing standard solutions of six concentrations from 0.01 to 5 mg l^{-1}. Recovery was conducted by fortifying two different concentrations (0.3 and 0.03 mg l^{-1}) of azoxystrobin. Six replicate determinations were made at each concentration level along with duplicate controls for comparison of interferences. The limit of quantification was established based on recovery study and minimum signal to noise ratio 10:1.

Degradation of azoxystrobin at different pH conditions

Photolysis of azoxystrobin in water at different pH levels under the influence of direct sun light was studied without catalyst.

Influence of catalyst

To determine nominal concentration of catalyst required for rapid degradation of residues, amount of ZnO nanorods added in aqueous solution was varied from 0.01 g to 0.15 g l^{-1} level. For this purpose the water samples were spiked with 2.0 mg l^{-1} of azoxystrobin and ZnO nanorods at 0.01, 0.03, 0.05, 0.07, 0.10 and 0.15 g l^{-1} levels. The solutions were exposed to sunlight during day time. The aliquots were collected at pre-determined intervals and quantified the residues. The optimum amount of photo-catalyst required to decontaminate the residues of azoxystrobin was established as 0.1 g l^{-1}.

Photo-catalysis with ZnO nanorods

Photo-catalysis of azoxystrobin in water was studied by spiking two different concentrations (1.0 and 2.0 mg l^{-1}) in three buffers of pH 4.0, 7.0 and 9.0 in triplicates along with a control. Two studies were conducted, one with catalyst (ZnO nanorods) and second without catalyst. The fortified samples were exposed to direct sunlight with continuous aeration and monitored the residues on different pre-determined sampling occasions. The temperature of water sample during the period was 27 to 44 °C. Aliquot of collected samples were filtered using 0.2 µ PTFE filter and centrifuged at 10000 rotations per minute for 3 minutes at 5°C and stored in dark at <4°C until analysis to avoid further degradation. The DT 50 and DT 90 values of azoxystrobin in presence and absence of photo-catalyst in water and at three different pH conditions presented in Table 1.

Table 1: DT 50 and DT 90 values of azoxystrobin in presence and absence of photo-catalyst in water and at three different pH conditions

Substrate	DT 50		DT 90	
	In Days	IN Hours	In Days	IN Hours
	Without Catalyst	With Catalyst	Without Catalyst	With Catalyst
milli Q water	14.36	13.02	48.96	45.77
Acidic water (pH - 4 water)	9.35	15.74	31.06	52.29
Neutral Water (pH - 7 water	15.17	13.94	50.39	46.29
Basic Water (pH - 9 water)	19.71	18.42	65.48	61.12

Effect of UV radiation in decontamination of residues in presence of catalyst

To analyze photo-catalytic activity under UV irradiation, the solution in water was exposed to UV light with and without catalyst and aerated continuously with constant stirring. The samples were exposed to UV radiation using a 75 W Philips UV lamp. The results are presented in Table 2.

Table 2: Effect of UV irradiation in the decontamination of residues of azoxystrobin in water

Sampling occasion in hours	Without catalyst	With Zinc oxide catalyst
	Concentration of residues in mg/L	
0	0.98	0.95
5	0.96	0.87
10	0.91	0.76
15	0.88	0.62
20	0.77	0.45
30	0.72	0.33
50	0.56	0.22
100	0.42	0.06

***** Residue values in mg/L presented are the average of three replicate determinations

Influence of catalyst in presence of cation and anion

To determine the influence of cation and anion, different concentrations of metal ions were (10^{-1}M, 10^{-2}M and 10^{-3}M) added along with ZnO catalyst. The metal ions used were ferrous sulfate (Fe^{2+}), copper sulfate (Cu^{2+}) and nickel sulfate (Ni^{2+}). The anions used are sodium chloride (Cl^-), sodium perchlorate (ClO_4^-) and sodium carbonate (CO_3^{2-}).

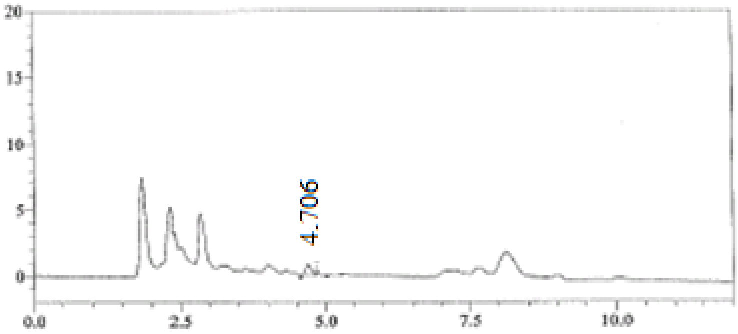
Influence of catalyst in presence of surfactants

The influence of cationic surfactant cetyltrimethylammonium bromide (CTAB), anionic surfactant sodium dodecylsulfate (SDS) and non ionic surfactant Brij-35 was studied with different concentration levels of surfactants (10^{-1}M, 10^{-2}M and 10^{-3}M).

RESULTS AND DISCUSSION

Specificity

Aliquots of azoxystrobin, control sample solutions, extracted solvents and mobile phase solvents were assayed to check the specificity. There were no matrix peaks in the chromatograms to interfere with the analysis of residues shown in (Figure 3, 4 and 5). Furthermore, the retention time of azoxystrobin was 4.7 min (Approximately).



Figu-3: Representative chromatogram of azoxystrobin test item in pH - 4 water - 0th Hour

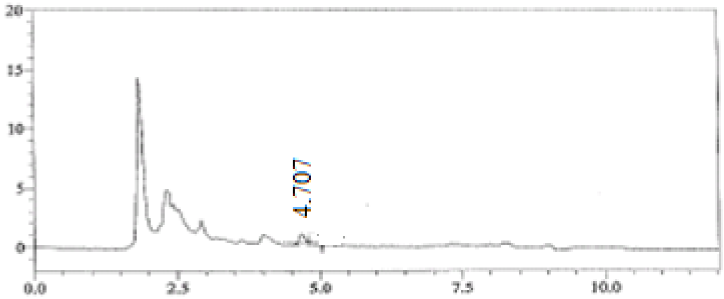


Fig-4: Representative chromatogram of azoxystrobin test item in pH - 7 water – 0th Hour

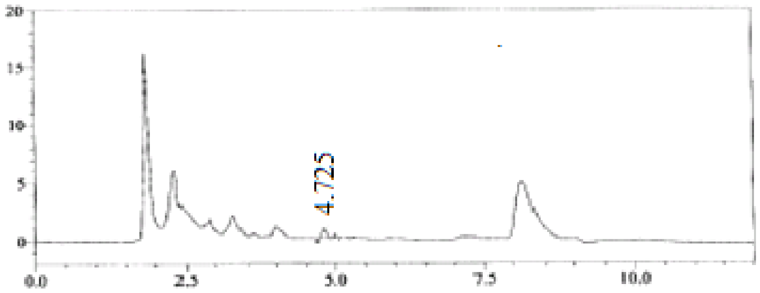


Fig-5: Representative chromatogram of azoxystrobin test item in pH - 9 water – 0th Hour

Linearity, Recovery and repeatability

Calibration curve of azoxystrobin is linear over the concentration range 0.01 to 5 mg l^{-1} with acceptable R^2 value of 0.9999. The LOD was established as 0.01 µg l^{-1} based on signal to noise ratio 3:1. The recovery of azoxystrobin in water was 82 to 92%. Repeatability of the method showed acceptable RSD%, 3.02% for 0.03 mg l^{-1} and 1.91% for 0.2 mg l^{-1} which is less than the maximum limit according to "Horwitz equation" RSD% < $2^{(1-0.5 \log C)}$ x 0.67. Where C is the concentration of the analyte expressed as percentage.

Photo-catalysis

The degradation results of azoxystrobin in water showed the residues are highly stable, the stability decreased with decreasing pH. The half life of azoxystrobin was 14.36, 9.35, 15.17, 19.71 days in milli Q water, acidic, neutral and basic pH's respectively without catalyst.

Adsorption on the catalyst

Recovery studies in water and different buffers were conducted with 0.1 g l^{-1} level of ZnO catalyst in dark. The adsorption of residues on catalyst was tested by quantifying the concentration of azoxystrobin in water for a period of three hours. The recovery was 90 to 95%, 87 to 92%, 89 to 93%, 90 to 97% in milli Q water, acidic water, neutral water and basic water respectively. The results clearly indicates that no significant loss of residues due to adsorption.

Influence of catalyst

The amount of catalyst required for the decontamination was optimized as 0.1 g l^{-1} for azoxistrobin, further increase of catalyst has no significant effect in degradation. The dissipation found rapid under sunlight in presence of catalyst.

Effect of aeration

The rate of degradation of contaminant in solutions is also influenced due to aeration in presence of catalyst. Due to aeration 91 to 94% of residues were degraded in 50 hours, in absence of aeration only 70 to 80% of residues only degraded. This may be due to increase in dissolved oxygen level in water, contributing the rapid degradation.

Influence of pH

The decontamination effect of ZnO under laboratory condition in water shows the residue of azoxystrobin was degraded rapidly within 100 hour of exposure with ZnO photo-catalyst under sunlight with continuous aeration.

The half life of azoxystrobin in presence of ZnO catalyst was 13.02, 15.74, 13.94 and 18.42 hours in milli Q water, acidic, neutral and basic pH conditions respectively. The time required for 90% degradation was 45.77, 52.29, 46.29 and 61.12 hours in milli Q water, acidic, neutral and basic pH conditions respectively**.** The photo-catalyst was highly influenced in neutral water when comparing the acidic and basic water. This is may be due to formation of Zn^{2+} ion formation in acidic and basic conditions.

Effect of UV irradiation in decontamination of residues

Effect of UV irradiation in decontamination showed UV source was found effective in decontamination, the residues degraded rapidly due to absorption of UV rays by photo-catalyst. When comparing the degradation of residues under sunlight in presence of catalyst was fast when comparing degradation under UV source.

Influence of cation and anion

The addition of cation and anion in the decontamination process with catalyst had no significant change.

Influence of surfactants

Study with cetyltrimethylammoniumbromide (CTAB), sodium dodecyl sulfate (SDS) Brij-35 in decontamination process showed the presence of CTAB and Brij-35 has no significant influence in the degradation of residues. The presence of anionic surfactant SDS has contributed the degradation of residues in presence of ZnO catalyst.

Dissipation kinetics

The rate constant k was calculated from the dissipation data using the following equation -

$$K = \frac{\ln (C_1/C_2)}{\Delta t}$$

Where, Δt is the time interval between t_1 and t_2 and C_1, C_2 are the concentration of residues at time t_1 and t_2 respectively. The higher correlation coefficient ($R^2 = 1.000$) for the least square indicates that the first order kinetics.

The rate constant values calculated for azoxystrobin under the influence of direct sun light (without the catalyst) are; milli Q water - 0.035; acidic water - 0.028, neutral water - 0.028, and basic water 0.031, The rate constant values of photo-catalytic reaction in presence of catalyst are; milli Q water - 0.094; acidic water - 0.077; neutral water - 0.089 and basic water – 0.106 at the tested concentrations. These results clearly indicate the ZnO nano rods enhancing the photo-catalytic degradation.

CONCLUSIONS

The photo-catalysis in water using ZnO nanorods showed the potential of catalyst in decontamination of metsulfuron methyl. The amount of catalyst required to decontaminate the residues is 0.1 g l^{-1} significantly very low quantity.

Dissolved oxygen, pH of water is influencing the decontamination of residues in presence of catalyst due to formation of $OH^{\cdot}$ radicals. The degradation rate was increased with increase in pH of water in presence of catalyst. The residues of azoxystrobin were found to be stable in basic pH than acidic pH in water without catalyst. The degradation of the residues was compared with data obtained by UV irradiation and in presence of catalyst. UV light contributed faster catalytic degradation reaction in aqueous solutions but slow when comparing the degradation under sunlight. The dissipation of residues of azoxystrobin followed first order kinetics.

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