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Research Article

Photocatalytic Degradation of Dinotefuran by Cerium-doped Zinc Oxide

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ABSTRACT

The study evaluated the photocatalytic degradation of the neonicotinoid insecticide dinotefuran. The degradation was evaluated with variable concentrations of cerium-doped ZnO and ZnO alone. The study was performed with mercury lamps as an artificial source of ultraviolet light. The rate of degradation was studied by using a variable percentage of cerium-doped catalyst, pH, amount of catalyst, pesticide concentration, and intensity of light. A UV spectrophotometer monitored the degradation. The optimum conditions were achieved as pH = 6.5, dinotefuran concentration 12 ppm, photocatalyst amount = 150 mg of 2% Ce-doped ZnO and light intensity is 19.2 mW cm^{-2}. About 77% dinotefuran degradation was achieved under these conditions.

Keywords: Cerium-doped zinc-oxide, Photocatalytic degradation, Dinotefuran, Oxidation.

INTRODUCTION

Dinotefuran is a systemic neonicotinoid broad-spectrum insecticide. It is used in its formulated form. The popular formulation of dinotefuran is 20% SG (water-soluble granules). The LC_{50} of dinotefuran is very low, >4.09 mg L^{-1} (4 h inhalation). The formulated pesticide directly spread over the crops to prevent it from whiteflies, plant bugs, leafhoppers, meal bugs and other sucking insects. While spraying over the crops, pesticides come in contact with the soil. As the water solubility of dinotefuran is high (i.e., 39.80g L^{-1}), it dissolves in water during irrigation and rainfall. The residual dinotefuran present in the soil can move towards the nearby water resources or the groundwater resources. This is one of the potential reasons for water pollution, which affects aquatic animals and human lives. The photocatalytic degradation methods are one of the popular and viable methods for the degradation of pesticides from contaminated water. The Ce-doped ZnO was used as a photocatalyst to degrade dinotefuran from contaminated aqueous solution. The variable parameters and experiments shows that approximately 77% dinotefuran was removed from contaminated aqueous solution (12 ppm) by using 2% cerium-doped ZnO as a photocatalyst under UV irradiation at pH 6.5.

Shanaah *et al.*[1] reviewed the photocatalytic degradation and adsorptive removal of emerging organic pesticides using metal oxide and their composites. A wide range of metal oxides, such as iron oxides, MgO, TiO_2, ZnO, WO_3, CuO, Cu_2O, metal oxides composites, and graphene–metal oxides composites, with variable structural, crystalline, and morphological features, were reviewed, for adsorptive removal and photocatalytic degradation of organic pollutants such as dyes, pesticides, phenolic compounds.

Huang *et al.*[2] investigated the catalytic degradation of dinotefuran (DIN) by dielectric barrier discharge plasma combined with La-doping TiO_2. The photocatalyst was prepared by the sol-gel method. The effect of various factors (initial concentration, initial pH, input power, and addition of metal ions) on the removal rate of dinotefuran was evaluated. The highest degradation of dinotefuran (99%) was achieved within 180 minutes at, when photocatalyst (10 wt% La-TiO_2), coupled with optimum conditions like pH:10.5, input power:150W, concentration: 100 mg/L, addition of Fe^{+2} ion catalyst 50 mg/L. The removal rate of DIN was decreased in the presence of H_2O_2, which makes a clear indication that the ($OH^{\cdot}$) radical takes part in degradation.

Liu *et al.*[3] studied the photocatalytic degradation of dinotefuran by layered phosphorus-doped carbon nitride and its mechanism. The layered phosphorus-doped carbon nitride ($HPCN_{0.5}$) was prepared by a simple hydrothermal method. The degradation efficiency of the catalyst for dinotefuran removal was 6 times higher than g-C_3N_4. According to the mechanism, the main photodegradation pathways were demethylation and hydroxylation. The toxicity test revealed that the toxicity of dinotefuran was greatly reduced to earthworms after photodegradation of $HPCN_{0.5}$.

Hamada *et al.*,[4] investigated the differential metabolism of imidacloprid and dinotefuran by *Bemisia tabaci* CYP6CM1 variants. Imidachloprid has been used to control silver leaf whitefly (*Bemisia tabaci*). The pest has developed resistance against imidachloprid by over-expressing the CYP6CM1 enzyme. It was reported that pests do not show or low level of resistance against dinotefuran. The additional studies showed that the combination of imidacloprid and pymetrozine competed efficiently against this enzyme (CYP6CM1) than dinotefuran.

Lee *et al*.,[5] studied the photocatalytic degradation of neonicotinoid insecticides using sulfate-doped Ag_3PO_4 with enhanced visible light activity. The sulfate-doped silver phosphate (SO_4-Ag_3PO_4) was prepared by a simple precipitation method, and its visible light photocatalytic activity was evaluated against seven neonicotinoid insecticides. The SO_4 doping decreases band gap energy and charge transfer resistance. It was reported that the first-order rate constant with sulfate-doped Ag_3PO_4 was 5.4 times higher than undoped Ag_3PO_4. The order of degradation rate constant was thiacloprid (TCP) > nitenpyram (NTP) > imidacloprid (ICP) > clothianidin (CTD) > acetamiprid(ATP) > thiamethoxam (TMX) > dinotefuran (DTF). Even after four reuse cycles, SO_4-Ag_3PO_4 maintained over 75% of its initial photocatalytic efficiency. Reactive species trapping experiments indicated that photo-induced electron holes (h^+) were most important oxidant for ICP degradation.

Khan and Pathak[6] presented a comprehensive review of zinc oxide-based photocatalytic degradation of persistent pesticides. It was observed and reviewed that the photocatalytic degradation of persistent pollutants with ZnO was, fast, cost-effective and eco-friendly for the clean-up of the environment. Dichlorvos, malathion, carbofuran, 4-nitrophenol, diazine, lambda-cyhalothrin, methyl parathion, phenol, chlorpyrifos, etc, were used in the study and find out the observations.

Mahalakshmi *et al*.[7] investigated the degradation of carbofuran in an aqueous solution by using Degusaa P-25 TiO_2 and ZnO as photocatalysts. The effects of various parameters like pH of solution, carbofuran concentration, catalyst loading and light intensity have been studied. The complete mineralization of carbofuran was confirmed with a TOC analyzer. The study and observation show that the degradation efficiency of TiO_2 was more effective than ZnO.

Fadehi and Moghadam[8] studied the photocatalytic oxidation of carbofuran pesticide using ZnO. The degradation of pesticides was studied under UV irradiation. The various operation parameters like initial concentration of catalyst, different pH, concentration of pesticide and light intensity have been studied. The optimum results were achieved with an initial concentration of carbofuran 50 mg/L, amount of photocatalyst (i.e., ZnO) 300 mg/L, pH 8.0, light intensity 125 W and reaction volume 150 mL.

Fenoll *et al*.[9] studied the degradation intermediates and reaction pathway of carbofuran in leaching water using TiO_2 and ZnO as photocatalysts under natural sunlight. The comparative results show that ZnO is a more efficient photocatalyst. At the end of the experiment (240 min) the residual levels of carbofuran were 0.1, 22.4, 62.8, 68.4 ppm for ZnO, TiO_2P25 Degussa (70A/30R), TiO_2 rutile (25A/75R) and TiO_2 anatase (90A/10R). The degradation follows pseudo-first-order kinetics.

Karidas *et al*.[10] studied the photodegradation of methylene blue (MB) using cerium-doped zinc oxide nanoparticles. The nanoparticles were prepared by the co-precipitation method. The nanoparticles were characterized by XRD and FESEM techniques. The optical properties were studied by using a diffuse reflectance ultraviolet visible (DRS UV–VIS) spectrophotometer. The band gap of doped particles was reduced as the doping concentration of cerium was increased. The comparative studies showed that cerium-doped ZnO decolorized methylene blue dye more efficiently (120 min, 92.62%) as compared to undoped ZnO (210 min., 81.93%).

MATERIALS AND METHODS/EXPERIMENTAL:

Zinc nitrate hexahydrate was obtained from Qualigens, USA, sodium hydroxide from Rankem, India, and cerium nitrate hexahydrate from SRL chemicals, India. A Teflon-coated autoclave of 1 liter capacity and a hot air oven were used for hydrothermal treatment. Centrifuge was used for liquor settlement after washing and a muffle furnace was used for calcination of dried material. A 250 W medium-pressure Hg vapor lamp was used as a UV light source. A continuous water supply and stirring were maintained for uniform irradiations.

Synthesis of ZnO and Cerium-Doped ZnO Nanostructure Material

The Ce-doped zinc oxide was prepared using the co-precipitation-hydrothermal method. A solution of 1.0M $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in water with continuous stirring at room temperature (25°C) for 30 min to form a clear solution. Then, 2.0M aqueous NaOH solution was added dropwise until a white precipitate was formed. The solution was transferred to a teflon-lined stainless-steel autoclave, and hydrothermal treatment was carried out at 160°C for 12 hours. The solution was then cooled to room temperature. The white precipitate was collected by centrifugation and was washed several times with deionized water. The precipitate was dried in an oven at 105°C and then calcinated in a muffle furnace at 750°C for 3 hours. The color of solid changed from white to light yellow after calcination.

The Ce-doped ZnO was synthesized by the same procedure. Cerium nitrate hexahydrate [$Ce(NO_3)_3.6H_2O$] was added to prepare Ce-doped ZnO (CZO) solutions with the concentration of 0.2, 1.0, 2.0, 3.0 and 4.0%.

X-ray Diffraction (XRD)

X-Ray diffraction (Bruker d8 ADVANCE X-ray diffractometer) was used for recording XRD of Ce-doped ZnO. The peaks were observed at 2θ value ranging from 20 to 80°. The XRD analysis was conducted for undoped ZnO and 2% Ce-doped ZnO. The results are given in Figs 1 and 2 respectively. The sharp peaks indicated that the particles of cerium-doped ZnO are highly crystalline in nature. Characteristic peaks of cerium and ZnO were observed separately and it indicating that the cerium was successfully incorporated in the ZnO. The Miller indices are clearly labelled on the peaks. The average particle size of undoped ZnO and 2% cerium-doped ZnO were found to be 27.59 and 67.71 nm, respectively. The particle sizes were determined using the Debye–Scherrer equation:

$$D = k\lambda/(\beta \cos\theta)$$

where D = Crystalline size, K is the Scherer's constant (K = 0.94), λ is the X-ray wavelength (1.54178Å) and β is full width at half maximum (FWHM).

Field Emission Scanning Electron Microscopy (FESEM)

The FESEM image of cerium-doped ZnO was recorded using a Quanta 200-3D FEI instrument. FESEM was used to study the morphological properties of ZnO nanostructures. The images obtained from FESEM indicated a sunflower-like (hexagonal)

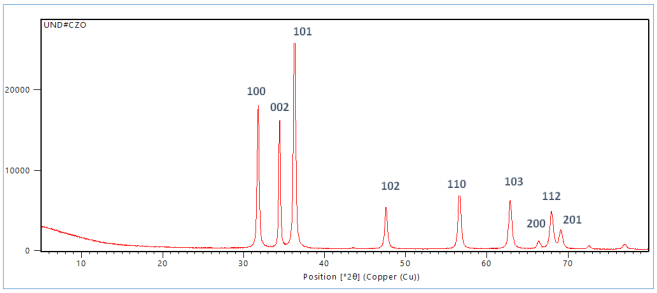

Figure 1: XRD of undoped ZnO

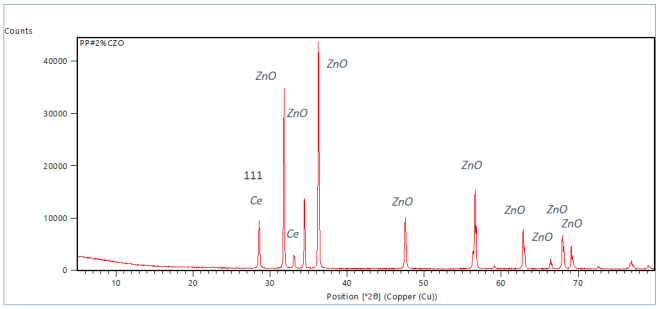

Figure 2: XRD of cerium-doped ZnO (2% CZO)

structure for ZnO nanomaterials and a nanorod-like structure for cerium-doped ZnO (Figures 3 and 4). As the cerium concentration increases, the size and shape of the nanorods are altered due to the nucleation of Ce ions.

Energy Dispersive Spectroscopy (EDS)

The elemental composition was investigated using energy dispersive spectroscopy (EDS) using an EDC Tecnai T-20 instrument. It was found that the undoped ZnO is a composition of only zinc and oxygen, while cerium-doped ZnO contains cerium in addition to zinc and oxygen (Figures 5, and 6). These images confirmed that cerium was successfully absorbed onto ZnO, and no other impurities were detected.

UV-Visible Spectroscopy

The absorbance was measured using a Shimadzu UV spectrophotometer (Model No.: 1800). The UV–visible spectra of undoped and Ce-doped ZnO nanorods show that undoped ZnO nanorods do not exhibit absorption in the visible region (>400 nm), while Ce-doped ZnO nanorods indicate a broad absorption tail between 400 and 500 nm. The doping increased the absorption intensity and the absorption band shifted towards the visible region (red shift). It indicated that Ce-doped ZnO exhibited better absorbance under sunlight irradiation.

The band gap of pure and Ce-doped ZnO nanorods can be calculated using the following equation.

$$E_b = \frac{1240}{\lambda}(eV)$$

The band gap energies (E_b) of undoped ZnO and 2% Ce-doped ZnO were calculated to be 3.25 and 3.04 eV, respectively.

The chemical structure of dinotefuran is presented in the Figure 7.

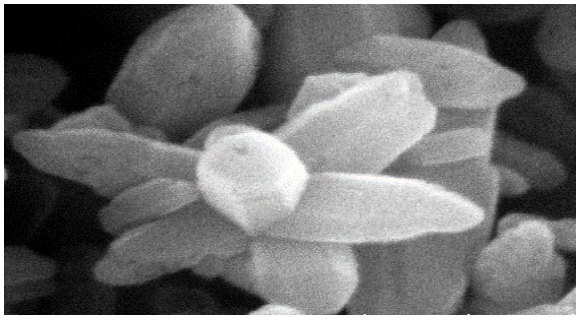

Figure 3: FESEM picture, undoped ZnO

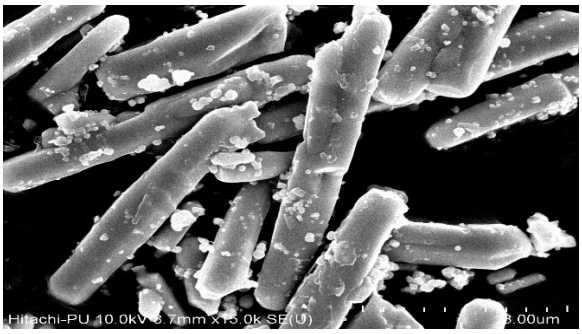

Figure 4: FESEM picture, 2% Ce-doped ZnO

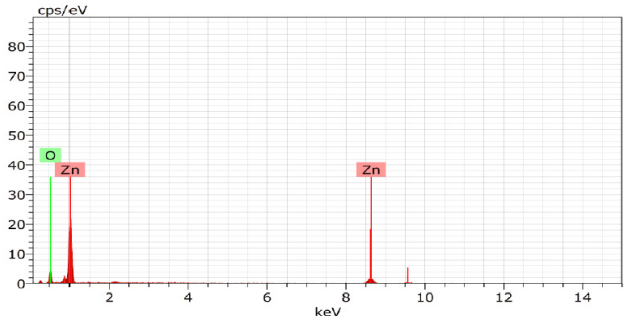

Figure 5: Undoped ZnO

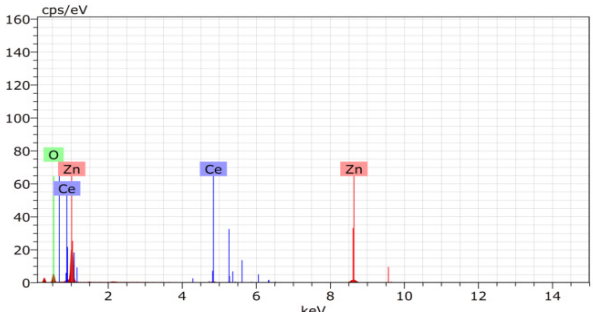

Figure 6: 2% Ce-doped ZnO

RESULTS AND DISCUSSION

The photocatalytic experiment was carried out with the photocatalyst and dinotefuran-contaminated water (12 ppm) under ultraviolet (UV) irradiation. The 50 mL of dinotefuran-contaminated water was placed in a 100 mL glass beaker. The pH of the solution was

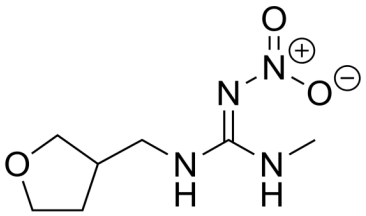

Figure 7: Structure of dinotefuran

6.5. Accurately 150 mg amount of photocatalyst was added and the solution was stirred vigorously. The reaction mixture was exposed to a 250 W mercury lamp. The sample solution was taken out in every 60 min to check percentage degradation of dinotefuran. The solution was kept for 10 min to achieve absorption/desorption equilibrium. Then, 5 mL of the solution was taken for centrifugation, and the solution was filtered through a 0.45 µm membrane filter to remove suspended particles. The filtered solution was then analysed using a Systronics UV spectrophotometer (Model No: 106) at 270 nm. The degradation of dinotefuran was observed at about 77% in 8 hours The extent of photodegradation was calculated using the formula mentioned below:

$$\text{Photodegradation (\%)} = \frac{(A_0 - A_t)}{A_0} \times 100$$

A_0 = absorbance at 0 min and

A_t = absorbance at regular time interval (Every 1 h).

It was observed that the absorbance of the solution decreased with increasing exposure time, indicating that dinotefuran was degraded photocatalytically in the presence of Ce-doped ZnO. The results are reported in Table 1.

A plot between the log of absorbance versus time was drawn, and it indicated that the reaction followed pseudo-first-order kinetics. The rate constant was calculated using the following relation:

$$k = 2.303 \times \text{Slope}$$

It was also confirmed that the degradation was not possible in the absence of either light or Ce-doped ZnO. This confirmed that the degradation reaction was photocatalytically in nature and not photochemical or thermal reaction. The highest degradation rate of dinotefuran-contaminated aqueous solution was observed with 2% Ce-doped ZnO.

$k = 5.0\times 10^{-5} s^{-1}$

Effect of Cerium Dopant

The photodegradation of aqueous solution of dinotefuran (concentration 15 ppm) was observed using undoped ZnO and various percentages of cerium-doped ZnO (0.2, 1.0, 2.0, 3.0 and 4.0%). The results are tabulated in Table 2.

Effect of pH

The pH is identified as an important factor affecting the photodegradation process. The surface of the photocatalyst may be either negatively or positively charged depending on the pH of the system. An acidic pH produces a positively charged catalyst surface while an alkaline pH produces a negatively charged surface. The experiment was conducted at different pH values (ranging from 5.5–8.5) of an aqueous solution contaminated with dinotefuran (15 ppm). It was observed that the highest degradation of dinotefuran occurred at pH 6.5 with 2% Ce-doped ZnO as the photocatalyst (Table 3).

Table: 1

Time	*Absorbance (A)*	*1 + log A*
0	0.875	0.94
60	0.685	0.84
120	0.554	0.74
180	0.496	0.70
240	0.433	0.64
300	0.375	0.57
360	0.321	0.51
420	0.256	0.41
480	0.199	0.30

Table 2: Effect of Ce-doping

Photocatalyst	*Rate Constant (K)× (10)^5*
Undoped ZnO	0.85
0.2% Ce-doped ZnO	0.88
1.0% Ce-doped ZnO	1
2.0% Ce-doped ZnO	3.3
3.0% Ce-doped ZnO	2.3
4.0% Ce-doped ZnO	1.6

Effect of Concentrations

The rate of photodegradation may be affected by different concentrations of dinotefuran and therefore, the concentration of dinotefuran was varied from 10 to 21 ppm. The results are summarized in Table 4. The highest rate of photocatalytic degradation was observed for 12 ppm of dinotefuran contamination.

Effect of Photocatalyst Amount

The degradation of dinotefuran is likely to be affected by the amount of photocatalyst and hence amount of photocatalyst was varied from 50 to 200 mg. The results are given in Table 5. The highest degradation of dinotefuran-contaminated water was observed with 150 mg of photocatalyst.

Effect of Light Intensity

The rate of degradation may also be affected by light intensity. The light intensity was varied from 13.4 to 23.7 mW cm^{-2} by changing the distance between the light source and the surface of the photocatalyst. The results are reported in Table 6. Optimum degradation of dinotefuran was observed at 19.2 mW cm^{-2}.

Scavenger Test

The radical capture experiment was carried out using ethylenediaminetetraacetic acid Na salt, potassium iodide,

Table 3: Effect of pH

Photocatalyst	*2.0% Ce-doped ZnO*
pH	Rate Constant (k) × 10^5 (s^{-1})
5.5	1.0
6.5	4.8
7.5	3.3
8.3	3.0
8.5	2.2

Table 4: Effect of dinotefuran concentrations

Photocatalyst	*2.0% Ce-doped ZnO*	
pH	6.5	
	Concentration in ppm	Rate Constant (k) × 10^5 (s^{-1})
	10	1.5
Dinotefuran	12	5.0
	15	4.8
	17	1.4
	21	1.2

Table 5: Effect of photocatalyst amount

Photocatalyst	*2.0% Ce-doped ZnO*	
pH	6.5	
Concentration in ppm	12 ppm	
	Amount of photocatalyst in mg	Rate Constant (k) × 10^5 (s^{-1})
	50	3.3
	100	3.4
	120	3.5
	150	5.0
	200	1.5

Table 6: Effect of light intensity

Photocatalyst	*2.0% Ce-doped ZnO*	
pH	6.5	
Concentration in ppm	12 ppm	
Amount of photocatalyst	150 mg	
Light intensity	mW cm^{-2}	Rate Constant (k) × 10^5 (s^{-1})
	23.7	3.7
	19.2	5.0
	15.9	3.0
	13.4	1.0

ammonium oxalate and isopropyl alcohol. It was observed that degradation was reduced in the presence of isopropyl alcohol and, therefore it was also concluded that the hydroxyl radical was the active oxidizing species in this degradation.

1DIN0----------> 1DIN1 ---------- (1)

ISC

1DIN1 ----------> 3DIN1 ----------(2)

SC + hν ------ > SC (e-CB + h+VB)-- ---------(3)

h+VB + OH- ---------- > .OH ---------- (4)

3DIN1 + ·OH -----> CO2 + H2O + Other Products -------- (5)

Where DIN = Dinotefuran and SC = Semiconductor (Ce-doped ZnO)
ISC = Intersystem crossing

CONCLUSION

The photocatalytic degradation of dinotefuran with undoped ZnO was found to be only 23% while optimum degradation was observed at pH (6.5), dinotefuran concentration (12 ppm), 2% Ce-doped ZnO (150 mg) and light intensity (19.2 mW cm^{-2}), where approximately 77% of dinotefuran was degraded.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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