Photocatalytic Degradation of Bispyribac Sodium by Cerium doped Zinc Oxide

Paliwal Praveen*, Ameta Rakshit and Chaudhary Varsha
Department of Chemistry, PAHER University, Udaipur-313024 (Raj.), INDIA
*paliwalpraveen@yahoo.co.in

Abstract

The performance of cerium dopped zinc oxide as a photocatalyst has been evaluated in the photodegradation of commercial herbicide, bispyribac sodium. The experiments were conducted by mercury lamps as source of ultra-violet radiation. The degradation of bispyribac sodium was studied by varying the percentage of cerium doping on ZnO (i.e. from 0.2, 1, 2,3 and 4%), pH, amount of photocatalyst, concentration of bispyribac sodium and the intensity of light.

The optimum conditions were: pH = 7.7, 3% Ce doped ZnO catalyst = 150 mg, bispyribac sodium concentration = 30 ppm and light intensity = 19.2mW/cm^{-2}. About 85% bispyribac degradation was achieved under this treatment.

Keywords: Cerium dopped ZnO, Photocatalytic degradation, Bispyribac sodium, Oxidation.

Introduction

Abri et al[1] used cerium doped ZnO in the degradation of pharma products like nizatidine, levofloxacin and acetaminophen under UV-B light irradiation. It was observed that about 95% degradation of these pharmaceuticals could be obtained within 4 h. Burbano et al[2] conducted the study of the photocatalytic degradation of commercial herbicide 2,4-D Amina (dimethylamine salt of 2,4-dichlorophenoxyacetic acid) by using ZnO as a photocatalyst under UV light. The various parameters like pH, catalyst concentration and flow rates were studied to check the effect on the pesticide degradation. The degradation was observed by quantifying the total organic carbon (TOC) in the aqueous solution. The optimum degradation was observed at pH 5.5, catalyst concentration 0.35 g L^{-1} and recirculation flow rate as 410 L h^{-1}. The TOC removal was found 38.1% in 8.0 h.

Chouchene et al[3] prepared, Ce doped ZnO nanorods and studied Ce doping effect on the structural, optical and electronic properties of ZnO nanorods. They showed that 5% Ce doped ZnO nanorods show highest photocatalytic degradation rate for the Orange-II dye under solar irradiations. The photocatalytic activity of Ce doped ZnO was enhanced and the catalyst was working in visible region too.

The various parameters like pH of the solution, catalyst amount and concentration of substances were also studied. Fierro et al[4] carried out the lanthanide doping (La, Ce and Eu) in TiO_2 for the treatment of cyanide contaminated water. The nanoparticles of TiO_2, La/TiO_2, Ce/TiO_2 and Eu/TiO_2 were synthesized to remove free cyanide from contaminated water. The photocatalytic process was followed by solar irradiations. The La/TiO_2 combination show highest percentage of removal of cyanide (i.e. 98%) from water it followed by Ce/TiO_2 (92%), Eu/TiO_2 (90%) and TiO_2 (88%). These results shows that doping of La, Ce and Eu improves the photocatalytic efficiency of TiO_2.

Gaggra and Ramesh[5] investigated the photocatalytic degradation of bispyribac sodium in an aqueous suspension using ZnO / $Na_2S_2O_8$ as photosensitizer and oxidant. The degradation of bispyribac sodium was studied under direct sun light with different pH 4, 7 and 9. The LC-MS/MS (Tandem Mass spectrometry) was used to identify the major transformed by products in water. The degradation of bispyribac sodium was increased by addition of ZnO as photosensitizer. The rate of degradation was also enhanced, by addition of oxidant ($Na_2S_2O_8$) in photosensitizer ZnO.

Gawarammana et al[6] have monitored that self-poisoning of herbicide is a potential reason for hospital admission and death. Bispyribac sodium is a selective herbicide and is a major cause of self-poisoning, when used in rice cultivation. The clinical data was collected from approximately 110 patients from the General Hospital of Shrilanka, who ingested bispyribac sodium. Most patients had self-limiting upper gestor intestinal symptoms. The clinical outcomes from acute self-poisoning from bispyribac sodium containing herbicide, was more favourable than other commonly used herbicide.

Kanwal et al[7] studied the Ag doped ZnO for the photocatalytic degradation of imidachlorprid in aqueous solution under UV irradiation. The investigation was performed under different parameters like pH of solution, catalyst amount and pesticide concentration. The results of the study revealed that the degradation of imidachlorprid increased with Ag doped ZnO as compared to pure ZnO.

Kuriakose et al[8] have demonstrated the photocatalytic degradation of methylene blue dye under sunlight irradiation, using Ag doped ZnO as a photocatalyst. The doping ratio of Ag^+/Citrate in ZnO has been established from the ratio of 1: 1 to 1: 10. The increase in citrate concentration is responsible for the formation of nano disklike structure. The decoration of ZnO with increasing doping ratio of Ag^+/Citrate concentration enhanced the photocatalytic activity of ZnO.

Niranjani and Devi[9] investigated the photocatalytic activity of chemically synthesize ZnO nanoparticles. The investigation was performed on organophosphorus pesticide, phorate. The observations showed that phorate was rapidly degraded with ZnO under solar light irradiation. The maximum degradation of phorate was observed with ZnO nanoparticles after 2 h. Rao et al[10] studied the photocatalytic degradation of bispyribac sodium in water by using Cu and Zn co-doped TiO_2 as a photocatalyst under UV irradiation. It was investigated that the degradation of bispyribac sodium was observed more efficient in the presence of Cu and Zn co-doped TiO_2 as compared to TiO_2 alone. The investigation was carried out in acidic, basic and neutral, media. The rate of degradation effectively increased under co-doped TiO_2 and basic medium.

Russo et al[11] investigated photocatalytic degradation of glyphosate by tungsten (W) doped ZnO under solar irradiation. After doping, the band gap energy of ZnO was down from 3.22 to 3.19 which allowed good photocatalytic degradation of glyphosate. The doping of tungsten in ZnO was performed in the range of 0.7 mole% to 2.9 mol%. The best photocatalytic degradation of glyphosate (i.e. up to 74% in 3 h) was obtained in the 1.5 mole% doping of tungsten in ZnO. Siboni et al[12] investigated the effect of photocatalytic efficiency of Cu doped ZnO in the degradation of organophosphorus pesticide diazinon. The photocatalytic experiment was supported by some experimental parameters like pH of solution, doses of Cu in ZnO, photocatalyst amount and concentration of pesticide. The efficiency of UV/Co doped ZnO for diazinon removal was approximately 96.97% which was more effective than UV/ZnO combination (58.52%).

Sukriti et al[13] studied the effect of different doses of cerium concentration in ZnO to check the photocatalytic efficiency. By decorating with different concentrations of Ce^{+3} in ZnO, the band gap was reduced from 3.17 eV to 2.72 eV. The ZnO doped with cerium in the ratio of 0.94: 0.06 exhibited 9.1times faster photocatalytic degradation activity against ZnO under visible light irradiation for methylene blue dye. Trandafilovic et al[14] used Eu-ZnO nanoparticles for the photocatalytic degradation of methylene blue and methyl orange dye. The photocatalytic activity of Eu-doped ZnO was observed better as compared to ZnO only. The photocatalytic study of methylene blue and methyl orange was observed under solar light. The degradation study was monitor by HPLC analysis. Veeraputhiran and Balasubramanian[15] described that bispyribac sodium is broad spectrum herbicide to control weeds in rice crops. It is a post emergence herbicide which is used in the later stages of crops. It has greater potential of weeds management and higher yield of crops.

Material and Methods

Ce doped zinc oxide was prepared using the co-precipitation-hydrothermal method. 1.0 M of 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, 2.0 M aqueous NaOH solution was added dropwise until a white precipitate formed. The solution was transferred to a teflon-lined stainless-steel autoclave and hydrothermal treatment was carried out at 160°C for 12 h. The solution was then cooled to room temperature. The white precipitate was harvested by centrifugation and was washed several times with deionized water. The precipitate was dried in an oven at 105 °C and then calcinated in Muffle furnace at 750°C for 3 hours. After calcination, the color of solid changed from white to light yellow. 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°. XRD analysis was conducted for undoped ZnO and 3% Ce doped ZnO in figures 1 and 2 respectively. The sharp peaks indicate that the particles of cerium doped ZnO are highly crystalline in nature. Characteristic peaks of cerium and ZnO were observed separately indicating that cerium was successfully incorporated in the ZnO structure. The Miller indices are clearly labelled on the peaks. The average particle sizes of undoped ZnO and 3% cerium doped ZnO were found to be 27.59 nm and 40.81nm respectively. Particle sizes were determined using Debye–Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos\theta)}$$

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 Quanta200-3D FEI instrument. Field Emission Scanning Electron Microscopy (FESEM) was used to study the morphological properties of ZnO nanostructure. The images obtained from FESEM indicate a sunflower like hexagonal structure for ZnO nanomaterials and a nanorod like structure for cerium-doped ZnO. As the cerium concentration increases, the size and shape of the nanorods are altered due to nucleation of Ce ions.

Energy dispersive spectroscopy (EDS): The elemental composition was investigated using energy dispersive spectroscopy (EDS) images. It was found that the undoped ZnO is composed of zinc and oxygen while cerium doped ZnO contains cerium in addition to zinc and oxygen (Figures 4 and 5). The images confirm that cerium was successfully absorbed onto ZnO and no other impurities were detected. This analysis was performed using an EDC Tecnai T-20 instrument.

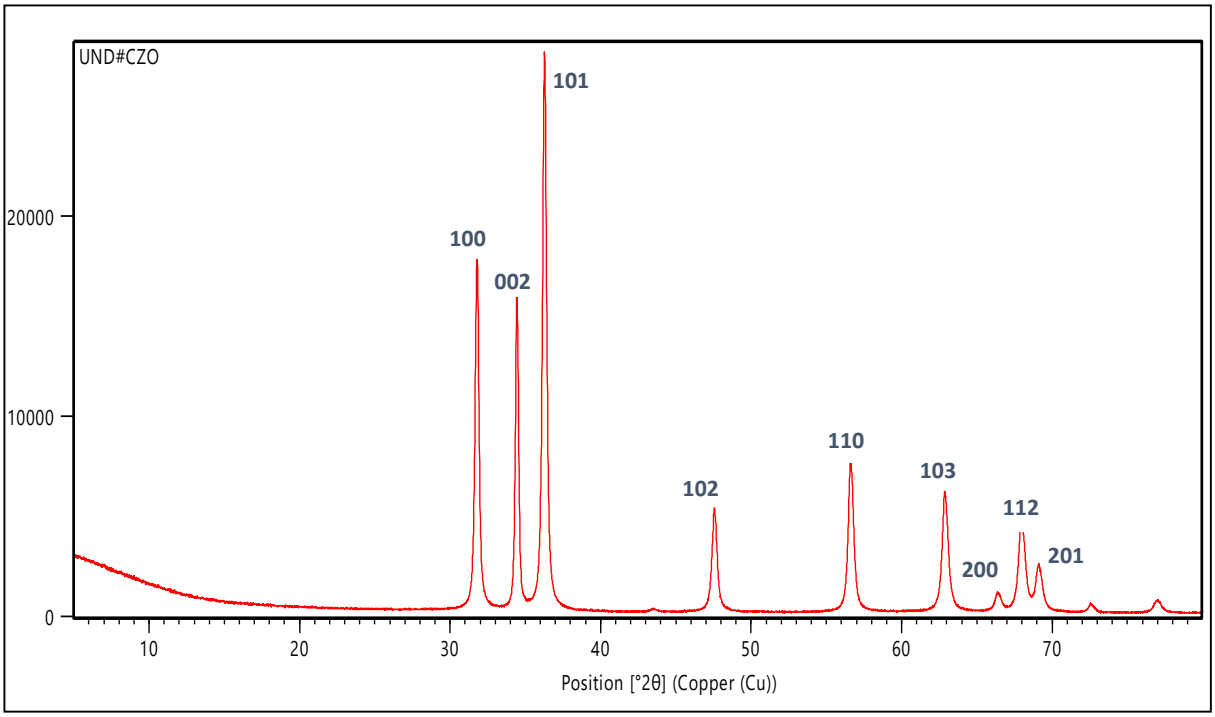


Figure 1: XRD of Undoped ZnO

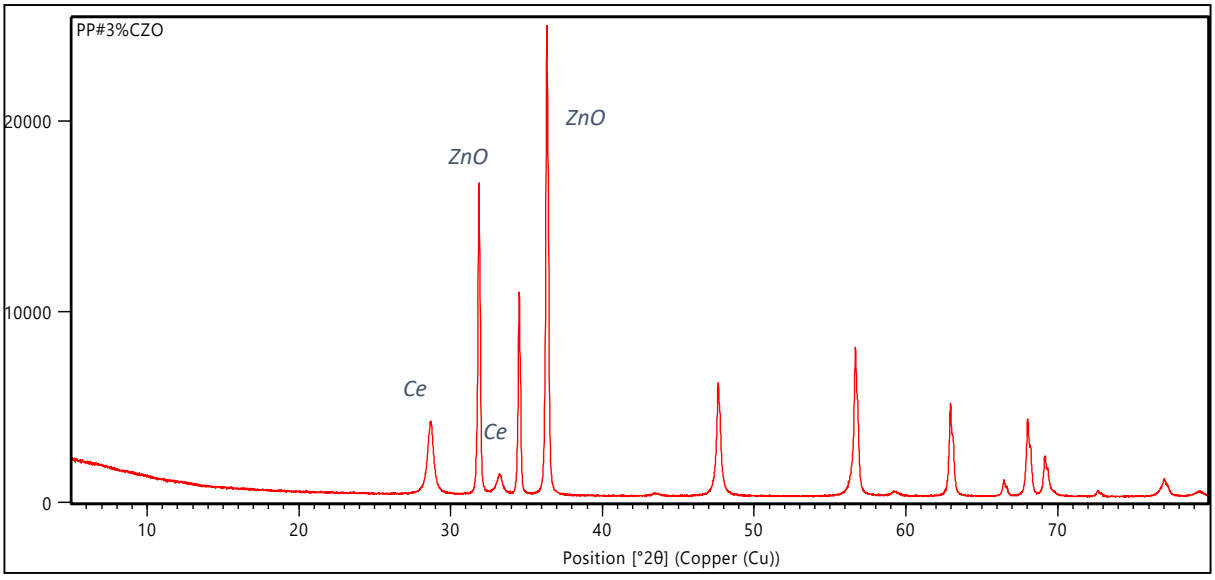
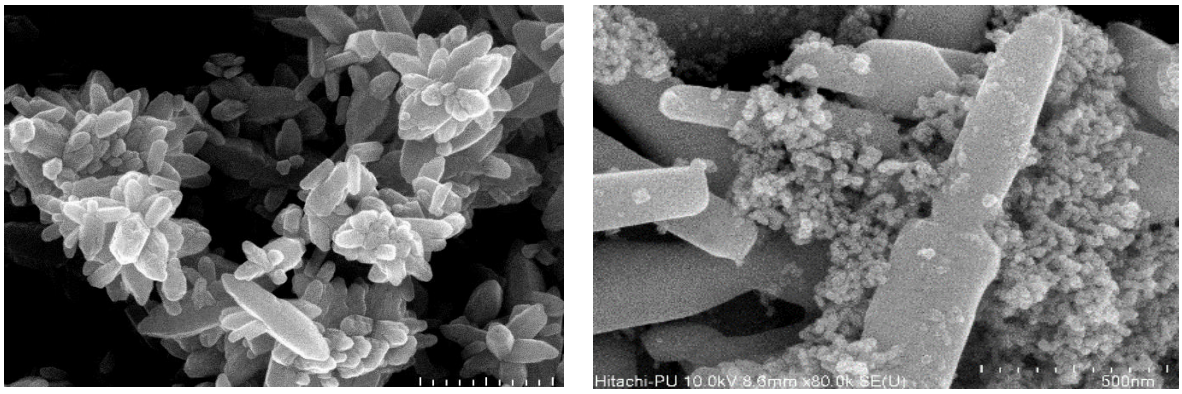


Figure 2: XRD of Cerium doped ZnO (3% CZO)



Undoped ZnO **3% Ce doped ZnO**

Figure 3: FESEM Images

UV Visible (UV) Spectroscopy: The UV absorbance was measured using a UV-Vis-spectrophotometer (Make: Shimadzu, Model: 1800). The UV–Visible spectra of undoped and Ce-doped ZnO nanorods showed that undoped ZnO nanorods do not exhibit any absorption in the visible region (>400 nm) while a broad absorption tail was observed for Ce-doped ZnO nanorods between 400 to 500 nm. While increasing the Ce doping in ZnO, the absorption intensity was increased and absorption band shifted towards the visible region (Red Shift). The doping of Ce exhibits better absorption under sunlight irradiations. 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 3% Ce doped ZnO were calculated to be 3.25 eV and 3.02 eV respectively. The structure of bispyribac sodium is presented in the figure 6.

Results and Discussion

Photocatalytic Experiment: The photocatalytic experiment was carried out with photocatalyst and bispyribac sodium contaminated water (i.e. 30 ppm) under UV irradiations. 50 mL of bispyribac sodium contaminated water was placed in a 100 mL glass beaker. The pH of the solution was 7.76. Accurately 150 mg of photocatalyst was added and the solution was stirred vigorously using magnetic stirrer. The reaction mixture was exposed to 250 W mercury lamp. The sample solution was taken to check percentage degradation of bispyribac sodium in every 1 h duration. Before analysis, the solution was allowed to equilibrate for 10 minutes to achieve absorption / desorption equilibrium.

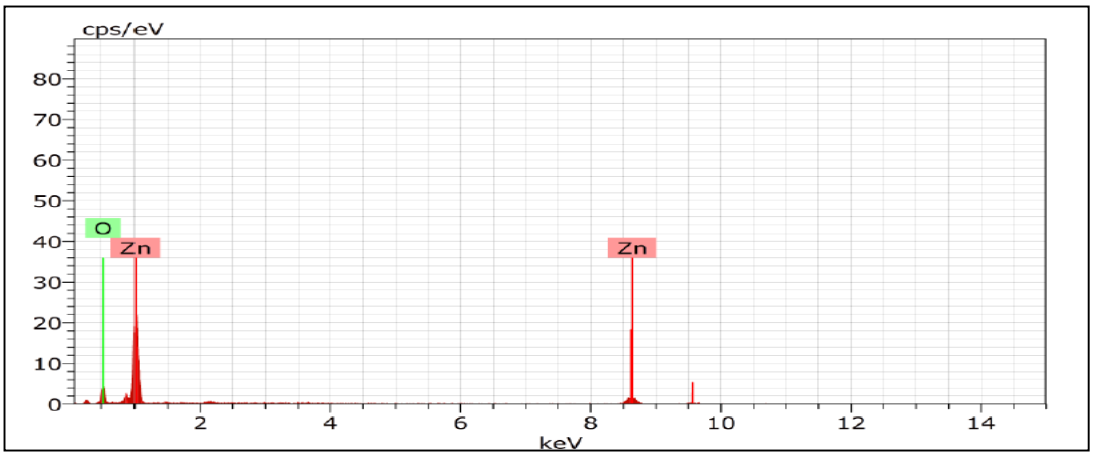


Figure 4: Undoped ZnO

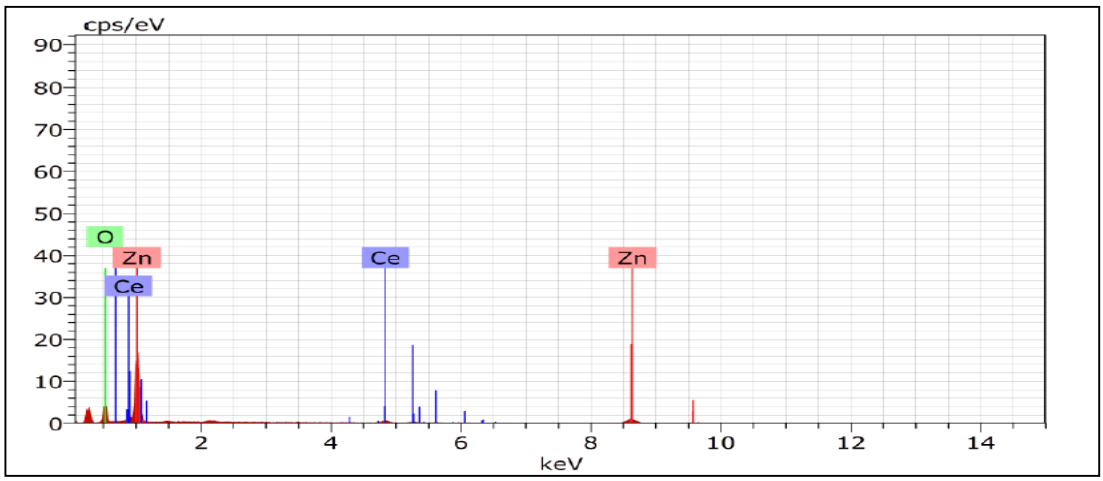


Figure 5: 3% Ce doped ZnO

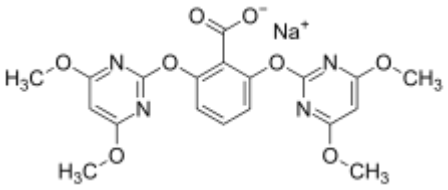


Figure 6: Chemical structure of Bispyribac Sodium

5 mL of solution was taken for centrifugation and the solution was filtered through a 0.45µm membrane filter to remove suspended particles. The filtered solution was then analysed using a UV spectrophotometer (Systronics Model No.: 106) at 245 nm. The degradation of bispyribac sodium was observed greater than 70% in 7 h. The extent of photodegradation was calculated using the formula as follows:

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

where A_0 = Absorbance at 0 minutes 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 bispyribac sodium was degraded photocatalytically in the presence of Ce-ZnO. The results are reported in table 1.

A plot between 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 photolytic in nature and not photochemical or thermal reaction. The highest degradation rate of bispyribac contaminated aqueous solution was observed with 3% Ce doped ZnO.

$k = 6.2 \times 10^{-5}\ s^{-1}$

Effect of Cerium dopant: The photodegradation of aqueous solution of bispyribac sodium 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 summarized in table 2.

The Effect of pH: The pH is a key 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 5.4 to 9.2) of an aqueous solution contaminated with bispyribac sodium (30 ppm). The study on pH showed that the highest degradation of bispyribac sodium occurred at pH 7.7 with 3% Ce-doped ZnO as the photocatalyst (Table 3).

Table 1
Relation of absorbance vs. exposure time

Time	Absorbance (A)	1 + log A
0	1.195	1.08
60	1.093	1.04
120	0.923	0.97
180	0.759	0.88
240	0.627	0.80
300	0.509	0.71
360	0.369	0.57
420	0.287	0.46

Table 2
Effect of Ce doping

Name of Photocatalyst	Rate Constant (k) × 10^5 (s^{-1})
Undoped ZnO	2.0
0.2% Ce doped ZnO	2.0
1.0% Ce doped ZnO	2.3
2.0% Ce doped ZnO	5.7
3.0% Ce doped ZnO	6.2
4.0% Ce doped ZnO	4.1

Table 3
Effect of pH

Photocatalyst	3% Ce doped ZnO
pH	Rate Constant (k) × 10^5 (s^{-1})
5.4	4.3
6.5	4.7
7.7	6.2
8.7	5.8
9.2	5.2

The effect of bispyribac sodium concentrations: The rate of photodegradation may be affected by different concentrations of bispyribac sodium and that is why concentration of bispyribac sodium varied from 25 ppm to 35 ppm. The pH of these solutions was 7.7 when treated with 3% Ce-doped ZnO for photocatalytic degradation. The highest rate of photocatalytic degradation was observed with 30 ppm of bispyribac sodium contamination (Table 4).

The effect of photocatalyst amount: The rate of degradation of bispyribac sodium in water may be affected by amount of photocatalyst. The amount of photocatalyst was varied from 50 mg to 200 mg. The highest rate of degradation was observed with 150 mg of photocatalyst.

The 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 $mWcm^{-2}$ by changing the distance between light source and surface of the photocatalyst. The results are tabulated in table 6. Optimum degradation of bispyribac sodium was observed at 19.2 mW cm^{-2}.

Scavenger Test: The radical capture experiment was conducted using ethylenediaminetetraacetic acid Na Salt, potassium iodide, 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.

$$^{1}BPS_{0} \xrightarrow{h\nu} {}^{1}BPS_{1} \quad (1)$$

$$^{1}BPS_{1} \xrightarrow{ISC} {}^{3}BPS_{1} \quad (2)$$

$$SC + h\nu \longrightarrow SC\,(e^{-}_{CB} + h^{+}_{VB}) \quad (3)$$

$$h^{+}_{VB} + OH^{-} \longrightarrow .OH \quad (4)$$

Table 4
Effect of bispyribac sodium concentrations

Photocatalyst	**3% Ce doped ZnO**	
pH	7.7	
Bispyribac Sodium	Concentration in ppm	Rate Constant (k) × 10^5 (s^{-1})
	25	5.0
	28	5.6
	30	6.2
	32	5.0
	35	3.5

Table 5
Effect of photocatalyst amount

Photocatalyst	**3% Ce doped ZnO**	
pH	7.7	
Concentration in ppm	30	
	Amount of photocatalyst (mg)	Rate Constant (k) × 10^5 (s^{-1})
	50	2.7
	100	3.8
	120	5.0
	150	6.2
	200	5.0

Table 6
Effect of light intensity

Photocatalyst	**3% Ce doped ZnO**	
pH	7.7	
Concentration of Bispyribac sodium	30 ppm	
Amount of Photocatalyst	150 mg	
Light intensity	mW cm^{-2}	Rate Constant (k) × 10^5 (s^{-1})
	23.7	5.9
	19.2	6.2
	15.9	4.0
	13.4	2.0

$$3BPS_1 + \cdot OH \longrightarrow CO_2 + H_2O + \text{Other Products} \quad (5)$$

where BPS = Bispyribac sodium, SC = Semiconductor (Ce doped ZnO) and ISC = Intersystem crossing.

Conclusion

The photocatalytic degradation of bispyribac sodium was observed 36% with undoped ZnO while maximum degradation was observed at pH (7.7), concentration (30ppm), Ce doped ZnO (150mg) and light intensity (19.2 $mWcm^{-2}$) where 76 % of bispyribac sodium was degraded.

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