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PHOTOCATALYTIC DEGRADATION STUDY OF BROAD-SPECTRUM INSECTICIDE (*carbofuran*) BY Ce DOPED ZnO

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ABSTRACT

The efficiency of cerium-doped zinc oxide was evaluated as a photocatalyst in the degradation of carbofuran. 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, concentration of catalyst, pesticide concentration, and intensity of light. The degradation was monitored by a UV spectrophotometer. The optimum conditions were achieved as pH=7.7, carbofuran concentration 14 parts per million, photocatalyst amount = 150 milligrams of 3% cerium-doped zinc oxide, and light intensity is 19.2 milliwatts per square centimetre. About 90% carbofuran degradation was achieved under these conditions.

Keywords: Cerium-doped Zinc-Oxide, Photocatalytic Degradation, Carbofuran, Oxidation
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INTRODUCTION

Carbofuran is a broad-spectrum carbamate insecticide. For crop protection, it is used in granular form. The water solubility of carbofuran is very good (700 mg / L). During irrigation or rainfall, carbofuran can easily dissolve in water and move towards nearby water reservoirs or groundwater resources. This water contamination can harm humans, animals, and aquatic life. The granules of carbofuran are also harmful to birds. The study shows that a single granule of carbofuran can kill a small, innocent bird. The purpose of this study is to remove carbofuran from contaminated water by photocatalytic degradation supported with ultraviolet irradiations. The use of photocatalysis in wastewater treatment was excellently reviewed.[1] The photocatalytic degradation of carbofuran in water was studied by using polychromatic light, zinc oxide (ZnO), and titanium oxide (TiO_2) as photocatalysts. The experiment demonstrated the complete removal of carbofuran (i.e., 88 milligrams/Liter) from water within two hours.[2] The cerium (Ce) doped ZnO nanorods were synthesized, and the Ce doping effect was studied on the structural, optical, and electronic properties of ZnO nanorods. The 5% Ce-doped ZnO nanorods show optimum degradation for the Orange-II dye under solar irradiation.[3] The response surface methodology (RSM) was used in the photocatalytic degradation of carbofuran in the presence of TiO_2 as a photocatalyst. The degradation efficiency of carbofuran was highly affected by the concentration of TiO_2, initial pH value, and the concentration of carbofuran.[4] The photocatalytic degradation of carbofuran in seeping water was studied by using ZnO and different mixed-phase (rutile/anatase) of TiO_2 under solar irradiation at pilot plant scale. The study investigated that ZnO is the most effective catalyst for the removal of carbofuran.[5] The photomineralization of carbofuran by TiO_2-supported catalyst was studied. The TiO_2 microcrystallites firmly affix to a glass plate without any deactivation, and total mineralization of carbofuran was achieved in 15 h under UV irradiation.[6] The removal of carbofuran by the photocatalytic degradation process using response surface methodology (RSM) was studied. The photocatalyst, GAC-TiO_2 [Granular activated carbon (GAC) supported TiO_2], was used to remove carbofuran, and the study was monitored up to 240 minutes. The optimum conditions were pH 7.9, concentration of carbofuran, and amount of photocatalyst, all of which were = 50 mg/L.[7] The photocatalytic degradation of carbofuran in water was investigated by using Degussa P-25 TiO_2 and ZnO as a photocatalyst under UV light irradiation. To achieve maximum degradation efficiency, observations on different conditions (i.e., carbofuran concentration, solution pH,

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amount of catalyst, and light intensity) were studied and recorded. The carbofuran removal and degradation was monitored by a TOC analyzer.[8] The Ce-doped zinc oxide was prepared for 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.[9] The carbofuran (Furadan) is a broad-spectrum systemic insecticide. The plant absorbs it through the roots and distributes it to those organs where insects like to attack. It is also known as a carbamate pesticide. Carbofuran is still used to protect crops like potatoes, corn, and soybeans from insects; however, it is one of the most toxic pesticides.[10] The effect of some transition metal ions on the photocatalytic strength of ZnO was studied. These transition metal ions were Fe^{+2}, Ni^{+2}, Ag^{+}, Cu^{+2}, Co^{+2}, V^{+2} and Mn^{+2}. The experiment was carried out for the bleaching of some dyes like erythrosin-B, fast green FCF, and eosin Y. It was observed that Fe^{+2} and V^{+2} are more effective in dye bleaching.[11] However, carbofuran is one of the most toxic pesticides, but it is still legally used in some parts of the world and countries, especially in Asia and Australia. The use of carbofuran has increased in recent times because it is reported to be an effective insecticide to protect soybean crops from aphids.[12] The toxicity of carbofuran was studied, and it was explained that it is extremely lethal to mammals, birds, fish, and wildlife. It is particularly toxic to birds in its granular form. By mistaking birds that eat carbofuran granules for seeds and dying shortly. It was claimed that millions of birds were killed by carbofuran granules. Carbofuran is a potential cause for acute and chronic toxicities in aquatic organisms by disrupting immune cells and biochemical and enzymatic activities.[13] The effect of different doses of Ce concentration on ZnO was studied to check its photocatalytic efficiency. By decorating with different concentrations of Ce^{+3} in ZnO, the band gap was reduced from 3.17eV to 2.72eV. The ZnO doped with cerium in the ratio of 0.94**:** 0.06 exhibits 9.1 times faster photocatalytic degradation activity against ZnO under visible light irradiation for methylene blue dye.[14]

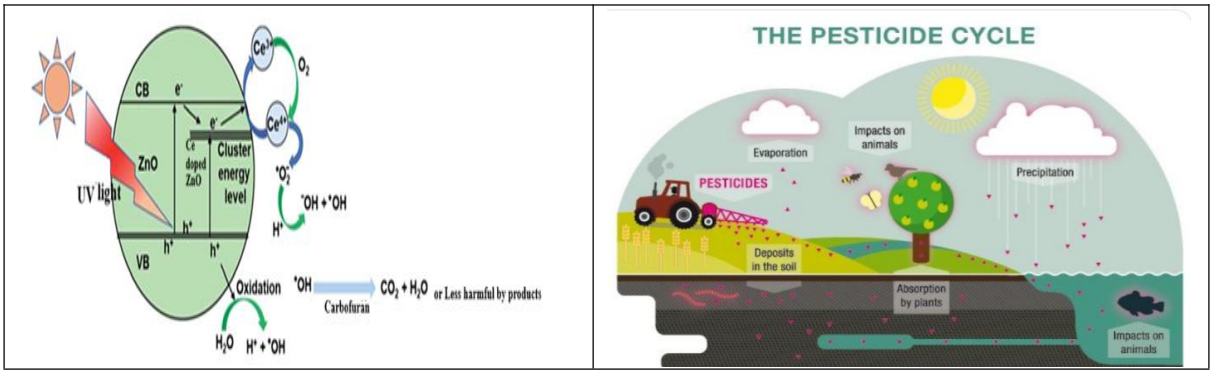

Fig.-1: Photocatalytic Mechanism of Ce-doped ZnO Nanoparticles in UV Light and Pesticide Cycle

EXPERIMENTAL

Material and Methods

Zinc nitrate hexahydrate (Zn $(NO_3)_2 \cdot 6H_2O$ from Qualigens, USA), sodium hydroxide (NaOH from Rankem, India), cerium nitrate hexahydrate (Ce $(NO_3)_3.6H_2O$ from SRL chemicals, India), and distilled water. A Teflon-coated autoclave of 1 Liter capacity and a hot air oven was used for hydrothermal treatment. A centrifuge was used for liquor settlement after washing, and a muffle furnace was used for the calcination of dried material. A 250-Watt mercury lamp was used as a UV light source. A continuous water supply and stirring was maintained for uniform irradiations.

General Procedure

The photocatalyst was synthesized by the hydrothermal method and washed with plenty of water to remove excess NaOH. After the addition of NaOH, a very fine white precipitate was formed. This precipitate was then washed and centrifuged to remove excess alkaline water and collect the white precipitate. The washed precipitate was dried in an oven (12 hours @160°C) and calcinated in a muffle furnace (3 hour @750°C).

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 1.0 mole 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. The aqueous NaOH (2.0 M) solution was prepared and added dropwise until a white precipitate was formed. The precipitated solution was filled in a Teflon-lined stainless-steel autoclave. This autoclave was mounted in a hot air oven for hydrothermal treatment (160°C @ 12 h). After treatment, the solution was allowed to attain room temperature. The precipitate was settled down, and the upper aqueous layer was decanted. The precipitate was washed several times with distilled water to remove excess NaOH. This precipitate was collected by centrifugation, and the upper water layer was discarded. The collected precipitate was dried in an oven (105°C @ 3.0 h) and calcinated in a muffle furnace (750°C @ 3h). The color of the solid changed from white to light yellow after calcination. The Ce-doped ZnO was synthesized by the addition of cerium salt in an aqueous solution of zinc nitrate hexahydrate. Accurately 37.5 g zinc nitrate hexahydrate [Zn $(NO_3)_2 \cdot 6H_2O$] was dissolved in 125 mL of water. The cerium nitrate hexahydrate [Ce $(NO_3)_3.6H_2O$] was weighed and added to this aqueous solution of Zn $(NO_3)_2 \cdot 6H_2O$ to prepare a photocatalyst of variable concentration of Ce doped in ZnO (i.e., 0.2, 1.0, 2.0, 3.0, and 4.0%). This doped solution was treated with aqueous NaOH solution. The observed precipitate was hydrothermally treated, washed, dried, and calcinated according to the above-described procedure to prepare a photocatalyst of Ce-doped ZnO (i.e., 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 values ranging from 20° to 80°. The XRD analysis was conducted for undoped ZnO and 3% Ce-doped ZnO. The results are given in Fig.-2 and 3, 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, 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 3% cerium-doped ZnO was found to be 27.59**nm** and 40.81nm, respectively. The particle sizes were determined using the Debye–Scherrer equation:

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

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

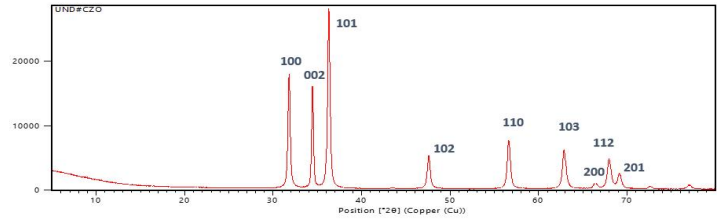

Figure-2: XRD of Undoped ZnO

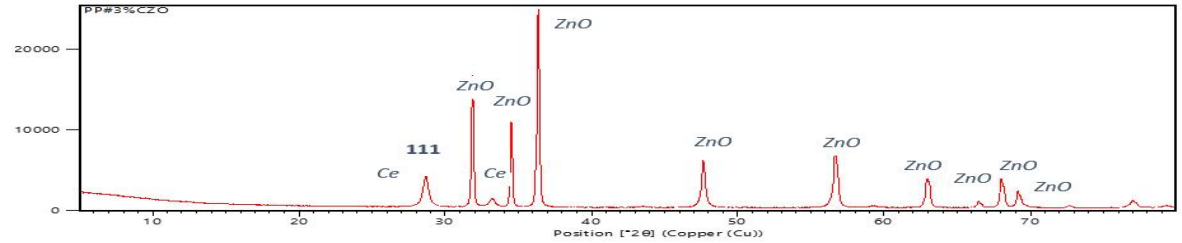

Figure-3: XRD of Cerium doped ZnO (3% CZO)

Field Emission Scanning Electron Microscopy (FESEM*)*

The images of cerium-doped ZnO were taken using a Quanta 200-3D FEI instrument. Field Emission Scanning Electron Microscopy (FESEM) was used to study the morphological properties of ZnO nanostructures. The images obtained from FESEM indicated a sunflower-like (hexagonal) structure for ZnO nanomaterials and a nanorod-like structure for cerium-doped ZnO, Fig.-4 and 5. As the cerium concentration increases, the size and shape of the nanorods are altered due to nucleation of Ce ions.

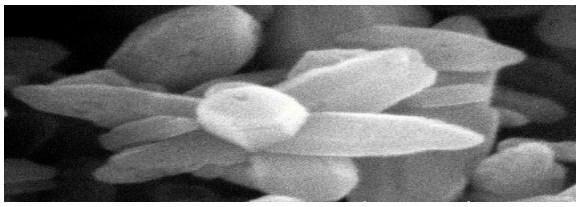

Fig.-4: FESEM Picture, Undoped ZnO

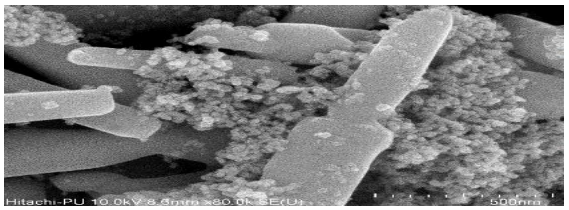

Fig.-5: FESEM Picture, 3% Ce-doped ZnO

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 (Fig.-6 and 7). These images confirmed that cerium was successfully absorbed onto ZnO, and no other impurities were detected.

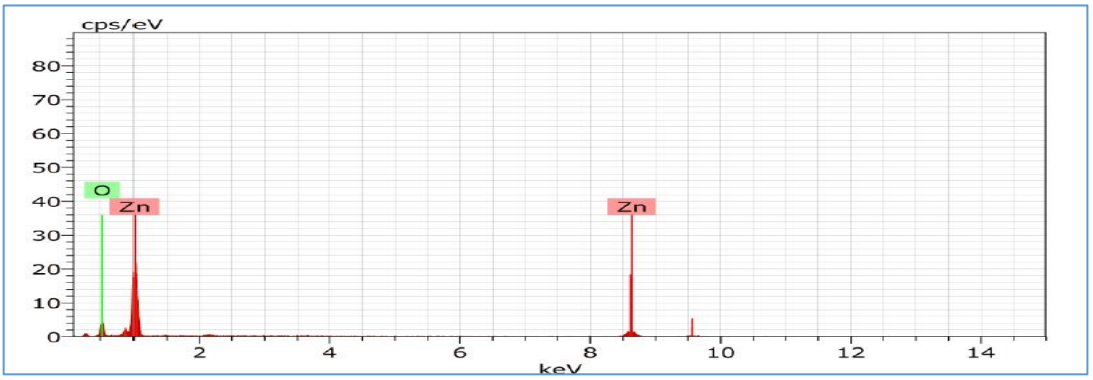

Fig.-6: Undoped ZnO

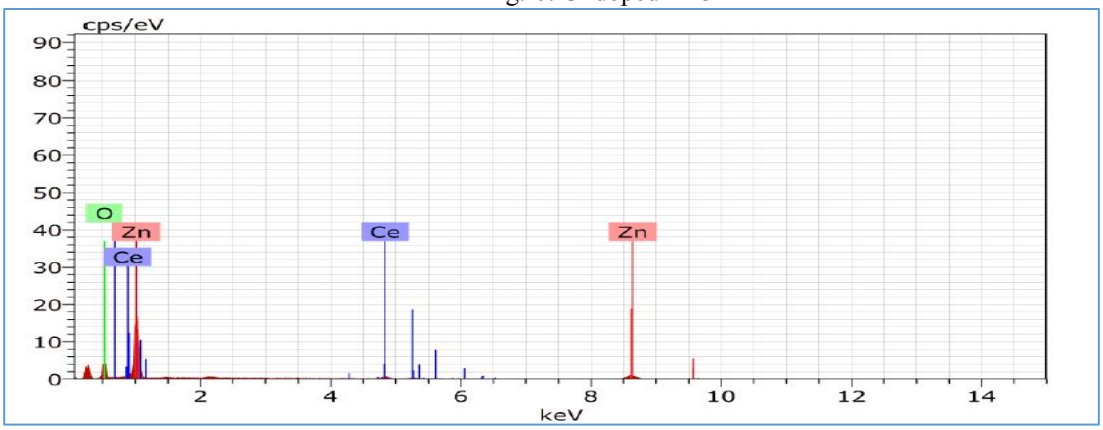

Fig.-7: 3% Ce-doped ZnO

UV-Visible Spectroscopy

The absorbance was measured using a Shimadzu UV spectrophotometer (Model No.: 1800). The comparative UV-Visible spectra of undoped ZnO and Ce-doped ZnO nanorods show that the spectra of Ce-doped ZnO exhibit absorption in the visible region (> 400 nm). This shifting in absorption indicated that Ce doping increased absorption intensity in the visible region (i.e., red shift). It indicated that Ce-

doped ZnO exhibited better absorbance under sunlight irradiation. The band gap of ZnO and Ce-doped ZnO can be calculated as:

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

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 chemical structure of carbofuran is presented in Fig.-8.

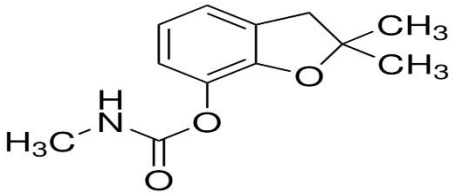

Fig.-8: Structure of Carbofuran

RESULTS AND DISCUSSION

The photocatalytic experiment was carried out with the photocatalyst and carbofuran-contaminated water (14 ppm) under ultraviolet (UV) irradiation. The 50 mL of carbofuran-contaminated water was placed in a 100 mL glass beaker. The pH of the solution was 7.7. An accurately measured 150 mg amount of photocatalyst was added, and the solution was stirred vigorously. The reaction mixture was exposed to a 250 W mercury lamp. Sample solutions were taken in every 60 min. to check the percentage degradation of carbofuran. The solution was kept for 10 minutes to achieve absorption /desorption equilibrium. Then, 5 mL of the 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 Systronics UV spectrophotometer (Model No: 106) at 280 nm. The degradation of carbofuran was observed to be more than 90 % in 6 h. 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 carbofuran was degraded photocatalytically in the presence of Ce-doped ZnO. The results are reported in Table-1. A plot of the log of absorbance versus time was drawn. The degradation reaction follows pseudo-first-order kinetics. The rate constant was calculated by the formula mentioned below:

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

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 photocatalytic in nature and not a photochemical or thermal reaction. The highest degradation rate of carbofuran-contaminated aqueous solution was observed with 3% Ce-doped ZnO.

Table-1: Effect of Absorbance

Time	Absorbance (A)	2 + log A
0	0.121	1.08
60	0.107	1.03
120	0.090	0.95
180	0.068	0.83
240	0.044	0.64
300	0.021	0.32
360	0.011	0.04

$k = 12.7 \times 10^{-5}\ s^{-1}$

Effect of Cerium Dopant

The photodegradation of an aqueous solution of carbofuran **(17 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.

Table-2: Effect of Ce-doping

Photocatalyst	Rate Constant (**k**) × $(10)^5$ **(s^{-1})**
Undoped ZnO	5.8
0.2 % Ce-doped ZnO	5.8
1.0 % Ce-doped ZnO	5.9
2.0 % Ce-doped ZnO	10.0
3.0 % Ce-doped ZnO	11.7
4.0 % Ce-doped ZnO	2.3

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 to 8.5) of an aqueous solution contaminated with carbofuran (17 ppm). It was observed that the highest degradation of Carbofuran occurred at pH 7.7 with 3% Ce-doped ZnO as the photocatalyst (Table-3).

Table-3: Effect of pH

Photocatalyst	3.0 % Ce-doped ZnO
pH	Rate Constant (k) × 10^5 (s^{-1})
5.5	4.5
6.5	4.7
7.7	11.7
8.3	7.5
8.5	4.7

Effect of Concentrations

The rate of photodegradation may be affected by different concentrations of carbofuran, and therefore, the concentration of carbofuran was varied from 12 to 20 ppm. The observations are summarized in Table-4. At 14 ppm of carbofuran contamination, the highest rate of photocatalytic degradation was observed.

Table-4: Effect of Carbofuran Concentrations

Photocatalyst	3.0 % Ce-doped ZnO	
pH	7.7	
Carbofuran	Concentration in ppm	Rate Constant (k) × 10^5 (s^{-1})
	12	6.3
	14	12.7
	17	11.7
	18	8.0
	20	3.3

Effect of Photocatalyst Amount

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

Table-5: Effect of Photocatalyst Amount

Photocatalyst	3.0 % Ce-doped ZnO	
pH	7.7	
Concentration in ppm	14 ppm	
	Amount of photocatalyst in mg	Rate Constant (k) × 10^5 (s^{-1})

	50	2.20
	100	5.80
	120	11.70
	150	12.70
	200	7.30

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 carbofuran was observed at 19.2 $mWcm^{-2}$.

Table-6: Effect of Light Intensity

Photocatalyst	3.0 % Ce-doped ZnO	
pH	7.7	
Concentration in ppm	14 ppm	
Amount of photocatalyst	150 mg	
Light intensity	mW cm^{-2}	Rate Constant (k) × 10^5 (s^{-1})
	23.7	12.3
	19.2	12.7
	15.9	7.3
	13.4	5.9

Scavenger Test

The radical capture experiment was carried out using ethylenediaminetetraacetic acid Na Salt, potassium iodide, ammonium oxalate, and isopropyl alcohol. It was observed that degradation was completely hindered in the presence of isopropyl alcohol, and, therefore, it was also concluded that the hydroxyl radical was the active oxidizing species in this degradation.

$$^1CAR_0 \xrightarrow{h\nu} {}^1CAR_1 \quad (1)$$

$$^1CAR_1 \xrightarrow{ISC} {}^3CAR_1 \quad (2)$$

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

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

$$^3CAR_1 + {}^{\cdot}OH \longrightarrow CO_2 + H_2O + \text{Other Products} \quad (5)$$

Where CAR = Carbofuran and SC = Semiconductor (Ce doped ZnO)
ISC = Intersystem crossing

CONCLUSION

The photocatalytic degradation of carbofuran with undoped ZnO was found to be only 40% while optimum degradation was observed at pH (7.7), carbofuran concentration (14 ppm), 3% Ce-doped ZnO (150mg), and light intensity (19.2 mW cm^{-2}), where more than 90% of carbofuran was degraded.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-6: Clean Water and Sanitation.* All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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