Indian Journal of Chemical Technology
Vol. 31, January 2024, pp. 39-43
DOI: 10.56042/ijct.v31i1.4985

# Synthesis and characterization of Fe doped ZnO nanoparticles for the photocatalytic degradation of eriochrome black-T dye

Dipak Giram & Arijit Das*
Department of Chemical Engineering, Visvesvaraya National Institute of Technology, Nagpur 440 010, Maharashtra, India
*E-mail: arijitdas@che.vnit.ac.in

*Received 18 August 2023; accepted 12 December 2023*

The current investigation presents the synthesis of zinc oxide (ZnO) and iron-doped zinc oxide (Fe:ZnO) nanoparticles using co-precipitation technique. A comprehensive characterization of the nanoparticles was conducted using XRD, FESEM, EDS and UV-visible spectroscopy. The XRD analysis revealed that both ZnO and Fe:ZnO nanoparticles exhibited a hexagonal wurtzite crystal structure. The average crystallite sizes are determined as 18.47 nm for ZnO and 15.32 nm for Fe:ZnO. Further, UV-visible absorption studies indicate a reduction in the band gap of ZnO upon Fe doping. The FE-SEM analysis confirms the irregular shaped morphology of the nanoparticles, while EDS analysis validates their elemental composition. The photocatalytic performance of the prepared nanoparticles has been investigated by employing eriochrome black T dye as a representative pollutant. Furthermore, the optimization of the photocatalytic degradation process is achieved by varying process variables like catalyst loading, initial dye concentration, and pH. The experimental finding demonstrated that Fe:ZnO nanoparticles exhibited significantly enhanced photocatalytic activity compared to pure ZnO nanoparticles, with a maximum degradation efficiency of 83.47% achieved within 150 min. The degradation kinetics followed a pseudo-first-order reaction.

**Keywords:** Co-precipitation method, Eriochrome black-T dye, Fe doped ZnO nanoparticles, Kinetics, Photocatalytic degradation

## Introduction

Textile industry plays a major role in water pollution as a result of the discharge of toxic and harmful dyes into water sources. According to literature, approximately 280,000 tons of synthetic dyes are released annually through industrial waste[1]. These dyes are not easily biodegradable and can persist in the environment for extended periods, causing severe health hazards. So, getting rid of water pollutants like dyes has become one of the most crucial issues for the environment. The photocatalysis technique has been widely used to remove several dyes due to its various advantages, which include high removal efficiency, low cost, and environmental friendliness. Photocatalysis involves the use of a suitable photocatalyst to activate the oxidation process under sunlight or artificial light. Nowadays, nanostructured semiconductors like $TiO_2$, ZnO, and $SnO_2$ have been extensively investigated as photocatalysts for the degradation of hazardous dyes, exhibiting remarkable degradation performance[2].

Zinc oxide (ZnO) has gained significant attention as a photocatalyst owing to its remarkable photocatalytic performance, notable stability, and minimal toxicity compared to other photocatalysts. However, the intrinsic properties of pure ZnO, such as its wide band gap energy (3.3 eV) and rapid recombination rate of electron-hole pairs generated during photocatalysis, impose limitations on its photocatalytic activity. Consequently, the photocatalytic capabilities of ZnO are predominantly limited to the UV region only. In order to increase its absorption of visible light, various strategies have been explored, including doping with transition metals[3]. Among various dopants, iron (Fe) was one of the best dopant for ZnO due to its superior chemical stability and comparable ionic radii dimensions. Thus, Fe could readily diffuse into the ZnO lattice without causing significant alterations to the crystal structure of the semiconductor. Additionally, the presence of Fe ions serves as electron traps, effectively promoting the separation of electron-hole pairs produced by light and inhibiting their recombination. As a result, this phenomenon leads to an improvement in the efficiency of photocatalytic processes[4].

In the literature, previous research studies have indicated that Fe-doped ZnO nanoparticles (Fe:ZnO) demonstrated exceptional photocatalytic activity in the degradation of diverse organic dyes, including congo red, crystal violet, methylene blue, methyl orange, and rhodamine B. However, a thorough review of the available literature suggests that the synthesis of

Fe-doped ZnO photocatalyst nanoparticles and their potential application in the degradation of eriochrome black T (EBT) dye under solar light remain uninvestigated. EBT is a well-known toxic azo dye that has several industrial and scientific applications, including silk, wool, and nylon dyeing. However, due to its poisonous and carcinogenic effects, EBT azo dye removal from water is an urgent priority[5].

Therefore, in this context, the present study focuses on the preparation of Fe:ZnO nanoparticles utilizingco-precipitation technique and their application for the degradation of EBT dye under sunlight. Moreover, the degradation of EBT was explored in detail, including the kinetics and optimization. The optimization of the photocatalytic degradation process was achieved by varying process variables like the initial dye composition, catalyst loading, and pH to enhance the overall efficiency.

## Experimental Section

### Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), iron nitrate ($Fe(NO_3)_3.9H_2O$), HCl, NaOH, and ethanol were obtained from Merck Chemical for the synthesis of Fe:ZnO nanoparticles. EBT dye was procured from Finar Company. Analytical grade chemicals were employed in the study.

### Synthesis of Fe doped ZnO nanoparticles

Zinc acetate dihydrate (5 g), iron nitrate (6.7 g) and sodium hydroxide (5 g) were introduced into an ethanol/water mixture. The resultant mixture was stirred properly (at 700 RPM) for 90 min using a magnetic stirrer. Subsequently, the solution was subjected to filtration to separate the desired nanoparticles. The solid residue obtained was then washed with distilled water to eliminate any residual impurities. Following the purification steps, the solid residue was subjected to drying in a hot air oven set at a temperature of 100°C. Finally, the dried residue was subjected to crushing using a mortar and pestle, resulting in the formation of Fe:ZnO nanoparticles. Also, ZnO nanoparticles were prepared in a similar way without the incorporation of iron nitrate in the above process.

### Photocatalytic activity of EBT dye degradation

The objective of the experiment was to assess the photocatalytic performance of the synthesized nanoparticles by degrading an EBT dye aqueous solution under sunlight. The batch experiment was conducted by introducing the necessary quantity of Fe:ZnO nanoparticles to 100 mL of EBT solution with the specified ppm composition. The resulting mixture was stirred vigorously by a stirrer in a light free environment for 30 min to establish a state of equilibrium between the adsorption and desorption process. At specific time intervals, 3 mL aliquots were extracted from the reaction mixture to evaluate the concentration of EBT. Further, the aliquots were centrifuged (4000 RPM), and the absorbance of the centrifuged sample was measured at $\lambda_{max}$ = 570 nm using a UV-visible spectrophotometer. Using the following formula, the percentage of EBT degradation was calculated.

$$\% \text{ Degradation} = \left(1 - \frac{C_t}{C_o}\right) * 100 \quad \text{... (1)}$$

Where $C_0$ and $C_t$ represent initial (t =0) and final concentration (t = t), respectively.

## Results and Discussion

### Characterization of ZnO and Fe:ZnO nanoparticles

#### *XRD analysis*

The XRD pattern of ZnO and Fe:ZnO was depicted in Fig. S1 (Supplementary Information).The XRD results showed key characteristic peaks at 2θ=31.88°, 34.46°, 36.35°, 47.64°, 56.69°, 62.94°, 68.34°, 69.04° are attributed to the plane of(100) (002) (101) (102) (110) (103) (112) (201) hexagonal wurtzite structure, respectively[6,7]. XRD analysis revealed that both samples show similar peak patterns, indicating that incorporation of Fe into ZnO matrix did not alter its crystal structure due to the lower concentration of the Fe precursor utilized. Furthermore, no secondary peaks were observed, indicating that both samples do not contain any other impurities. Additionally, the crystallite size of as synthesized samples was estimated using Debye-Scherrer's equation[8]. The nano crystallite size of ZnO and Fe:ZnO samples was measured to be 18.47 nm and 15.32 nm, respectively.

#### *UV-visible analysis*

The UV-visible absorption spectra of synthesized samples were obtained by measuring the absorbance over the wavelength range of 200 to 800 nm, as illustrated in Fig. S2. The resulting UV-visible absorption spectrum of the synthesized materials primarily reflects changes in the band gap energy. Subsequently, the incorporation of iron (Fe) particles into the ZnO matrix caused a blue shift in the absorption edge, indicating a shift towards longer wavelengths. This shift in the absorption peaks can be assigned to the incorporation of Fe dopant in ZnO, which induces

modifications in the band structure and energy gap of the nanoparticles. The determination of the energy gap for both samples was calculated using the Tauc plot equation[8]. The respective band gap energies of ZnO and Fe:ZnO nanoparticles were determined to be 3.31 eV and 3.10 eV (shown in Fig. 1). This reduction in band gap improved the optical characteristics of the synthesized nanoparticles, which can be favourable for photocatalytic applications.

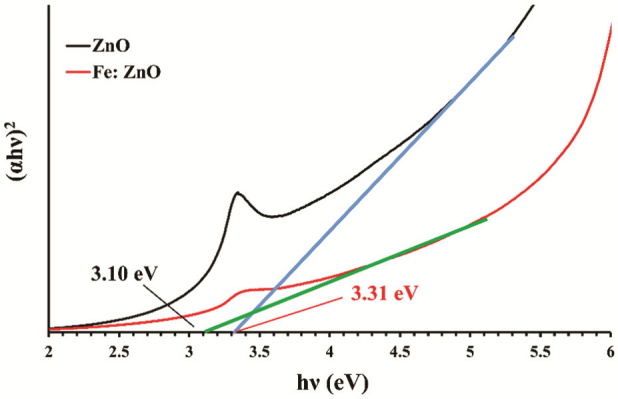


Fig. 1 — Tauc plot for ZnO and Fe:ZnO photocatalysts

**Photocatalytic activity**

***Effect of catalyst loading***

Fig. 2a illustrates the impact of catalyst loading (50-400 mg) on the photo degradation of EBT dye

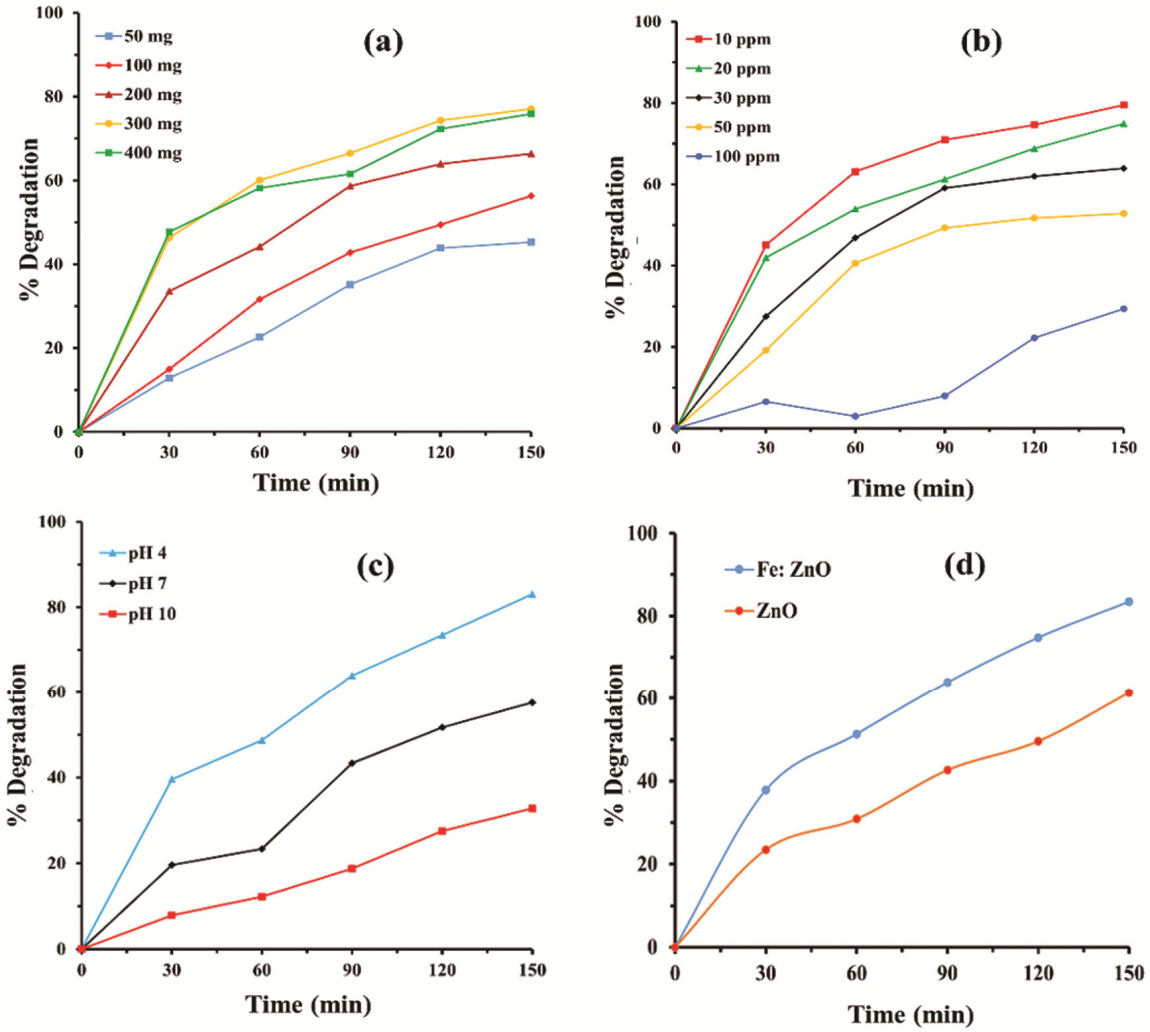


Fig. 2 — Effect of different parameters on degradation of EBT dye using Fe:ZnO nanoparticles: (a) Effect of catalyst loading [conditions: initial dye concentration 20 ppm, irradiation time 150 min and pH 6.5]; (b) Effect of initial dye concentration [conditions: photocatalyst loading 300 mg, irradiation time 150 min and pH 6.5]; (c) Effect of pH [conditions: photocatalyst loading 300 mg, initial dye concentration 10 ppm and irradiation time 150 min]; (d) Effect of doping [conditions: photocatalyst loading 300 mg, initial dye concentration 10 ppm, pH 4 and irradiation time 150 min]

using Fe:ZnO nanoparticles. The initial conditions of the experiment included a 100 ml dye solution with a pH of 6.5 and a concentration of 20 ppm. The experimental findings indicated that an increase in photocatalyst loading from 50 mg to 300 mg resulted in a corresponding increase in the degradation of EBT dye, with the percentage of degradation rising from 45.25% to 77.06% over a 150 min period. This enhancement can be attributed to the increase in the number of active sites within the photocatalyst, which play a major role in enhancing the degradation of the dye. However, upon further increasing the catalyst loading from 300 mg to 400 mg, the degradation decreased from 77.06% to 75.90%. This decline can be attributed to the excessive use of the catalyst, which leads to the formation of aggregates, which diminishes the photocatalysts performance[2]. Therefore, it was determined that a catalyst dose of 300 mg is optimal in this context.

***Effect of initial dye concentration***

Fig. 2b depicts the impact of the initial dye concentration (10-100 ppm) on the photocatalytic degradation of dye. The catalyst loading remains constant at 300 mg/100 mL, and the pH level is maintained at 6.5. Experimental findings indicate a diminishing trend in the degradation of dye as the initial dye concentration increases. After an irradiation time of 150 min, the percentage of EBT dye degradation is observed to be 79.50% for a concentration of 10 ppm, whereas it decreases to 29.37% for a concentration of 80 ppm.This decrease can be attributed to two main factors: (1) as the dye concentration rises, the adsorption of dye molecules on the catalyst surface reaches an optimal level, resulting in a saturation of available active sites for the photodegradation process and (2) an increase in dye concentration results in a reduction in the number of incident photons reaching the photocatalyst surface. Consequently, the excitation of the photocatalysts is reduced, thereby affecting the overall photodegradation efficiency[2].

***Effect of pH***

Fig. 2c depicts the effects of different pH values (4, 7, and 10) on the degradation of EBT dye. The obtained experimental results demonstrate that the photocatalytic degradation process exhibits higher efficiency in an acidic environment (pH 4) compared to an alkaline environment. The percentage of dye degradation at the end of 150 min of irradiation was measured as 83.04% for a pH value of 4, while it was found to be 57.5% and 35.75% for pH values of 7 and 10, respectively. The alteration of pH modulates the surface properties of Fe doped ZnO photocatalyst. The pH at the point of zero charge for the catalyst determines its surface charge. In acidic solutions, the surface of the catalyst exhibits a positive charge, while in alkaline solutions, it carries a negative charge. The maximum adsorption of EBT dye occurs at an acidic pH of 4. At this pH, the catalyst surface becomes positively charged, facilitating the interaction with EBT, which is an anionic dye, through electrostatic forces of attraction. Conversely, in a basic medium, both the dye solution and the catalyst surface possess a negative charge, resulting in repulsive forces between them. As a result, the degradation of EBT is hindered, and a lower level of degradation is observed under these conditions.

***Effect of doping at optimized conditions***

This study employed optimized loading of ZnO and Fe:ZnO photocatalysts with a catalyst loading of 300 mg, an initial EBT concentration of 10 ppm, and pH of 4. The experimental findings demonstrated that the Fe:ZnO nanocomposite displayed a superior degradation efficiency (83.47%) compared to pure ZnO (61.30%) under identical conditions, as depicted in Fig. 2d. The enhancement in photocatalytic activity of the Fe:ZnO photocatalyst can be associated to its efficient charge separation mechanism, resulting in a substantial decrease in the recombination rate of electron and hole pairs.

***Kinetic study***

The current study evaluated the kinetics of the degradation of EBT dye in the presence of synthesized ZnO and Fe:ZnO photocatalysts under optimized conditions. The experimental conditions included a dye concentration of 10 ppm, pH of 5, and a catalyst loading of 300 mg/100 mL. The degradation of the dye followed pseudo-first-order reaction kinetics. The rate constant ($k$) for the photocatalytic degradation process was determined using the equation

$$In\left(\frac{C_o}{C}\right) = kt \quad \ldots (2)$$

In this equation, $C_0$ represents the initial concentration of the dye, $C$ represents the final concentration after an irradiation period of t min, and $t$ represents the time in minutes. Further, the fitting correlation coefficient ($R^2$) was calculated and

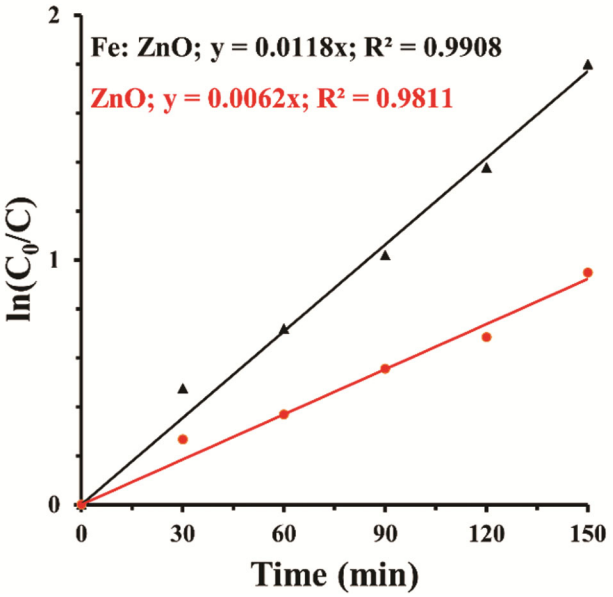


Fig. 3 — Pseudo-First order kinetics of EBT dye degradation using Fe:ZnO nanoparticles

depicted in Fig. 3. The $R^2$ values indicated that the experimental data and the model are strongly correlated. Notably, the rate constant of Fe:ZnO was determined to be greater than that of bare ZnO, indicating that Fe:ZnO expresses superior photocatalytic efficiency compared to ZnO.

## Conclusion

ZnO and Fe doped ZnO (Fe:ZnO) nanoparticles were synthesized via co-precipitation method. These nanoparticles were effectively employed as photocatalysts for the photodegradation of EBT dye. Additionally, the optimization of different process variables, including catalyst dosage, initial concentration of EBT, and pH, was conducted to achieve the highest degradation efficiency of EBT. The optimized conditions yielded a maximum degradation efficiency of 83.47%, with a catalyst dosage of 300 mg, initial EBT concentration of 10 ppm, and pH of 4. Notably, the Fe:ZnO nanoparticles showed better photodegradation performance compared to pure ZnO, assigned to the reduction in band gap and suppression of electron-hole pair recombination.

## Acknowledgement

The authors acknowledge the contribution of Visvesvaraya National Institute of Technology, Nagpur, India, for providing financial support, experimental facilities, and other necessary facilities to carry out this research work.

## Supplementary Information

Supplementary information is available on the website http://nopr.niscpr.res.in/handle/123456789.

## References

1 Al-Ghouti M A & Dib S S, Utilization of nano-olive stones in environmental remediation of methylene blue from water, *J Environ Heal Sci Eng*, 18 (2020) 63.

2 Giram D, Das A & Bhanvase B, Comparative study of ZnO-$TiO_2$ nanocomposites synthesized by ultrasound and conventional methods for the degradation of methylene blue dye, *Indian J Chem Technol*, 30 (2023) 693.

3 Sanakousar F M, Vidyasagar C C, Jiménez-Pérez V M & Prakash K, Recent progress on visible-light-driven metal and non-metal doped ZnO nanostructures for photocatalytic degradation of organic pollutants, *Mater Sci Semicond Process*, 140 (2022) 106390.

4 Mancuso A, Sacco O, Mottola S, Pragliola S, Moretta A, Vaiano V & De M I, Synthesis of Fe-doped ZnO by supercritical antisolvent precipitation for the degradation of azo dyes under visible light, *Inorg Chim Acta*, 549 (2023) 121407.

5 Franco P, Sacco O, De M I, Sannino D & Vaiano V, Photocatalytic Degradation of eriochrome black-T azo dye using Eu-doped ZnO prepared by supercritical antisolvent precipitation route: A preliminary investigation, *Top Catal*, 63 (2020) 1193.

6 Ferin F A, Jothi M R, Sakthipandi K, Manimala K & Hossain A, Enhanced antifungal activity of pure and iron-doped ZnO nanoparticles prepared in the absence of reducing agents, *J Inorg Organomet Polym Mater*, 30 (2020) 2397.

7 Selvanayaki R, Rameshbabu M, Muthupandi S, Razia M, Sasi F S, Ravichandran K & Prabha K, Structural, optical and electrical conductivity studies of pure and Fe doped zinc oxide (ZnO) nanoparticles, *Mater Today Proc*, 49 (2021) 2628.

8 Satdeve N S, Ugwekar R P & Bhanvase B A, Ultrasound assisted preparation and characterization of Ag supported on ZnO nanoparticles for visible light degradation of methylene blue dye, *J Mol Liq*, 291 (2019) 111313.