



Photocatalytic Degradation of Bg by Zr Doped Co₃O₄ Nanoparticles

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ABSTRACT: The synthesis of Co₃O₄ and Zr-Co₃O₄ nanoparticle using a co-precipitation method for efficient photocatalytic degradation of Brilliant green (BG) dye under UV and natural sunlight. Characterization through, Elemental mapping of FE-SEM, HR-SEM, XRD, HR-TEM, EDAX, PL and UV-DRS techniques confirmed the successful synthesis and structural integrity of the materials sheet-like structures and Chain spherical, tetragonal structures for Zr-Co₃O₄ and Zr-Co₃O₄ and while the composite maintained the crystallinity of both phases, Low intensity very high Photocatalytic activity by PL and UV-DRS analysis demonstrated a reduction in the band gap from 3.3 eV (Co₃O₄) to 2.6 eV (Zr-Co₃O₄) enhancing photocatalytic efficiency. Photocatalytic degradation tests indicated Zr-Co₃O₄ achieved (98% Natural sun light) Brilliant green (BG) removal, outperforming Zr-Co₃O₄ (96% UV) this performance enhancement is attributed to the synergistic interaction between Zr-Co₃O₄ nanoparticles under solar irradiation,

Introduction: The current living standards, coupled with a growing population, have resulted in a notable rise in the demand for vital resources, including food, water, energy, and raw materials, across multiple industrial sectors. A significant array of strategies has been formulated to eliminate synthetic dyes from wastewater to mitigate their environmental impact. Each year, more than 70,000 tons of approximately 10,000 varieties of colors and shades are distributed globally. Approximately 20–30% of colors are wasted in mechanical effluents during the processes of material coloring and finishing through the undoped Co₃O₄ and doped Zr-Co₃O₄

Methods: Synthesis of Zr-doped Co₃O₄ nanoparticles by A straight forward co-precipitation method

Results: Photocatalytic degradation tests indicated Zr-Co₃O₄ achieved (98% Natural sun light) Brilliant green (BG) removal, outperforming Zr-Co₃O₄ (96% UV) this performance enhancement is attributed to the synergistic interaction between Zr-Co₃O₄ nanoparticles under solar irradiation,

Conclusions:

Using the precipitation approach, we were then able to successfully synthesize Zr-doped Co₃O₄ nanomaterial. This nanomaterial was examined using an HR-SEM, which showed that the Zr-doped Co₃O₄ nanomaterial has a well-defined multilayer structure. An X-ray (EDX) study also verified that Zr, Co and O are present in the nanomaterial. When the generated the generated spherical-like and flower structure nanomaterial PL to Co₃O₄ a significant photocatalytic activity is observed. Because of its low band gap energy, the UV-Vis DRS spectrum is a good choice for photocatalysis. In the end, the photocatalytic efficiency of BG dye was found to be almost Zr-doped Co₃O₄ higher than photocatalytic activity that of Co₃O₄. After providing a workable procedure and thoroughly reviewing the created nanomaterial for industrial use, it was shown to be stable and reusable by highest catalytic ability of the Zr-doped Co₃O₄ nanoparticles.

1. Introduction

The current living standards, coupled with a growing population, have resulted in a notable rise in the demand

for vital resources, including food, water, energy, and raw materials, across multiple industrial sectors. A significant array of strategies has been formulated to eliminate synthetic dyes from wastewater to mitigate



their environmental impact. Each year, more than 70,000 tons of approximately 10,000 varieties of colors and shades are distributed globally. Approximately 20–30% of colors are wasted in mechanical effluents during the processes of material coloring and finishing [1]. The majorities of dyestuffs, including azo colors, are toxic and must be removed before being discharged into receiving waters, as their effluents can reduce light penetration and hinder photosynthesis [2]. In the past ten years, photocatalytic degradation processes has been utilized extensively as methods for the deletion of whole pollutants in wastewater and effluents, particularly the degradation of dyes [3–11]

Spinel cobalt oxide (Co_3O_4), known for its high thermodynamic stability, presents promising applications across various significant technological domains. This encompasses heterogeneous catalysis for carbon monoxide oxidation and the degradation of industrial contaminants, along with anode materials in lithium-ion rechargeable, sensor advantages, pigments, batteries, and energy storage applications. Nonetheless, insufficient performance across diverse applications presents a significant challenge for scaling this material to an industrial level. Nano-structured Co_3O_4 has demonstrated remarkable catalytic properties, primarily due to its morphology, dimension, large surface-to-volume atomic ratio, and shape-dependent characteristics, as these factors significantly affect the preferentially exposed catalytic sites [12]. Cobalt oxide nanoparticles serve as effective semiconductor materials for photocatalytic activity. Cobalt oxide nanoparticles exhibit a suitable band gap [13–16]. The incorporation of dopants in semiconductors represents a significant method to enhance their photocatalytic performance. The removal of various dyes can be enhanced through the doping of metals like Ni^{2+} and Co^{2+} [17, 18].

This study focuses on the synthesis of nanoparticles of Co_3O_4 catalysts. The impact of size distribution of nanoparticles on catalysis was investigated by analyzing their catalytic performance in the degradation of BG dye.

2. Objectives

- ❖ To prepare modified photocatalysts viz. Co_3O_4 and Zr-doped Co_3O_4
- ❖ To characterize these nanomaterials using SEM., EDX, XRD, PL and UVDR Quantifications.

- ❖ To study the activity of the prepared materials Co_3O_4 and Zr-doped Co_3O_4 by the photocatalytic decomposition of Brilliant Green (BG) dye in aqueous solution under UV and solar light irradiation.
- ❖ To study the effect of the various rate influencing factors on the photodegradation of BG
- ❖ To investigate the mechanism of the degradation
- ❖ To demonstrate the antibacterial activity of (a) TiO_2 &Zr-doped TiO_2 , (b) SnO_2 &Zr-doped SnO_2 (c) Co_3O_4 & Zr-doped Co_3O_4 and (d) ZnO&Zr-doped ZnO nanocomposites against G^{+Ve} and G^{-Ve} bacterial strains.
- ❖ To demonstrate the photovoltaic characteristics of the modified photocatalysts by Dye Sensitized Solar Cells (DSSCs).
- ❖ To test the stability and reusability of the catalysts
- ❖ To compare the photocatalysts and propose the general mechanism for the synthetic and commercial dyes

3. Methods

3.1 MATERIALS

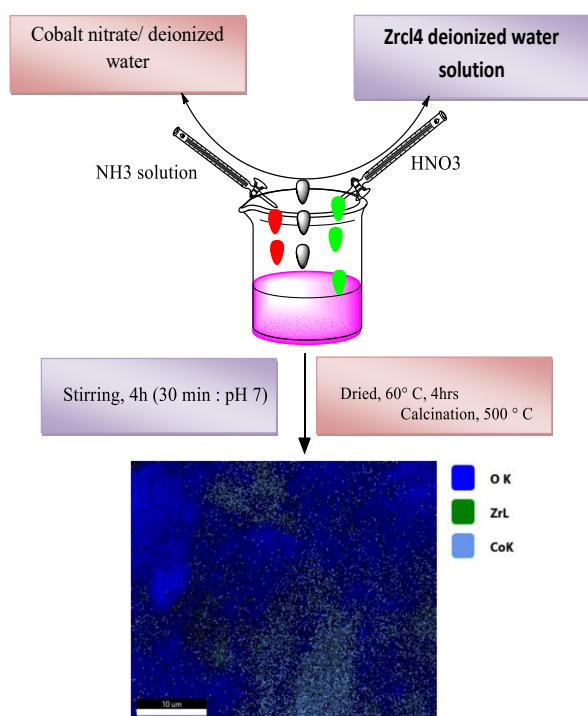
Zirconium chloride, Titanium (IV) isopropoxide, Oxalic acid, Stannous chloride pentahydrate, Cobalt nitrate, Zinc nitrate, NH_3 solution, nitric acid (HNO_3 -65%), Brilliant Green (BG) and ruthenium dye (535-bisTBA, N719) were utilized in their received form. Isopropyl alcohol and coumarin were sourced from Sigma Aldrich and utilized as specified. The solutions were prepared using H_2O .

3.2 Synthesis of Zr-doped Co_3O_4 nanoparticles

A straight forward co-precipitation method combined with sonication was employed to synthesize a Zr-doped Co_3O_4 nanocomposite material. Zirconium chloride (0.5g) at 0.1 M was dissolved in 100 mL of DI-water (Solution A), while Cobalt nitrate (2.1g) at 0.2 M was dissolved in 50 mL of DW (Solution B). With nonstop stirring, solution B was added to solution A gradually, drop by drop, before adjusting the pH to 9 by incorporating NH_3 solution. The resulting solution underwent agitation for duration of 3 hours. Ultrasonic



treatment is applied for duration of 40 minutes to facilitate the precipitate formation. The precipitate obtained was subjected to filtration and subsequently rinsed with distilled water, ethanol, and deionized water. The precipitate was subsequently gathered and subjected to drying at a temperature of 100°C in an oven for 24 hours. The powder underwent calcination in a MF at 500°C for duration of 2 hr as presented in Scheme 1



Scheme.1. Preparation of the Zr doped Co_3O_4 nanoparticles

4. Results and Discussion

4.1 SEM analysis

SEM is extensively employed to examine the morphological characteristics and surface features of the catalyst surfaces. The SEM analysis of pure cobalt oxide nanoparticles prior to the photocatalytic degradation is depicted in **Figure 1**. Surface texture and porosity are evident in the SEM micrographs. Its surface micrograph also shows the microspores and mesopores with heterogeneous nature.

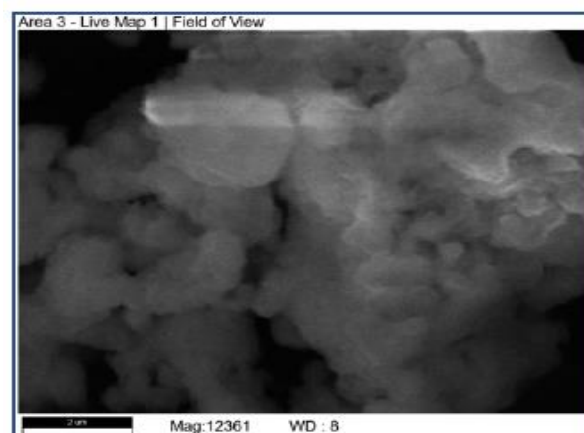


Figure. 1 SEM image of Co_3O_4 nanoparticles

4.2 Energy-dispersive spectroscopy (EDS)

Numerous outflows are produced when an electron interacts with a test target. The distinctive X-ray emissions are analyzed using energy dispersive spectroscopy (EDS). EDS can provide material composition across a point down to a few microns. Together, these capabilities supply critical compositional data for a large assortment of materials. The analysis shows that pure and doped cobalt oxide nanoparticles have the exact natural composition of certain elements in pure cobalt oxide Co and O, as shown in **Figure**.

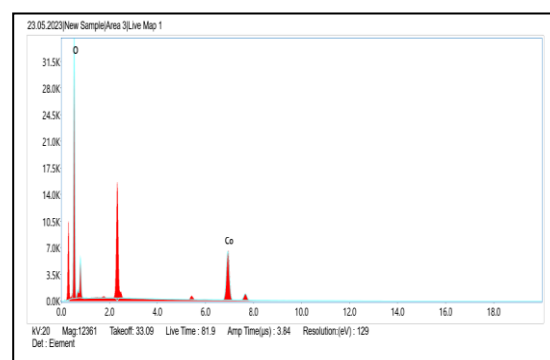


Figure.2.EDX analysis of Co_3O_4 nanoparticles

4.3 Elemental mapping

Elemental mapping of FE-SEM is performed to verify the composition of Co and O on the nanoparticle surface. While the FE-SEM image of Co_3O_4 is shown in **Figure 3a-c**, elemental mappings are displayed in **Figure 3 b and c** for Co (Block) and O (Red). As shown in



Figure 3a, the densities of Co and O are uniformly distributed in the catalyst. Elemental

mapping demonstrates the catalyst consists of Co and O and its purity .

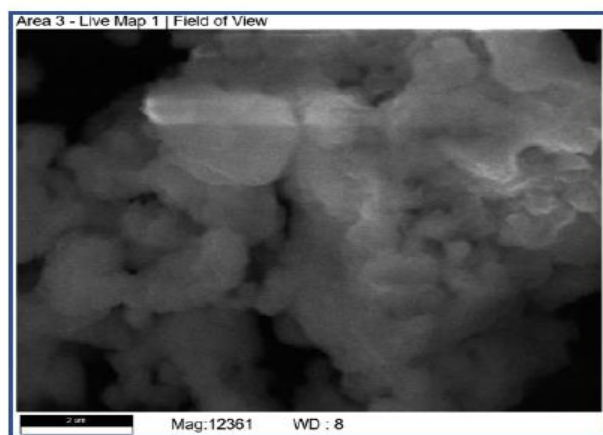


Figure 3. SEM image of Co_3O_4

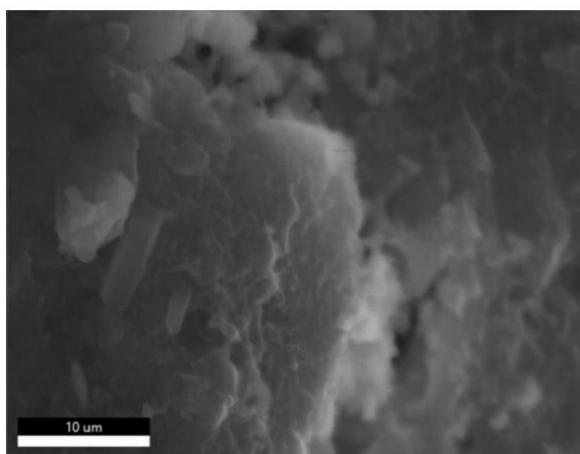


Figure.4 SEM image of $\text{Zr-Co}_3\text{O}_4$ nanomaterial

4.4 SEM analysis

Scanning electron microscopy is extensively employed to examine the morphological characteristics and surface features of the catalyst surfaces. The SEM analysis of Zr-doped cobalt oxide nanoparticles occurs prior to the photocatalytic degradation of GB dye, as depicted in **Figure 4**. Surface texture and porosity are evident in the SEM micrographs of both pure and doped cobalt oxide nanoparticles

4.5 EDS analysis

EDS is used to analyze the characteristic X-ray emissions sections into a vast range. It can provide component composition maps across a considerably larger raster zone. Together the analysis shows that Zr-doped cobalt oxide nanoparticles have the exact composition as expected Zr, Co and O as shown in **Figure 5**

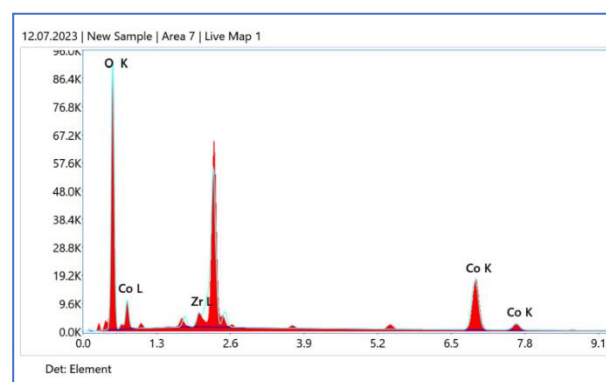


Figure. 5 EDX spectrum of $\text{Zr-Co}_3\text{O}_4$ nanomaterial

4.6 Elemental mapping

FE-SEM image of $\text{Zr-Co}_3\text{O}_4$ is shown in **Figure 6 a-d**, elemental mappings are displayed for Zr (Green), Co (Block) and O (Blue). As shown in **Figure 6a**, the densities of Zr, Co and O are uniformly distributed in the catalyst. Therefore, elemental mapping demonstrates that the catalyst consists of Zr, Co and O. It also demonstrates how pure the catalyst $\text{Zr-Co}_3\text{O}_4$

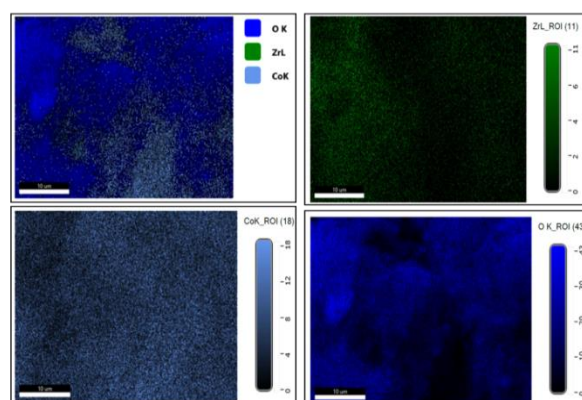


Figure .6 (a-d) Elemental mapping of $\text{Zr-Co}_3\text{O}_4$.

4.7. HR-TEM analysis

HR-TEM images of $\text{Zr-Co}_3\text{O}_4$ nanoparticles at magnification demonstrate that the $\text{Zr-Co}_3\text{O}_4$ particles



have a distinctly spherical morphology with significant aggregation. Additionally, the presence of Zr is indicated as dark spots on the Co_3O_4 nanoparticles, as illustrated in Figure 5.7 $\text{Zr-Co}_3\text{O}_4$ at aggregation of 200 nm clearly exhibit lattice structures, indicating that the particles are well crystalline. Figures 7 b and c illustrate the plot profile and image profile, whereas Figure 7 d indicates an average particle size of 120 nm, with the selected particle length depicted in Figure 7 a. The previously obtained TEM designs exhibited crystallite sizes comparable to those calculated using Scherrer's equation, so confirming that the synthesized $\text{Zr-Co}_3\text{O}_4$ possesses a robust crystalline structure.

3.8 X-ray diffraction analysis

The phase and crystalline structure of Co_3O_4 and $\text{Zr-Co}_3\text{O}_4$ nanoparticles are examined via X-ray powder diffraction, as illustrated in Figure 8 a and b. The diffraction peaks at 2θ values of 19.18° , 31.90° , 36.35° , 38.25° & 56.13° correspond to the (111), (220), (311), (222), & (422) planes of Co_3O_4 (JCPDS card no. 76-1802), respectively [19]. The diffraction peaks at 2θ values of 35.10° , 51.15° & 58.97° correspond to the (200), (220), and (311) planes of Zr (JCPDS card no. 50-1089), accordingly towards smaller angles indicates the successful Zr-doping in the Co_3O_4 structure. Average crystallite size of Co_3O_4 and $\text{Zr-Co}_3\text{O}_4$ is estimated from the Scherrer's equation as about 44 and 19 nm for bare and doped catalyst. The small crystalline particle size helps for higher photocatalytic activity.

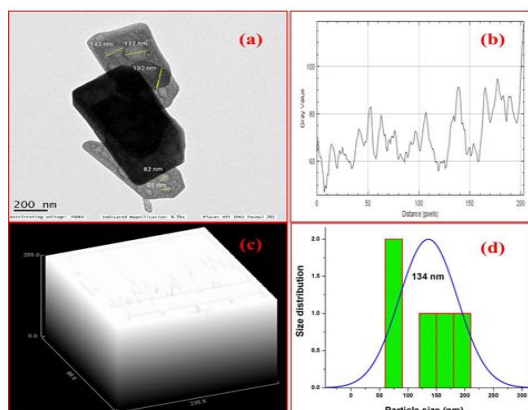


Figure.7 TEM study of (a) Image (b) Plot profile, (c) Surface plot and (d) Particle size of $\text{Zr-Co}_3\text{O}_4$ Nanoparticle

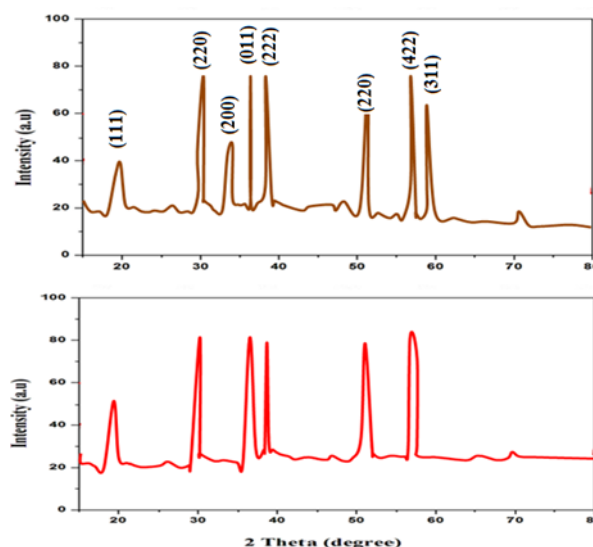


Figure.8 XRD analysis of (a) Co_3O_4 and (b) $\text{Zr-Co}_3\text{O}_4$ nanoparticles

4.9 Photoluminescence analysis

Semiconductors PL spectra can show recombination, migration, and transfer of photo generated electron-hole pairs. **Figure 9a and b** shows the PL spectra of bare Co_3O_4 and Zr doped Co_3O_4 . Three distinct peaks are visible at 425, 490 & 540 nm, respectively. The intensity of bare Co_3O_4 is greater than that of Zr-doped cobalt oxide, indicating a higher rate of e^- and h^+ recombination. The lower intensity of $\text{Zr-Co}_3\text{O}_4$ implies that Zr doping helps successful preventing of unwanted e^-/h^+ pair recombination. Increasing charge carrier separation allowing more free charge carriers to participate and boosting the photocatalytic activity.

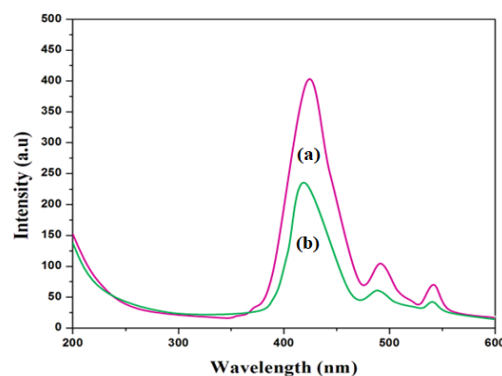


Figure.9 PL analysis of (a) Co_3O_4 and (b) $\text{Zr-Co}_3\text{O}_4$ nanoparticles



4.10 UV-Vis-DRS analysis

The UV-Vis-DRS for both Co_3O_4 & the doped semiconductor oxide $\text{Zr-Co}_3\text{O}_4$ is presented in **Figure 10 a and b**. The $\text{Zr-Co}_3\text{O}_4$ exhibits enhanced absorption in both the UV & visible regions compared to Co_3O_4 . This indicates that $\text{Zr-Co}_3\text{O}_4$ can serve as an effective semiconductor photocatalytic nanomaterial active under UV and visible light. The result Co_3O_4 and doped $\text{Zr-Co}_3\text{O}_4$ have been determined to be 2.7 eV and 2.25 eV, respectively.

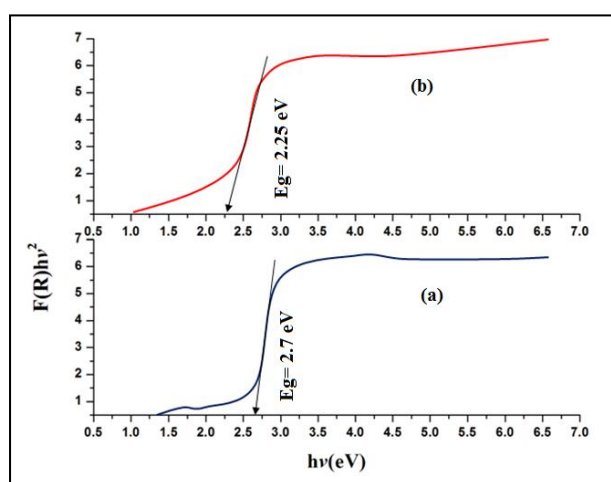


Figure 10. Direct band gap of (a) Co_3O_4 and (b) $\text{Zr-Co}_3\text{O}_4$ nanoparticles

4.11. PHOTOCATALYTIC DEGRADATION OF BG UNDER SOLARLIGHT

4.11.1. Preliminary analysis

The degradation of BG through photocatalysis using the synthesized Co_3O_4 and $\text{Zr-Co}_3\text{O}_4$ catalysts is illustrated in **Figure 11**. (without nanoparticles 5%). In the equal experiment, when conducted in the absence of solar light with $\text{Zr-Co}_3\text{O}_4$, there was a decrease of 10% in the dye concentration. The dye experiences a degradation rate of 96.0% when exposed to $\text{Zr-Co}_3\text{O}_4$ under solar light for duration of 60 minutes. Under identical conditions, the use of prepared SnO_2 resulted in only 40% of the expected degradations. This indicates that $\text{Zr-Co}_3\text{O}_4$ exhibits greater efficiency in the degradation of BG compared to Co_3O_4 .

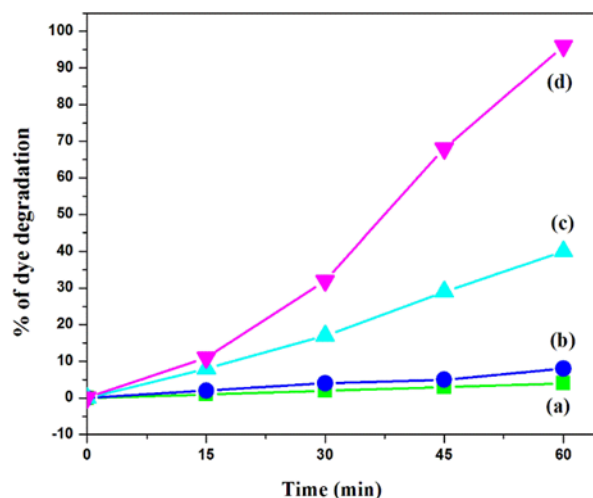


Figure 11. Degradation of BG dye under solar irradiation: (a) dark, (b) without catalyst, (c) Co_3O_4 , and (d) $\text{Zr-Co}_3\text{O}_4$ catalyst.

4.11.2 Influence of catalyst loading

Figure 12 & b illustrates the effect of photocatalyst dosage on the degradation of BG using varying concentrations of Co_3O_4 and $\text{Zr-Co}_3\text{O}_4$. The degradation rises as the catalyst dosage increases. However, an excessive dosage leads to a reduction in light penetration due to the heightened light scattering effect caused by catalyst particles. The optimum result of BG dye is determined to be 0.6g, consistent with previous findings

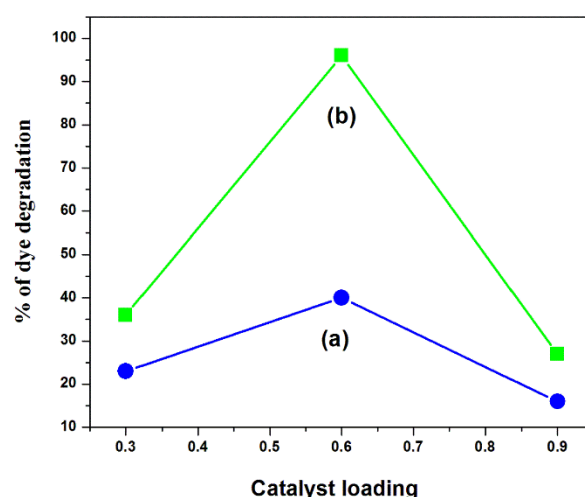


Figure 12. The impact of (a) Co_3O_4 and (b) $\text{Zr-Co}_3\text{O}_4$ catalyst



4.11.3 Impact of initial dye concentration and pH influence

Figures 13a-d and 14a and b illustrate the consistent trend observed under the same conditions applied in the study. As the concentration of dye rises, the quantity of dye that adheres to the catalytic surface also increases, subsequently influencing the catalytic activity of the nanocatalyst.

The influence of starting pH on BG dye is examined within the pH range of 3-11. The degradation of the dye solution shows an increase as the pH transitions from 3 to 7, followed by a subsequent decline. The result intricate for Zr-Co₃O₄ at pH 7 exhibits superior photocatalytic activity.

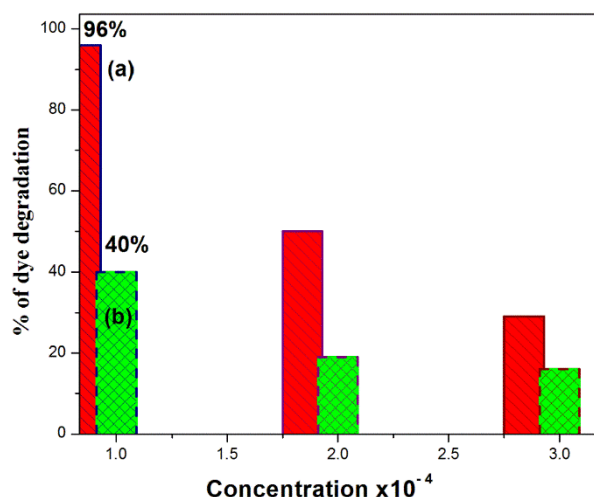


Figure 13(a) Zr-Co₃O₄ and (b) Co₃O₄ catalyst

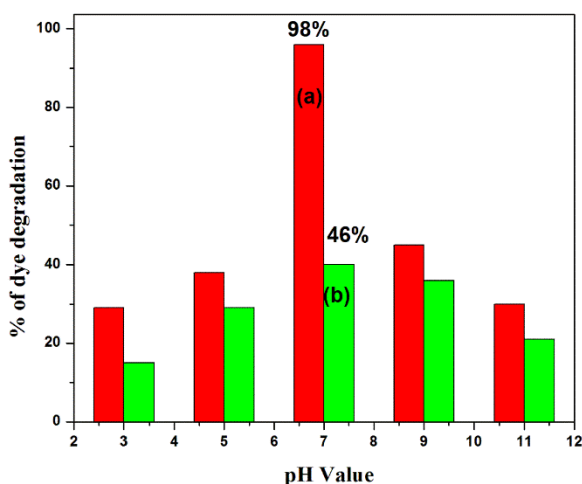


Figure 14 (a) Zr-Co₃O₄ and (b) Co₃O₄ catalyst

4.11.4 Reusability of photocatalytic activity

As shown in the Figure 15 a and b. The complete degradation for 0-60 minute indicates the percentage of degradation of the Co₃O₄ and Zr-Co₃O₄ on BG dye as follows 100, 90, 84, 81 & 81 and 100, 95, 93, 90 & 90%. The outcome indicates that the doped catalyst exhibits stability and reusability, unlike the bare nanoparticles

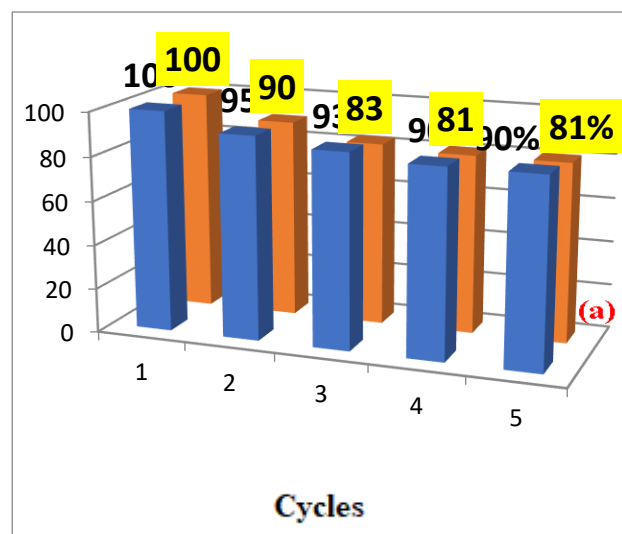


Figure 15 Stability and reusability (a) Co₃O₄ and (b) Zr-Co₃O₄ catalyst

4.11.5 PHOTOCATALYTIC DEGRADATION OF BG UNDER UV LIGHT

Preliminary analysis

The photocatalytic degradation of BG using the synthesized Co₃O₄ and Zr-Co₃O₄ catalysts is illustrated in Figure 16. When the dye is on irradiation in the absence of a catalyst, degradation is low (0.5%). Conversely, in the same experiment conducted without UV light and with Zr-Co₃O₄, there is a 5% reduction in dye concentration. The dye experiences 90% degradation when exposed to Zr-Co₃O₄ and UV light for 60 minutes. When produced Co₃O₄ (Merck) was utilized under same conditions, only 35% deterioration was observed. This indicates that Zr-Co₃O₄ has superior efficiency in GB degradation compared to prepared Co₃O₄ (Merck) under UV light

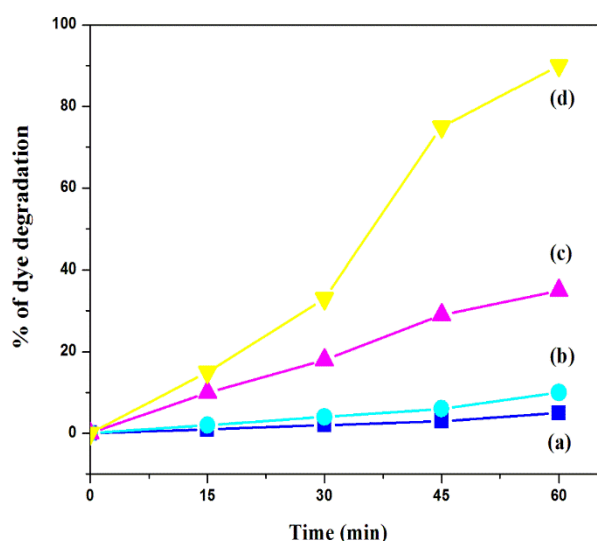


Figure 16 Degradation study of BG dye under UV irradiation: (a) in dark, (b) without catalyst, (c) with Co₃O₄, and (d) with Zr-Co₃O₄ catalyst.

3.11.6 Analysis of chemical oxygen demand (COD)

To COD measurements are conducted for the degradation of BG dye using Co₃O₄ and Zr-Co₃O₄ nanoparticles, with a loading amount of 0.6 g in a suspension of initial ion (1×10^{-4}) in 40 mL of neutral pH solution, while subjected to air flow under UV and solar light irradiation. The percentage of Chemical Oxygen Demand (COD) decrease achieved by Co₃O₄ over 60 minutes is 35%, whereas Zr-Co₃O₄ demonstrates a reduction of 90% in the same timeframe. Additionally, Co₃O₄ shows a 41% reduction, while Zr-Co₃O₄ achieves a 97% reduction over 60 minutes.

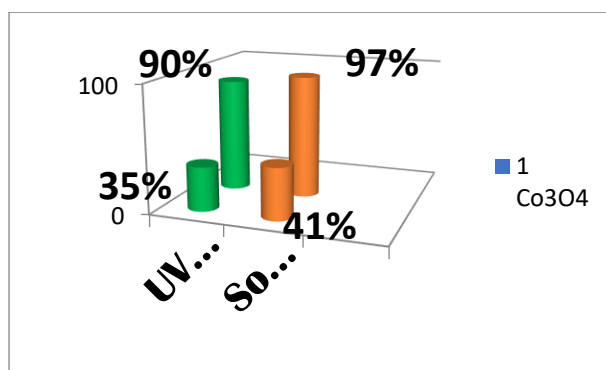


Figure 17 COD analysis under UV and Solar Light Irradiation

4.11.7 Analysis of Hydroxyl Radicals

Figures 18 a and b demonstrate that Zr-Co₃O₄ has significant photocatalytic activity as evidenced by the increased fluorescence intensity, while the •OH analysis confirms that the reaction mechanism involves •OH generated from water splitting by the semiconductor metal oxides. The photocatalytic activity mechanism of Zr-Co₃O₄ nanoparticles is directly linked to the rate of hydroxyl radical (•OH) formation.

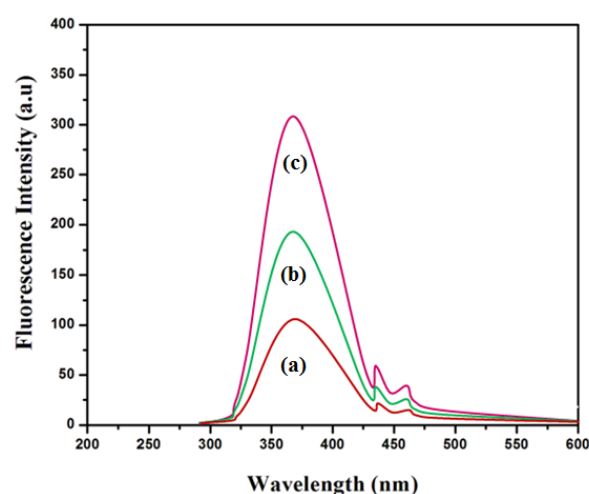


Figure 18. Fluorescence spectra recorded at $\lambda_{\max} = 310$ nm for Zr-doped Co₃O₄: (a) 0, (b) 30 & (c) 60 minutes.

4.12 ANTIMICROBIAL EFFICACY

Co₃O₄ and Zr-doped Co₃O₄ nanoparticles exhibit significant antibacterial action against G^{+ve} & G^{-ve}. *S. aureus* & *E. coli* as demonstrated in Table 5.1 and Figure 19. The table illustrates the enhanced antibacterial activity of the Zr-doped Co₃O₄ nanocomposite material

Table 1. Antibacterial efficacy against Gram-positive and Gram-negative microorganisms with the disc diffusion method

S. No	Bacteria- G ^{+ve} & G ^{-ve}	Standard disk	(mm)		
			1 [Co ₃ O ₄]	2 [Zr-doped Co ₃ O ₄]	Control (DMSO)
1	<i>Staphylococcus</i>	25	11	20	20



	<i>aureus</i> (Positive)				
2	<i>Escherichia coli</i> (Negative)	25	13	18	18

*Ciprofloxacin

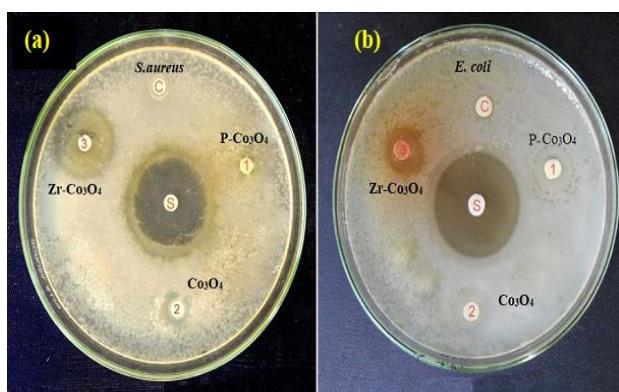


Figure 19 Antibacterial activity of (a) Co_3O_4 and (b) $\text{Zr-Co}_3\text{O}_4$ nanoparticles by disc diffusion method against (a) *S.aureus* and (b) *E.coli*

4.13 DYE SENSITIZED SOLAR CELLS (DSSCS)

The Zr-doped Co_3O_4 utilized in the fabrication of a typical solar cell employing Ruthenium dye exhibits superior electro-efficiency in terms of short-circuit current density compared to Co_3O_4 . The Zr-doped Co_3O_4 exhibits a J_{sc} value of (4.5 mA/cm^2), whereas the Co_3O_4 displays a J_{sc} value of (4.0 mA/cm^2) [20,21].

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Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

Compliance with Ethical Standards

The authors declare that they have no conflict of interest. This research and the manuscript are original and unpublished. All authors have read and approved the final version of the article

Author contributions

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