

Study on the Photocatalytic Activity of Bimetallic-Semi-Aromatic Polyester Nanocomposite

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Abstract: Metallo-Polyester Nanocomposite (MPN) has played a pivotal role in environmental remediation. These hybrid nanomaterials have demonstrated photocatalytic activity in degrading organic pollutants and killing microorganisms, thereby mitigating environmental pollution. In the present study, we have utilised a novel bimetallic-semi-aromatic polyester nanocomposite (NC) composed of poly(*t*-BGE-*alt*-PA) copolymer and Zinc Ferrite nanoparticles (ZnFe₂O₄ NPs). The NC was physicochemically characterized and tested for *in vitro* and *in vivo* toxicity studies in our previous study. The ZnFe₂O₄@poly(*t*-BGE-*alt*-PA) composite was fabricated in NP form and then tested for photocatalytic action on methylene blue (MB) dye under sunlight. As a result, the ZnFe₂O₄@poly(*t*-BGE-*alt*-PA) composite degraded 91.73% MB dye in 150 minutes, compared with ZnFe₂O₄ NPs, which degraded only 83.10% MB dye. Additionally, the ZnFe₂O₄@poly(*t*-BGE-*alt*-PA) composite was found to be reusable and more stable during the recycling study.

Keywords: ZnFe₂O₄, Poly(*t*-BGE-*alt*-PA) copolymer, Nanocomposite, Methylene blue, Photocatalytic.

ABBREVIATIONS

| | |
|--------------------------------------|---|
| MPN | Metallo-Polyester Nanocomposite |
| NC | Nanocomposite |
| ZnFe ₂ O ₄ NPs | Zinc Ferrite Nanoparticles |
| MB | Methylene Blue |
| PPNCL | Bis (Triphenylphosphine) Iminium Chloride |
| Et ₃ B | Tri-ethyl Borane |
| <i>t</i> -BGE | Tert-Butyl Glycidyl Ether |
| PA | Phthalic Anhydride |
| DMSO | Dimethyl Sulfoxide |
| DCM | Dichloromethane |

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|------------------|---|
| FTIR | Fourier Transform Infrared Spectroscopy |
| XRD | X-Ray Diffraction |
| TGA | Thermogravimetric Analysis |
| DSC | Differential Scanning Colorimetry |
| e ⁻ | Electron |
| OH | Hydroxyl Group |
| GQDs | Graphene Quantum Dots |
| PEG | Polyethylene Glycol |
| CV | Crystal Violet |
| CO ₂ | Carbon Dioxide |
| H ₂ O | Water |

I. INTRODUCTION

In recent years, a surge in environmental pollution has been observed due to rapid urbanisation and industrialisation. This could lead to the release of several toxic inorganic and organic pollutants into the soil, water, and air without their proper disposal and treatment, thus causing serious harm to public health [1]. Various textile industries use several dyes and dispose them of into the water, which are mutagenic and thus cause many life-threatening diseases in humans. Therefore, there is a need to develop an eco-friendly and sustainable approach to remove these pollutants or dyes from the environment [2]. To date, several metal-oxide NPs have been utilised in the photocatalysis of industrial effluent dyes due to their lesser toxicity, higher stability, and better oxidation capability [3]. However, when these metal-oxide NPs are combined with polyesters or adsorbed on their surface, they form an NC [4]. Several researchers have investigated the photocatalytic activity of such NCs under sunlight to study the degradation of dyes [5]. However, no reports were available on the photocatalytic activity of the ZnFe₂O₄@poly(*t*-BGE-*alt*-PA) composite. Therefore, we will study the degradation

of the MB dye by $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC under the sunlight and calculate the percentage of dye degradation efficiency. Furthermore, we will also analyse the stability and reusability of the NC during the recycling study.

II. MATERIALS AND METHODS

A. Materials

Zinc nitrate hexahydrate, Ferric nitrate nonahydrate, Phthalic anhydride (PA), Tert-butyl glycidyl ether (*t*-BGE), Bis (triphenylphosphine) iminium Chloride (PPNCL), Tri-ethyl borane (Et_3B), and Methylene blue dye were procured from Sigma Aldrich, Merck, India. All organic solvents, like Dimethyl Sulfoxide (DMSO), Dichloromethane (DCM), chloroform, and ethanol, were purchased from Merck India. All glasswares were procured from Borosil, India. All the plasticware was purchased from Abdos Labtech Pvt. Ltd., India.

B. Methods

i. Development and Characterization of $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC

The $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC was developed by physical blending of ZnFe_2O_4 NPs and $\text{poly}(t\text{-BGE-}alt\text{-PA})$ copolymer and then heating at 200°C as reported in our previous study [6]. The composite was physicochemically characterized by Fourier Transform Infrared Spectroscopy (FTIR), powder X-Ray Diffractometer (XRD), Thermogravimetric Analyzer (TGA), Differential Scanning Colorimetry (DSC), and a nanozeta sizer in our earlier report [6].

ii. Photocatalytic Study

The photocatalytic property of $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC was tested on MB dye under the sunlight. In brief, 20 mg of the NC was dispersed in 20 mL of the MB dye solution (7.5 mg/L). The solution was shaken for 1 h under dark conditions so that the equilibrium constant could be reached. Then, eight aliquots of the MB dye solution treated with $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC were taken and irradiated with sunlight to analyze the photocatalytic activity using a UV-Visible spectrophotometer (Shimadzu Corp., Japan) [7]. Along with this test, the photocatalytic activity of ZnFe_2O_4 NPs was also studied on the MB dye solution using a similar method. During the test, the percentages of removal/degradation efficiency for both ZnFe_2O_4 NPs and NC on MB dye molecules were calculated. Next, the catalytic performance of $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC was also tested on the MB dye solution in three cycles to study its reusability [7].

iii. Statistical Analysis

All data were analyzed using Origin 8 software (OriginLab, USA).

III. RESULTS AND DISCUSSION

A. Development and Characterization of $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC

The $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC was prepared by the physical blending method followed by heating. Next, the physicochemical properties of the NC were studied and reported in our previous study [6].

B. Photocatalytic Study

The photocatalytic action of $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC was studied on the MB dye solution under the sunlight. The change in absorbance of the MB dye solution was recorded at 664 nm by a UV-Visible spectrophotometer. Fig. 1 shows the UV-Visible spectra of the MB dye solution treated with $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC and ZnFe_2O_4 NPs, where the absorbance of the degraded MB dye solutions was recorded at 0, 15, 30, 45, 60, 90, 120, and 150 minutes. We observed a significant reduction in the absorbance peak of the MB dye at 664 nm for both $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC and ZnFe_2O_4 NP treatments with increasing time (0–150 minutes) (Fig. 1). We observed a significant decrease in the absorbance of MB dye molecules in the case of NC treatment when compared with ZnFe_2O_4 NPs treatment (Fig. 1). The $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC degraded/removed 91.73% MB dye molecules in 150 minutes, compared with ZnFe_2O_4 NPs, which degraded/removed only 83.10% MB dye molecules (Fig. 2). Furthermore, the reusability of ZnFe_2O_4 NPs and $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC was examined for MB dye degradation. After three cycles of photocatalytic reaction, the ZnFe_2O_4 NPs and $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC exhibited negligible reduction in their photocatalytic performance (Fig. 3, but data for two additional cycles are not shown). Next, Fig. 4 shows the possible photocatalytic mechanism. Under sunlight, the dye molecules present in the MB dye solution adsorb onto the surface of the $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ composite. These dye molecules excite under the sunlight and transfer their electrons (e^-) to the conduction bands of the composite. During this period, electrons were excited from the valence bands of the composite to its corresponding conduction bands, resulting in the formation of e^-/h^+ hole pairs. These holes react with an OH group and produce a free radical of the hydroxyl group ($*\text{OH}$). The reactive radicals involved in MB dye degradation yield water and carbon dioxide [7].

In 2023, Perveen *et al.*, synthesized an NC made up of graphene quantum dots (GQDs), polyethylene glycol (PEG), and ZnFe_2O_4 NPs. They tested the photocatalytic action of GQDs@PEG- ZnFe_2O_4 composite on both MB and crystal violet (CV) dye molecules. They observed a significant degradation efficiency (98%) for both MB and CV dye molecules within 120 minutes under sunlight. This indicated that the GQDs@PEG- ZnFe_2O_4 composite may act as an efficient photocatalyst [5].

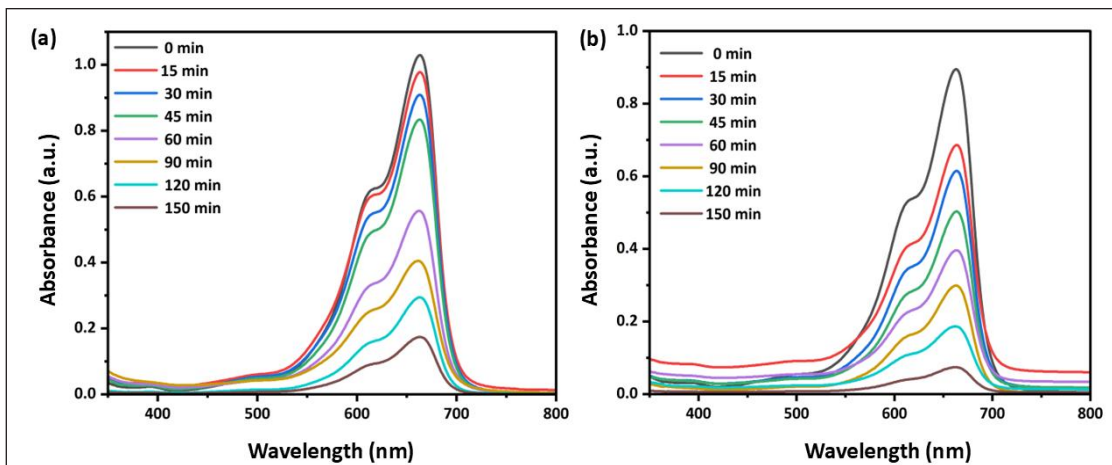


Fig. 1: Photocatalytic Action of (a) $ZnFe_2O_4$ NPs and (b) $ZnFe_2O_4@poly(t-BGE-alt-PA)$ Nanocomposite on MB Dye Molecules in an Aqueous Solution Studied by UV-Visible Spectral Analysis

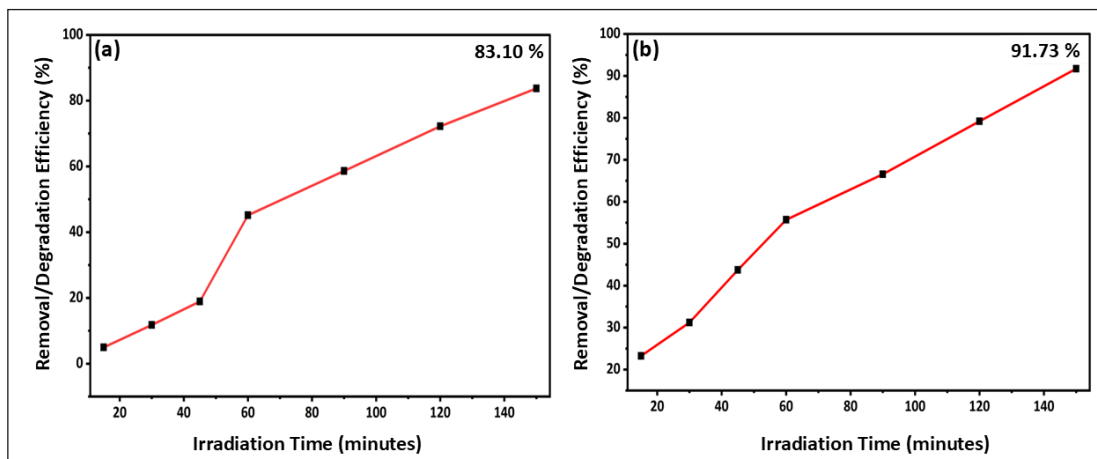


Fig 2: Photocatalytic Action of (a) $ZnFe_2O_4$ NPs and (b) $ZnFe_2O_4@poly(t-BGE-alt-PA)$ Nanocomposite on MB Dye Molecules in an Aqueous Solution Studied by Plotting Their Graphs Between Percentages of Removal/Degradation Efficiency and Irradiation Time

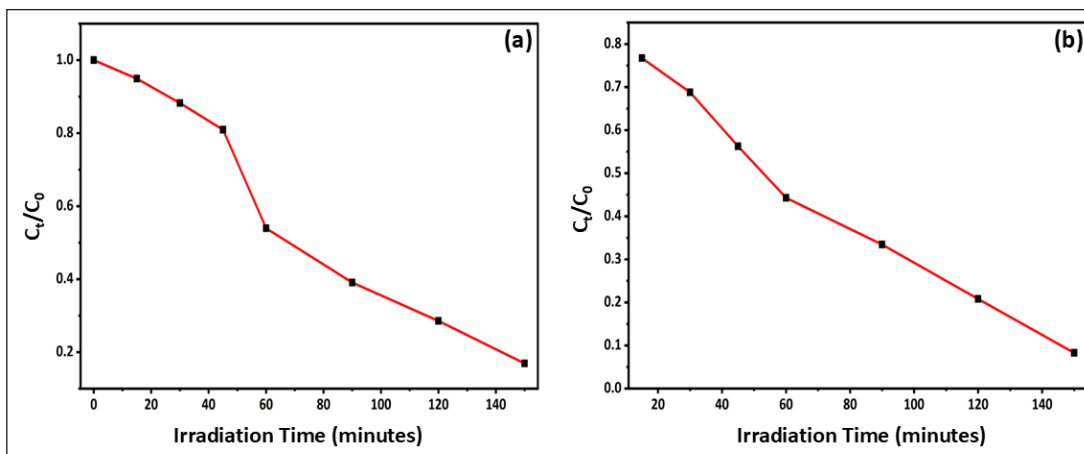


Fig. 3: Recycling Test (One Cycle Shown) Performed to Study the Reusability of (a) $ZnFe_2O_4$ NPs and (b) $ZnFe_2O_4@poly(t-BGE-alt-PA)$ Nanocomposite

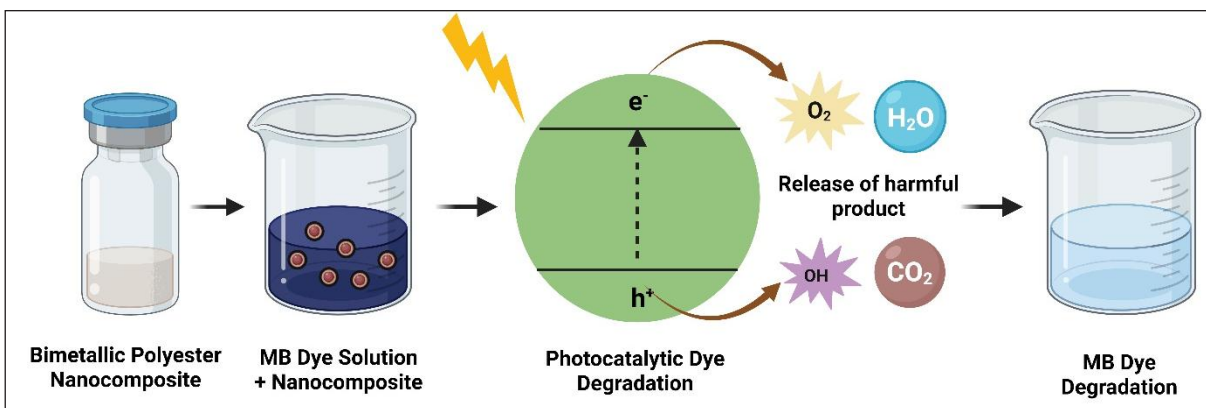


Fig. 4: Schematic Diagram Showing the Photocatalytic Mechanism of Bimetallic Polyester Nanocomposite ($\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$) on MB Dye Molecules in Aqueous Solution Under the Sunlight. After the Degradation of MB Molecules, Water (H_2O) and Carbon Dioxide (CO_2) were Produced, resulting in a Clear Aqueous Solution

IV. CONCLUSION

In this study, we analyzed for the first time the photocatalytic action of $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC on MB dye molecules in aqueous solution under sunlight. We compared the obtained results with the photocatalytic activity of ZnFe_2O_4 NPs in the conducted experiments. We observed a significant reduction in the absorbance peak of MB dye molecules at 664 nm, resulting in a better removal or degradation efficiency for the $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ composite compared to ZnFe_2O_4 NPs. We also found the reusability of both ZnFe_2O_4 NPs and $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ NC after each photocatalytic cycle. Based on the results of this study, the $\text{ZnFe}_2\text{O}_4@\text{poly}(t\text{-BGE-}alt\text{-PA})$ composite may be utilized for removing organic pollutants during wastewater treatment.

Consent for Publication: All authors have given their consent for publication.

Availability of Data: The data reported in this manuscript will be available on request.

Competing Interests: The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Funding: No funding was obtained from any funding agencies to support this research.

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