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***Journal of Scientific and Engineering Research*, 2025, 12(12):90-95**

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Photocatalytic Activity of Green-Synthesised ZrO_2 Nanoparticles Using *Aegle marmelos* Fruit Extract

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Abstract: The present work investigates the photocatalytic efficiency of *Aegle marmelos* (Bael) fruit–mediated ZrO_2 nanoparticles, synthesised through an eco-friendly method using $ZrOCl_2 \cdot 8H_2O$, for the degradation of methylene blue under both UV and visible light. The fruit-based ZrO_2 nanoparticles displayed notable photocatalytic activity, with performance strongly dependent on the irradiation source and solution pH. The highest degradation was achieved under UV light in alkaline conditions (pH 9), where favourable surface charge interactions enhanced dye adsorption and subsequent breakdown. Kinetic analysis revealed that the degradation process followed a pseudo-first-order model, indicating effective electron–hole generation and reaction progression. Overall, the findings confirm that green-synthesised ZrO_2 nanoparticles. Derived from the *Aegle marmelos* plant. fruit are promising, sustainable photocatalysts for wastewater treatment, with optimised pH and light conditions significantly improving their dye removal efficiency.

Keywords: *Aegle marmelos*, green synthesis, ZrO_2 nanoparticles, photocatalysis, methylene blue degradation, UV and visible light irradiation, pH effect, pseudo-first-order kinetics, eco-friendly nanomaterials, wastewater treatment.

1. Introduction

The discharge of synthetic dyes from industries such as textiles, leather processing, and printing represents a major threat to aquatic ecosystems. Methylene blue (MB), a widely used cationic dye, is recognised for its exceptional stability, toxicity at elevated concentrations, and resistance to traditional treatment methods. These challenges have driven the development of sustainable and eco-friendly approaches for efficient dye removal. Among them, photocatalysis has emerged as a prominent advanced oxidation process, valued for its capability to harness light energy to degrade organic contaminants into harmless end products.[1], [2].

Metal oxide nanoparticles—especially zirconium dioxide (ZrO_2)—"These materials have been thoroughly investigated for their photocatalytic applications." because of their strong thermal and chemical stability, wide bandgap, and high oxidising ability [13]. Despite their potential, many conventional synthesis methods involve harmful chemicals that raise environmental and safety concerns. This has shifted research interest toward green synthesis routes that employ plant extracts as natural reducing and stabilising agents. Such phytochemical-assisted synthesis avoids toxic by-products and enhances nanoparticle stability and reactivity [3], [4].

Aegle marmelos (Bael) fruit contains abundant phytochemicals, including phenolics, flavonoids, and alkaloids, which facilitate the reduction of metal ions and the stabilisation of nanoparticles [11]. These characteristics make *Aegle marmelos* an efficient and sustainable alternative for producing metal oxide nanomaterials. Additionally, fruit-based synthesis is cost-effective, eco-friendly, and suitable for large-scale applications.

In this research, ZrO_2 nanoparticles were produced using *Aegle marmelos* fruit extract and examined for their photocatalytic efficiency under UV and visible light. The study focuses on evaluating their ability to degrade the methylene blue dye and assessing the effects of pH, irradiation source, and kinetic behaviour. The results offer

valuable insight into the development of green-synthesised nanomaterials and demonstrate the potential of plant-mediated ZrO_2 nanoparticles as effective photocatalysts for wastewater treatment.

Applications in Photocatalysis and Environmental Remediation

The growing concern over environmental pollution has driven extensive research toward the development of safe and sustainable materials for remediation applications. In this context, green-synthesised metal oxide nanoparticles have emerged as promising alternatives to conventional photocatalysts, offering environmentally benign synthesis routes along with enhanced performance [3], [4]. These biologically fabricated nanomaterials are increasingly valued for their high efficiency, low toxicity, and eco-friendly production methods, making them well suited for advanced environmental purification technologies.

A comparative investigation examined zirconium dioxide (ZrO_2) nanoparticles prepared via conventional chemical routes and green synthesis using Passiflora edulis extract. The results revealed that plant-mediated synthesis yields nanoparticles with superior structural characteristics and enhanced biological activity, while also being more environmentally compatible than chemically synthesised counterparts [5].

ZrO_2 is widely recognised as an effective photocatalyst owing to its excellent thermal and chemical stability, high mechanical strength, and strong resistance to photocorrosion [13]. Moreover, its wide band gap and highly negative conduction band facilitate the generation of reactive oxygen species, which play a key role in driving photocatalytic reactions.

In another study, ZrO_2 nanoparticles were successfully synthesised using Ficus benghalensis leaf extract, further highlighting the potential of green synthesis strategies [6]. Additionally, biogenic ZrO_2 nanoparticles prepared from plant sources demonstrated significant adsorption capacity toward methylene blue dye, indicating their strong dye-removal efficiency [7].

Green synthesis using Ficus carica fruit extract has also been reported, where the extract served as a natural reducing and stabilising agent, leading to enhanced photocatalytic degradation of pollutants [8]. Likewise, ZrO_2 nanomaterials fabricated through an eco-friendly approach employing dragon fruit peel extract exhibited notable photocatalytic performance, showing efficient degradation of methyl orange under UV light irradiation [9].

Furthermore, a green nano-zirconia–doped ZnO catalyst was found to effectively promote the photodegradation and mineralisation of contaminants under light exposure, reinforcing the advantages of green-derived hybrid photocatalysts for environmental remediation [10].

2. Material and Methods

Photocatalytic Degradation Methodology

(UV–Visible Assisted Photocatalytic Degradation; Modified Ahmad–Iravani Approach)

The photocatalytic experiments were performed using a combined visible–UV light irradiation system, following a modified protocol adapted from Ahmad et al. and Iravani, which are widely used to evaluate dye degradation efficiency when working with metal oxide nanocatalysts.

1. Preparation of Methylene Blue (MB) Solution

A stock solution of MB dye was prepared with deionised (DI) water. For each experimental run, a fresh working solution of 5 $mg \cdot L^{-1}$ MB was prepared in a 50 mL volume to maintain consistency in reaction conditions.

2. Catalyst Loading

A fixed amount of 150 mg of the synthesised ZrO_2 nanopowder was added to 50 mL of MB solution, corresponding to a catalyst concentration of 3 $g \cdot L^{-1}$. This dose was selected based on prior optimisation studies, which indicated effective radical generation, reduced electron-hole recombination, and minimal light scattering at this loading.

3. pH Optimisation

To examine the effect of pH on photocatalytic efficiency, the MB solution was adjusted to pH 3, 7, and 9 using diluted HCl or NaOH. Measurements were taken with a calibrated digital pH meter. pH 7 was considered neutral, while pH 3 (acidic) and pH 9 (alkaline) were evaluated to investigate the influence of surface charge interactions on dye adsorption and subsequent degradation.

4. Irradiation Setup

Experiments were conducted in a borosilicate glass reactor placed beneath a 200 W visible light source. For UV-assisted experiments, a UV lamp of similar geometry was used. Continuous magnetic stirring ensured

uniform dispersion of the catalyst and prevented sedimentation during irradiation.

5. Photocatalytic Reaction Procedure

Before irradiation, the MB–ZrO_2 suspension was kept under continuous stirring in the dark for 30 minutes to establish adsorption–desorption equilibrium between the dye molecules and the nanoparticle surface. Once equilibrium was attained, the mixture was exposed to either visible or UV light, with illumination times varying from 60 to 250 minutes based on the experimental conditions.

6. Sampling and Analytical Measurements

Aliquots of 2 to 3 mL were withdrawn at 30-minute intervals throughout the irradiation period. Each sample was promptly centrifuged to separate and remove the suspended catalyst particles. During the experiments, an aeration pump provided a continuous flow of oxygen to enhance the generation of reactive oxygen species and promote dye degradation. The clear supernatant was analysed using a UV–Visible spectrophotometer at the characteristic absorption wavelength of methylene blue (MB) ($\lambda_{max} \approx 664$ nm). The degradation efficiency (%) was determined based on the reduction in absorbance relative to the initial concentration.

7. Kinetic Analysis

The photocatalytic degradation behaviour was analysed using a pseudo-first-order kinetic model, which helped determine the reaction rate and evaluate the performance of the ZrO_2 nanoparticles under both UV and visible light irradiation.

3. Result and Discussion

Table 1: Photocatalytic Degradation of Using *Aegle marmelos* Fruit–Mediated ZrO_2 ($ZrOCl_2 \cdot 8H_2O$) Nanoparticles (UV Irradiation)

Time (min)	pH 3 (%)	pH 7 (%)	pH 9 (%)
60	20	33	41
100	37	51	62
150	48	68	79
200	59	83	91
250	67	93	97

Table 1 presents the photocatalytic degradation of methylene blue (MB) using *Aegle marmelos* fruit-mediated ZrO_2 nanoparticles under UV irradiation at pH 3, 7, and 9 over 250 minutes. The degradation efficiency showed a clear time-dependent increase. After 60 minutes of UV exposure, MB removal was 20%, 33%, and 41% for pH 3, 7, and 9, respectively. At 100 minutes, the degradation improved to 37%, 51%, and 62%, rising further to 48%, 68%, and 79% at 150 minutes. By 200 minutes, the efficiencies reached 59%, 83%, and 91%, and near-complete degradation was observed at 250 minutes, with 67% at pH 3, 93% at pH 7, and 97% at pH 9.

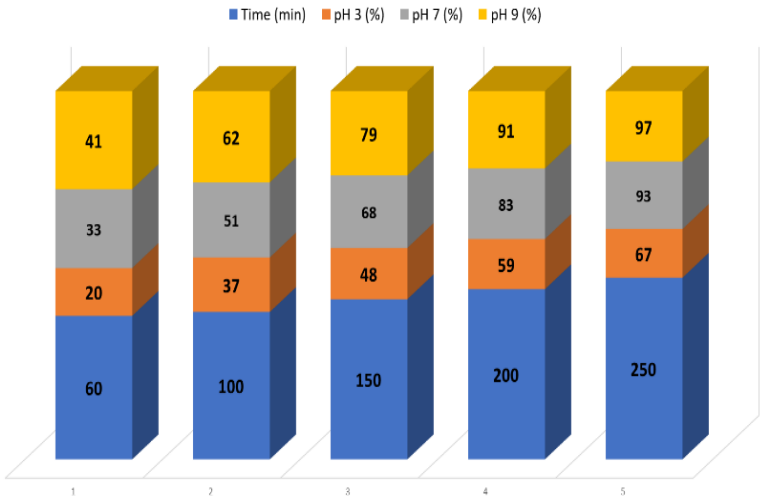


Figure 1: Time-dependent photocatalytic degradation using aegle Marmelos fruit-mediated ZrO_2 ($ZrOCl_2.8H_2O$) nanoparticles under UV Irradiation

Table 2: Time-Dependent Photocatalytic Degradation Using *Aegle marmelos* Fruit–Mediated ZrO_2 Nanoparticles Under (Visible Irradiation)

Time (min)	pH 3 (%)	pH 7 (%)	pH 9 (%)
60	12	21	29
100	25	38	50
150	39	57	68
200	51	72	82
250	60	86	93

Table 2 illustrates The photocatalytic degradation of methylene blue (MB) was studied using ZrO_2 nanoparticles mediated by *Aegle marmelos* fruit under visible light irradiation. Similar to the experiments conducted with UV light, the degradation efficiency increased gradually over time. However the overall degradation efficiency was comparatively reduced relative to the results obtained under UV illumination. After 60 minutes, MB degradation reached 12%, 21%, and 29% at pH 3, 7, and 9, respectively. At 100 minutes, the efficiencies improved to 25%, 38%, and 50%, and further increased to 39%, 57%, and 68% at 150 minutes. By 200 minutes, degradation reached 51%, 72%, and 82%, and the highest removal at 250 minutes was observed as 60% at pH 3, 86% at pH 7, and 93% at pH 9.

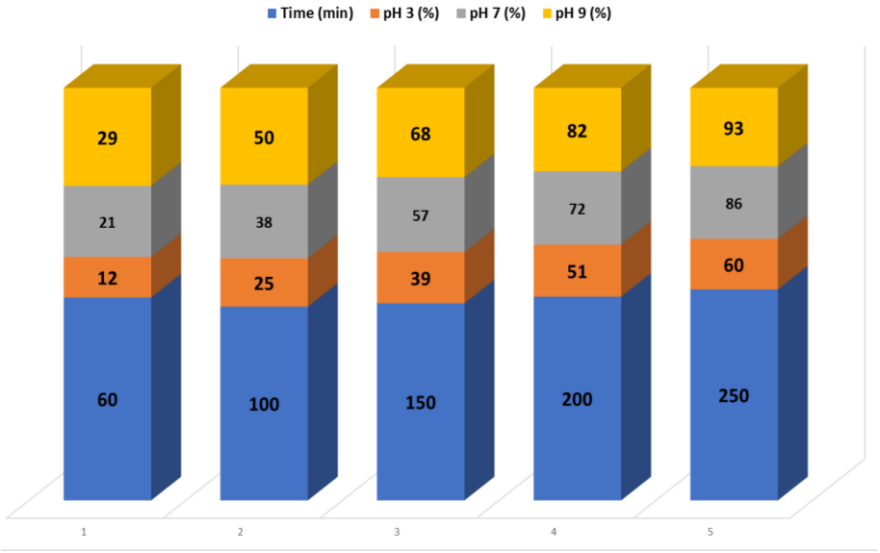


Figure 2: Time-Dependent Photocatalytic Degradation of Methylene Blue Using Aegle Marmelos Fruit-Mediated ZrO_2 $Zr(NO_3)_4$ Nanoparticles Under Visible Irradiation

4. Discussion

The study demonstrates that *Aegle marmelos* fruit-mediated ZrO_2 nanoparticles effectively degrade methylene blue (MB) under both UV and visible light, with UV irradiation showing superior performance due to higher photon energy and enhanced generation of reactive oxygen species (ROS) [1], [2], [13].

Photocatalytic efficiency was strongly influenced by solution pH, with alkaline conditions (pH 9) achieving the highest MB removal. The gradual increase in degradation over time indicates that the process follows a pseudo-first-order kinetic model, consistent with earlier photocatalytic studies [1].

Overall, the results confirm the potential of these green-synthesised nanoparticles as effective photocatalysts for environmental applications. Particularly in treating dye-contaminated wastewater, optimised light and pH conditions enhance their performance.

5. Conclusion

The study confirms that *Aegle marmelos* fruit-mediated ZrO_2 NPs are efficient photocatalysts for degrading methylene blue under both UV and visible light. Photocatalytic performance was influenced by light type and solution pH, with UV light and alkaline conditions (pH 9) providing the highest degradation rates. The process

followed a pseudo-first-order kinetic model, and the results highlight the critical role of surface charge in dye adsorption. These findings demonstrate the potential of these green-synthesised nanoparticles for environmentally friendly wastewater treatment, with optimised light and pH conditions enhancing their practical applicability.

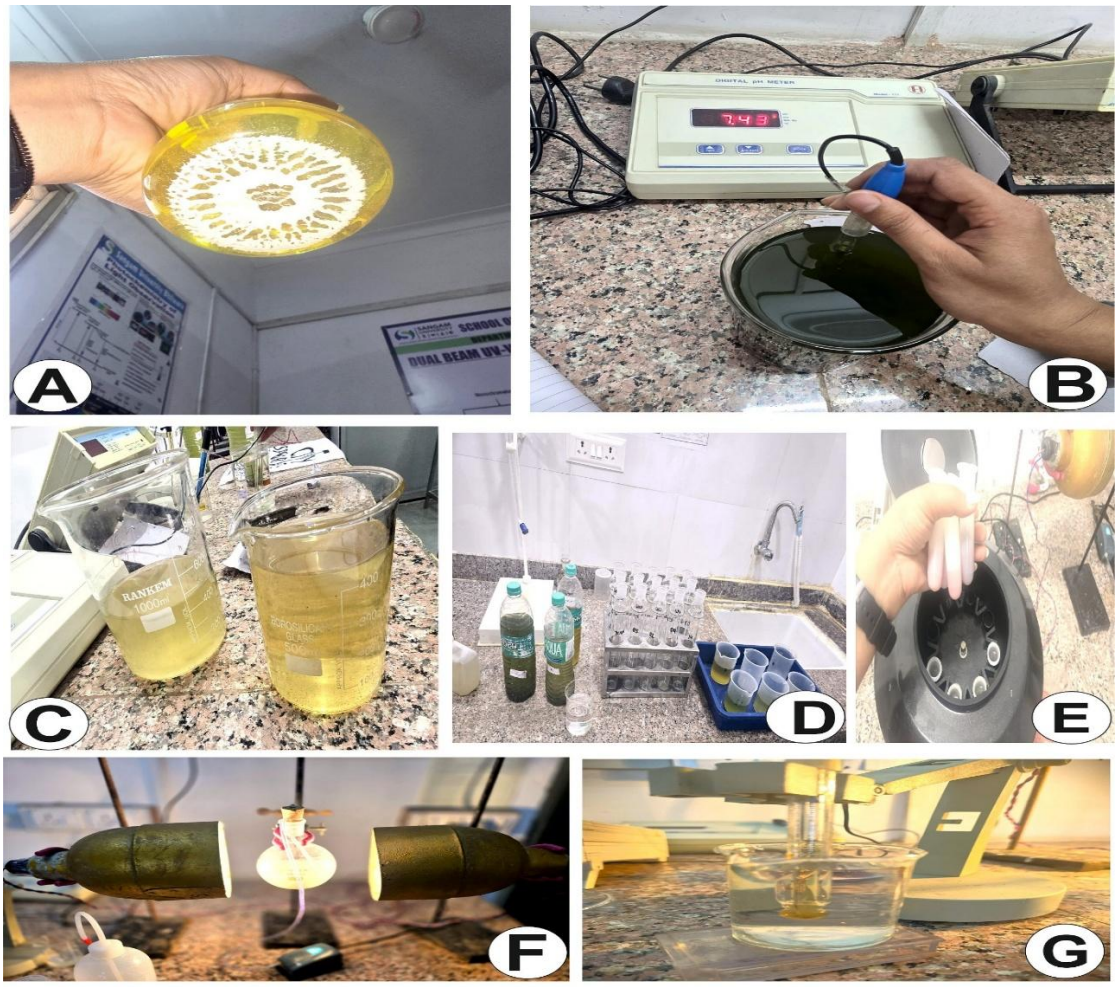


Figure 3: Photocatalytic Study: Instrumentation and Experimental Setup

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