Research Article

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Photoremediation of methylene blue by biosynthesized ZnO/Fe₃O₄ nanocomposites using Callistemon viminalis leaves aqueous extract: A comparative study

Abstract: This article reports a simple, cost-effective, and eco-friendly biosynthesis of ZnO/Fe₃O₄ nanocomposites using Callistemon viminalis leaves’ water extract. For the first time, we used a green synthetic route via C. viminalis leaves’ extract to prepare ZnO/Fe₃O₄ nanocomposites (NCs) using zinc acetate and ferric chloride as precursor materials. Fourier transform infrared (FTIR) spectroscopic results revealed polyphenolic compounds mainly phenolic acids present in the plant extract acted as both reducing and stabilizing agents to synthesize ZnO/Fe₃O₄ NCs. Outcomes of XRD and X-ray photoelectron spectroscopy confirmed the formation of ZnO–Fe₃O₄ heterojunction in ZnO/Fe₃O₄ NCs, with crystallite sizes of 45, 35, and 60 nm, respectively, according to Debye–Schererrer’s formula. EDX confirmed Zn, Fe, and O in the ZnO/Fe₃O₄ nanocomposite. Scanning electron microscopy and transmission electron microscopy (TEM) analyses revealed the existence of both ZnO and Fe₃O₄ in the NCs with some agglomeration. The thermal stability of NCs was evaluated using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in a nitrogen atmosphere. In addition, as-prepared ZnO/Fe₃O₄ NCs along with biosynthesized ZnO and Fe₃O₄ (prepared by C. viminalis extract) nanoparticles were examined for photodegradation of methylene blue under visible light irradiation for 150 min. The result reveals that the photodegradation efficiency of ZnO/Fe₃O₄ NCs (99.09%) was higher compared to that of monometallic ZnO (84.7%) and Fe₃O₄ (37.1%) nanoparticles.

Keywords: ZnO/Fe₃O₄ nanocomposites, Callistemon viminalis, XPS, photodegradation, methylene blue

1 Introduction

Industrialization and urbanization have increased water pollution to a great extent because of the direct disposal of organic and industrial waste into water bodies [1]. Among all, dyeing industries produce an enormous amount of wastewater containing unused dye along with other chemicals [2]. It reported that the majority of dyes are toxic and nonbiodegradable [3]. Hence, the dye effluent contaminates surface and underground water, which brings out adverse effects on flora and fauna [4,5]. Methylene blue (MB) is the most popular thiazine dye used in textile industries. The prolonged exposure to MB results in harmful effects, such as cyanosis, skin irritation, and gastrointestinal irritation, in living beings [6]. To solve this challenge, many physical and chemical techniques including flocculation–coagulation, surface adsorption, ion-exchange, chemical precipitation, and photocatalytic degradation have been used to remove the dye from waste water [7,8]. Because of the simple experimental procedure and decomposition of organic dye molecules into nontoxic simple
products in the presence of semiconductors under proper light irradiation, the photodegradation process proves its superiority over other methods [9, 10]. For semiconductor-assisted photocatalytic process, various materials, such as ZnO, CuO, TiO2, and more, have been widely used as photocatalysts previously [11–13]. Among different semiconductor materials, ZnO is a nontoxic, easily available, and cost-effective material with a bandgap of 3.2 and 60 MeV exciton binding energy [14]. That is why ZnO became the priority to many researchers working in the photocatalytic degradation of dyes using semiconductors. But ZnO semiconductor has a rapid tendency of recombination of photo-induced electron–hole pairs, which makes it difficult to gain the practical demand [15]. To overcome this problem, many metallic or nonmetallic materials, such as CdS, Ag2O, CuO, and g-C3N4, have doped with ZnO and showed improved efficiency toward photodegradation process [16–19].

However, the removal of nanocomposites (NCs) from the treated solution is very tedious and expensive, which is still a challenge. In this concern, magnetite nanoparticles (Fe3O4 NPs) play an effective role as they are easily separable from the solution by applying an external magnetic field [20]. Apart from this, doping of metallic NPs with magnetite NPs improves their functionality and recyclability and in turn cost effectiveness of the process [21,22]. Inspired by this, many researchers have synthesized and investigated the results of magnetite NCs [23]. After reviewing the literature, we observed that various approaches, such as sol–gel, hydrothermal synthesis, precipitation, and microemulsion, have been adopted for preparing magnetite composites [24–27]. But many of these methods have certain demerits, such as the use of expensive and hazardous chemicals and the formation of toxic byproducts, which makes it difficult to achieve the requirement of green synthesis. In recent decades, the use of bioproducts (including biomolecules, bacteria, fungi, or plant extracts) for the synthesis of NPs has attracted researchers as well [28]. Metals and metal oxide nanoparticles have also been used as homogeneous or heterogeneous nanocatalysts in various organic syntheses due to the large surface-to-volume ratio of nanoparticles compared to bulk materials [29,30]. This strategy provides a simple, cost-effective, and eco-friendly route for the fabrication of nanomaterials [31]. Although synthesis of ZnO/Fe3O4 NCs by different routes has been reported [32,33], a few reports on a green synthesis of ZnO/Fe3O4 NCs are available [34,35]. In our present study, we have synthesized ZnO/Fe3O4 NCs using Callistemon viminalis leaves’ extract as a green reducing and stabilizing agent. C. viminalis is a small tree that belongs to the family Myrtaceae with a characteristic brushlike flowers. It is a traditional medicine to treat hemorrhoids, gastroenteritis, diarrhea, and skin infection [36–38]. The phytochemical study reported that C. viminalis is rich in biomolecules, including viminadiones, quercetin, and betulinic acid, and can act as a green reducing and capping agent during the fabrication of nanomaterials.

After reviewing the literature, we understand that C. viminalis leaves’ extract-mediated biomimetic synthesis of ZnO/Fe3O4 has not been reported till date. In this study, we have attempted to understand the role of biomolecules present in leaves’ extract as a reducing and stabilizing agent for the fabrication of ZnO/Fe3O4 NCs. The novelty of this study is to show the efficacy of biosynthesized ZnO/Fe3O4 NCs as a photocatalyst in contrast to ZnO or Fe3O4 NPs for the degradation of MB solution under visible light irradiation.

2 Experimental methodology

2.1 Chemicals

All chemicals applied in this research study, including zinc acetate dihydrate (Thermo Fisher Scientific India Pvt. Ltd.), ferric chloride (Thermo Fisher Scientific India Pvt. Ltd.), sodium hydroxide (Merck Life Science India Pvt. Ltd.), and methylene blue (Merck Life Science India Pvt. Ltd.), were of analytical grade and used as received commercially without further purification. Deionised water was used throughout the experiment wherever required.

2.2 Preparation of C. viminalis leaves’ extract

Leaves of C. viminalis were collected from Jaipur National University campus, India. The collected leaves were thoroughly washed under tap water and finally washed using deionised water. After drying in shade, the leaves were powdered in an electrical grinder. About 25 g of the powdered leaves in 100 mL deionised water was refluxed in a Soxhlet apparatus (Sigma-Aldrich, India) for 2 h at 80°C on a magnetic stirrer. On cooling, the suspension was filtered through Whatmann’s filter paper, and the filtrate was collected as leaves’ extract and stored in a refrigerator at 2°C for further studies.

2.3 Biosynthesis of ZnO/Fe3O4 NCs

The ZnO/Fe3O4 NCs were prepared through an eco-friendly green route, and the synthesis procedure is briefly illustrated
as follows: 30 mL of *C. viminalis* leaves' extract was added slowly in a round-bottom flask containing 30 mL of zinc acetate solution (0.01 M) under stirring. After 10 min, 0.16 g of ferric chloride in 10 mL deionised water was introduced dropwise into the flask and heated to 60°C, followed by the addition of NaOH (0.1 M) to maintain pH 10. The color of the solution changes from black to blackish brown after 1 h stirring, which indicated the formation of ZnO/Fe₃O₄ NCs. Afterward, the solution was cooled to room temperature, centrifuged, collected in a China dish, washed several times with ethanol to remove unused extract and NaOH, dried in an oven at 80°C, and finally calcined at 300°C before storing for further studies. For comparison, monometallic nanoparticles (ZnO and Fe₃O₄) had also been synthesized using *C. viminalis* leaves' extract. A schematic of aforementioned green synthesis is shown in Figure 1.

### 2.4 Characterization

FTIR spectral analysis in the range of 4,000–400 cm⁻¹ was carried out to investigate the role of *C. viminalis* leaf extract in the fabrication of ZnO, Fe₃O₄, and ZnO/Fe₃O₄ nanoparticles using a PerkinElmer spectrophotometer (MNIT, Jaipur). A powder X-ray diffraction technique was performed to determine the crystallinity and particle size of biosynthesized product by PAN analytical (XPART PRO) diffractometer in the scattering range (2θ) of 20–80° using Cu Kα radiation (λ = 1.5406 Å). The surface morphology of green synthesized samples was determined by scanning electron microscopy (SEM) using Nova Nano SEM 450 (MNIT, Jaipur) and transmission electron microscopy (TEM) at IIT Roorkee. The elemental composition was investigated using EDX analysis. Chemical states of elements present in ZnO/Fe₃O₄ NCs were analyzed by X-ray photoelectron spectroscopic technique (XPS, PHI 5000 Versa Probe III, IIT Roorkee). The thermal stability of ZnO/Fe₃O₄ sample was recorded in a nitrogen atmosphere at a heating rate of 5°C min⁻¹ by TGA/DTA analyzer (EXSTAR TG/DTA 6300, IIT Roorkee).

### 2.5 Designing of the photocatalytic activity experiment

The photocatalytic efficiency of biosynthesized ZnO, Fe₃O₄, and ZnO/Fe₃O₄ nanomaterials for the degradation of MB dye was evaluated under visible light at pH 7. For the
photodegradation study, three experimental sets were prepared. Each set comprised seven beakers (100 mL) with 25 mL solution of MB (32 mg L$^{-1}$) in each. The dose of biosynthesized ZnO, Fe$_3$O$_4$, or ZnO/Fe$_3$O$_4$ nanoproducts taken was 0.004 g in each beaker. After certain intervals of time (15, 30, 45, 60, 75, 90, and 150 min), one beaker from each set was removed from irradiation, and dye solutions were centrifuged at 8,000 rpm followed by filtration to remove the photocatalyst. MB degradation was examined by measuring the absorbance of the dye solution at $\lambda_{max} = 665$ nm using a UV-Vis spectrophotometer. The percentage of MB degradation was determined by the following equation:

$$\eta = \frac{A_0 - A_t}{A_0} \times 100.$$  

In equation (1), $\eta$ is the degradation percentage and $A_0$ and $A_t$ are the absorbances of MB dye solution at $t = 0$ and after time $t$, respectively.

3 Results and discussion

3.1 FTIR analysis

The involvement of biomolecules present in C. viminalis leaves’ extract, for the fabrication of nanomaterials, was screened by FTIR spectroscopic analysis. Figure 2 depicts the FTIR spectra of C. viminalis leaves’ extract as well as biosynthesized ZnO, Fe$_3$O$_4$, and ZnO/Fe$_3$O$_4$ nanomaterials. The FTIR spectrum of C. viminalis leaves’ extract (Figure 2a) showed some major absorption bands at 3,419, 2921.76, 1718.16, 1451.86, 1368.87, and 1180.95 cm$^{-1}$ were assigned to O–H stretching of phenolic acids and phenols, C–H stretching in CH$_3$ and CH$_2$, C=O groups in phenolic acids and flavonoids, C=C stretching of the aromatic ring, and C–H deformation in CH$_3$ and C–OH stretching in phenolic acids, respectively, as reported in various literature [39–41].

However, after the reduction of metal precursors into their respective metal nanoparticles, a remarkable difference in intensity, position, and shape of absorption peaks had been observed, which showed the participation of biomolecules (present in leaves’ extract) in the reduction and capping of nanomaterials. The additional peaks in the spectra of monometallic NPs at 466.53 cm$^{-1}$ (Figure 2(b)) and 612 cm$^{-1}$ (Figure 2(c)) were allocated to Zn–O and Fe–O stretching vibrations, respectively, confirming the formation of ZnO and Fe$_3$O$_4$ NPs [42]. Moreover, shifting in absorption peak values of Zn–O (452.93 cm$^{-1}$) and Fe–O (591.63 cm$^{-1}$) towards lower wave numbers in ZnO/Fe$_3$O$_4$ (Figure 2(d)) indicated the formation of bimetallic nanocomposite. Furthermore, shrinkage/shifting of peaks corresponding to C==O, C==C, and C–OH groups (1718.16, 1451.86, and 1180.95 cm$^{-1}$) in the spectra of nanoproducts...
suggests that polyphenolic compounds mainly phenolic acids are responsible for the bioreduction of metal ions and capping of as-prepared nanoproducts.

3.1.1 Mechanism of biosynthesis

On the basis of FTIR results, a possible mechanism for the *C. viminalis* leaves' extract-mediated synthesis of ZnO, Fe$_3$O$_4$, and ZnO/Fe$_3$O$_4$ has been proposed.

In short, betulinic acid present in leaves' extract undergoes oxidation according to the free radical mechanism, that is, betulinic acid to dehydro betulinic acid (Scheme 1). Zn$^{2+}$/Fe$^{3+}$ ions (present in solution) form complex with dehydro betulinic acid via transfer of electrons from anionic dehydro betulinic acid to metal ions. On calcination, the resulting complex is converted into respective metal oxide nanoparticles because of the capping effect of biomolecules [43].

3.2 XRD analysis

The phase and crystal structure of biosynthesized ZnO, Fe$_3$O$_4$, and ZnO/Fe$_3$O$_4$ nanomaterials were examined by powder X-ray diffraction analysis. Figure 3 depicts the

![Scheme 1: Proposed mechanism for the biosynthesis of ZnO, Fe$_3$O$_4$, and ZnO/Fe$_3$O$_4$ NCs.](image1)

![Figure 3: Powder XRD pattern of biosynthesized NPs: (a) ZnO, (b) Fe$_3$O$_4$, and (c) ZnO/Fe$_3$O$_4$ NCs.](image2)
X-ray patterns of ZnO (a), Fe$_3$O$_4$ (b), and ZnO/Fe$_3$O$_4$ (c). In Figure 3(a), XRD peaks at 2θ values = 32.03°, 34.73°, 36.66°, 48.03°, 57.05°, 68.32°, and 69.49° were indexed to the respective (100), (002), (101), (102), (110), (112), and (201) crystalline planes of hexagonal wurtzite phase of ZnO (JCPDS Card No. 36-1451), whereas in Figure 3(b), diffraction peaks at 2θ values = 30.16°, 35.29°, 43.12°, 56.83°, and 62.59° correspond to the miller indices (220), (311), (400), (511), and
(440), respectively (JCPDS Card No. 19-0629), which confirm the face-centered cubic structure of Fe₃O₄ [44]. For ZnO/Fe₃O₄ NCs (Figure 3c), peaks at 32.56°, 34.87°, 36.07°, 57.28°, 68.92°, and 69.58° corresponding to (100), (002), (101), (110), (112), and (201) planes infer the presence of ZnO in hexagonal wurtzite phase, whereas peaks at 2θ = 30.10°, 35.65°, 43.15°, and 62.86° represent (220), (311), (400), and (440) planes of face-centered cubic structure of iron. The identification of a dual phase with shifting of the respective peak values in the XRD pattern of NCs indicates the formation of Zn–Fe heterojunction. Moreover, the crystallite size (D) of as-prepared nanoproducts is calculated using Debye–Scherrer’s formula (D = kλ/βcosθ) and at maximum intense peaks, the size of ZnO, Fe₃O₄, and ZnO/Fe₃O₄ is found to be 45, 35, and 60 nm, respectively.

3.3 SEM and TEM analysis

Morphology and nanoscale of the biosynthesized samples were analyzed using SEM and TEM. An overview of SEM images of Zn, Fe₃O₄, and ZnO/Fe₃O₄ samples is shown in Figure 4(a–c). As observed from images, the morphology of ZnO/Fe₃O₄ differs from ZnO or Fe₃O₄, which suggested the formation of ZnO/Fe₃O₄ NCs. Furthermore, in the SEM image of ZnO/Fe₃O₄, rod-shaped particles of ZnO and cubic-shaped structures of Fe₃O₄ are clearly visible, which interprets the interaction of Fe₃O₄ with ZnO. Morphological differences among as-prepared samples were also identified by TEM micrographs (Figure 4(d–f)). The spherical shape of ZnO NPs with a particle size of ~45 nm can be seen in Figure 4(d), whereas Fe₃O₄ NPs have an irregular shape (Figure 4(e)) with a particle size of ~35 nm. The coexistence of ZnO and Fe₃O₄ can be clearly identified in the TEM micrograph of NCs (Figure 4(f)), wherein Fe₃O₄ can identify as dark particles with some agglomeration because of its highly magnetic nature and ZnO as bright particles surrounding Fe₃O₄. Moreover, selected area electron diffraction (SAED) image of ZnO/Fe₃O₄ NCs (Figure 4(g)) also interprets the incorporation of Fe₃O₄ in the crystalline lattice of ZnO NPs, which resulted in a comparatively less crystalline and large-sized ZnO/Fe₃O₄ NCs. Thus, the results obtained from SEM and TEM analyses were in close agreement with XRD results.

Figure 5: EDX spectrum of (a) ZnO, (b) Fe₃O₄, and (c) ZnO/Fe₃O₄ NCs.
3.4 EDX analysis

To determine the chemical composition of ZnO, Fe3O4, and ZnO/Fe3O4 nanoproducts, EDX analysis was carried out and results are displayed in Figure 5(a–c). It can be seen in Figure 5(a) that the EDX spectrum consists of strong peaks for Zn and O, whereas Figure 5(b) shows Fe and O elemental peaks. In case of ZnO/Fe3O4 NCs (Figure 5(c)), strong signals for Zn, Fe, and O elements were well recognized, which further confirmed the coexistence of ZnO and Fe3O4. The appearance of carbon in all three spectra may be due to biomolecular capping on the surface of nanoproducts [45]. Based on EDX outcomes, the weight percentage of elements in ZnO/Fe3O4 NCs was 32.56, 38.67, and 28.77% for Zn, Fe, and O, respectively.

3.5 XPS analysis

XPS analysis was carried out to demonstrate the chemical nature of the surface of biosynthesized ZnO/Fe3O4 NCs. Figure 6(a) depicts the full scan spectrum of ZnO/Fe3O4 and the appearance of major peaks at binding energies of 1,021 eV (Zn2p), 725 eV (Fe2p), 530 eV (O1s), and 284 eV (C1s) confirms the fabrication of ZnO/Fe3O4 NCs. High-resolution XPS spectra of Fe2p, Zn2p, O1s, and C1s are shown in Figure 6(b–e). In Figure 6(b), a doublet for Fe2p at 711.94 and 726.93 eV was assigned to respective binding energies of Fe2p3/2 and Fe2p1/2 of Fe3O4 [46,47]. In the Zn2p spectra (Figure 6(c)), the spin-orbit doublet Zn2p3/2 and Zn2p1/2 peaks were centered at binding energies of 1021.7 and 1044.65 eV, respectively [48]. It is evident from the literature that Zn2p3/2 and Zn2p1/2 peaks are separated by 23 eV in pure ZnO. From the XPS results, peaks of Zn2p in NCs were separated by 21 eV, which strongly manifests the synergistic effect between ZnO and Fe3O4 NPs, contributing to the enhancement in photocatalytic activity of NCs [49]. XPS spectrum of C1s (Figure 6(d)), consists of three peaks at 283 eV (C–C) [50], 284 eV (C=C) [46,51], and 285 eV (C==O) [52], attributed to the polyphenolic compounds of leaves’ extract acting as a stabilizing agent for ZnO/Fe3O4 NCs [53]. In the O1s spectrum shown in

![Figure 6](https://example.com/figure6.png) 

**Figure 6:** XPS spectra of ZnO/Fe3O4 NCs: (a) survey spectrum, (b) Fe2p, (c) Zn2p, (d) C1s, and (e) O1s.
Figure 6(e), the peak position at 529.89 eV was assigned to oxygen in Fe–O of ZnO/Fe3O4, corresponding to ferro–ferric oxide. The deconvolution of O1s signals revealed the presence of Zn–O of ZnO at a binding energy of 530.89 eV. The peak at 531.89 eV may be due to the hydroxyl group of biomolecular capping and oxygen chemisorbed onto the surface of ZnO/Fe3O4 NCs [54]. Under visible light irradiation, these active oxygen species on the surface of NCs may contribute to MB degradation via oxygen ions, such as O−1 and O−2, which in turn improves the photocatalytic activity of ZnO/Fe3O4 NCs [55].

3.6 Thermal analysis

Thermal characteristics of ZnO/Fe3O4 NCs were determined simultaneously in a single run by using TGA and DTA (Figure 7). TGA results showed that the thermal decomposition of ZnO/Fe3O4 NCs occurred in four steps. Initially, up to 100°C, the weight loss of 5.2% was due to the loss of adsorbed water on the surface of NCs. The weight loss observed in the second step (200–400°C) was 17.3%, which might be due to the dismissal of biomolecules capped on the surface of NCs. The loss in weight observed in between 400 and 600oC (third step) was assigned to the adsorbed oxygen species [56]. In the last step, a loss of 7.5% in weight was observed up to 800°C. DTA thermogram (Figure 7) displayed energy changes irrespective of change in weight. The peaks observed at 328 and 599°C were associated with the release of bioactive molecules and adsorbed oxygen, respectively.

Table 1: Comparative analysis on the photoremediation of MB in the presence of biosynthesized ZnO, Fe3O4, and ZnO/Fe3O4 NCs for a period of 150 min

| Sr. no. | Time (min) | ZnO (E_{max}) | Fe3O4 (E_{max}) | ZnO/Fe3O4 (E_{max}) |
|---------|------------|----------------|-----------------|---------------------|
| 1       | Initially  | 1.32           | 1.32            | 1.32                |
| 2       | 15         | 1.239          | 1.29            | 0.956               |
| 3       | 30         | 0.987          | 1.19            | 0.854               |
| 4       | 45         | 0.916          | 1.12            | 0.806               |
| 5       | 60         | 0.865          | 1.023           | 0.772               |
| 6       | 75         | 0.722          | 0.992           | 0.578               |
| 7       | 90         | 0.682          | 0.93            | 0.485               |
| 8       | 150        | 0.202          | 0.829           | 0.012               |
respectively. A peak at 927°C in DTA thermogram probably infers a crystalline transition of ZnO/Fe₃O₄ NCs.

3.7 Assessment of the photocatalytic activity

The photodegradation of MB in the presence of as-prepared nanoproducts was examined under visible light, and the extent of degradation was measured in terms of absorbance of MB solution using a UV-Vis spectrophotometer after certain intervals of time for 150 min. The results of degradation studies are showcased in Figures 8 and 9, and Table 1, which revealed that the degradation of MB increases with an increasing irradiation time. From the absorbance spectra of MB (Figure 8 and Table 1), it can be seen clearly that initially, 15 min of exposure to sunlight, MB solution was degraded by 6.14, 2.27, and 28.03% and after 90 min, MB solution was degraded by 48.3, 29.94, and 63.25% in the presence of biosynthesized ZnO, Fe₃O₄, and ZnO/Fe₃O₄ samples, respectively.

As shown in Figure 8, MB dye was almost completely degraded (99.09%) by ZnO/Fe₃O₄ NCs in 150 min, whereas ZnO and Fe₃O₄ NPs degraded it by 84.7 and 37.1%, respectively. These outcomes of MB absorbance spectra revealed that the degradation efficiency of ZnO NPs was increased in the presence of Fe₃O₄ NPs. The enhancement in MB removal by ZnO/Fe₃O₄ NCs compared to ZnO NPs indicated the synergistic effect between ZnO and Fe₃O₄, assigning to the degradation of MB.

Moreover, the degradation efficiency of ZnO/Fe₃O₄ NCs was examined for three consecutive runs, and the results are shown in Figure 10.

From the results, it is clear that the composites were active up to three cycles. Although in the third cycle, the degradation efficiency was decreased (90.1%). This decrement may be due to the adsorbance of some MB on the surface of photocatalyst, which perhaps blocks some active sites of NCs and can also be due to some loss of NCs during the recovery process.

The possible mechanism for the photodegradation of MB dye over biosynthesized ZnO/Fe₃O₄ NCs under visible light is shown in Figure 11.

The phenomenon of photodegradation of MB takes place when visible light is irradiated on the photocatalyst (ZnO, Fe₃O₄, or ZnO/Fe₃O₄), which leads to the generation of electron–hole pairs in conduction/valence bands (VBs) simultaneously on the surface of the photocatalyst.

Figure 8: UV-Vis absorbance spectra of MB solution during the photocatalytic process with biosynthesized: (a) ZnO, (b) Fe₃O₄, and (c) ZnO/Fe₃O₄ NCs.

Figure 9: Graphical portrayal of percentage removal of MB at 15, 90, and 150 min in the presence of as-prepared ZnO, Fe₃O₄, and ZnO/Fe₃O₄.
In the conduction band (CB), oxygen on the surface of the photocatalyst combines with the excited electron and forms \( \cdot O_2^- \) (superoxide radical; equation (3)). This radical checks the recombination of \( e^-/h^+ \) pairs by converting into \( \cdot OH \) radicals through hydroperoxyl radicals (HOO) and \( H_2O_2 \) intermediates (equation (4)). Simultaneously, holes produced in VB react with the surface water to produce hydroxyl radicals (\( \cdot OH \); equation (5)). The hydroxyl radicals produced in CB and VB, on the surface of photocatalyst, act as a strong oxidizing agent, which in turn degrade MB molecules into simple inorganic molecules, such as water, carbon dioxide, and inorganic ions (equation (6)). The survey of the previous literature also reveals that \( \cdot O_2^- \) (superoxide) radicals and hydroxyl radicals (\( \cdot OH \)) are the leading reactive species for the photodegradation of MB dye [57].

As shown in Figure 8 and Table 1, the absorption intensity of dye gradually decreases with an increasing irradiation time and finally diminished in case of ZnO/Fe\(_3\)O\(_4\). This is because of a breakdown of the heterocyclic conjugated structure of MB molecule into simple molecules, such as water, carbon dioxide, and inorganic ions. Apart from this, the photocatalytic efficiency of ZnO/Fe\(_3\)O\(_4\) NCs was greater compared to ZnO NPs, and this can be summarized as follows: Fe\(_3\)O\(_4\) NPs possess a narrow bandgap, and hence, \( e^-/h^+ \) pairs produced in it under irradiation recombines fastly, as a result charge carriers could not survive for a long time for the photocatalysis process [58]. In ZnO/Fe\(_3\)O\(_4\) NCs, the energy level of CB and VB of ZnO differs from that of Fe\(_3\)O\(_4\). During irradiation, some photogenerated electrons from ZnO are captured by Fe\(_3\)O\(_4\) NPs at the composite’s interface, where they react with the surface oxygen to form superoxide radicals. However, some holes transfer to VB of Fe\(_3\)O\(_4\) from ZnO and react with the surface water to produce hydroxyl radicals (\( \cdot OH \)). This phenomenon at the interface restricts an electron–hole recombination in ZnO. As a resultant, the generation of reactive species increases at the junction of ZnO–Fe\(_3\)O\(_4\), which accelerates the degradation of dye molecules [59]. Hence, the efficient charge transfer separation at heterojunction of two different semiconductor materials attributes to an enhanced photo-catalytic activity of ZnO/Fe\(_3\)O\(_4\) NCs to degrade MB.
solution. However, a comparison data for photodegradation of MB dye solution by ZnO/Fe₃O₄ NCs synthesized by different routes are displayed in Table 2. The results show considerable proficiency for the current study of MB degradation by C. viminalis-synthesized ZnO/Fe₃O₄ NCs.

\[
\text{Photocatalyst surface} + \text{hv} \rightarrow e_{cb}^- + h_{vb}^+. \\
2e_{cb}^- + 2O_2 \rightarrow 2O_2. \\
2O_2^- + 2H^+ \rightarrow 2HOO \rightarrow H_2O_2 \rightarrow 2OH \text{ (oxidizing agent),} \\
h_{vb}^+ + H_2O \rightarrow H^+ + OH \text{ (oxidizing agent),} \\
OH + MB \rightarrow \text{Degradation products (CO}_2 + \text{H}_2O + \text{Simple inorganic ions).}
\]

\section{4 Conclusion}

In this study, ZnO/Fe₃O₄ NCs as well as ZnO and Fe₃O₄ NPs were successfully synthesized via eco-friendly route using C. viminalis leaves’ extract without using any toxic additives. FTIR study indicated that the leaves’ extract played a key role in the reduction and stabilization of ZnO/Fe₃O₄ NCs, ZnO NPs, and Fe₃O₄ NPs, through the interaction of O–H, C=O, and C–C groups of phytocemicals present in C. viminalis leaves’ extract. Nanosize and the presence of pure phase in the crystal structure of biosynthesized products without major impurities, were confirmed by XRD analysis. XRD results were supported by XPS outcomes and revealed the formation of Zn–Fe heterojunction in ZnO/Fe₃O₄ NCs. Evidence of SEM, TEM, and EDX analyses also confirms the existence of Zn and Fe in composite nanoparticles. In addition, the photodegradation of MB under visible light irradiation was carried out using synthesized ZnO, Fe₃O₄, and ZnO/Fe₃O₄ as a photocatalyst. The results obtained in this study demonstrate that compared to monometallic (ZnO and Fe₃O₄) NPs, bimetallic NCs of Zn and Fe (ZnO/Fe₃O₄) accelerated the degradation of MB. The enhanced photocatalytic activity was attributed to the synergistic effect between ZnO and Fe₃O₄ nanoparticles in ZnO/Fe₃O₄ NCs. Moreover, ZnO/Fe₃O₄ NCs can be reused for three successive runs. Therefore, these findings suggest that ZnO/Fe₃O₄ NCs synthesized via C. viminalis leaves’ extract have a potential as an efficient photocatalyst for water purification.

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