

PAPER



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Single-phase BiFeO₃ and BiFeO₃–Fe₂O₃ nanocomposite photocatalysts for photodegradation of organic dye pollutants†

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The application of a novel BiFeO₃ (BFO)–Fe₂O₃ composite (called BFOF) as a photocatalyst for the degradation of methylene blue is reported. To improve the photocatalytic effectiveness of BiFeO₃, we synthesized the first BFOF photocatalyst by adjusting the molar ratio of Fe₂O₃ in BiFeO₃ using microwave-assisted co-precipitation. The UV-visible properties of the nanocomposites showed excellent absorption of visible light and reduced electron–hole recombination properties compared to the pure phase BFO. Photocatalytic studies on BFOF10 (90% BFO, 10% Fe₂O₃), BFOF20 (80% BFO, 20% Fe₂O₃), and BFOF30 (70% BFO, 30% Fe₂O₃) have shown that they decompose Methylene Blue (MB) in sunlight better than the pure BFO phase in 70 minutes. The BFOF30 photocatalyst was the most effective at reducing MB when exposed to visible light (94%). Magnetic studies confirm that the most effective catalyst BFOF30 has excellent stability and magnetic recovery properties due to the presence of magnetic phase Fe₂O₃ in the BFO.

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1. Introduction

Due to the difficulty in recovering photocatalysts from the majority of treated solutions and reusing them, it is challenging to bring composite photocatalysis to the practical application because it is difficult to recover them from treated solutions. Nano and microparticles with a large surface area possess high photocatalytic activity,^{1,2} allowing better spreading in aqueous media.³ They efficiently pass the light needed for the catalysts to be photoactivated. However, recovering those tiny particles through filtration or centrifugation typically results in higher operating costs for photocatalyst reuse in subsequent cycles. During the past decade, researchers have used external magnetic fields to separate magnetized photocatalytic materials from aqueous phases. Various pure and composite materials have been widely studied, including single-phase ferromagnetic

BiFeO₃, Fe₃O₄/TiO₂, Fe₂O₃/ZnO, BiFeO₃/SrTiO₃, Fe₂O₃/TiO₂, and BiFeO₃/Fe₂O₃.^{4–10}

Most of the above-mentioned magnetic materials have shown excellent photocatalytic activity and performance for degrading organic pollutants and other dyes, as well as practical ways to quickly recover powder (catalyst) from the suspension.^{4–10} Among the oxide semiconductors, BiFeO₃ and Fe₂O₃ have attracted particular attention because of their chemical stability, magnetic properties and excellent optical properties in visible light, which could make a significant difference in the absorption of visible light by solar energy over other semiconductors such as GaS, CdS and ZnS.^{11,12} Although numerous studies have demonstrated a bit of improvement in the photocatalytic activity of BFO and Fe₂O₃, still the photocatalytic performance of the pure phase BFO and pure phase Fe₂O₃ is lower than those of other oxide semiconductor visible light-active photocatalysts, such as BiVO₄,^{13,14} BiOX (X = Cl, I, Br)^{15–17} or Bi₂O₃ (ref. 18–20) due to their wide energy bandgap, improper optical band positions and high rates of electron and hole recombination compared to other commercially available semiconductors mentioned above.^{21–23}

Combining multiple photocatalysts and creating a composite photocatalyst system are among the advantageous techniques for promoting photogenerated electron–hole pairs and their separation.^{24–26} Recently, researchers have developed several composites of visible photocatalysts such as CuO/BFO,²⁷ BFO/polymer g-C₃N₄, g-C₃N₄/BFO,²⁸ BaTiO₃/α-Fe₂O₃ (ref. 29) and core–shell structures Fe₂O₃@CeO₂ (ref. 30) showing improved photocatalytic activity. Like the BiFeO₃ system,³¹ α-

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Fe₂O₃ (hematite) possesses a canted antiferromagnetic alignment and a rhombohedral crystal structure.³² Both crystal systems exhibit small optical band gaps ($E_{g(\text{BiFeO}_3)} = 2.2\text{--}2.8$ eV (ref. 33 and 34) and $E_{g(\alpha\text{-Fe}_2\text{O}_3)} = 2.2$ eV), making them suitable for photocatalysis and photoelectrochemical applications.³⁵ In addition, the particle's size, strain, and defect impact its magnetic and optical properties.³⁶ It has been reported that γ - and α -Fe₂O₃ in BiFeO₃ increase strain and magnetization, with the feasibility of α -Fe₂O₃ to be easily incorporated into a BiFeO₃ matrix.³⁷ Therefore, BiFeO₃/ α -Fe₂O₃ composites are interesting to study in terms of their structural and physical properties.³⁸

In the present work, we have synthesized the BFO-based composites BiFeO₃-Fe₂O₃ by loading different ratios of hollow micro spherical Fe₂O₃ (10, 20 and 30%) into the BFO micro flowers. Very few studies have been done on the BiFeO₃/Fe₂O₃ composites.³⁹⁻⁴² A novel aspect of the current study is that the α -Fe₂O₃ hollow spheres have been collected from the slags generated by the steel industry. Moreover, the microwave-assisted co-precipitation method was used to construct BFO-Fe₂O₃ composites by mixing different molar ratios of BFO and Fe₂O₃ hollow microspheres. Despite irradiation for 70 min under sunlight illumination, the BFO-Fe₂O₃ composite (also known as BFOF in the rest of the paper) has shown outstanding photocatalytic activity for eliminating methylene blue. After adding different ratios of Fe₂O₃ into the BFO, the BFOF composites have shown enhanced magnetic properties, photocatalytic activity and magnetic recovery compared to the pure phase BFO.

2. Experimental section

2.1. Materials used for the preparation of BiFeO₃-Fe₂O₃ composites

For this procedure, ethanol, double-distilled water (DDW), pure potassium hydroxide (KOH, SRL, 98%), pure ferric chloride (FeCl₃·6H₂O, SRL, 98%), ferric nitrate nonahydrate [Fe(NO₃)₃·9H₂O, SRL, 98%], mono-hydrated citric acid (C₆H₈O₇·H₂O, Sigma, 99.99%), and pure bismuth chloride (BiCl₃, SRL, 98%) are all used.

2.2. Preparation of BiFeO₃ micro flowers

The pure phase BFO is synthesized by the microwave-assisted-solvothermal (MWAST) method in a domestic solo-microwave oven with power 800 W and operating at 2.45 GHz. We have prepared the BFO in powder form with two metal precursors (BiCl₃, FeCl₃·6H₂O) and a mineralizer (KOH). A solution of equimolar concentrations (0.05 M) of BiCl₃ and FeCl₃·6H₂O was dissolved in ethanol and mechanically stirred for 1 hour. The dropwise addition of 8 M KOH solution altered the original solution. A hydroxide precipitate of bismuth and iron was obtained after 30 minutes of magnetic stirring. Later, 10 ml of this mixture was poured into a customized sealed microwave acid digestion vessel (model 4782 from Parr) of 45 ml capacity and then placed in a homemade microwave oven. The chemical reactions were carried out by applying a microwave power level of 800 W at a constant microwave heating time of 3 minutes and allowing the reaction vessel to cool down to room temperature.

The final reaction residue was washed in DDW several times and dried at 80 °C for 4 hours.⁴³

2.3. Preparation of hollow Fe₂O₃ microspheres

The hematite sample was collected from slag generated during the hot rolling process from the steel industry in Kazakhstan. It is obtained as a secondary product during steel production described elsewhere which can produce iron oxide particles.^{44,45,53} The collected samples were used as such without treatment with any harmful compounds. In previous studies we have characterized these steel slags, see ref. 44 and 45. They consist of stable polycrystalline α -Fe₂O₃ hollow spheres with diameters around 1 μm . More detailed information about the formation of the hematite during steel production is described in the ESI.†

2.4. Synthesis of BFO-Fe₂O₃ composites

BFO-Fe₂O₃ composites are prepared by a simple coprecipitation method following microwave heating at 360 W for 3 min. We dissolved a stoichiometric ratio of BFO and Fe₂O₃ powders in 40 ml of ethanol and sonicated it for six hours at 80 °C to evaporate the solvent and obtain the gel. Finally, the gel was heated at 360 W for 3 min in a domestic microwave oven. Following the above procedure, we have synthesized three different series of BFO-Fe₂O₃ composites by loading different ratios of Fe₂O₃ into the BFO. The prepared composites BFO-Fe₂O₃ (10, 20 and 30%) are named BFOF10, BFOF20, and BFOF30, respectively.

3. Characterization

The synthesized BFO, Fe₂O₃ and composites were characterized using UV-visible spectroscopy (Jasco V-670 UV-visible double beam spectrophotometer) against deionized water as blank. The absorption spectra were recorded in the 200–800 nm wavelength range. By analysing XRD data (PANalytical, X'Pert Powder Diffractometer), we have confirmed the formation of the pure phases of BFO, Fe₂O₃ and composites. In this diffractogram, the scanning range was between 20° and 80° (2 θ value) at a scan rate of 4° min⁻¹, and the step size was 0.02°. Field emission scanning electron microscopy (FESEM: Carl Zeiss Smart Sem) and energy dispersive X-ray analysis (EDAX) were used to study the morphology of the synthesized samples. A vibrating sample magnetometer (VSM) measured the magnetic properties of synthesized samples at room temperature (VSM, Model: LakeShore).

4. Photocatalysis

Using a model pollutant dye Methylene Blue (MB), each prepared sample was assessed for its photocatalytic activity for degrading dye pollutants. Photodegradation was conducted in heavy sunlight (200 mW cm⁻²). A total of 40 mg of each photocatalyst powder was initially added to 100 ml of MB solution at a concentration of 10 mg L⁻¹ and neutral pH. Following continuous magnetic stirring, the slurry was irradiated with heavy sunlight. We monitored the decolourization of the dye

solution using UV-visible spectroscopy in the range of 200 to 800 nm.

5. Results and discussion

5.1. X-ray diffraction (XRD) analysis of the composites

We synthesized BFO-Fe₂O₃ composite powders, along with content levels (mass%) of Fe₂O₃ of 10% (BFOF10), 20% (BFOF20) and 30% (BFOF30) using the chemical coprecipitation method. The XRD patterns of the BFO, Fe₂O₃ and BFO-Fe₂O₃ composites are displayed in Fig. 1.

According to XRD analysis, the BFO exhibited Rhombohedral crystal structures with the *R3c* space group, which is in perfect agreement with the previous crystallographic data (ICSD 98-019-1940), exhibiting no secondary phases within the detection limits of the technique. It was determined that the Fe₂O₃ XRD pattern showed Rhombohedral symmetry (*R3c* space group, ICSD: 98-005-6372). After adding 10% of Fe₂O₃ (BFOF10), the XRD patterns showed all peaks corresponding to pure phase BFO with a slight trace of the two prominent peaks (104) and (110) of Fe₂O₃. As the Fe₂O₃ loading ratio increased to 20% (BFOF20), more Fe₂O₃ peaks appeared. In particular, the increased intensity of the two most intense Fe₂O₃ peaks found at about 33.38 and 35.83°, corresponding to (104) and (110) crystal orientations, confirms the higher Fe₂O₃ content. Finally, after loading 30% Fe₂O₃, the composite sample BFOF30 presents all the Fe₂O₃ peaks besides the diffraction pattern corresponding to pure BFO.

5.2. FE-SEM images of BFO-Fe₂O₃ composites

As shown in Fig. 2, FE-SEM was used to analyse the microstructures of the BFO-Fe₂O₃ composites. Fig. 2(a) shows that pure phase BFO powder was composed of many BFO micro flowers where hundreds of BFO nano petals were closely packed on the BFO micro flowers.⁴⁶ Microstructures of pure phase

Fe₂O₃ are shown in Fig. 2(b), confirming the formation of hollow Fe₂O₃ microspheres. As illustrated in Fig. 2(c)–(e), the microstructure of the BFO-Fe₂O₃ composite is drastically altered after different molar ratios of Fe₂O₃ hollow microspheres were loaded on BFO. It is worth mentioning that after heating the BFO-Fe₂O₃ composites with high microwave energy (350 W, 3 min), both BFO micro flowers and hollow Fe₂O₃ microspheres were destroyed. From Fig. 2(c), it can be seen that there is partial contact between the BFO and Fe₂O₃ phases. It is believed that the destroyed nano petals from BFO micro flowers enter into the hollow Fe₂O₃ microspheres and make the coupling between the BFO and Fe₂O₃ phases, which is a crucial factor for enhancing the photocatalytic activity. As the amount of Fe₂O₃ increases, the contact between both phases increases, as shown in Fig. 2(d) and (e). The EDAX spectra of BFOF10, BFOF20, and BFOF30 are shown in Fig. 2(f)–(h). It is proven that the Bi, Fe, and O components are the source of the signal peaks, indicating that Fe₂O₃ was successfully loaded into the BFO.

5.3. TEM images of the BFO-Fe₂O₃ composite

Fig. 3(a)–(c) show the TEM images of the BFO-Fe₂O₃ composite. This figure shows that the composite material was composed of BFO nanoflowers with thin nanocrystalline petals of size 50 nm on the surface and Fe₂O₃ spheres. One can clearly see the contact between the two phases in the composite. To further investigate the detailed structural information of contact between both phases in the BFO-Fe₂O₃ composite, high-resolution transmission electron microscopy (HRTEM) was performed. In the HRTEM image (Fig. 3(d)), the BFO nano petals collected from the BFO-Fe₂O₃ composite revealed well-resolved lattice fringes with an interplanar distance of 0.281, 0.396 and 0.239 nm corresponding to the (104), (012) and (113) planes of the BFO rhombohedral structure respectively in all the composite materials [Fig. 3(d) and (e)]. The Fe₂O₃ hollow spheres with small size showed lattice fringes with 0.251 and 0.367, and 0.269 nm interplanar distances corresponding to the (110), (012) and (104) planes of the Fe₂O₃ hexagonal structure, respectively [Fig. 3(d) and (e)]. As a result, the TEM analysis also confirms the phases of BFO and Fe₂O₃ in the BFO-Fe₂O₃ composite, which is consistent with the FESEM and EDAX analysis.

5.4. Optical properties of BFO-Fe₂O₃ composites

The UV-vis absorption spectrum of all the prepared samples is shown in Fig. 4. Each sample demonstrated an excellent visible light absorption that matches extremely well with the majority of the UV-vis spectra of single-phase Fe₂O₃ and their composites that have been published.^{47,48} BFOF10, BFOF20, and BFOF30 exhibit excellent optical absorption in the visible range, demonstrating their suitability for visible photodegradation of organic dyes. The shoulder peaks observed besides the prominent peak in all the samples correspond to the metal-to-metal transitions. The absorption of light in the visible spectral range from 500–800 nm increased as the amount of Fe₂O₃ increased, revealing that the visible light absorbance of these composites improved more than the pure phase BFO. The improvement in

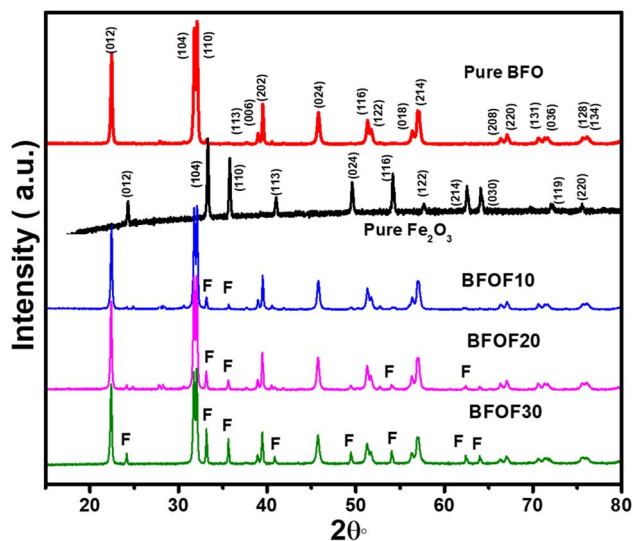


Fig. 1 XRD patterns of pure BFO, pure Fe₂O₃, BFOF10, BFOF20, and BFOF30.

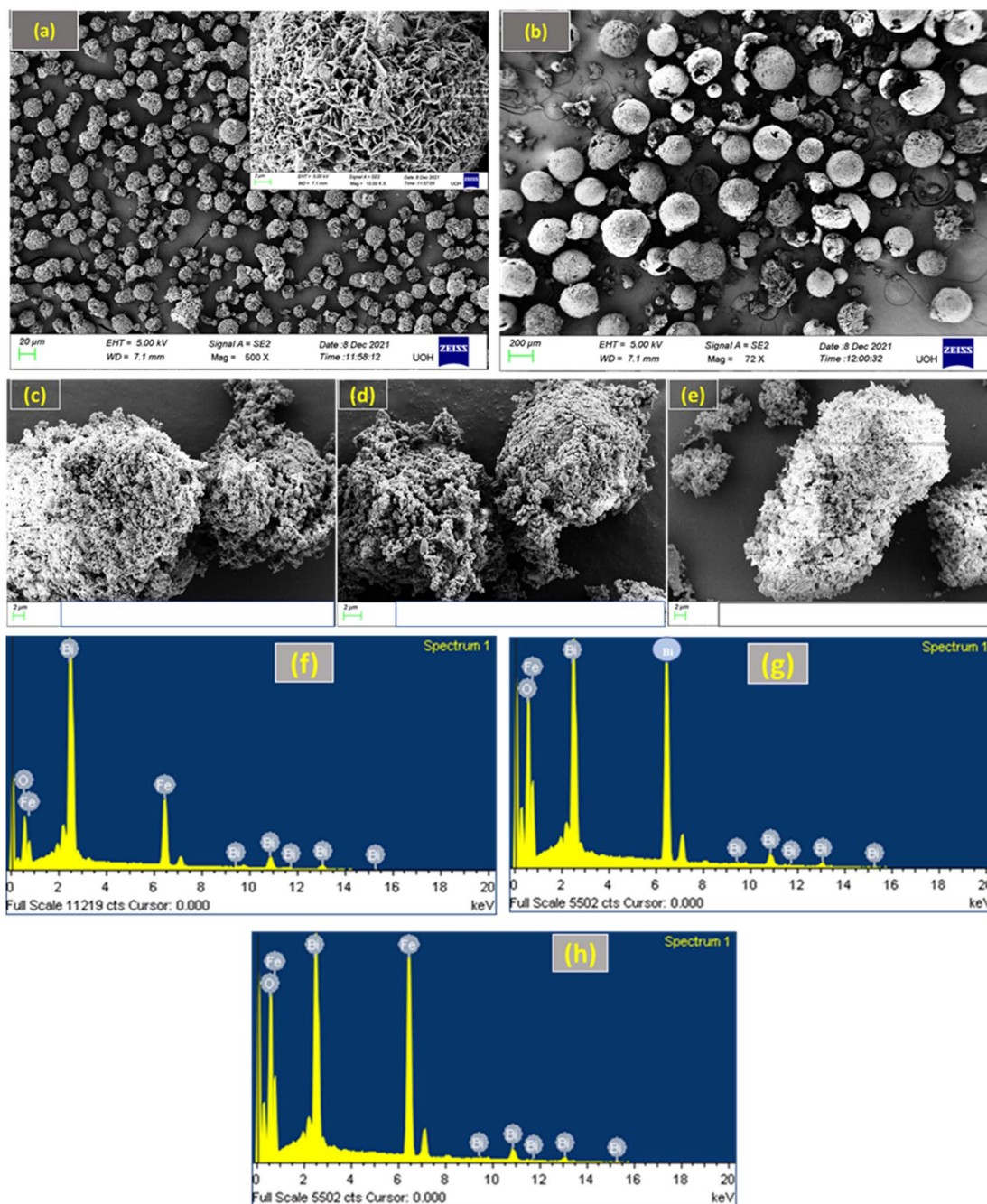


Fig. 2 FE-SEM images of (a) pure BFO, (b) pure Fe_2O_3 , (c) BFO10, (d) BFO20, and (e) BFO30, and EDAX spectra of (f) BFO10, (g) BFO20, and (h) BFO30.

light absorption is most probably due to the enhancement in the production of photo-excited electrons and holes. When we combine two different semiconducting materials, there will be heterojunction formation at the interface due to the coupling of the two different energy band gaps. Due to the Schottky effect, there will be inhibition of the transformation of hole–electron pairs from one semiconductor to another, which results in a reduction in the hole–electron recombination rate; thus, there is an enhancement in the light absorption property of the material. Every material from the BFO– Fe_2O_3 composite will provide a high number of photoexcited electrons and holes and

produce a high number of oxidation and reduction reactions, resulting in reactive species production. This results in an increment in the photocatalytic activity of any material. The obtained band energies of these composites, BFO10 (570 nm), BFO20 (579 nm), and BFO30 (620 nm), were 2.17, 2.14, and 2.0 eV [Table 1]. According to the results of the bandgap studies, the energy band gap of these composites is smaller than that of the pure phase BFO, which might be because two semiconductors' interfaces combine two different energy band gaps. This study observed that BFO30 has a higher absorption of light in the visible range with a lower bandgap than the other

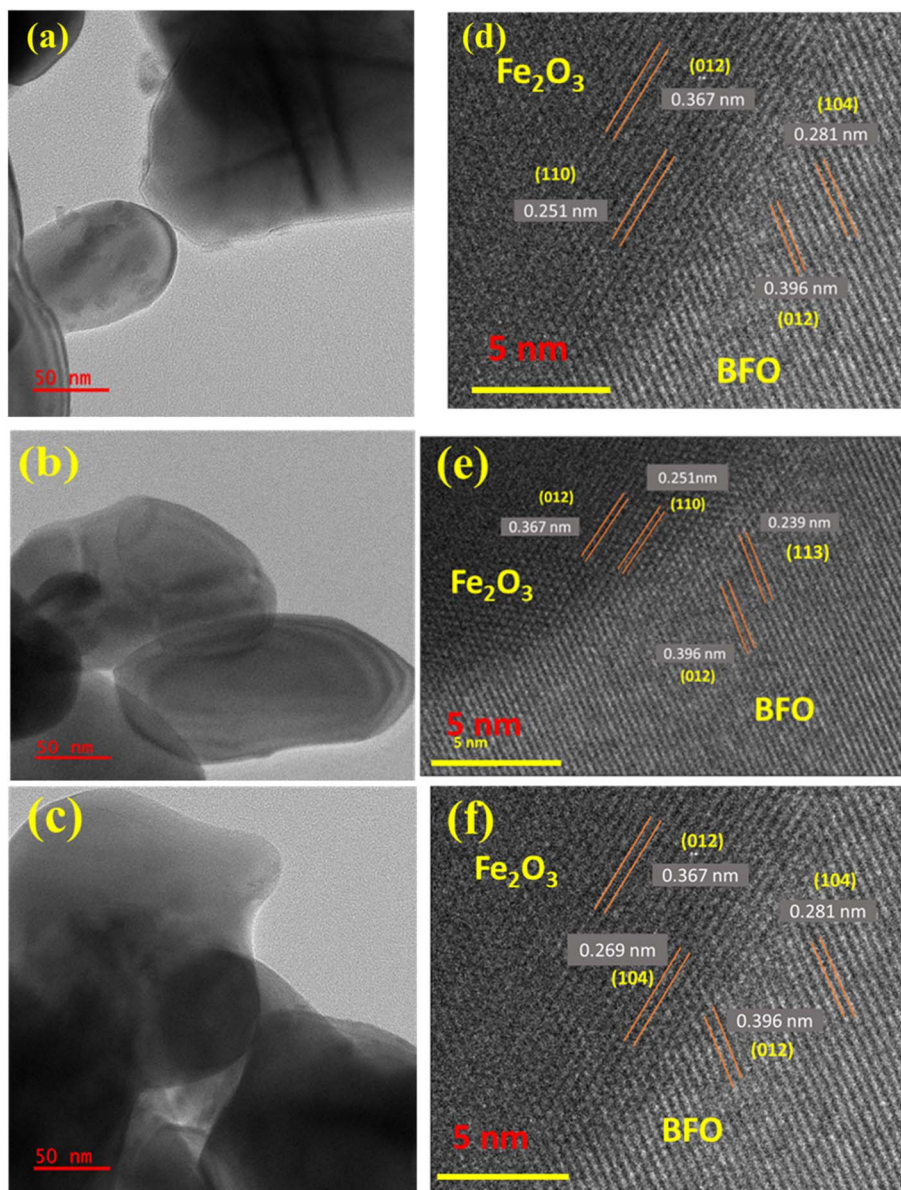


Fig. 3 TEM images of (a) BFOF10, (b) BFOF20, and (c) BFOF30 and HRTEM images of (d) BFOF10, (e) BFOF20 and (f) BFOF30.

two (BFOF10 and BFOF20) and is expected to produce a higher number of photogenerated electron holes. Using Tauc's plot, we calculated the optical band edges as follows:

$$(\alpha h\nu) = A(h\nu - E_g)^n$$

α is the absorption coefficient, E_g represents the energy band gap, A is constant, and depending on transition, we have to consider n values.

- Directly permitted transitions, $n = 1/2$.
- Directly forbidden transitions, $n = 3/2$.
- Permitted indirect transitions, $n = 2$.
- Indirect prohibited transitions, $n = 3$.

5.5. Photocatalytic activity of BFO-Fe₂O₃ composites

Fig. 5 displays the photocatalytic capabilities of BFO, Fe₂O₃, and BFO-Fe₂O₃ composites under heavy sunlight. The complete degradation of MB using the BFO, Fe₂O₃ and BFO-Fe₂O₃ composite took 70 minutes to complete. The equation for calculating the performance of the photocatalyst is given below. C_0 is an initial concentration of MB, and C_t is the concentration at time t .

$$\text{Efficiency} = \frac{C_0 - C_t}{C_0} \times 100$$

After adding 10% Fe₂O₃ [BFOF10], we observed less degradation (72%) in the MB solution compared to the other two composites [BFOF20, BFOF30]. The photocatalytic efficiency of

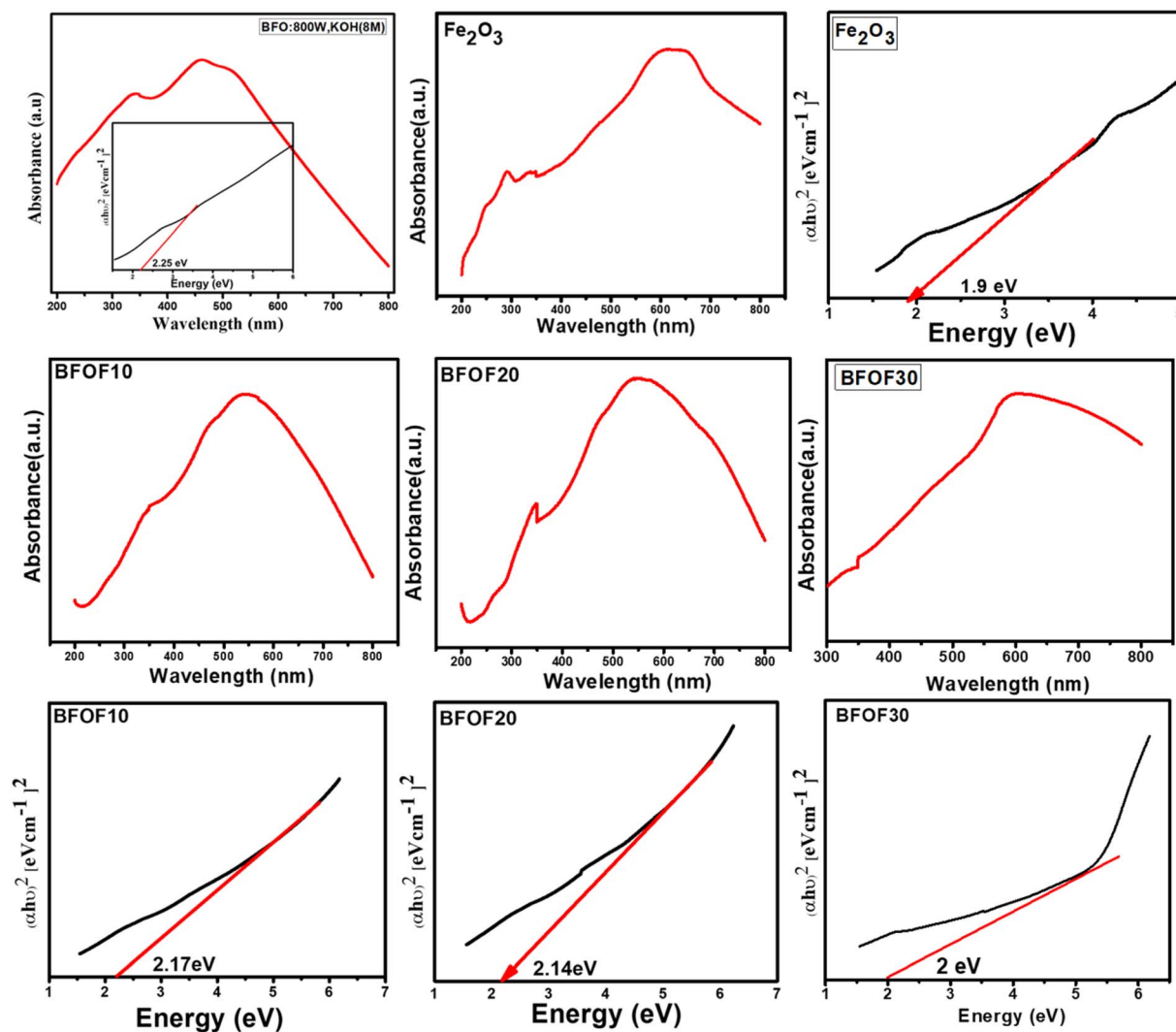


Fig. 4 UV-vis absorption spectra and energy band gaps of Fe_2O_3 , BFOF10, BFOF20, and BFOF30.

Table 1 Band energies obtained from optical property studies

S. no	Sample	The band gap (eV)
1	BFO	2.25
2	Fe_2O_3	1.9
3	BFOF10	2.17
4	BFOF20	2.14
5	BFOF30	2.0

BFOF20 and BFOF30 has increased to 86, and 94%, respectively. The increased photocatalytic performance of the samples BFOF20 and BFOF30 demonstrates how efficiency increased for higher concentrations of Fe_2O_3 . The composite's microstructural characteristics may cause this improvement in photodegradation efficiency. The BFO surface is entirely coupled with Fe_2O_3 in this situation (BFOF20 and BFOF30), making it easier for the light to form electron-hole pairs at the BFO- Fe_2O_3

surface, and also the band gaps of BFOF20 and BFOF30 are narrower than that of the pure BFO sample. As a result, their photocatalytic efficiency is improved. In this photodegradation test, the composites demonstrated significantly higher photodegradation efficiency than pure phase BFO, demonstrating the ability of these composites to degrade MB in sunlight.

5.6. Effect of photocatalyst concentration on efficiency

The degradation of MB dye was carried out at a constant dosage of 10 mg L^{-1} using different composites of BFOF10, BFOF20, and BFOF30 at different catalyst dosages (10, 20, 30 and 40 mg). The catalyst dosage, the initial dosage of dye, the type of dye, the pH value of the dye, and most microstructures of the catalysts were all factors that affected the dye degradation.⁴⁹ Fig. 6 demonstrates that the catalyst concentration significantly impacts the photodegradation efficiency by showing that the photodegradation efficiency of MB decreases as the catalyst concentration increases (all values obtained are presented in Table 2). According to the literature, microstructure, pH level,

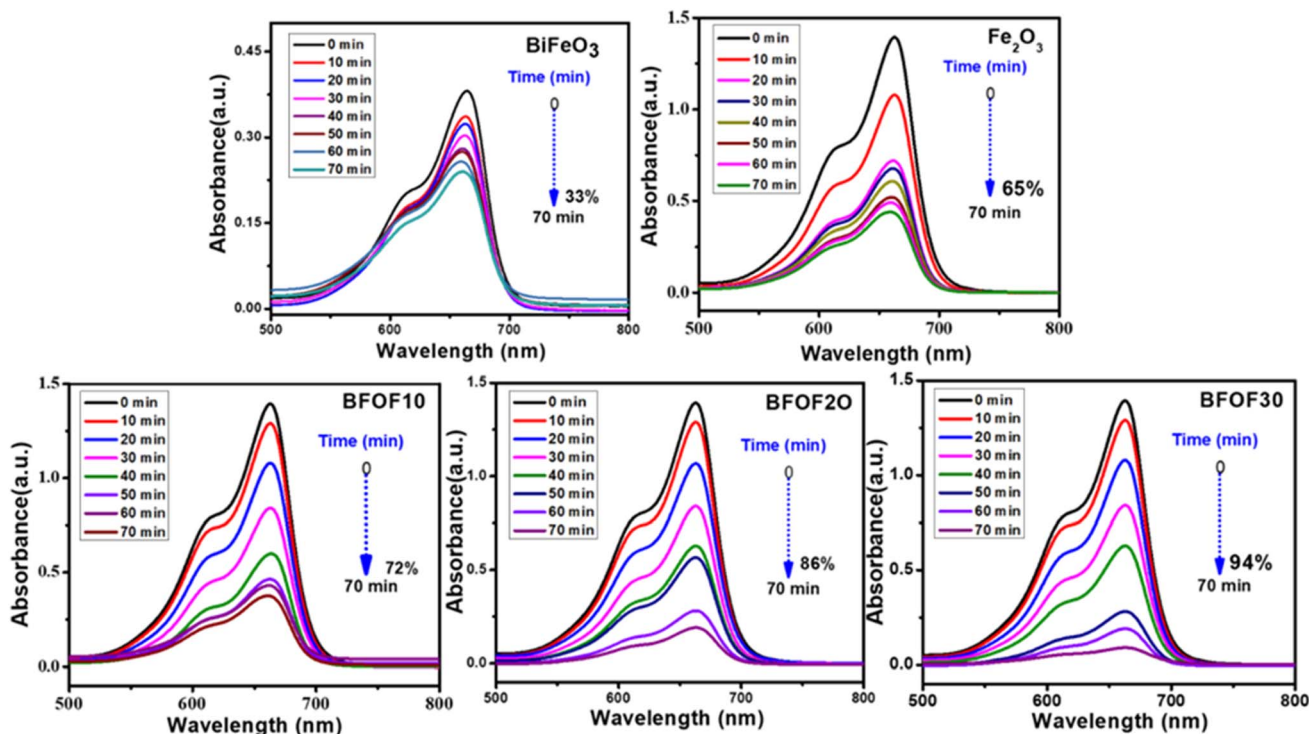


Fig. 5 Time dependent UV-vis spectral changes of methylene blue in the presence of BFO, Fe_2O_3 , BFOF10, BFOF20, and BFOF30.

dye concentration, and other factors significantly impact photodegradation efficiency.^{49–52}

5.7. Stability and magnetic recovery of photocatalysts

The catalyst stability of the most active powders, BFOF20 and BFOF30, was investigated by recycling them for four cycles. Fig. 7 shows no difference in the photodegradation efficiencies of the BFOF20 and BFOF30 catalysts for the first two cycles. Only a 6% and 4% decline in the efficiency of BFOF20 and BFOF30, respectively, is visible after four cycles, demonstrating the stability of the suggested catalysts for the first four cycles.

The magnetization curves for the composites and the pure phase BFO and Fe_2O_3 are shown in Fig. 8(a) and (b). Compared to BFO (1.25 emu g^{-1}), the magnetization value of BFO– Fe_2O_3 composites increases with increasing Fe_2O_3 content (1.84 emu

Table 2 Influence of catalyst dosage (mg) on photodegradation (%)

Catalyst name	Catalyst dosage (mg)	Degradation (%)
BFOF10	10	54
	20	62
	30	68
	40	72
BFOF20	10	58
	20	62
	30	75
	40	86
BFOF30	10	71
	20	76
	30	89
	40	94

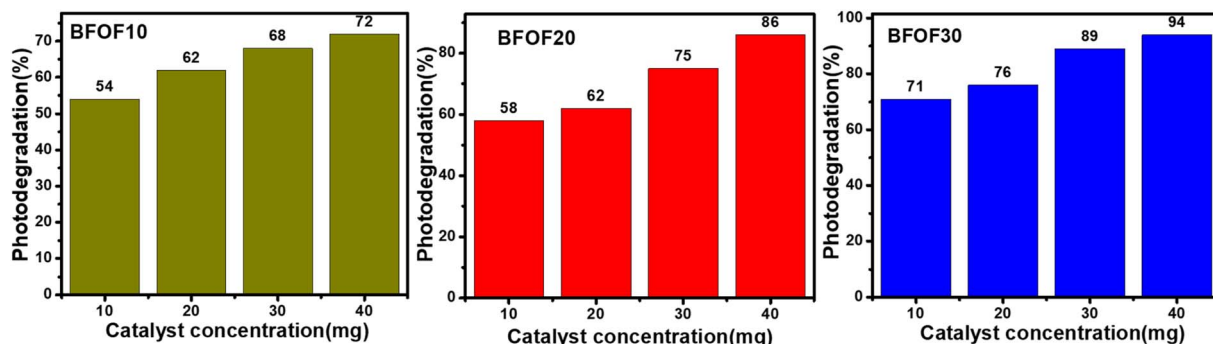


Fig. 6 Effect of photocatalyst dosage on the photodegradation efficiency of composites BFOF10, BFOF20, and BFOF30.

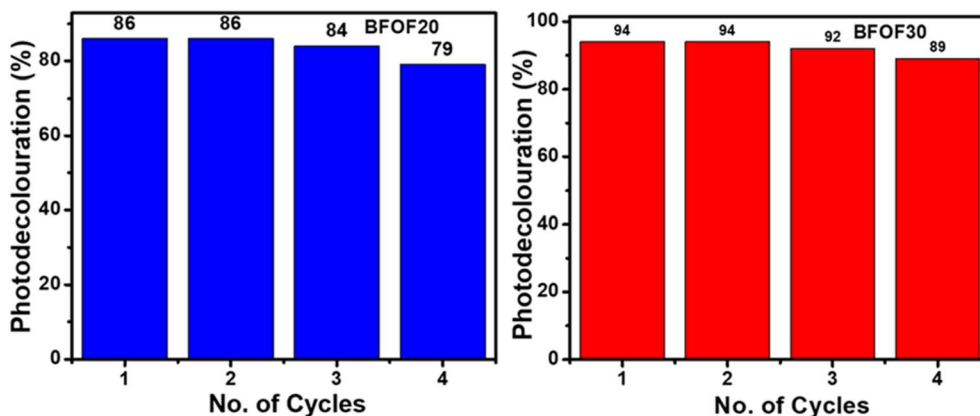


Fig. 7 Photodegradation efficiency of composites BFOF20 and BFOF30 after four cycles.

g^{-1}). The most efficient sample, BFOF30, had a maximum magnetism of $1.58 \text{ emu } g^{-1}$, which is adequate for magnetic recovery. Fig. 8(c) displays the magnetization values for the prepared samples. The improvement in the magnetization value of BFOF composites is due to the presence of magnetic phase Fe_2O_3 in the BFO phase.

We have tested the magnetic recovery property of BFOF30 since it is the most efficient catalyst among the three BFO- Fe_2O_3 composites. As shown in Fig. 9, using a magnetic field enables us to recover the BFOF30 catalyst quickly since it has an excellent magnetic response to the applied magnetic field. A permanent magnet is used to study the magnetic recovery of the

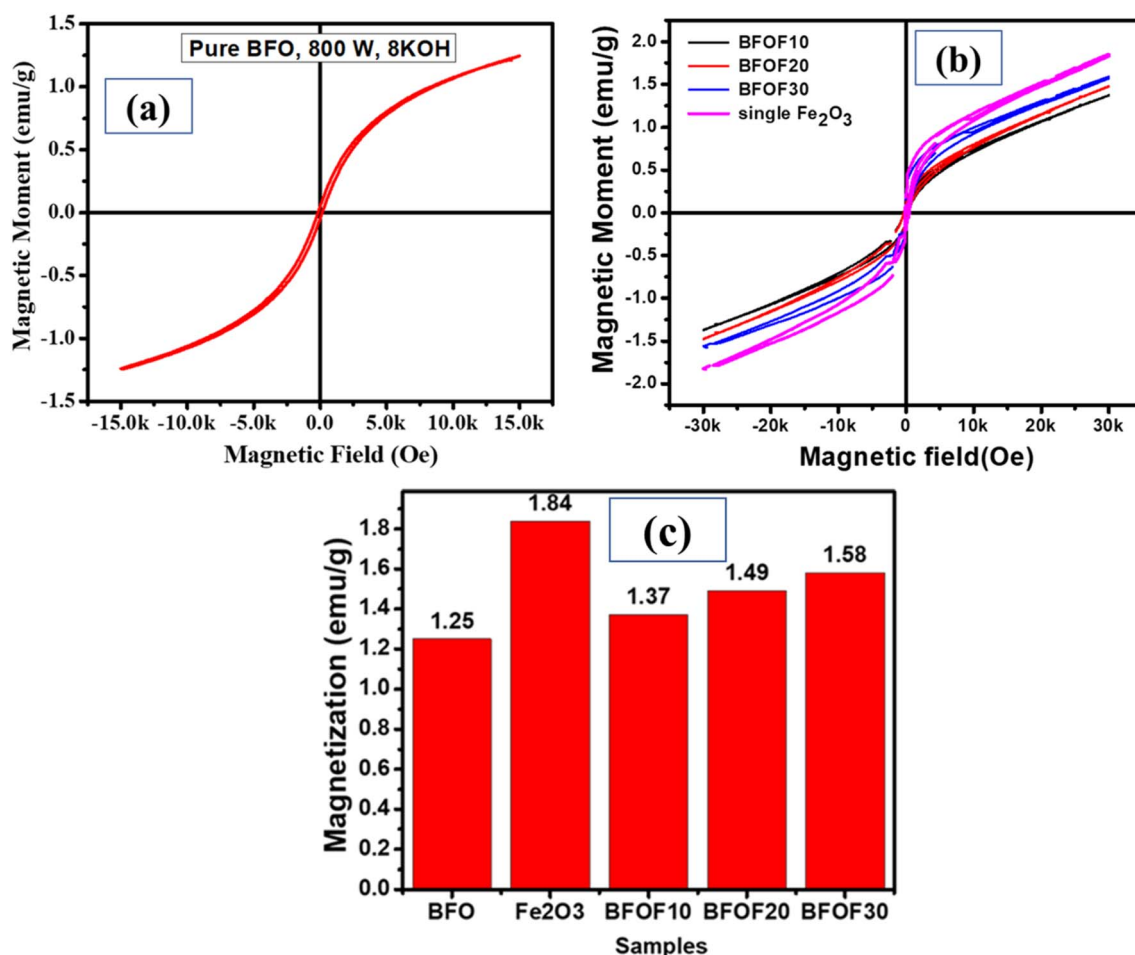


Fig. 8 Magnetic properties of (a) pure BFO, (b) Fe_2O_3 , and the BFO- Fe_2O_3 composite and (c) magnetization values of pure phase BFO, Fe_2O_3 , and the BFO- Fe_2O_3 composite.

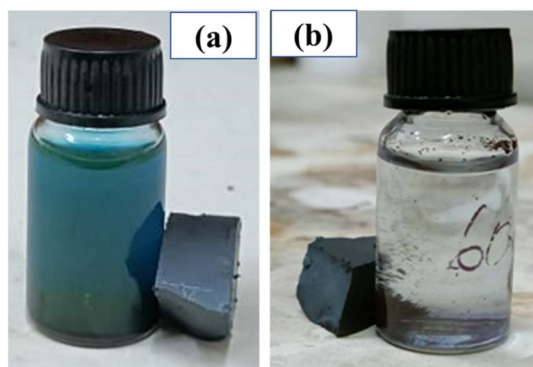


Fig. 9 Methylene blue solution post-photocatalytic test for pure (a) BFO and (b) BFOF30 and their magnetic recovery.

BFO and BFOF30 catalysts from the MB solution by applying a 1.5 T magnetic field for 6 minutes. Fig. 9(a) highlights how pure-phase BFO magnetic responses fail to recover particles when magnetic fields are applied after the photodegradation experiment. Therefore, additional filtering or centrifugation is required to separate the pure-phase BFO catalyst from the MB solution.

To study the magnetic recovery of the most effective photocatalyst, BFOF30, we have applied the magnetic field, as shown in Fig. 9(b). Fig. 9(b) shows that BFOF30 could be recovered when applying a magnetic field, confirming its excellent magnetic recovery. It is essential to highlight that the BFOF30 magnetic response is strong for recovering particles by applying magnetic fields, indicating no further filtering or centrifugation methods are required. The results of these stability and recovery studies indicate that the stability and magnetic recovery properties of BFO improved when hollow spherical Fe_2O_3 was added to BFO.

At the beginning and end of the photocatalytic process and recovery test for BFOF30, XRD was used on the BFOF30 powder

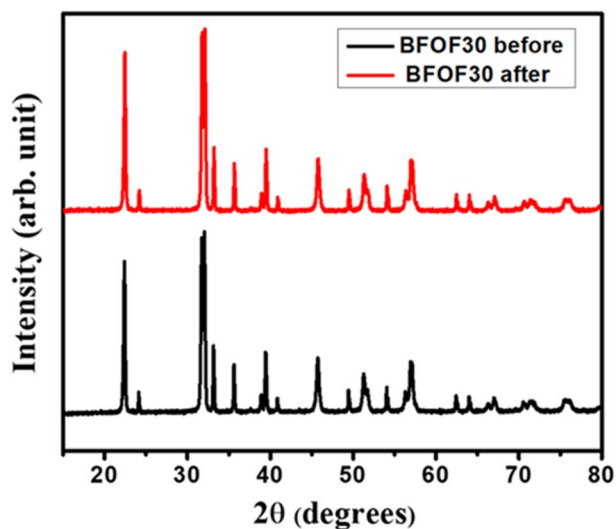


Fig. 10 XRD patterns of the BFOF30 composite pre and post photocatalytic tests for BFOF30.

to determine if it could be recovered. Fig. 10 shows the XRD patterns of BFOF30 pre- and post-degradation of MB. For the BFOF30 catalyst used in the photocatalysis experiment, we found no variations in the XRD patterns or traces from MB. Therefore, magnetically recovered BFOF30 catalysts maintain their original structural features, improving their reuse potential.

5.8. Conclusion

In summary, $\text{BiFeO}_3\text{-Fe}_2\text{O}_3$ composites were successfully synthesized by a microwave-assisted co-precipitation method for MB degradation. UV-vis absorption spectroscopy and microstructural analysis demonstrate that micro interfaces between BFO and Fe_2O_3 microspheres can alter band gaps and change work functions at their surface. Due to this, it is simpler to form electron-hole pairs and more difficult for them to recombine. In the best results, BFOF30 showed 94% degradation of MB after 70 minutes of exposure to sunlight. According to the magnetic study, BFOF10, BFOF20, and BFOF30 phases have the highest magnetization values compared to pure phase BFO. A stability and recovery test showed that the photocatalyst BFOF30 could be recovered and reused at least four times with an average efficiency reduction of 4%. Therefore, the $\text{BFO-Fe}_2\text{O}_3$ composites display enhanced photocatalytic efficiency when a direct Fenton-like mechanism and an electron drain process coexist.

Conflicts of interest

There are no conflicts to declare.

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