



Use of Treated Fly Ash in the Design of a $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ Nanocomposite Photocatalyst for Dye Removal from Aqueous Solutions

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Abstract

A visible-light photocatalyst for methyl orange (MO) degradation was synthesised and evaluated as a $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ magnetic nanocomposite. Treated fly ash, a byproduct of a power plant, was employed as mesoporous support to facilitate the adhesion of the dye to the surface and the dispersion of the active sites. BiOCl was the shell that reacted to visible light, graphene oxide allowed charges to move easily between the two materials and Fe_3O_4 enabled the use magnets to recover the material. Structural analyses revealed the formation of a stable core/shell heterojunction with soft magnetic properties. Under ideal conditions, MO was completely decolorised in 45 min, a process that followed pseudo-first-order kinetics. After 90 min of irradiation, 92.4% of the total organic carbon had been removed, indicating substantial mineralisation aside from adsorption. The photocatalyst exhibited stability after three applications and could be recovered with a magnet. The integration of fly ash valorisation and visible-light photocatalysis is a sustainable approach for wastewater remediation in a circular economy, as evidenced by the current findings.

Keywords: $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$; visible light photocatalysis; fly ash; methyl orange degradation; core/shell heterojunction; magnetic nanocomposite; advanced oxidation processes (AOPs); wastewater treatment

1. Introduction

Rapid industrial expansion has considerably diminished the availability and safety of water resources globally, posing a serious environmental challenge [1], [2]. Water resources are extensively utilised in textile and related industries [3]. Synthetic dyes are one of the most persistent types of water pollutants. Annually, thousands of tons of chemicals used in dyeing are dumped into natural bodies of water, damaging the environment and public health [4]. Numerous studies have linked dye-contaminated wastewater to mutagenic and carcinogenic effects resulting from the formation of stable aromatic intermediates [5], [6]. Concerns about dyes arise from their potential to harm marine

life, hinder photosynthesis and disrupt ecosystem balance [7]. Some traditional treatment methods that do not mineralise enough, generate secondary waste or work well in real wastewater matrices that contain salts and surfactants are adsorption, coagulation–flocculation, membrane filtration, biological degradation and chemical oxidation [8]–[10].

Advanced oxidation processes can quickly remove colour, but they do not always guarantee that all intermediate species will be completely broken down by oxidation. These limitations reveal that the need for treatment technologies that combine high degradation efficiency, deep mineralisation, ease of use and long-term cost effectiveness. Heterogeneous semiconductor

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photocatalysis has recently emerged as a viable method for the degradation of persistent organic pollutants via oxidation [11]–[13].

Many common photocatalysts, such as TiO_2 , have wide band gaps (>3 eV), so they work well when exposed to UV light [14], [15]. The majority of recent research has focused on materials that respond to visible light and can use a wide range of the solar spectrum [16]–[18]. Layered bismuth oxyhalides (BiOX , $X = \text{Cl, Br, I}$) have elicited substantial attention because their internal electric field and anisotropic crystal structure that make it easy for charges to move in one direction and for carriers to separate [19], [20]. Heterojunction engineering strategies have been widely used to combine BiOCl with conductive and/or magnetic materials to improve charge separation at the interface and allow the recovery of the catalyst [21]. In these heterostructures, an internal electric field forms at the interface, making photogenerated electrons and holes move in a certain direction. This situation inhibits recombination and extends the lifespan of the carriers. In addition, the fact that charge carriers are spread out in space allow multistep redox reactions to occur on the surface of the catalyst, creating reactive oxygen species (ROSs), such as superoxide radicals ($\bullet\text{O}_2^-$), hydroxyl radicals ($\bullet\text{OH}$), hydrogen peroxide (H_2O_2), electrons (e^-) and holes (h^+), that are made by light. These species work together to oxidise organic pollutants and convert them into minerals [22].

Graphene oxide (GO) is a good electron mediator because of its π -conjugated structure and its numerous functional groups that contain oxygen. Consequently, electrons can traverse surfaces efficiently, thus reducing recombination losses [23], [24]. Magnetite (Fe_3O_4) can separate magnetic

materials and change $\text{Fe}^{2+}/\text{Fe}^{3+}$, which can help create ROS when light is present [25]. Photocatalysis works well with heterojunction systems that contain Fe_3O_4 , GO and BiOCl [26]. However, these structures mostly work to separate charges and recover magnetic properties. They do not improve adsorption nor increase the value of waste.

Fly ash (FA), a major by-product of thermal power plants, is a serious problem in environmental management. Composed primarily of silica and several metal oxides [27], [28], FA has natural porosity and surface functionality that allow it adsorb organic pollutants when it is treated properly [29], [30]. Recently, researchers have examined FA-supported magnetic and multicomponent photocatalysts to take advantage of synergistic adsorption–photocatalytic interactions. Table 1 shows a comparison of some common FA-based and heterojunction magnetic nanocomposite (MNC) devices that have been documented in the last few years. Most modern systems still have a binary or ternary design, but they work well in degradation. They often focus on one of the following functions: charge separation, adsorption enhancement and magnetic recovery. Instead of combining these functions into a single hierarchical structure, they focus on one.

The current study systematically tests how well the system works in breaking down and mineralising methyl orange (MO) when exposed to visible light. Special attention is given to identifying reactive species, studying their kinetic behaviour, validating the results statistically and checking if the system can be reused. This work contributes to the development of sustainable photocatalytic platforms for wastewater treatment by valorising treated FA as a functional structural component.

Table 1,
Comparison of photocatalytic degradation efficiencies reported in recent studies

Photocatalyst	Light source	Pollutant	Reaction time (min)	Degradation efficiency (%)	Ref.
$\text{MnFe}_2\text{O}_4/\text{CFA}$	Sunlight	Methylene blue	30	99.9%	[31]
$\text{CFA-ZnFe}_2\text{O}_4$	UV light	Methyl orange	60	97%	[32]
$\text{GO/ZnO/Fe}_2\text{O}_3/\text{ZnFe}_2\text{O}_4$	Visible light	Methyl orange	180	98%	[33]
BiOCl/rGO	Visible light	Methyl orange	80	99.07%	[34]
$\text{Fe}_3\text{O}_4/\text{BiOCl}$	Sunlight	Rhodamine B	90	100%	[35]
$\text{BiOCl/Fe}_3\text{O}_4$	Sunlight	Carbamazepine (CBZ)	120	90.3%	[36]
$\text{TiO}_2/\text{fly ash}$	Visible light	Methylene blue	180	100%	[37]
$\text{TiO}_2@\text{GO}$	UV light	Rhodamine B	25	100%	[38]
$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{BiOCl}$	Sunlight	Rhodamine B	60	95%	[39]
$\text{CFA-CuFe}_2\text{O}_4$	UV light	Methyl orange	60	98%	[40]
$\text{BiOI/Fe}_3\text{O}_4@\text{GO}$	Visible light	2,4 dinitrophenol	100	99%	[17]
$\text{Fe}_3\text{O}_4@\text{BiOCl}@\text{GO}$	Visible light	Methyl orange	120	100%	[26]

2. Materials and Methods

2.1 Materials

The following materials were used in this study: sodium chloride (NaCl, 99.9%; RCI Labsacan Limited, Thailand), sodium dodecyl sulfate (SDS, $C_{12}H_{25}SO_4Na$, 99.9%; Direvo Industrial Biotechnology, Germany), sodium hydroxide (NaOH, 99.88%; BDH Limited, England), ammonia solution ($NH_3 \cdot H_2O$, 25%; Thomas Baker, India), ethanol (C_2H_5OH , 99.9%; RCI Labsacan Limited, Thailand), sulfuric acid (H_2SO_4 , 98%; Thomas Baker, India), nitric acid (HNO_3 , 69–72%; Sigma-Aldrich, China), hydrogen peroxide (H_2O_2 , 35%; Panreac, China), sodium nitrate ($NaNO_3$, 99%; RCI Labsacan Limited, Thailand), potassium permanganate ($KMnO_4$, 99%; CDH, India), graphite powder (C, 99.5%; Sigma-Aldrich, China) and chloroform ($CHCl_3$, 99%; CDH, India). All reagents were of analytical grade and used as received without further purification. Deionised water was employed throughout all experimental procedures.

2.2 Synthesis of Fe_3O_4 Magnetic Nanoparticles

The co-precipitation method was used to create Fe_3O_4 magnetic nanoparticles (MNPs). In 100 mL of deionised water, a $2Fe^{3+}:1Fe^{2+}$ molar ratio was combined. Before the suspension was heated to 60 °C, the solution was heated to 60 °C whilst being stirred continuously. NaOH in water was added drop by drop until basic pH was reached. After the resulting black magnetite precipitate was collected magnetically, the solid was cleaned three times by using distilled water and ethanol alternately. The product was dried for 16 h at 60 °C to obtain 0.35 g of Fe_3O_4 MNPs [41], [42].

2.3 Preparation of the Fly Ash Sample

FA generated at the Al-Musayyib Thermal Power Station in Iraq represents a persistent disposal concern because the facility produces approximately 5,000 t of ash annually, but its available storage capacity is limited. Material characterisation showed that the ash had about 6.8 wt.% silicon and a high ignition loss, indicating that it contained volatile components and leftover carbon [43]. The first step was to heat 10 g of raw FA for 3 h at 900 °C in a vacuum oven (P 330, Nabertherm, Germany). In the second step, the calcined material was mixed with 100 mL of 3.5 M

hydrochloric acid and stirred for 3 h after it had cooled to room temperature [44]. Third, after the suspension was filtered, the left-over solid was washed with deionised water several times until the pH level was neutral. Finally, the modified FA that was used to create the photocatalyst composite was dried at 120 °C for 12 h.

2.4 Preparation of Graphene Oxide

GO was synthesised using a modified Hummers method. Graphite flakes (0.75 g) and $NaNO_3$ (0.375 g) were added to 17.25 mL of concentrated H_2SO_4 under stirring in an ice bath. $KMnO_4$ (2.25 g) was introduced slowly whilst maintaining the temperature below 20 °C. The mixture was then stirred at 35 °C for 30 min. Deionised water (34.5 mL) was added carefully, causing the temperature to rise to ~98 °C, which was maintained for 15 min. After cooling, 0.75 mL of 35% H_2O_2 and 105 mL of deionised water were added. The product was washed repeatedly with deionised water and dried to obtain GO powder [45].

2.5 Synthesis of $Fe_3O_4@FA$ MNC

Thermal-assisted mixing was performed to create the $Fe_3O_4@FA$ nanocomposite. Ultrasonic dispersion of Fe_3O_4 MNPs in deionised water for 10 min with a probe-type ultrasonic homogeniser (MSK-USP-12N, 1,200 W, MTI Corporation, the USA) resulted in a stable and even suspension. The mixture was stirred for an hour at 60 °C after adding pre-treated FA at a 1:1 mass ratio. An external magnetic field was employed to recover the solid product. Then, the product was cleaned with distilled water repeatedly until the pH was neutral and dried afterwards for 16 h at 60 °C. The dried composite was further calcined in air at 400 °C by using a controlled heating program with a ramp rate of 8 °C min^{-1} and a holding period of 130 min [46].

2.6 Synthesis of $Fe_3O_4@FA@GO$ MNC

$Fe_3O_4@FA$ and GO were combined to create the $Fe_3O_4@FA@GO$ nanocomposite. In this step, $Fe_3O_4@FA$ and GO were blended at a mass ratio of 4:1. GO was ultrasonically dispersed in deionised water for 20 min to obtain a stable suspension. Simultaneously, an equivalent mass of $Fe_3O_4@FA$ was dispersed in 100 mL of ethanol and subjected to 20 min of ultrasonication. The aqueous GO suspension was then continuously stirred whilst the ethanolic $Fe_3O_4@FA$ dispersion was added

dropwise. Afterwards, the homogeneous slurry was transferred to a 100 mL autoclave and maintained at 180 °C for 12 h. After cooling to room temperature, the precipitate was separated, repeatedly washed and dried at 80 °C for 24 h [47]. The finished powder was referred to as the $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}$ nanocomposite.

2.7 Synthesis of $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ MNC

$\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ MNC was synthesised through a two-step process involving the incorporation of BiOCl into pre-formed $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}$. In the first step, $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}$ (0.25 g) was ultrasonically dispersed in ethanol to achieve a uniform, stable suspension for 20 min. In the second step, precipitation was used to directly form BiOCl on $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}$ MNC. Exactly 1.40 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 20 mL of 4 M nitric acid whilst being stirred to create a clear Bi^{3+} precursor solution. Afterwards, 0.54 g of sodium chloride was added as the chloride source, and 40 mmol of SDS was added to control the morphology and growth of the particles. The solution was then mixed with the recently made $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}$ suspension (0.30 g) whilst being continuously stirred magnetically. Exactly 18 mL of deionised water and 9 mL of aqueous ammonia were added gradually to adjust the pH of the solution. The product slurry was moved to a 100 mL autoclave and processed at 180 °C for 12 h after the reaction mixture was kept at 80 °C for 4 h. The powder was collected, thoroughly cleaned with distilled water in five cycles and dried for 24 h at 60 °C after naturally cooling to room temperature [48]. Figure 1 shows the core and shell of the synthesised photocatalyst $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$.

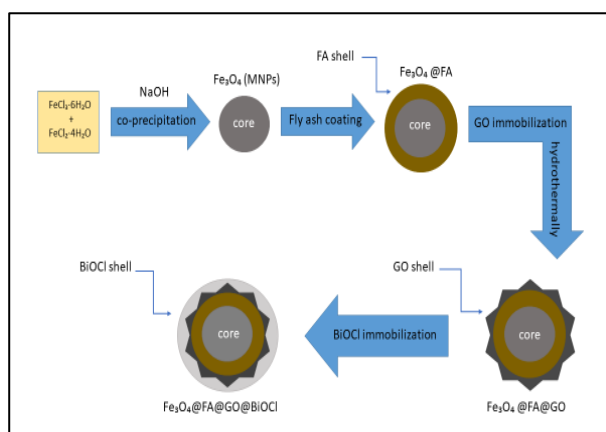


Fig. 1. Steps to prepare core/shell MNPs ($\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$) by using co-precipitation and hydrothermal methods.

2.8 Characterisation and Instrumentation

An AL-2700B X-ray diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm) was used to examine the crystallographic phases and structural purity of the photocatalysts. Diffraction patterns were obtained in a 2θ range of about 10°–160°. The instrument worked at accelerating voltages of 10–60 kV and currents of 5–80 mA. Fast scans (up to 50° min⁻¹) were employed to quickly obtain complete phase information, and slow high-resolution acquisition (0.0012° min⁻¹) was applied to view very small structural details.

Field-emission scanning electron microscopy (FESEM, ZEISS Ultra Plus) was implemented to determine the shape of the surface and the distribution of the particles. Nitrogen adsorption–desorption isotherms from a BELSORP MINI II BET analyser were employed to assess the porosity and textural properties. The Barrett–Joyner–Halenda (BJH) method was used to determine the average size of the pores. A vibrating sample magnetometer (VSM1100, Weistron, Taiwan) was utilised for magnetic property testing over a field range of ± 10 kOe to determine saturation magnetisation and coercivity. Moreover, UV-vis diffuse reflectance spectra obtained with a Hitachi U-3900H spectrophotometer were employed to determine the optical absorption properties and band gap energies, and Tauc plots were used to estimate the materials' optical band gaps.

2.9 Photocatalytic Performance

The photocatalytic activity towards MO degradation was evaluated in a batch-type system using a 500 mL Pyrex reactor. The reactor was irradiated with a visible-light assembly consisting of four 30 W xenon lamps, each providing an average light intensity of 20 mW/cm² at the reactor surface. The spatial arrangement of the lamps and the reactor geometry are schematically shown in Fig. 2. All experiments were conducted at room temperature.

During each experiment, the photocatalyst was dispersed in an aqueous MO solution. For the initial tests, 100 mL of MO solution with 20 mg L⁻¹ concentration and pH = 7.5 was prepared, and the catalyst was added at a dosage of 1 g L⁻¹. Before illumination, the suspension was magnetically stirred in the dark for 60 min to establish adsorption–desorption equilibrium. After equilibrium was reached, the reactor was irradiated for 90 min to initiate the photocatalytic reaction. Aliquots (2 mL) were withdrawn at 15 min intervals and filtered; the residual MO concentration was

determined by UV-vis spectrophotometry at 465 nm, as illustrated in Fig. 3. Degradation performance was calculated using [49]

$$D.P. \% = \frac{C_0 - C_t}{C_0} \times 100\%, \quad \dots(1)$$

where D.P. denotes degradation performance, C_0 is the initial concentration (20 mg L^{-1}) and C_t corresponds to the concentration at a given irradiation time.

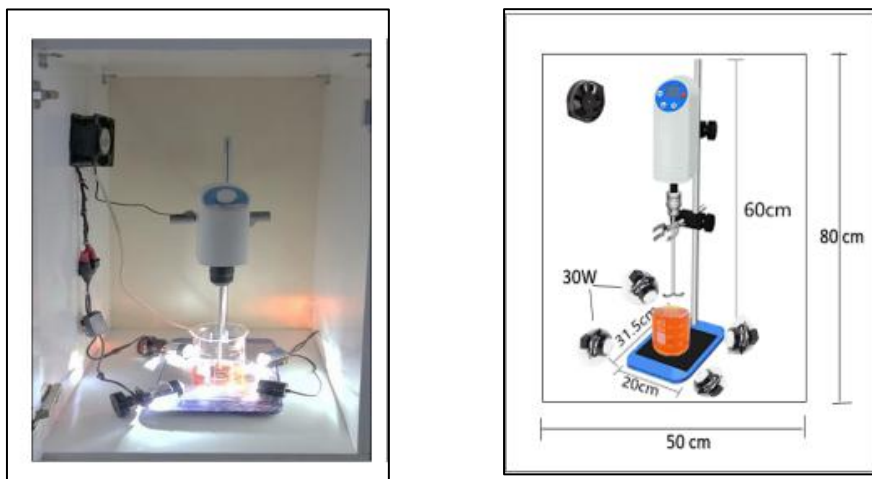


Fig. 2. Image and schematic of the photocatalytic batch reactor system for MO dye degradation under visible light irradiation.

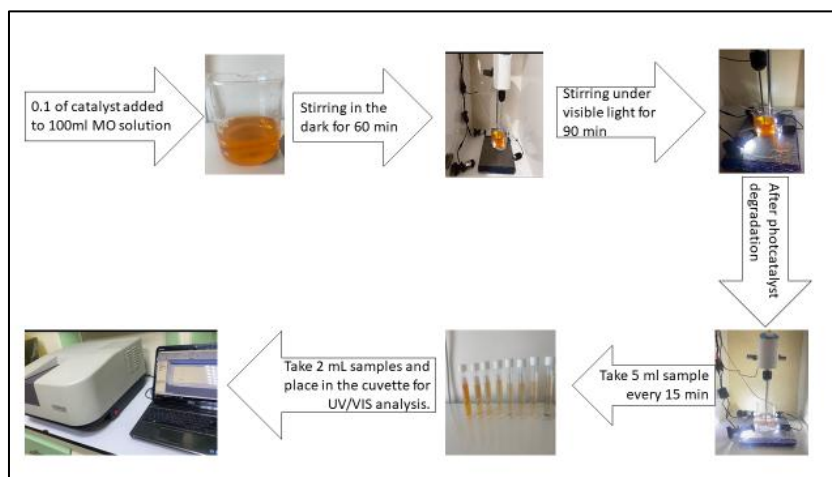


Fig. 3. Schematic of the procedure of MO dye photocatalytic degradation under a visible light source

2.10 Determination of Point of Zero Charge

The point of zero charge (PZC) of the synthesised $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ photocatalyst was determined using the pH drift method. A series of 0.01 M NaCl solutions (50 mL) was prepared, and the initial pH values were adjusted between 2 and 10 by using 0.1 M HCl or 0.1 M NaOH. Subsequently, 0.1 g of the photocatalyst was added to each solution, and the suspensions were magnetically stirred for 24 h at room temperature to reach equilibrium. The final pH values were recorded. PZC was determined from

the point where the curve of ΔpH ($\text{pH}_{\text{final}} - \text{pH}_{\text{initial}}$) versus $\text{pH}_{\text{initial}}$ intersected zero [50].

2.11 Cytotoxicity Test

A common way to test the cytotoxicity of nanomaterials stuck to membranes is to use a standard red blood cell (RBC) hemolysis assay [51], [52]. In this study, plasma was obtained from fresh human red blood cells by washing them several times in phosphate-buffered saline (PBS). Then, a 5% RBC solution was made in PBS and added to composites at different amounts (100%, 80%, 60%,

40% and 20%). The positive control (+C) was 1% Triton X-100, which caused all of the blood cells to break down. The negative control (–C) was PBS. After incubation, the absorbance of the supernatant was measured at 520 nm. The hemolysis ratio (HR%) was derived as

$$\text{Hemolysis ratio (HR\%)} = \frac{\text{OD test} - \text{OD negative control}}{\text{OD positive} - \text{OD negative control}} \times 100\%, \quad \dots(2)$$

where OD test represents the optical density measured for the sample and OD negative and OD positive correspond to PBS and the Triton-treated control, respectively.

3. Results and Discussion

3.1 Characteristics Results

3.1.1 X-ray Diffraction

Powder X-ray diffraction (XRD) was used to determine the crystalline phases present in the synthesised materials. All diffractograms in Fig. 4 exhibit six intense reflections near $2\theta \approx 30^\circ, 35^\circ, 43^\circ, 53^\circ, 57^\circ$ and 62° , which correspond to the (220), (311), (400), (511), (440) and (611) planes of the inverse-spinel magnetite lattice, respectively. The fact that these peaks are the same in the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{FA}$, $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}$ and $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ samples shows that the Fe_3O_4 core retained its crystalline structure during the coating process. The $\text{Fe}_3\text{O}_4@\text{FA}$ pattern has a small shoulder at $2\theta = 26.6^\circ$. This reflection matches the (101) plane of quartz, indicating that the FA shell contains solid SiO_2 [53]. The $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}$ sample's magnetite peaks have low intensity, revealing that the amorphous GO layer is blocking them in part. GO usually has poor crystallinity, which means that instead of sharp diffraction peaks, it has large, low-intensity humps.

Incorporation of bismuth oxychloride yielded additional reflections at $2\theta = 26.3^\circ, 33.2^\circ, 47.1^\circ, 54.7^\circ, 59^\circ$ and 77.9° , which are indexed to the (101), (200), (103), (212), (220) and (321) planes of tetragonal BiOCl , respectively. The observed peaks match the Joint Committee on Powder Diffraction Standards card for BiOCl (06-0249), indicating that the oxychloride phase precipitated in situ [54]. The XRD pattern still shows different diffraction peaks related to Fe_3O_4 . The data indicate that magnetite was the main crystal phase in $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$. The absence of extra or unknown reflections supports the idea that no impurities were added during synthesis. The

Debye–Scherrer equation was used to determine the size of the crystallite on the basis of the strongest magnetite reflection; the size was determined to be about 13 nm. This size is expected for nanoscale Fe_3O_4 domains. In general, these XRD results show that magnetite, FA, GO and BiOCl were slowly combined into a hierarchical structure and that the desired crystalline phases were retained during the creation process.

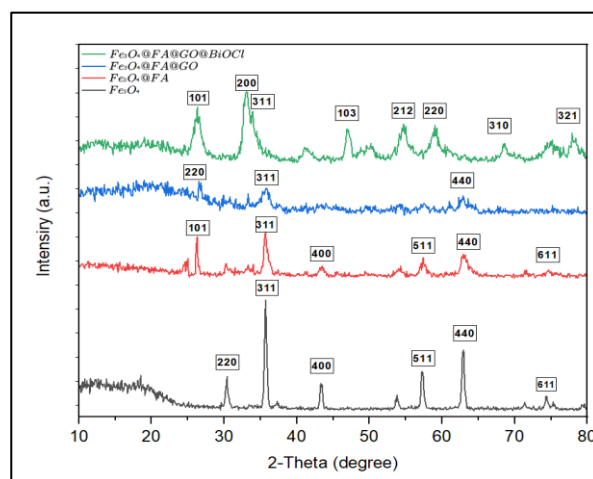


Fig. 4. XRD patterns of the synthesised MNCs.

3.1.2 Optical Characteristics of the Synthesised Photocatalysts

Diffuse reflectance spectroscopy (DRS) was employed to analyse the optical characteristics of the produced photocatalysts. Figure 5a illustrates that $\text{Fe}_3\text{O}_4@\text{FA}$ MNC displayed elevated reflectance and diminished absorption in the visible and UV spectra. This optical characteristic indicates restricted visible-light absorption, which may partially account for $\text{Fe}_3\text{O}_4@\text{FA}$ MNC's diminished photocatalytic efficiency. The optical profile of $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}$ was distinctly altered after the integration of GO. Remarkably reduced reflectance and increased absorption were noted over the visible spectrum (400–700 nm). These alterations may be associated with the π – π conjugated domains present in GO; these domains can contribute additional electronic states and facilitate interfacial charge transport, consequently influencing the reported optical band structure of MNC [33]. The $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ system exhibited the highest absorption enhancement amongst the photocatalysts analysed. A redshift in the absorption edge, extending far into the visible spectrum, was detected. The broadened spectrum response indicates improved use of visible light. The

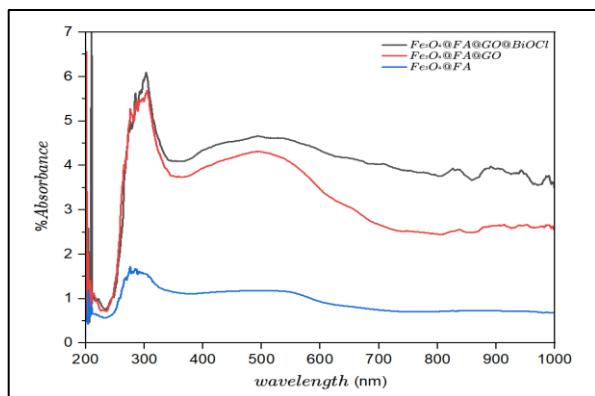
enhanced absorption properties may have been due to the synergistic interactions of GO and BiOCl within the heterostructure, modifying the electronic environment and promoting interfacial interactions. Moreover, the stratified architecture of BiOCl may enhance light absorption and charge separation during visible-light exposure [53]. The Kubelka–Munk function transforms diffuse reflectance data into absorption-equivalent values as follows:

$$F(R) = \frac{(1-R)^2}{2R} \quad \dots(3)$$

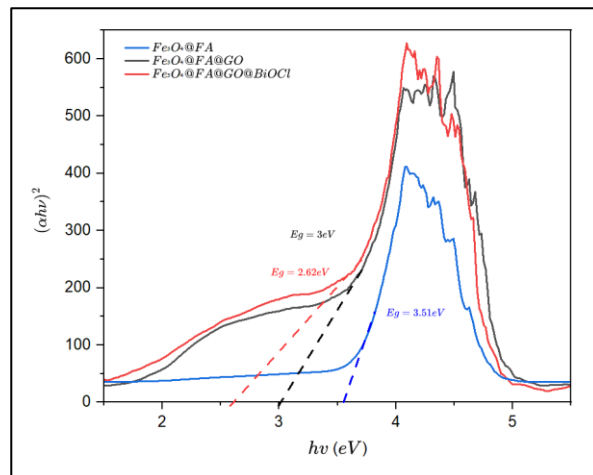
The resultant function was subsequently examined using the Tauc relation for indirect electronic transitions.

$$[F(R)h\nu]^{\frac{1}{2}} = A(h\nu - E_g), \quad \dots(4)$$

where A is a constant indicating the extent of light reflection from a surface, $h\nu$ represents the energy of a photon (eV), $F(R)$ denotes the Kubelka–Munk function and R signifies the diffuse reflectance [55]. $\text{Fe}_3\text{O}_4@FA$ displayed the highest band gap energy of 3.51 eV, with an absorption edge at approximately 353 nm, as shown in Figure 6b. The band gap diminished to 3 eV upon GO inclusion, signifying an alteration of the electrical structure. The $\text{Fe}_3\text{O}_4@FA@GO@BiOCl$ MNC had the lowest estimated band gap value (2.62 eV), indicating enhanced responsiveness to visible light. The progressive reduction in the observable band gap and the corresponding red shift in $\text{Fe}_3\text{O}_4@FA@GO@BiOCl$ MNC indicate enhanced light-harvesting efficiency. The optical characteristics align with the superior photocatalytic performance of $\text{Fe}_3\text{O}_4@FA@GO@BiOCl$ in comparison with the $\text{Fe}_3\text{O}_4@FA$ and $\text{Fe}_3\text{O}_4@FA@GO$ systems.



(a)



(b)

Fig. 5. Photocatalysts' optical characteristics: (a) UV-vis light adsorption and (b) optical band gap energy.

3.1.3 Magnetic Properties of the Photocatalysts

Room-temperature vibrating sample magnetometer (VSM) measurements (Fig. 6) revealed S-shaped hysteresis loops with a very small opening, indicative of a soft magnetic material with a superparamagnetic-like response across the series. Pure Fe_3O_4 exhibited the highest saturation magnetisation (M_s) of 60 emu g^{-1} , which is in line with the ferrimagnetic nature of magnetite. After treated FA was introduced, M_s decreased to 37.3 emu/g for $\text{Fe}_3\text{O}_4@FA$ because of dilution by the non-magnetic matrix and partial surface spin disorder at the $\text{Fe}_3\text{O}_4@FA$ interface. Subsequent incorporation of GO further lowered the magnetisation to 21.8 emu/g , representing the large fraction of the non-magnetic carbonaceous phase and enhanced interfacial exchange frustration that suppressed the net moment of surface spins. $\text{Fe}_3\text{O}_4@FA@GO@BiOCl$ showed the lowest magnetisation of 8.5 emu/g , as expected from the additional loading of diamagnetic BiOCl and the increased core/shell interfacial volume, where spin canting becomes prominent. Coercivity (H_c) and remanence (M_r) were small for all samples (narrow loop around the origin), a hallmark of superparamagnetic/ultrasoft behaviour in nanoscale Fe_3O_4 composites. Multiple photocatalytic cycles without clumping were made possible by the magnetic property. Particles move when the magnetic field is turned off, but an external magnet can quickly reconnect them for recovery after the reaction [36]. Even though M_s decreased with the non-magnetic shells (FA, GO and BiOCl), the

composites' magnetic responsiveness prevented them from mixing with water.

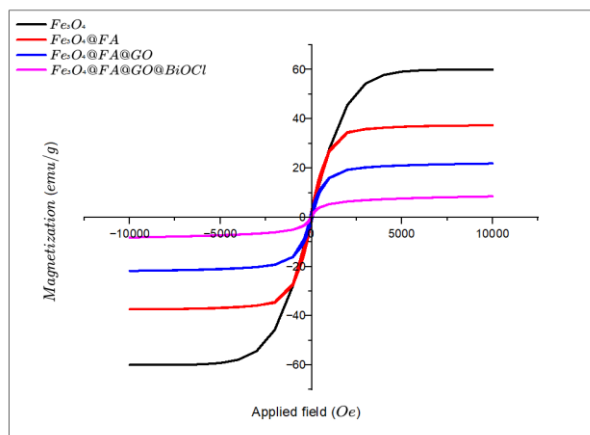


Fig. 6. Synthetic photocatalysts' magnetic hysteresis curves.

3.1.4 Scanning Electron Micrograph

Figure 7 shows the geometry and microstructure of the photocatalysts derived using FESEM and TEM. The FESEM images of the clean Fe_3O_4 nanoparticles (Fig. 7a) show that they are almost spherical and range in size from 75 nm to 200 nm. Magnetite nanoparticles frequently aggregate into substantial clusters because of intense magnetic dipole–dipole interactions that fail to provide cohesion [56]. The Fe_3O_4 clusters show that the surface was magnetic; the clusters grouped together to lower the energy of the surface. The addition of treated FA changed how the surface looked. Figure 7b indicates that $\text{Fe}_3\text{O}_4@\text{FA}$ MNC had magnetite nanoparticles all over its FA structure, which was not regular and had holes in it. FA's different textures and rough surface provided the particles a place to stick to and start to grow. This phenomenon caused the Fe_3O_4 particles to spread out more than they did in the sample that was not affected. FA's structural role as a stabilising agent decreased aggregation and encouraged magnetic phase

uniformity [57]. The corrugated GO layers made the surface area increasingly useful and prevented the magnetic particles from sticking together. GO has functional groups that contain oxygen. These groups create strong bonds between Fe_3O_4 and FA. Putting the composite together might help it absorb pollutants well [17], [26]. $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ MNC (Fig. 7d) is not exactly the same. The $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}$ framework is covered in BiOCl nanosheets that are 20–40 nm thick and look like flakes. The stacked domains create large areas where the photoactive BiOCl phase and the conductive/magnetic substrate come in contact. In the presence of light, this helps charges move and stay apart.

TEM (Fig. 7e) was employed to examine $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ MNC. The TEM picture is dark because the atomic number difference in the Fe_3O_4 core is large, which means that this area has many electrons. FA, GO and BiOCl create light, semi-transparent layers around these dark spots. The thick parts in the middle and the tiered structure around them make the design look like it is made up of different parts. Layered structures that are about 30–50 nm thick can be created by placing BiOCl nanosheets on top of the composite structure. Individual lattice fringes cannot be seen at this level of magnification, but the interface is smooth enough that the phases can touch each other tightly.

Moreover, statistical analysis of several SEM micrographs (Fig. 8) was conducted to assess how the particles were spread out by size. The average size of the 102 particles was 83.34 nm, with a standard deviation of 67.15 nm. The sizes ranged from 4.01 nm to 286.64 nm, with an average size of 60.01 nm. The histogram's right-skewed shape indicates that most of the particles were less than 100 nm in size, and only a few aggregates were large. This statistical study supports the microstructural findings that the composite is mostly made up of nanoscale domains with approximately the same size.

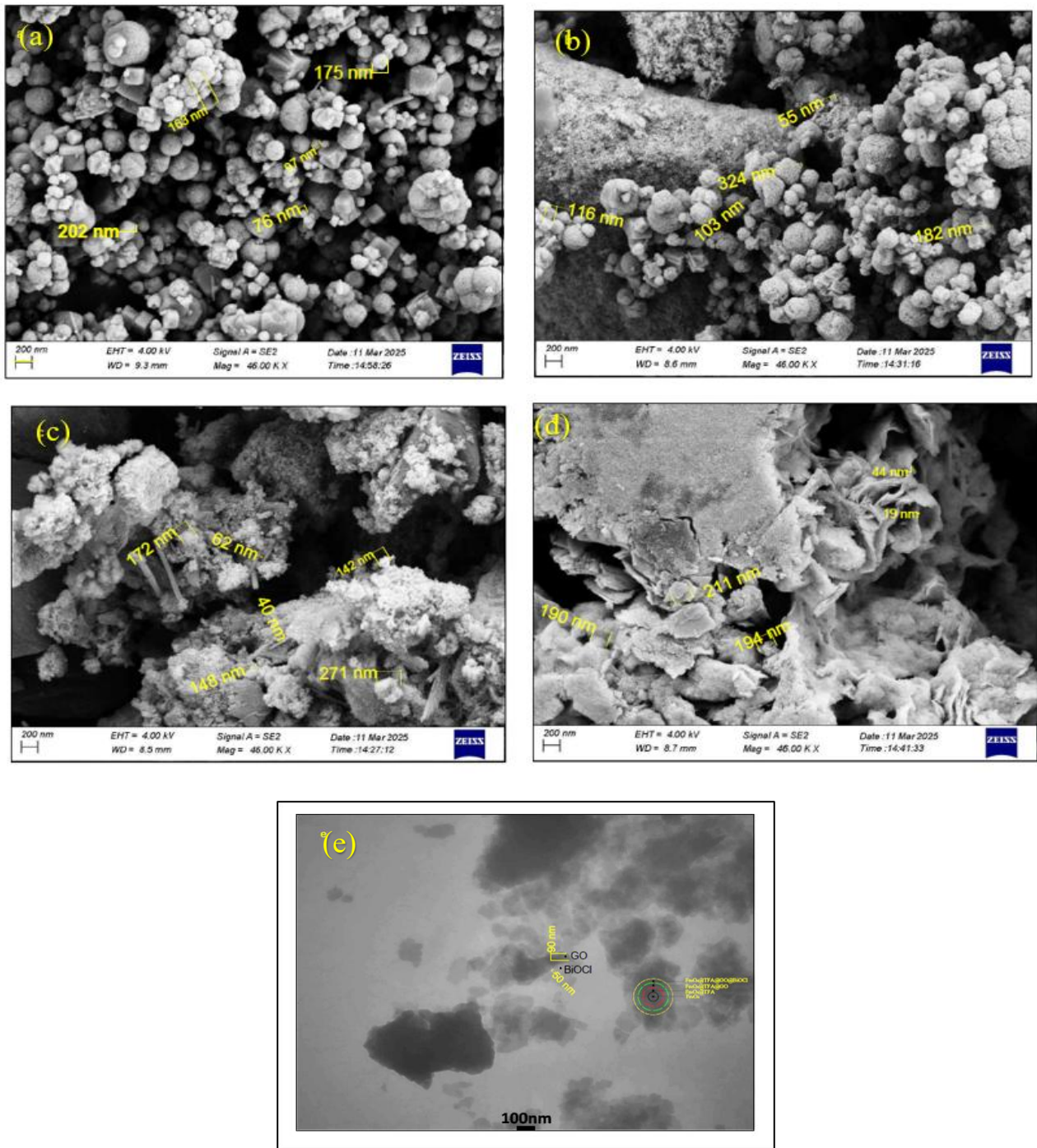


Fig. 7. TEM and FESEM of the photocatalysts. (a) SEM of Fe_3O_4 , (b) SEM of $\text{Fe}_3\text{O}_4@FA$, (c) SEM of $\text{Fe}_3\text{O}_4@FA@GO$, (d) SEM of $\text{Fe}_3\text{O}_4@FA@GO@BiOCl$ and (e) TEM of $\text{Fe}_3\text{O}_4@FA@GO@BiOCl$.

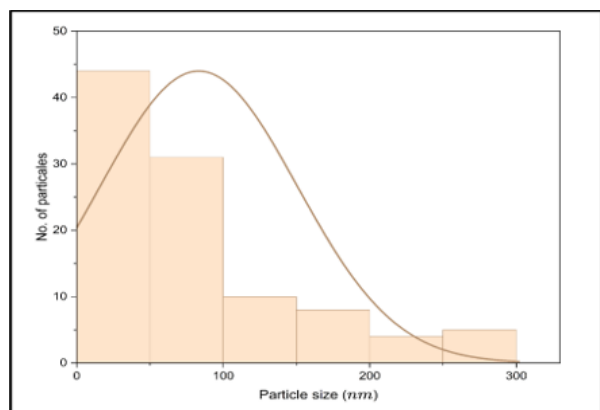


Fig. 8. Histogram of the $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ nanocomposite.

3.1.5 Surface Area and Porosity Analysis

Examination of the surface area and porosity was also conducted. The nitrogen adsorption–desorption isotherm of $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ MNC (Fig. 9) shows a type IV isotherm with an H3 hysteresis loop, which is a common feature in mesoporous materials. These materials usually have plate-like particles that stick together or nanosheets that are stacked on top of each other [58]. The gradual rise in adsorption at high relative pressures ($P/P_0 > 0.6$) suggests that mesopores existed between the particles. The FA-supported Fe_3O_4 framework holds the BiOCl nanosheets and GO layers together to make these pores. The Brunauer–Emmett–Teller (BET) specific surface area is $19.65 \text{ m}^2 \text{ g}^{-1}$, the total pore volume is $0.0526 \text{ cm}^3 \text{ g}^{-1}$ and the average pore width is 10.7 nm. The surface area is smaller than that of silica-based materials that are highly porous, but the pore diameter is in the mesoporous range (2–50 nm), allowing dyes to easily spread in water. The BET value is slightly smaller than the Langmuir surface area ($28.22 \text{ m}^2 \text{ g}^{-1}$), indicating that the surface is not uniform and has substantial microporosity.

The BJH pore size distribution, shown in Fig. 10, has a clear peak at about 4.65 nm. This result means that most of the pores are in the lower mesoporous range. Mesopores and interparticle spaces may facilitate molecular transport to photoactive sites whilst maintaining adequate surface accessibility [59]. Similar mesoporous materials can effectively combine adsorption and photocatalysis when exposed to visible light [60].

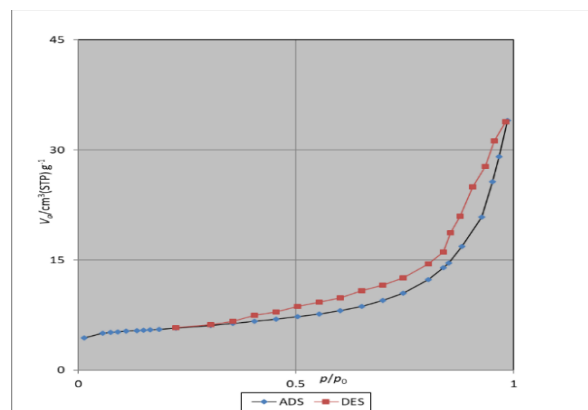


Fig. 9. BET analysis of $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$.

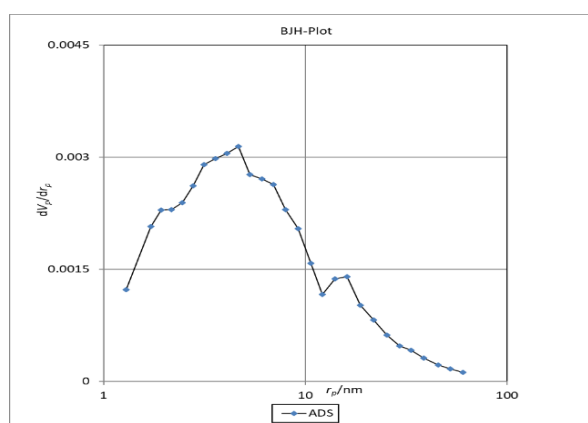


Fig. 10. BJH analysis of $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$.

3.2 Effect of Operating Conditions

3.2.1 Effect of Catalyst Loading

The amount of photocatalyst plays a key role in determining the overall photocatalytic performance because it directly influences the availability of active surface sites and the interaction between incident light and suspended particles [60]. Figure 11 shows that when the amount of $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ increased from 0.5 g L^{-1} to 2 g L^{-1} (with an MO concentration of 20 mg L^{-1} and pH of 7.5), degradation efficiency improved gradually from 70.4% to 96.5%. This improvement emerged because many active sites could be reached, and the catalyst surface and MO molecules could contact one another effectively. High catalyst loading also promotes the formation of ROS, thereby facilitating effective oxidative degradation of the dye [61].

However, a further increase in catalyst loading to 3 g L^{-1} resulted in a marked decline in degradation efficiency to 62.8%. Such behaviour is frequently observed in heterogeneous

photocatalytic systems and is generally associated with excessive particle concentration in suspension. At elevated loadings, particle agglomeration, increased turbidity, and light scattering become more pronounced, leading to reduced photon penetration into the reaction medium. Consequently, the effective irradiation of catalyst particles is limited, which decreases the generation of electron-hole pairs and lowers photocatalytic activity [62]. These results indicate the existence of an optimal catalyst dosage at 2 g L^{-1} , where a balance is achieved between sufficient surface-active sites and effective light utilisation. At this loading, the $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ MNC demonstrates maximum visible-light-driven degradation efficiency without significant optical shielding effects.

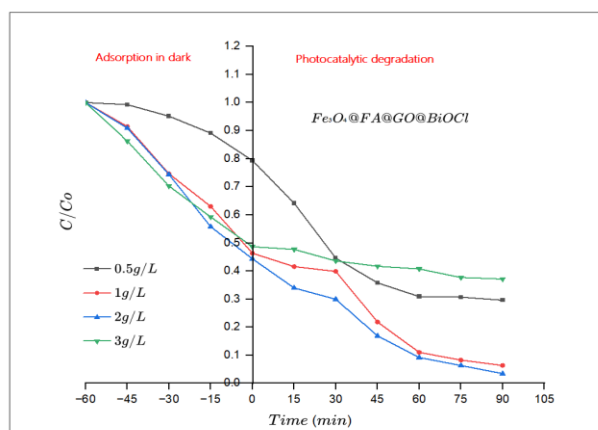


Fig. 11. Effects of $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ dosage at initial pH = 7.5 and dye concentration = 20 mg L^{-1} for photocatalyst doses of 0.5, 1, 2 and 3 g L^{-1} .

3.2.2 Effect of Initial Dye Concentration

The initial concentration of MO has a notable effect on how well $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ works as a photocatalyst. Figure 12 shows that raising the dye concentration to 30 mg L^{-1} substantially lowered the photocatalytic activity, but decreasing it from 20 mg L^{-1} to 10 mg L^{-1} improved degradation efficiency. After exposure to visible light for 90 min, the removal rates were 98.4%, 93.6% and 78.5% for MO concentrations of 10, 20 and 30 mg L^{-1} , respectively.

This concentration-dependent behaviour is due to surface reaction kinetics and optical attenuation. The optical density of the solution decreases as the dye concentration increases, making it difficult for light to get through and for the catalyst particles to hit it. Light blocking reduces the amount of light that photocatalysts can absorb, thus decreasing the

number of charge carriers that are created. Similar to the amount of catalyst used, the amount of surface active sites that are available stays the same at 1 g L^{-1} . High pollution levels may slow down degradation by making it difficult for reactive and adsorption sites to compete [63], [64]. However, a low initial concentration of 10 mg L^{-1} , reduced optical shielding and high dye-to-active-site ratio make it easy for photons to be used and for MO catalytic sites to interact with one another. Thus, long production of ROS and good charge separation make degradation effective. High concentrations cause kinetic and optical problems because of active site saturation and reduced light transmission. However, an initial MO concentration of 10– 20 mg L^{-1} results in excellent system performance.

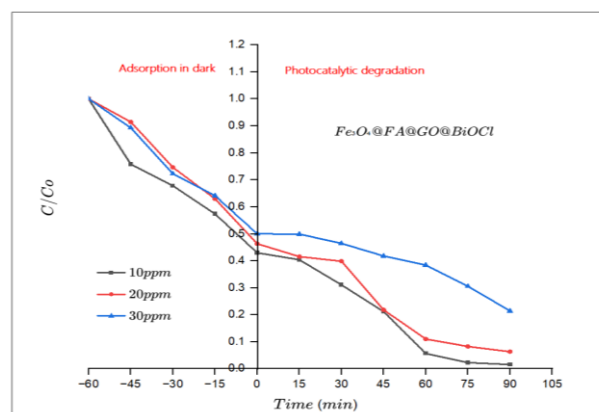


Fig. 12. Effect of MO dye concentration on the photocatalytic degradation activity of MO dye for $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ at catalyst dose = 1 g L^{-1} , initial pH = 7.5 and MO initial concentration = 10, 20 and 30 mg L^{-1} .

4.2.3 Addition of H_2O_2

Under visible light, H_2O_2 accelerated the breakdown of MO much more than the $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ photocatalyst ($C_0 = 20 \text{ mg L}^{-1}$, pH = 7.5, catalyst dosage = 1 g L^{-1}) did (Fig. 13). After 90 min, 93.6% of the irradiated material disappeared. The treatment time was reduced to 45 min by raising the oxidant concentration to 0.10 M. Colour removal with 0.05 M H_2O_2 took 75 min.

This improvement is due to H_2O_2 , which can take in electrons and generate ROS. H_2O_2 takes in electrons created by light to prevent electrons and holes from recombining, thereby generating very reactive species, such as hydroxyl radicals ($\bullet\text{OH}$), and accelerating deterioration [65]. In experimental settings, Fenton-like reactions may enhance oxidative pathways by promoting $\bullet\text{OH}$ generation through $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couples in the Fe_3O_4 core

[66]. H_2O_2 likely increases the charge separation potential of the $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ heterojunction by causing Fenton-type reactions and electron-mediated reduction. Thus, the oxidant increases steady-state ROS, and the multi-component structure maximises the use of the charge. Excessive H_2O_2 can function as a radical scavenger and diminish photocatalytic efficiency; however, within the analysed concentration range (0–0.10 M) characterised by reaction enhancement, no such inhibition was observed. Accordingly, an H_2O_2 dosage between 0.05 and 0.10 M can be considered effective for accelerating MO removal under the present experimental conditions.

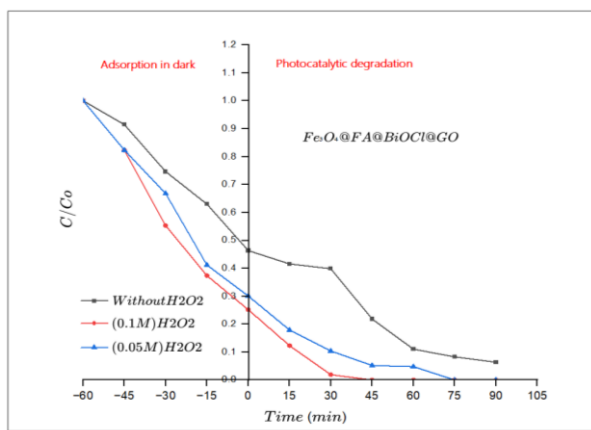


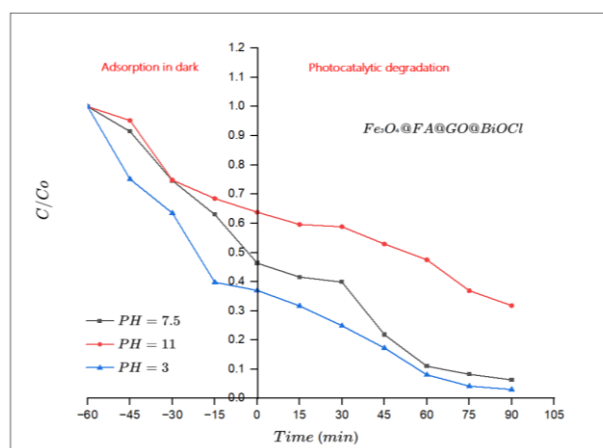
Fig. 13. Effect of H_2O_2 concentration on MO degradation efficiency at dosage = 1 g L^{-1} , pH = 7.5 and $C_0 = 20 \text{ mg L}^{-1}$.

4.2.4 Effect of pH and Surface Charge

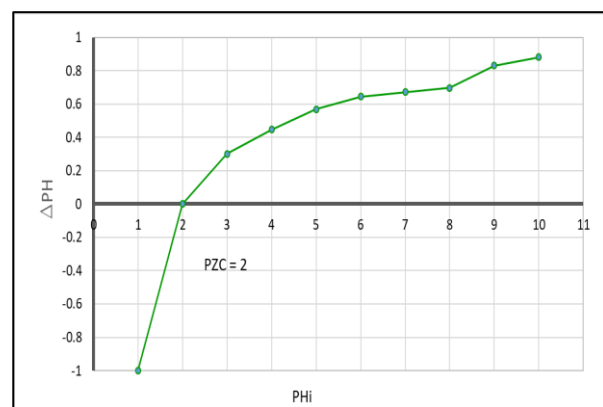
The pH of the reaction medium plays a critical role in regulating the surface charge of $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ and the speciation of MO. As illustrated in Fig. 14a, varying the pH from 3 to 11 produced a clear performance trend. The highest degradation efficiency (96.9% after 90 min of visible-light irradiation) was obtained at pH = 3, whereas the efficiency decreased substantially to 68.2% at pH = 11 under identical experimental conditions ($C_0 = 20 \text{ mg L}^{-1}$, catalyst dosage = 1 g L^{-1}). The observed behaviour can be interpreted by considering the measured PZC (PZC = 2), as shown in Fig. 14b. When pH is above PZC, the catalyst's surface is either neutral or has a small positive charge, allowing it to use electrostatic forces to interact with MO molecules that have negative charges. Photogenerated carriers in dyes can easily move charge around because of acidic adsorption. The catalyst's surface acquires a negative charge when pH is alkaline (pH > PZC). This phenomenon

pushes away MO molecules with a negative charge. This repulsion makes it difficult to reach reactive sites and stick to surfaces, making it less effective to break things down [67]. Dark adsorption studies have demonstrated that MO absorption is augmented in acidic environments and diminished in alkaline ones.

pH affects redox reactions, ROS generation and electrostatic forces. When pH is slightly high, water and surface hydroxyl groups help oxidation occur through holes. When pH is low, H_2O_2 may speed up Fenton-like reactions in Fe_3O_4 cores with $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox centres, making $\bullet\text{OH}$ formation likely. When pH is high, extra OH^- ions may reach the active sites before the dye molecules do, causing recombination to occur often and reducing the usefulness of charge carriers created by light [68]. Interfacial interactions and the breakdown of anionic azo dyes, such as MO, by visible light are highly pronounced at low pH levels.



(a)

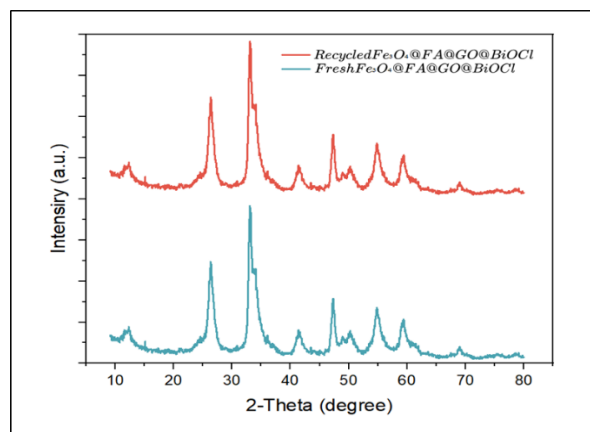
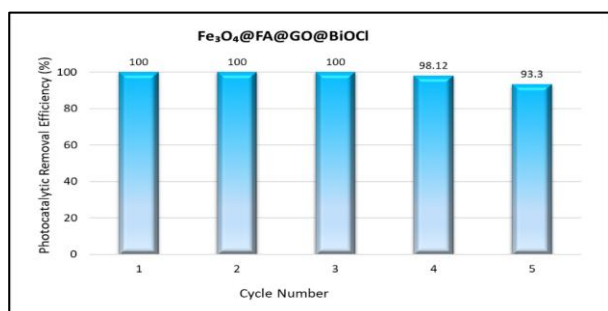


(b)

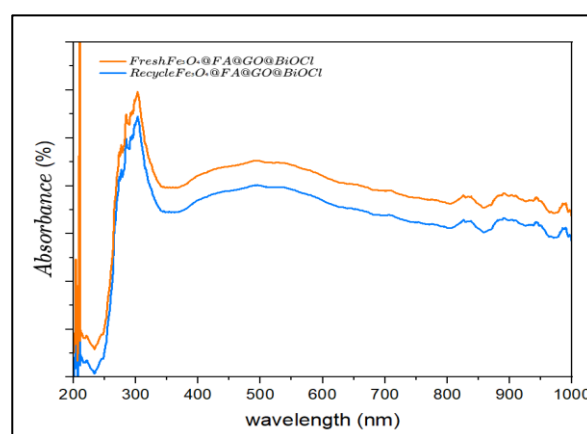
Fig. 14. (a) Photocatalytic degradation activity of MO dye as affected by solution pH and (b) PZC of $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$.

4.2.5 Stability and Reusability of the Photocatalyst

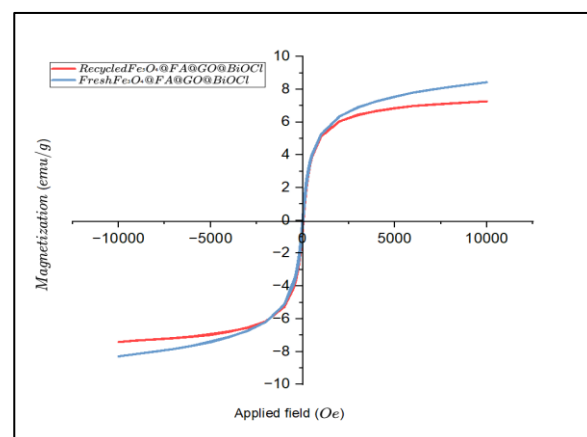
When evaluating the efficacy of photocatalysts in wastewater treatment systems, their longevity and recyclability must be considered [69]. $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ MNC underwent five consecutive photocatalytic cycles under optimal conditions ($\text{MO} = 10 \text{ mg L}^{-1}$, catalyst dose = 2 g L^{-1} , $\text{pH} = 3$, $\text{H}_2\text{O}_2 = 0.1 \text{ M}$ and visible-light irradiation duration = 90 min) to ensure the catalyst's stability and efficacy. Figure 15 shows that the photocatalyst kept breaking down completely during the first three cycles. In the fourth cycle, the amount of activity decreased to 98.12%, and in the fifth cycle, it dropped to 93.3%. After five cycles, 93.3% of the activity was still occurring, indicating that efficiency decreased by only 6.7%. Many researchers believe that this slow decline is due to reaction intermediates sticking to surface active sites, thereby slowing down slightly. Others posit that catalysts do not work ideally when they undergo extensive washing and magnetic separation [70]. In this study, the shape and function of MNC did not change after the reaction (Figs. 16a–16d). The XRD patterns of the recycled sample still had all the unique diffraction peaks linked to BiOCl , Fe_3O_4 , FA and GO, indicating that the structure and phase did not change. No remarkable alterations in the UV-vis diffuse reflectance spectra at the absorption edge were observed, revealing that the optical properties did not change substantially even after being used a few times. The magnetic tests showed that the VSM hysteresis loops before and after cycling were the same. This result means that the Fe_3O_4 magnetic core could still become magnetic and recover its magnetic properties. The FESEM data indicate that the shape stayed mostly the same. Slight surface aggregation was observed, but it did not affect how well the catalyst worked.



(a)



(b)



(c)

Fig. 15. Reusability and stability of the synthesised photocatalysts after five running cycles at MO dye concentration = 10 mg L^{-1} , photocatalyst dosage = 2 g L^{-1} , running time = 45 min, $\text{pH} = 3$ and $\text{H}_2\text{O}_2 = 0.1 \text{ M}$.

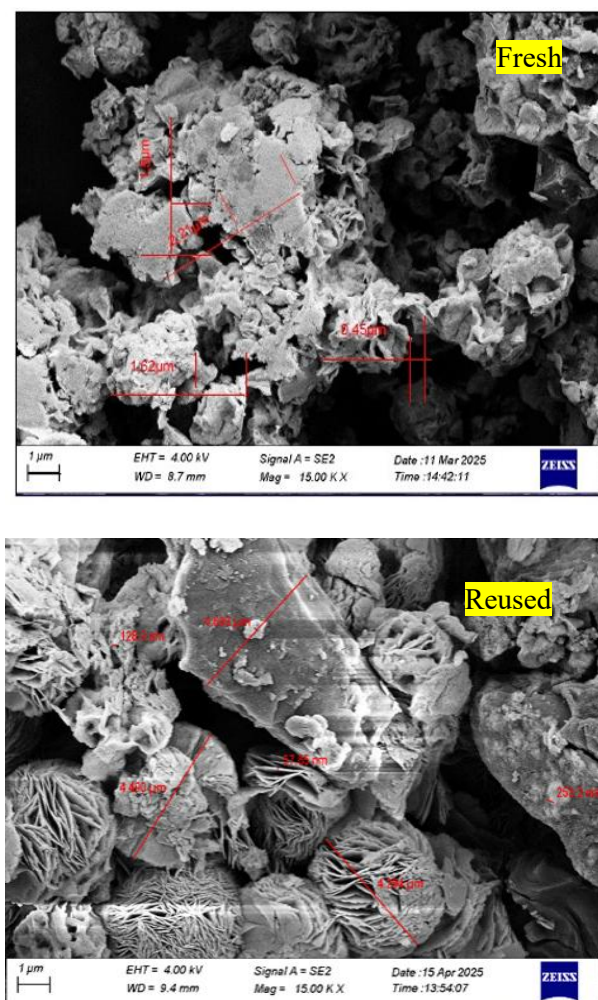


Fig. 16. Characterisation of fresh and reused $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$. (a) XRD patterns, (b) DRS, (c) VSM and (d) FESEM.

4.2.6 Evaluation of the hemocompatibility of the photocatalysts

Table 2 shows the hemolytic response of $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ MNC, and Fig. 17 presents the response in a picture. The effect depended on the concentration. At high concentrations, particularly 100% and 80%, substantial hemolysis occurred, as evidenced by the intense red colour of the supernatant and the elevated HR% values. At 60%, some damage to the membrane was still observed, but at 40%, hemolysis was reduced substantially. The hemolysis rate was very low at a concentration of 20%, similar to the negative control. This finding means that the membranes of the red blood cells were not considerably damaged when the solution was diluted. Microscopic analysis yielded additional corroborative evidence for these findings. At high

concentrations, all of the cells were lysed, but at 20%, the erythrocytes still had their normal biconcave shape. At intermediate levels, only small changes to the structure were observed.

Nanoparticle membrane interactions produce the hemolytic behaviour that depends on concentration. At high concentrations, increased surface contact and possible oxidative stress may damage the integrity of the phospholipid bilayer. Meanwhile, dilution reduces direct membrane contact, thus improving hemocompatibility. Similar findings have been recorded for other oxide-based nanocomposites, showing a notable reduction in hemolysis with decreased concentration [51], [52]. Table 2 presents the percentage of hemolytic rate for human red blood cells resulting from the $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ synthesis concentrations and the hemolysis percentage (HR%).

Table 2,
Percentage of hemolytic rate for human red blood cells resulting from the $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ synthesis concentrations and hemolysis percentage (HR%)

Dilutions	Hemolysis Percentage (HR%)
100%	83.33%
80%	79.16%
60%	78.33%
40%	75%
20%	N.H (0)
+ C Triton X 100	100%
- C (PBS)	N.H

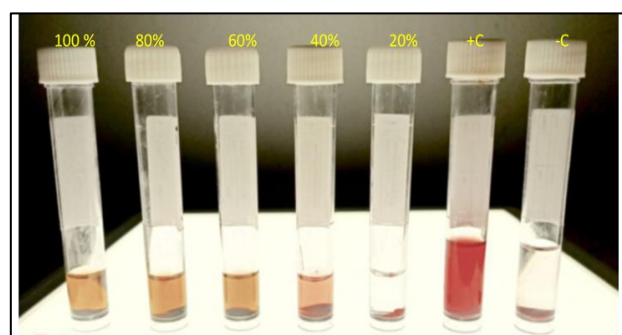


Fig. 17. Different amounts of $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ hemolysis.

4.3 Scavenger Experiments and Proposed Mechanisms

The $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ core/shell MNCs' photocatalytic performance was tested via electronic band structure analysis (Fig. 18a) and radical scavenger studies. The quenching data

indicate that isopropanol and Fe(II)–EDTA substantially influenced MO degradation, corroborating the hypothesis that $\bullet\text{OH}$ radicals and H_2O_2 are the principal oxidative agents governing MO degradation. However, p-benzoquinone and sodium oxalate did not considerably affect the process, suggesting that h^+ and $\bullet\text{O}_2^-$ were involved. These findings are consistent with those for the heterojunction system. They show that the order of reactive species is $\bullet\text{OH} > \text{H}_2\text{O}_2 > \text{h}^+ > \bullet\text{O}_2^- > \text{e}^-$ [71].

The observed H_2O_2 was produced through oxygen-reduction processes that occurred in the same place, driven by electrons created by light. In this setup (Fig. 18b), the FA shell help up other parts. It spread Fe_3O_4 , prevented magnetic clumping and strengthened the contact amongst Fe_3O_4 , GO and BiOCl . Enhanced dispersion creates many surface active sites, allowing contaminants to accumulate near redox centres. This phenomenon allows $\bullet\text{OH}$ to grow in the light. As a conductive electron mediator, GO absorbs and moves electrons created by light. Photocatalysts with GO shells stop recombination and enable electrons to move to surfaces with abundant oxygen [72]. The electronic band positions were estimated using the electronegativity method in accordance with Equations (5) and (6) [73].

$$E_{VB} = X - E_e + 0.5E_g, \quad \dots(5)$$

$$E_{CB} = E_{VB} - E_g, \quad \dots(6)$$

where E_e is the free electron energy on the hydrogen scale (4.5 eV) and X is the geometric mean of Pearson's absolute electronegativity. X is determined from the relation

$$X(A_mB_nC_l) = \sqrt[m+n+l]{X_A^m X_B^n X_C^l}, \quad \dots (7)$$

where A, B and C are the elements and m , n and l are the moles of these elements. The absolute electronegativities of Fe_3O_4 and BiOCl were estimated to be 2.75 and 2.87 eV, respectively. Notably, these values provide only a thermodynamic approximation and do not fully represent the complex interfacial electronic structure of multicomponent MNCs [74]. Under visible-light irradiation, BiOCl acts as the primary photoactive semiconductor, generating electron/hole pairs. Through GO-mediated interfacial charge transfer, less reactive carriers undergo internal recombination, preserving highly oxidative holes on the BiOCl side and highly reductive electrons that accumulated on the Fe_3O_4 side. Electrons available at the Fe_3O_4 conduction

level are thermodynamically capable of activating dissolved oxygen to form superoxide radicals ($\bullet\text{O}_2^-$), which subsequently participate in oxygen-reduction pathways for H_2O_2 formation.



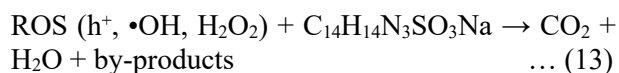
The $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple that is part of Fe_3O_4 initiates the H_2O_2 produced through Fenton-like reactions.



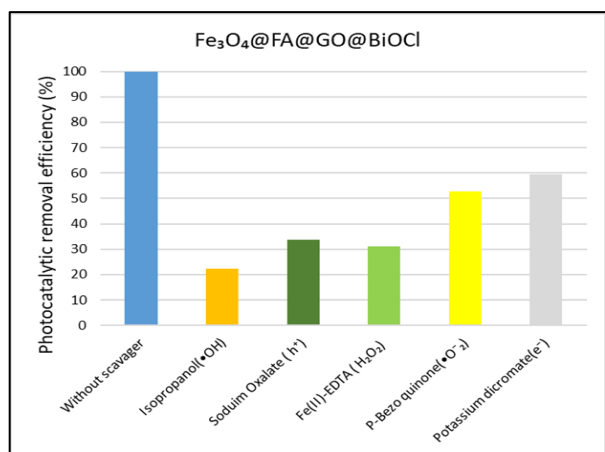
Holes created by light on the BiOCl surface oxidise existing H_2O or OH^- , thus generating additional $\bullet\text{OH}$ radicals.



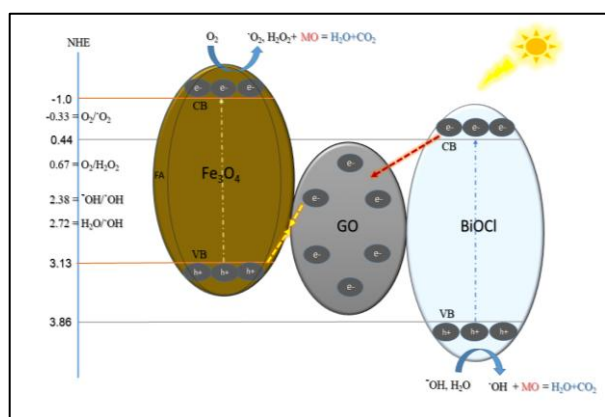
The presence of photocatalytic oxidation and Fenton-like activation creates a cooperative redox cycle that maintains a high steady-state concentration of $\bullet\text{OH}$ radicals, a finding that is in line with the scavenger results. Hence, MO molecules break down into intermediate species through a series of oxidative cleavages, and eventually, they transform into CO_2 and H_2O .



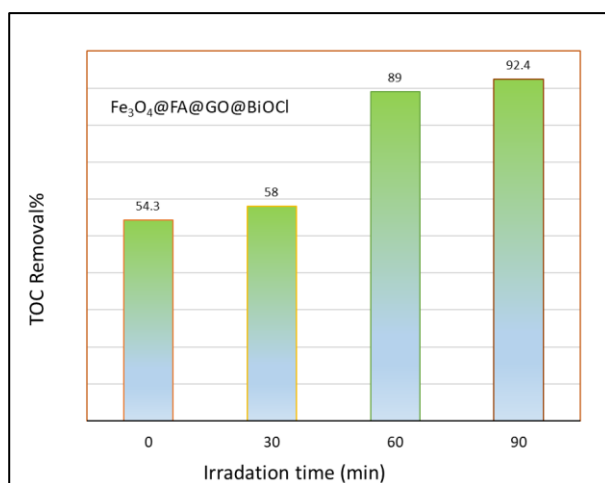
The total organic carbon (TOC) results (Fig. 18c) also support this interpretation because they show that mineralisation was highly effective when exposed to visible light. The remarkable decrease in organic carbon confirms that the process transcends mere decolorisation or surface adsorption, suggesting efficient oxidative degradation of aromatic structures, although precise intermediate identification is not within the purview of this study. In general, the way through which $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ breaks down can be better described as a synergistic photocatalytic–Fenton-like system than as a regular semiconductor heterojunction. BiOCl excites visible light, GO helps charge move, Fe_3O_4 helps reduce oxygen and activate H_2O_2 and FA enhances adsorption and structural stability. This integrated mechanism reinforces the fact that $\bullet\text{OH}$ radicals are highly common in experiments and that mineralisation is efficient when visible light is used.



(a)



(b)



(c)

Fig. 18. Photodegradation of the $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ photocatalyst under visible light. (a) Scavenger experiments at 20 mg L^{-1} MO concentration, 1 g L^{-1} catalyst dosage, 90 min reaction time and pH 7.5. (b) Proposed mechanism of MO degradation over the heterojunction. (c) TOC removal efficiency.

4.4 Photocatalytic Degradation and Kinetics

Figures 19a and 19b show how MO breaks down in visible light over Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{FA}$, $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}$, $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$, BiOCl, FA and GO. The experiments were conducted under the same conditions (catalyst dosage = 1 g L^{-1} , $C_0 = 20 \text{ mg L}^{-1}$, pH = 7.5). After 90 min, photolysis removed only 1%, indicating that visible light alone was not enough to break down MO. Pure Fe_3O_4 had very little activity (3%) because it could not absorb much visible light, and charges quickly recombined. FA addition substantially improved performance because FA's mesoporous aluminosilicate structure makes it easy for Fe_3O_4 MNPs to stick to it and prevents them from clumping together [63], [75]. Even though some of the pores were covered, which made adsorption slightly less effective than that under FA alone, $\text{Fe}_3\text{O}_4@\text{FA}$ MNC still had a 50.2% removal rate after 90 min. This result shows that interfacial charge transfer and surface hydroxyl availability were improved [46]. Adding GO enhanced the material by increasing adsorption and photocatalytic efficiency. This enhancement was achieved by creating conductive pathways for interfacial electron transport and lowering recombination losses [76]. The $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ MNC system worked the best amongst all the systems, removing 93.6% of MO after 90 min without adding H_2O_2 from outside. This enhancement resulted from the synergistic combination of FA-assisted adsorption, GO-mediated charge transport, BiOCl visible-light excitation and Fe_3O_4 redox contribution whilst preserving magnetic recoverability [57], [77], [78]. The overall performance trend under visible-light irradiation followed the order $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl} > \text{Fe}_3\text{O}_4@\text{FA}@\text{GO} > \text{BiOCl} > \text{FA} > \text{Fe}_3\text{O}_4@\text{FA} > \text{GO}$. Kinetic modelling (Fig. 20) confirmed pseudo-first-order behaviour, namely,

$$\ln\left(\frac{C_0}{C_t}\right) = k \cdot t, \quad \dots(14)$$

where t is time (min), C_0 and C_t are MO concentrations (mg L^{-1}) at $t = 0$ and time t , respectively; and k (min^{-1}) is the apparent rate constant. As summarised in Table 3, amongst the systems examined, $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ exhibited the highest rate constant ($k = 0.01299 \text{ min}^{-1}$, $R^2 = 0.95877$), which was approximately 1.74 times higher than that of $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}$ ($k =$

0.00744 min⁻¹, R² = 0.93792). The high correlation coefficients (R² = 0.94–0.96) and ANOVA significance (p < 0.05) confirm the statistical reliability of the kinetic fitting under the applied irradiation conditions. The residual distribution showed no systematic deviation, supporting the suitability of the apparent first-order description for comparative purposes.

Table 3,
Kinetic study on the photocatalytic degradation of MO dye

Catalysts	<i>k</i> (min ⁻¹)	(R ²)
Photolysis	0.0000906	0.71768
Fe ₃ O ₄	0.0003065	0.85522
Fe ₃ O ₄ @FA	0.00506	0.96417
Fe ₃ O ₄ @FA@GO	0.00744	0.93792
Fe ₃ O ₄ @FA@GO@BiOCl	0.01299	0.95877
FA	0.00447	0.80922
BiOCl	0.00612	0.93147
GO	0.00191	0.91173

Fe₃O₄@FA@GO and Fe₃O₄@FA@GO@BiOCl. (b) Fe₃O₄, BiOCl and GO.

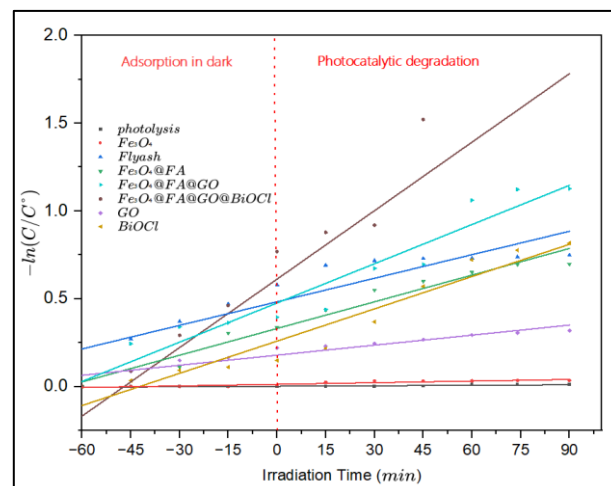
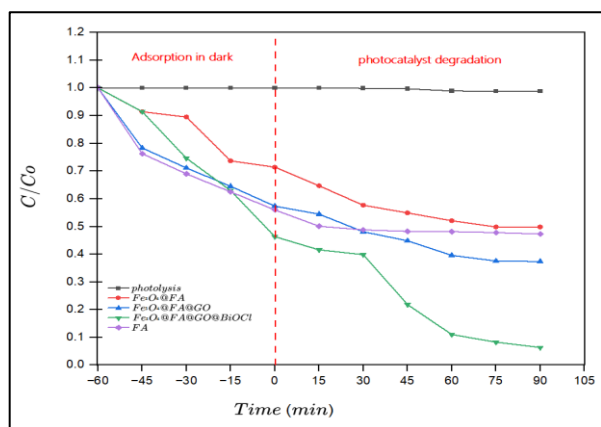
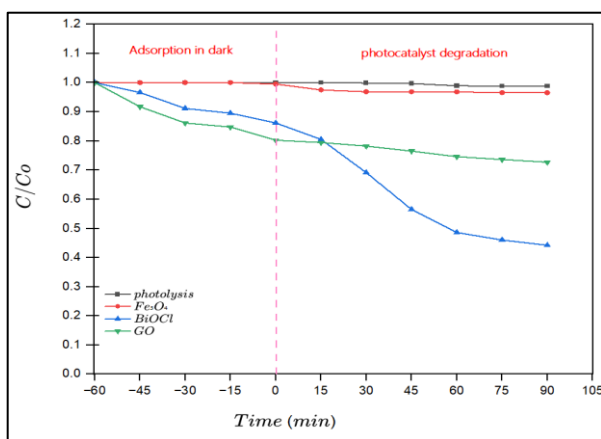


Fig. 20. Kinetic reaction plot for the photocatalytic degradation of MO dye.



(a)



(b)

Fig. 19. MO dye photocatalytic degradation performance for core/shell MNC catalysts at initial concentration of MO dye = 20 mg L⁻¹, photocatalyst dose = 1 g L⁻¹, and pH = 7.5. (a) Fe₃O₄, Fe₃O₄@FA,

4.5 Statistical Analysis of MO Dye Photodegradation

Multiple linear regression models were employed to analyse the MO dye photodegradation performance results of the core/shell (Fe₃O₄@FA@GO@BiOCl) MNC. Irradiation time, photocatalyst dose, MO dye concentration, solution pH and H₂O₂ concentration were selected as independent variables, and removal efficiency (%) was considered the dependent variable. Given that the Enter model yielded the best regression coefficient (R²), it was employed to analyse the photodegradation performance results of MO dye. The correlation equation utilised in this model is

$$X = AY_1 + BY_2 + CY_3 + DY_4 + EY_5 + F, \quad \dots (15)$$

where

X = removal efficiency (%) = (1 - C/C₀) × 100%,

A, B, C, D, E: coefficients,

Y₁: detention time (min),

Y₂: photocatalyst dose (g L⁻¹),

Y₃: concentration of MO dye, (mg L⁻¹),

Y₄: solution pH,

Y₅: H₂O₂ concentration (M),

F: constant.

Table 4 shows the photodegradation performance results of the MO dye for core/shell MNC. The dependent (X) values for

(Fe₃O₄@FA@GO@BiOCl) photocatalysts can be derived using

$$X_I = 0.529Y_1 + 7.148Y_2 - 0.660Y_3 - 3.593Y_4 + 211.209Y_5 + 65.385. \quad \dots (16)$$

The model demonstrated strong statistical reliability, with a correlation coefficient (R) of 0.956, coefficient of determination (R²) of 0.914 and adjusted R² of 0.910. About 91% of the differences in removal efficiency can be explained by the operational parameters used in the experiments.

ANOVA demonstrated that the regression model was statistically significant at the 95% level of confidence. This result suggests that the examined variables had a substantial effect on how well MO was removed. The standard error (8.56) indicates that the expected and actual values were close. The amount of irradiation time was the most critical aspect because long exposure accelerates ROS generation and improves degradation. Using proper amounts of H₂O₂ and the catalyst resulted in enhancements. However, improper pH or low dye concentration yielded poor performance because they affected the surface and how they were absorbed. The linear model effectively explained how the system functioned, but it was not fully linear, as evidenced by the slight variations at high H₂O₂ levels or lengthy irradiation interval

Table 4,
Statistical analysis results of core/shell (Fe₃O₄@FA@GO@BiOCl) MNC

Model	Variable	Coefficient	Value	R ²
Inter	Detention time (min)	A	0.529	0.914
	Photocatalyst dose (g L ⁻¹)	B	7.148	
	Concentration of MO dye (mg L ⁻¹)	C	- 0.660	
	Solution pH	D	- 3.593	
	H ₂ O ₂ concentration (M)	E	211.209	
	Constant	F	65.385	

5. Conclusions

A magnetically recoverable Fe₃O₄@FA@GO@BiOCl core/shell MNC was successfully developed by integrating FA, GO and visible-light-active BiOCl into Fe₃O₄ cores.

Fe₃O₄@FA@GO@BiOCl MNC removed 93.6% of MO in 90 min when exposed to visible light without the addition of H₂O₂. This pseudo-first-order rate constant was the highest amongst all the constants tested. Statistical analysis (R² = 0.914, p < 0.001) verified the significant correlation between degradation efficiency and irradiation duration and between oxidant-related variables. The scavenger experiments showed that •OH was the most reactive species, followed by H₂O₂ created in situ. This phenomenon supports a photocatalytic–Fenton-like process. The combined roles of FA in adsorption and dispersion, GO in charge transport, BiOCl in visible-light excitation and Fe₃O₄ in redox mediation and magnetic recovery helped separate charges and generate ROS. Mineralisation analysis revealed a 92.4% decrease in TOC after 90 min, confirming that oxidative degradation did not just change the colour of the surface. The reusability tests conducted under ideal conditions demonstrated that the material performed similarly after several cycles, indicating that it is structurally strong and can be easily separated by magnets.

Conflicts of Interest

The authors declare no conflict of interest regarding the publication of this paper.

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استثمار الرماد المتطاير المعالج في تصنيع مترابك نانوي $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ فعال ضوئياً لإزالة الأصباغ من المحاليل المائية

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المستخلص

تم في هذه الدراسة تصميم وتحضير المركب النانوي المغناطيسي $\text{Fe}_3\text{O}_4@\text{FA}@\text{GO}@\text{BiOCl}$ وتقييمه كمحفز ضوئي فعال يعمل تحت الإضاءة المرئية لتحلل صبغة الميثيل برتقالي. اعتمد التصميم على استثمار الرماد المتطاير المعالج، بوصفه ناتجاً ثانوياً صناعياً منخفض الكلفة، كدعامة مسامية تساهم في زيادة تركيز الملوثات على السطح، وتعزيز توزيع الأطوار النشطة داخل البنية المترابكة. مثل BiOCl الطور الفعال المستجيب للضوء المرئي، بينما أدى أكسيد الغرافين دوراً محورياً في تحسين انتقال الشحنة وتقليل إعادة اتحاد أزواج الإلكترون-الفجوة، في حين أتاح Fe_3O_4 إمكانية الاسترجاع المغناطيسي السريع للمحفز بعد انتهاء التفاعل. أكدت التحليلات البنوية والبصرية تكوين وصلة غير متجانسة مستقرة من نوع لب-قشرة ذات خصائص مغناطيسية لينية واستجابة فعالة للضوء المرئي. تحت الظروف التشغيلية المثلى، تحققت إزالة كاملة للون الصبغة خلال ٤٥ دقيقة، متبعة بحركية من الدرجة الأولى الظاهرية. والأهم من ذلك، أظهرت النتائج انخفاضاً في إجمالي الكربون العضوي (TOC) بنسبة ٩٢,٤٪ بعد ٩٠ دقيقة، مما يدل على تمعدن حقيقي للمركبات العضوية الوسيطة وليس مجرد امتزاز سطحي. كما حافظ النظام على كفاءته البنوية والوظيفية خلال ثلاث دورات متتالية من إعادة الاستخدام. تؤكد هذه النتائج أن دمج ثمين الرماد المتطاير مع منظومة تحفيز ضوئي مغناطيسية يعمل بالضوء المرئي يمثل توجهاً واعداً لتحقيق معالجة مستدامة وفعالة لمياه الصرف، مع دعم مبادئ الاقتصاد الدائري وتقليل الأثر البيئي للنفايات.