



Visible-Light-Activated CuFe₂O₄/Zn-BTC Photocatalyst for Efficient Mineralization and Detoxification of Carbofuran in Industrial Effluents

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Received: 17 February 2026 / Accepted: 18 May 2026

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Abstract

Growing concern over carbofuran (CBF) contamination present in water bodies has increased the need for effective remediation strategies. Herein, CuFe₂O₄ nanoparticles, Zn-BTC MOF (H₃BTC; 1,3,5-benzenetricarboxylic acid), and CuFe₂O₄/Zn-BTC composite were successfully synthesized and characterized using various analytical techniques to investigate physiochemical and electrochemical properties. These photocatalysts were subsequently employed for the CBF degradation in wastewater. The CuFe₂O₄/Zn-BTC composite degraded (96%) 20 mg/L CBF in 90 min under optimized conditions (0.01 g/L catalyst loading, 7 pH, and light intensity 50 W LED). The superoxide ions ($\cdot\text{O}_2^-$) and hydroxyl radicals ($\cdot\text{OH}$) were identified as the main oxidants, due to the strong interaction between CuFe₂O₄ and Zn-BTC, which promoted the separation of electrons and holes and increased the number of reactive sites. The photocatalytic activity remained stable in five successive cycles with a slight decrease in efficiency from 96% to 91%. When exposed to real pesticide effluent, total organic carbon (TOC) was reduced 69% and chemical oxygen demand (COD) was reduced 77%. A near complete detoxification of CBF was confirmed by *Escherichia coli* assays and degradation intermediates were identified by LC-MS, and a plausible reaction pathway was suggested. The results indicate that CuFe₂O₄/Zn-BTC is stable and effective photocatalyst for the removal of CBF from contaminated water.

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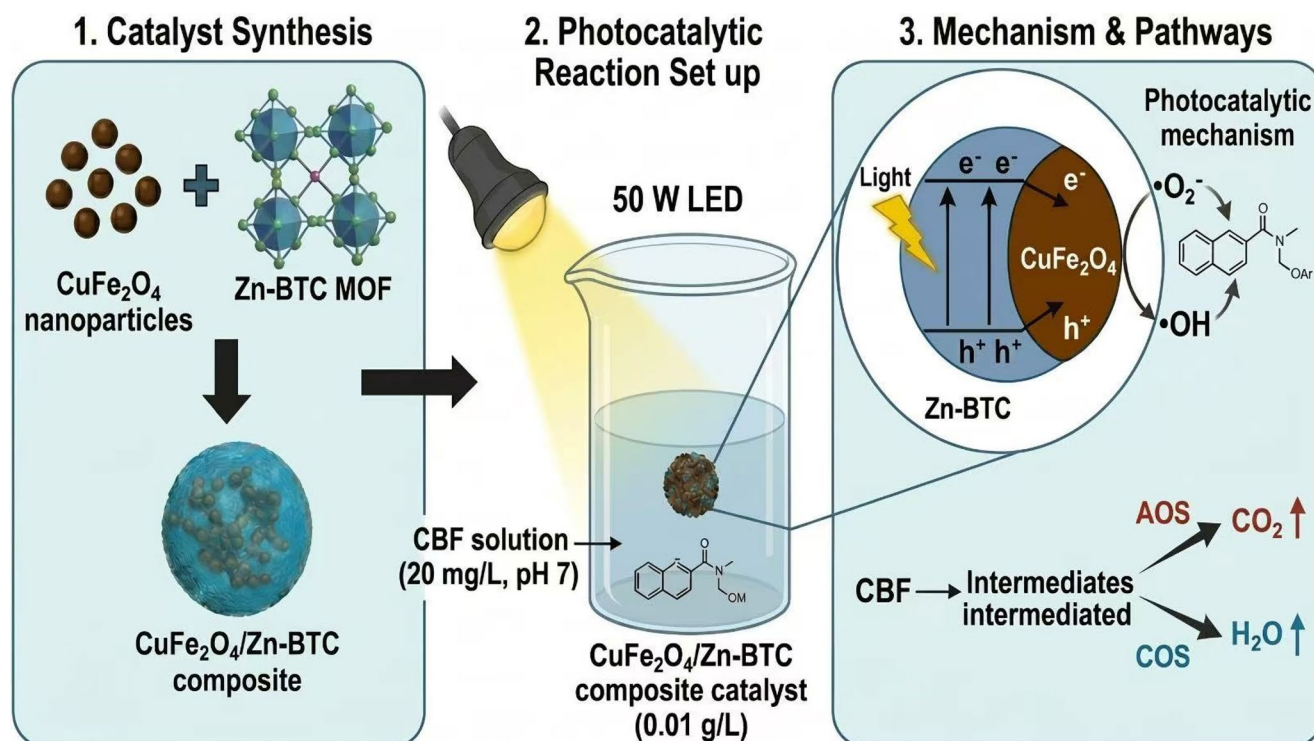
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Graphical Abstract



Keywords $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ composite · Photodegradation · Carbofuran · Water treatment · Pesticide effluents

Abbreviations

TOC	Total organic carbon
COS	Carbon oxidation state
CBF	Carbofuran
MOFs	Metal-organic frameworks
PVP	Polyvinylpyrrolidone
EDX	Energy-dispersive X-ray spectroscopy
FTIR	Fourier-transform infrared spectroscopy
PZC	Point of zero charge

1 Introduction

With the rise in demand for agricultural products, the agrochemical industry has gained a lot of growth, resulting in the use of pesticides in large numbers [1]. However, the misuse and excessive use of these materials are a significant problem for freshwater resources and aquatic ecosystems [2]. Chemically, pesticides are generally grouped into four classes: carbamates, organophosphates, organochlorines and pyrethroids. Organophosphates and carbamates are among the most commonly used pesticides as they are effective against pests that have developed resistance to organochlorines. As a carbamate-derived insecticide and

nematicide, CBF inhibits acetylcholinesterase, resulting in disrupted nervous system function [3]. The continual discharge of CBF into surface waters poses a risk to non-target species, including humans. Only approximately 1% of pesticides used effectively end up on the target. pests, whereas the remaining 99% stay in the environment, frequently bioaccumulating at higher trophic levels [4].

The conventional wastewater treatment techniques (disinfection, sedimentation, filtration and adsorption) are generally not effective enough to completely eliminate pesticide residues [5]. Other methods like biodegradation, ozonation, membrane filtration and oxidation by UV have been studied, but their efficiency is frequently constrained by the resistance of these compounds [6]. Furthermore, many advanced oxidation processes (AOPs) are able to achieve greater efficiencies of removal but are often limited by high operating costs [7]. In this regard, heterogeneous photocatalysis is a promising alternative because it can be easily synthesized, is inexpensive, and can lead to complete mineralization of organic pollutants [8]. When the photocatalyst is illuminated, it generates reactive oxygen species (ROS) that cause the degradation of pesticide molecules to harmless products [9, 10].

Metal-organic frameworks (MOFs) have become an appealing photocatalytic material due to their large surface area, adjustable physicochemical characteristics, and light absorption [11]. Unlike conventional semiconductors, MOFs use organic linkers and metal nodes to promote the adsorption and degradation of pollutants [12]. For the degradation of organic pollutants, some MOFs like Co-MOF (ZIF-67), Ti-MOF (MIL-125-NH₂), and Zn-BTC (MOF-5), exhibit good photocatalytic performance [13]. Despite these advantages, their practical application remains limited due to insufficient visible-light absorption and challenges in post-reaction separation [9]. Coupling MOF with spinel ferrites like CuFe₂O₄, which offers magnetic properties, a narrow bandgap, and high thermal and chemical stability [14], offers a potential solution. Despite these benefits, pure CuFe₂O₄ exhibits fast electro-hole recombination, affecting its photocatalytic activity performance [12]. Therefore, these complementary properties provide a strong basis for constructing spinel ferrite/MOF composites, where each component helps overcome the limitations of the other.

In this study, we report a facile hydrothermal synthesis of CuFe₂O₄/Zn-BTC nanocomposite and evaluated the performance in photodegrading the CBF in water. The aim was to combine the high surface area of Zn-BTC and the structured morphology of CuFe₂O₄, which enhanced charge separation and photocatalytic efficiency. Systematized studies were conducted on the effects of CBF concentration, pH, catalyst dosage, and light intensity. Reaction kinetics, degradation pathway, scavenger experiments, stability and recyclability tests, mineralization, and toxicity assessments were also performed. Electrochemical and spectroscopic studies clarified the charge-transfer mechanism of the catalyst, providing a deeper understanding of CBF decontamination. This work contributes to the understanding of spinel ferrite/MOF composites and their potential in wastewater treatment.

2 Experimental Procedures

2.1 Materials

In this study reagents comprised of trimesic acid (H₃BTC, 1,3,5-benzene tricarboxylic acid), polyvinylpyrrolidone (PVP), ferric(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O), copper(II) nitrate hexahydrate (Cu(NO₃)₂·6H₂O), zinc(II) nitrate hexahydrate (Zn(NO₃)₂·6H₂O), and N, N-dimethylformamide (DMF), carbofuran (CBF), NaOH, HCl, and ethanol (C₂H₅OH). All reagents of analytical grade (>99%; Sigma Aldrich) were used as received.

2.2 Photocatalyst Synthesis Procedure

The technique of co-precipitation was employed to synthesize CuFe₂O₄ nanoparticles [12], and for this purpose, two distinct aqueous solutions (200 mL), 0.1 M (Cu(NO₃)₂·6H₂O) and 0.2 M (Fe(NO₃)₃·9H₂O), were prepared. Each was stirred at 300 rpm for 30 min, then combined dropwise under continuous stirring. After adding 2.0 M NaOH to bring the pH down to 10, the solution was heated to 80 °C (3 h) until a brown precipitate appeared. Then, the precipitate was separated by centrifugation (10,000 rpm), washed with ethanol and DI water. After drying for 24 h at 75 °C and calcining for 6 h (600 °C), CuFe₂O₄ nanoparticles were obtained.

For Zn-BTC synthesis, a standard hydrothermal method was employed [15]. For this purpose, the reaction medium consisted of H₂O and DMF in a 1:6 v/v ratio, into which a precursor solution of 2.0 mmol H₃BTC, 2.0 mmol PVP, and 1.0 mmol Zn(NO₃)₂·6H₂O was dissolved. After that, the precursor solution was thoroughly and uniformly mixed by stirring for 1 h at 75 °C, then transferred to a 50 mL Teflon-lined autoclave and treated hydrothermally for 12 h at 180 °C. After natural cooling, the Zn-BTC crystals were separated by filtration, thoroughly washed, and dried to yield the purified product. To prepare the CuFe₂O₄/Zn-BTC nanocomposite, pre-synthesized CuFe₂O₄ nanoparticles were introduced into the Zn-BTC precursor solution in a 1:1 mass ratio and then placed under hydrothermal conditions (12 h; 180 °C) [16]. Here, the PVP function was to reduce agglomeration and ensure uniform dispersion of CuFe₂O₄ and Zn-BTC particles [17, 18].

2.3 Characterization and Analytical Techniques

The surface morphology and particle size were investigated using a TESCAN MIRA3 field-emission scanning electron microscope (FE-SEM) at 15 kV accelerating voltage, 4.89 mm working distance, and ×30,000 magnification in InBeam mode. The elemental composition was measured using energy-dispersive X-ray spectroscopy (EDX). The chemical composition and functional groups were investigated employing Fourier-transform infrared spectroscopy (FTIR; Bruker 8400 S, KBr pellet technique) over 400–4000 cm⁻¹ at 4 cm⁻¹ resolution and an average of 32 scans at a scan speed of 2 cm⁻¹s⁻¹. Crystalline structure and phase purity were confirmed by X-ray diffraction (Bruker D8 diffractometer with Cu Kα radiation, λ=1.5406 Å) at 40 kV and 40 mA spanning 2θ=10–80° (step size 0.02°, scan speed 2°·min⁻¹). The Quantachrome Autosorb-iQ analyzer analyzed nitrogen adsorption-desorption isotherms at 77 K using the BET method (P/P₀ range 0.05–0.30) and the BJH method was used to quantify pore size distribution. UV-vis

diffuse reflectance spectra (DRS) were acquired using a U-3900 H spectrophotometer and the magnetic properties of the samples were examined using vibrating sample magnetometry (VSM) using a Quantum Design; VersaLab system. Mineralization was measured using a total organic carbon analyzer (Shimadzu TOC-L). The photocatalytic degradation intermediates were detected using liquid chromatography mass spectrometry (LCMS) on a JEOL JMS-T100LP AccuTOF LC-plus 4G system with positive-mode electrospray ionization (ESI+). Charge carrier recombination was examined by photoluminescence (PL, HITACHI F-7000 spectrofluorometer, 450 nm excitation, xenon lamp). Reactive radicals during photocatalysis were detected by an electron spin resonance (ESR, Bruker MEX nano) spectrometer with DMPO as a spin trap (100 kHz modulation, 15 mW microwave power). The secondary cutoff binding energy was measured using ultraviolet photoelectron spectroscopy (UPX, ESCALAB 250Xi) spectrometer with He I ($h\nu=21.22$ eV) as the excitation source. Photoelectrochemical tests were performed on a CHI 660E workstation with Pt counter, SCE reference, and Na_2SO_4 electrolyte.

2.4 Experimental Procedures

Adsorption-desorption equilibrium was established by suspending 0.01 g of photocatalyst in 100 mL of a 10 mg/L CBF solution (pH 7.0, adjusted with 1 M NaOH or HCl), and the mixture was agitated for 30 min at 300 rpm and 25 °C in the dark. The suspension was irradiated with visible light of 20 W (LED lamp; Philips CorePro; 420–700 nm) placed at a distance of 15 cm on top of the mixture. After every 10 min, aliquots (3 mL) were withdrawn, filtered (0.22 μm nylon membrane), and analyzed by UV-Vis spectrophotometry. After each run, the reaction solutions were centrifuged to recover the catalyst. By applying the One-Factor-at-a-Time (OFAT) approach, the influence of catalyst dosage, initial carbofuran (CBF) concentration, solution pH, and visible light intensity was investigated independently. Each experiment run was carried out in triplicate under controlled conditions [19]. The photodegradation (%) was calculated using Eq. (1) [8].

$$\text{Degradation (\%)} = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 ; initial concentration of CBF (mg/L), while A_t ; its concentration at a given reaction time.

The surface charge of $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ composite was determined by the pH equilibration method. To produce suspensions, 30 mg of catalyst was dispersed in 10 mL of 0.01 M NaCl and adjusted to their initial pH values 2 to 11 with dilute HCl or NaOH and continuously agitated (300 rpm;

24 h; 25 °C. Point of zero charge (pHpzc) was taken as the initial pH where $\Delta\text{pH} = 0$ [12].

To elucidate the degradation mechanism, scavenger experiments were performed using 10 mmol/L of each trapping agent. Benzoquinone (BQ) act as a scavenger for superoxide ($\cdot\text{O}_2^-$) radicals; ethylene diaminetetraacetic acid (EDTA) is an excellent hole (h^+) trapper; tert-butyl alcohol (TBA) quenches the hydroxyl radicals ($\cdot\text{OH}$), and silver nitrate (AgNO_3) captures conduction band electrons (e^-) [20].

The kinetics of CBF degradation were analyzed with a pseudo-first-order rate equation as given in Eq. (2) [20].

$$\ln\left(\frac{C_0}{C_t}\right) = kt \quad (2)$$

where C_0 is the initial concentration of CBF (mg/L), while C_t is its concentration at a given reaction time t , and k is the apparent rate constant.

2.5 Photocatalytic Treatment of Pesticide Wastewater and Toxicity Evolution

Wastewater specimens were collected from a pesticide production plant in Multan, Pakistan. The samples were sieve filtered to remove suspended solids and subsequently stored under refrigeration until analysis. Thereafter, the wastewater underwent photocatalytic treatment under optimized conditions using the $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ composite, and mineralization was evaluated by COD (measured by the dichromate method) and TOC analyses and calculated by following Eqs. (3) and (4), respectively [21].

$$\text{COD reduction (\%)} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100 \quad (3)$$

$$\text{TOC reduction (\%)} = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100 \quad (4)$$

Where COD_0 and TOC_0 denote the initial and COD_t and TOC_t are the time-dependent concentrations (mg/L).

Since real industrial samples contain a complex mixture of organics, the samples were spiked with CBF to achieve a final 20 mg/L concentration to facilitate the identification of its specific intermediate products.

To evaluate toxicity during photocatalysis, CBF solutions were tested with the agar well diffusion assay. Growth inhibition of *E. coli* (ATCC 25922) served as a bioindicator to assess the antibacterial effect of CBF solutions [22–24]. Initially, nutrient agar was prepared and subjected to sterilization, and the molten agar was subsequently dispensed into Petri dishes and left to solidify. Six sets of plates were

prepared as follows: (i) ciprofloxacin solution (5 mg/L) (positive control), (ii) DI water (negative control), (iii) untreated CBF solution (5 mg/L), (iv-v) partially treated CBF solutions (collected at 60 and 90 min), and (iv) fully treated CBF solution (120 min). Once the agar plates were solidified and ready, fresh overnight cultures of *E. coli* were evenly spread on each agar plate using a sterile cotton swab. A 5 mm well was punched at the center of each plate using a sterilized micropipette tip. Each well was filled with 20 μ L of the corresponding solution. The agar plates were incubated (35 °C, 24 h) following a diffusion time of 15 min, and then the diameters of the inhibition zones in each well were measured.

To supplement the agar diffusion assay, a liquid broth inhibition test was performed. Activated *E. coli* (Optical Density; OD₆₀₀ = 0.6–0.8) was inoculated (10 μ L) into 10 mL of photocatalytically treated CBF solutions. Following incubation (12 h, 37 °C), bacterial growth was quantified spectrophotometrically at 600 nm. The inhibition % was determined using Eq. (5) [25].

$$\text{Inhibition (\%)} = \frac{A_{\text{control}} - A_{\text{sample}}}{A_{\text{control}}} \times 100 \quad (5)$$

where A_{sample} is the absorbance of the treated sample, and A_{control} is the absorbance of the control.

2.6 Stability and Reusability Study

The stability of the CuFe₂O₄/Zn-BTC photocatalyst was systematically evaluated over five consecutive photocatalytic cycles. After each 90-min run, the catalyst was magnetically recovered, filtered, and thoroughly washed (ethanol and deionized water), and dried before reuse. FTIR/XRD analyses were conducted after the fifth cycle to assess structural integrity [22].

3 Results and Discussion

3.1 Characterization by Composition, Structure, and Morphology

XRD analysis was conducted to elucidate the crystalline phases of CuFe₂O₄, Zn-BTC, and the CuFe₂O₄/Zn-BTC composite (Fig. 1a). The CuFe₂O₄/Zn-BTC composite displayed diffraction peaks at 30.15°, 33.41°, 35.84°, 39.02°, 54.29°, and 62.24° that matched with the spinel structure of CuFe₂O₄ (JCPDS card no. 34–0425) [26]. Zn-BTC showed characteristic peaks at 7.57°, 11.16°, 13.32°, 14.86°, 18.55°, 22.54°, 25.67°, 38.98°, and 45.25°, consistent with its crystalline framework [27]. The simulated PXRD pattern

of Zn-BTC further validated phase purity. The composite retained the characteristic peaks of both components with no significant shift in 2 θ , indicating that the crystalline structure remained unchanged during composite formation.

FTIR spectra (Fig. 1b) revealed characteristic vibrational modes confirming composite formation [10]. The composite spectrum retained all characteristic peaks, such as C = O stretching at 1614 cm^{−1} and asymmetric/symmetric carboxylate stretches at 1560/1530 cm^{−1} [16]. Additional bands included unsaturated C = C (1710 cm^{−1}), C–O stretching of uncoordinated carboxyl groups (1120 cm^{−1}), and aromatic C–H bending (782–720 cm^{−1}) [8]. characteristic peaks included unsaturated C = C bonds (1710 cm^{−1}), C–O stretching of uncoordinated carboxyl groups (1120 cm^{−1}), and aromatic C–H bending vibrations (782–720 cm^{−1}) [28]. Pristine CuFe₂O₄ displayed metal-oxygen vibrations at 474 cm^{−1} (Cu–O) and 582 cm^{−1} (Fe–O) [29]. A wide absorption near 3390 cm^{−1} was observed in all samples, which indicated stretching of O–H or an adsorbed water molecule [12]. These results confirm successful hybridization without compromising structural integrity.

The nitrogen adsorption-desorption isotherms (Fig. 1c) of CuFe₂O₄, Zn-BTC and CuFe₂O₄/Zn-BTC composite showed type IV isotherms with H3 hysteresis, characteristics of meso-porous materials [30]. The nitrogen uptake was higher for Zn-BTC which has a larger surface area (1032 m²/g) than CuFe₂O₄ (125.4 m²/g) [29]. The surface area of composite was reduced to 722.6 m²/g from that of bare Zn-BTC [16] due to partial pore blockage of CuFe₂O₄ nanoparticles. The BJH pore size distribution curves (Fig. 1d) indicated that CuFe₂O₄ had a wide mesoporous distribution while Zn-BTC had relatively narrow but uniform pores [31]. The composite had an intermediate pore structure, which provided enough active sites for photocatalysis. All sample BET surface area and BJH pore distribution results are summarized in Table 1.

The FESEM micrograph, EDS spectrum and grain size distribution profiles of all the synthesized materials are shown in Fig. 2. The CuFe₂O₄ nanoparticles (Fig. 2a) had a uniform surface texture, were mostly spherical in shape with some aggregation [32] and their grain sizes were between 10 and 100 nm, with a dominant peak around 50 nm. The crystals of Zn-BTC (Fig. 2b) were faceted with sharp edges and the particle size was in the range of 20–100 nm with a major peak around 60 nm. The composite (Fig. 2c) had a hybrid form, with the spherical and faceted domains being connected in cluster structures, which is indicative of strong interaction between both the oxide and MOF phases. The distribution of O, C, Cu, Zn and Fe was confirmed by EDS element mapping (Fig. S1) to be uniform. This even dispersion proves successful integration of both phases and structural stability of the composite [33].

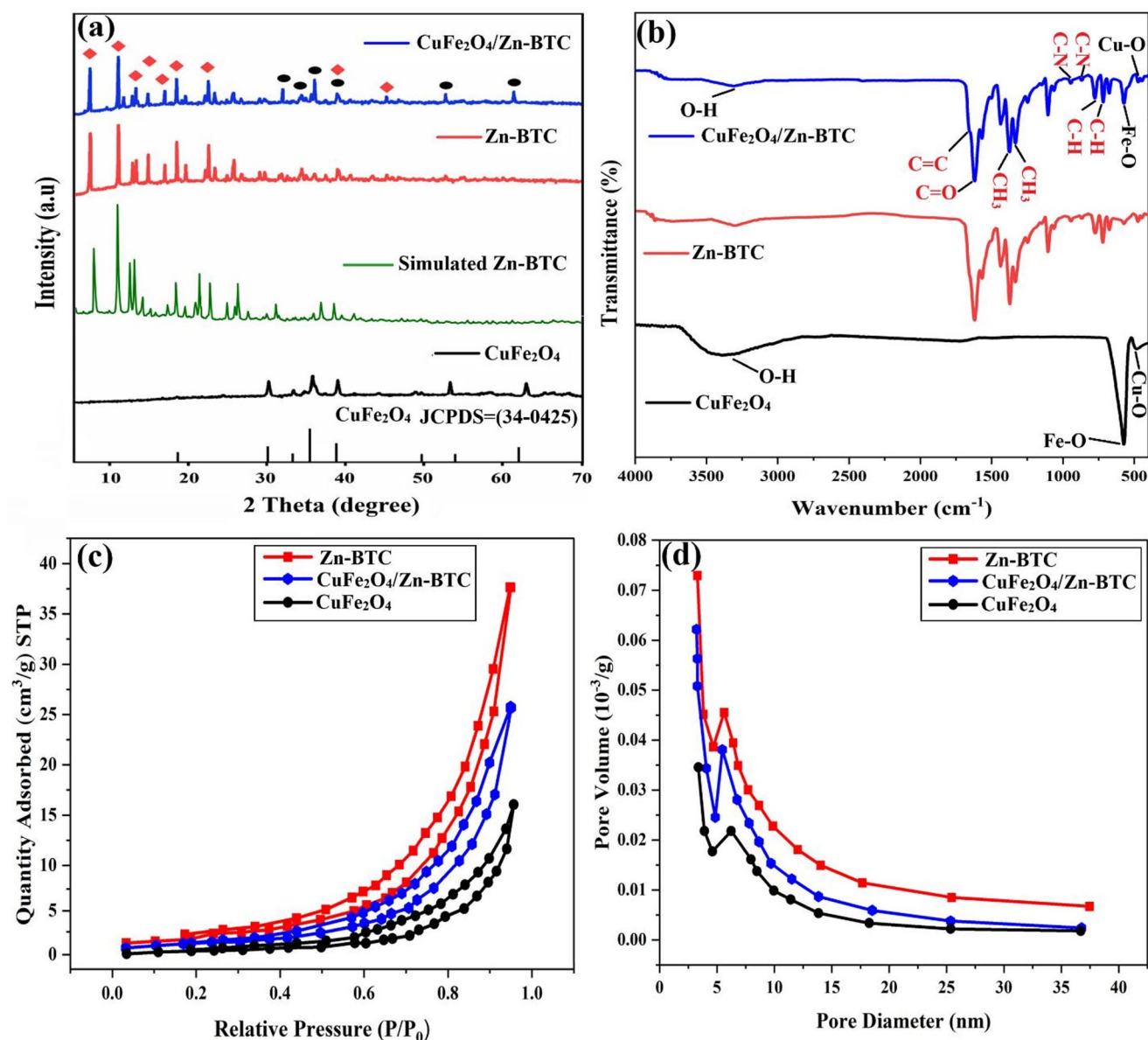


Fig. 1 Structural and surface characterization: **a** XRD patterns, **b** FTIR spectra, **c** N_2 adsorption-desorption isotherms, **d** BJH pore size distribution of $CuFe_2O_4$, Zn-BTC, and $CuFe_2O_4/Zn-BTC$

Table 1 Textural characteristics of $CuFe_2O_4$, Zn-BTC, and $CuFe_2O_4/Zn-BTC$ nanocomposite as determined from BET and BJH analyses

Photocatalyst	Surface area (m ² /g)	Average pore diameter (nm)	Total pore volume (cm ³ /g)
$CuFe_2O_4$	125.4	4.2	0.26
Zn-BTC	1032	3.4	0.43
$CuFe_2O_4/Zn-BTC$	722.6	3.9	0.36

All materials showed strong absorbance in the UV region as indicated in the UV-Vis DRS spectra (Fig. 3a). The composite exhibited a higher visible-light absorption than the Zn-BTC, and a slightly lower absorption than the

pure $CuFe_2O_4$. The bandgap energies were calculated using Tauc's relation, as expressed in Eq. (6) [10].

$$\alpha h\nu = \beta(h\nu - E_g)^n \quad (6)$$

Here, α donates the absorption coefficient while $h\nu$ represents photon energy, and E_g bandgap energy. Tauc plots (Fig. 3b) showed band gap energies of 1.86 eV for $CuFe_2O_4$, 3.29 eV for Zn-BTC, and 2.14 eV for the $CuFe_2O_4/Zn-BTC$. The intermediate bandgap shows effective coupling between the two components that improved the visible-light absorption while maintaining suitable redox ability for photocatalysis [34].

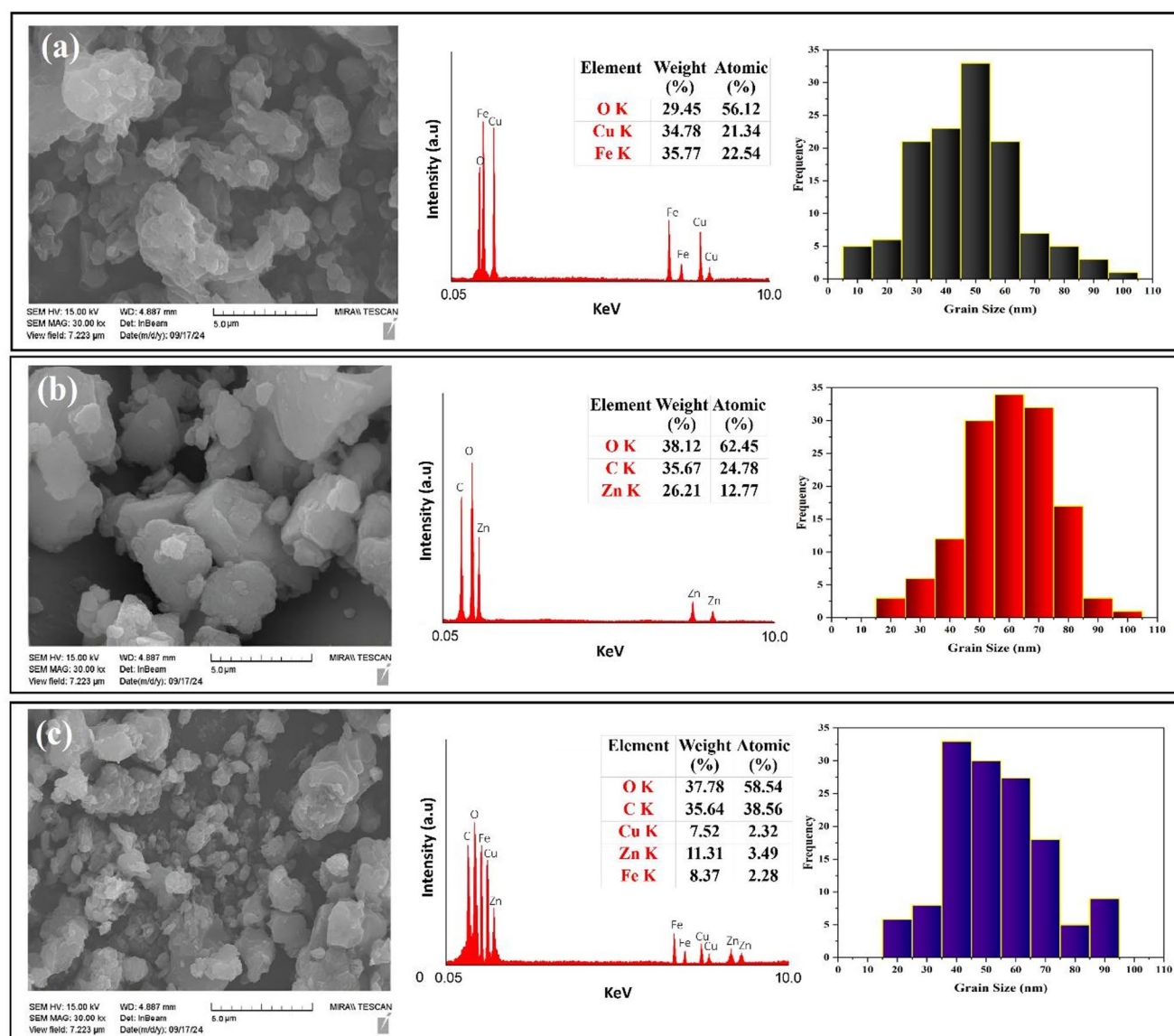


Fig. 2 FESEM imaging, grain size distribution, and EDX elemental analysis: **a** CuFe_2O_4 , **b** Zn-BTC, and **c** $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ nanocomposite

VSM analysis (Fig. 3c) reveals that pure CuFe_2O_4 exhibited significant ferrimagnetic behavior with a saturation magnetization (M_s) of 45.20 emu/g, and Zn-BTC showed a low magnetic response (13.18 emu/g) that correlated to poor intrinsic magnetism [35–37]. The $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ composite displayed an intermediate M_s value of 23.51 emu/g, lower than pure CuFe_2O_4 but still sufficient for practical purposes. This preserved magnetization allows efficient recovery of the nanocomposite from aqueous suspensions using an external magnet, a key advantage for reusable photocatalysts. Recovery efficiency remained consistently high, exceeding 97% after each catalytic cycle (Fig. S2) and showed excellent recyclability and practical applicability of the photocatalyst.

The point of zero charge (pHpzc) of the $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ composite was determined to be 6.30, as shown in Fig. 3d. The surface has a net positive charge below pH 6.30 and a net negative charge above it. Adsorption behavior and photocatalytic performance in water are modulated by this pH-responsive surface characteristic. The intermediate pHpzc indicates that the material can be used for environmental remediation in a variety of pH ranges [38, 39].

3.2 Key Parameters Affecting CBF Photodegradation

In an initial screening study, the photocatalytic efficiency of each material (CuFe_2O_4 , Zn-Zn-BTC, and $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ composite) was assessed under visible-light irradiation

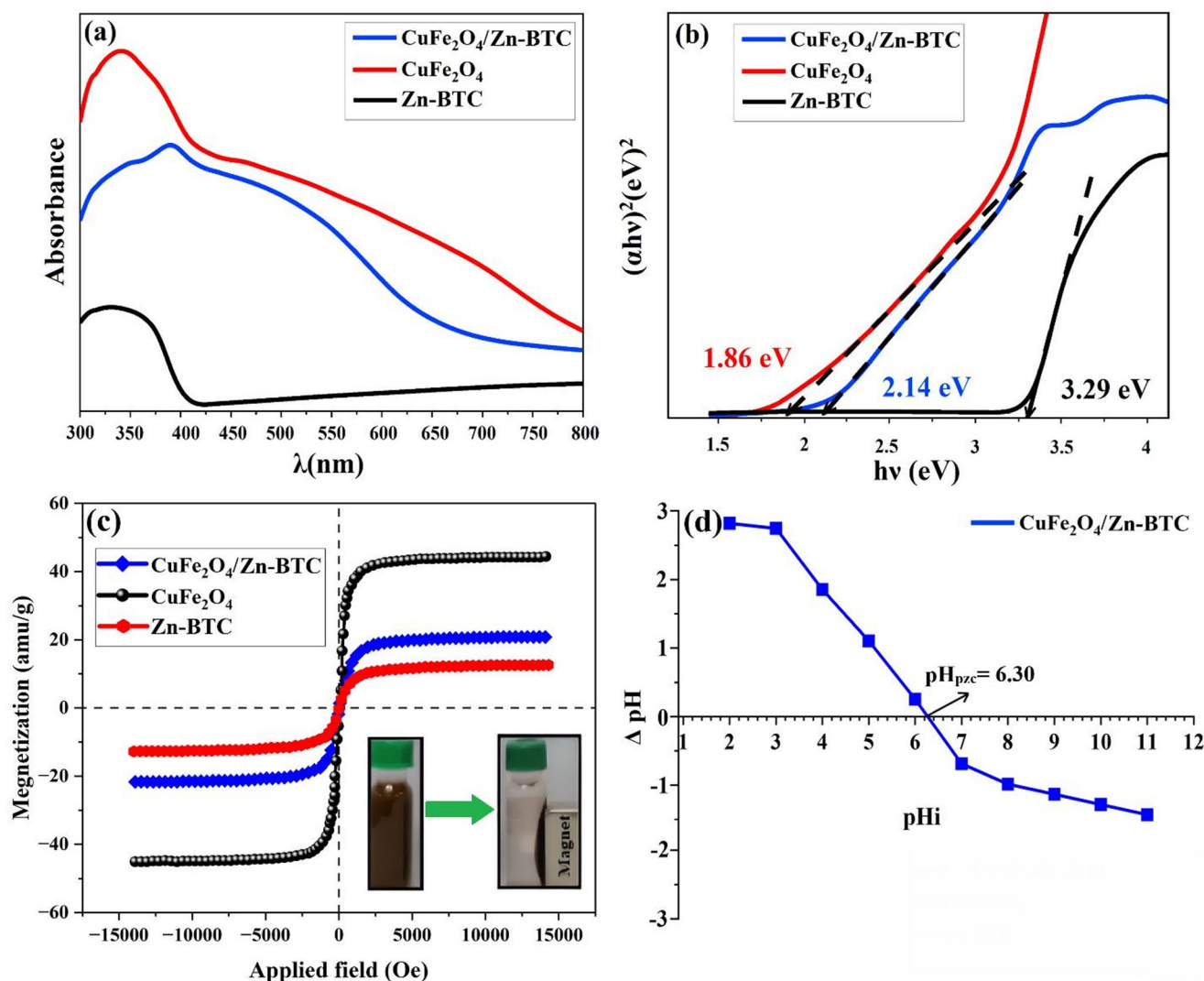


Fig. 3 Optical, magnetic, and surface charge analysis: **a** UV-Vis spectra, **b** Tauc plots, **c** VSM magnetization curves, **d** pH_{pzc} of CuFe₂O₄, Zn-BTC, and CuFe₂O₄/Zn-BTC nanocomposite

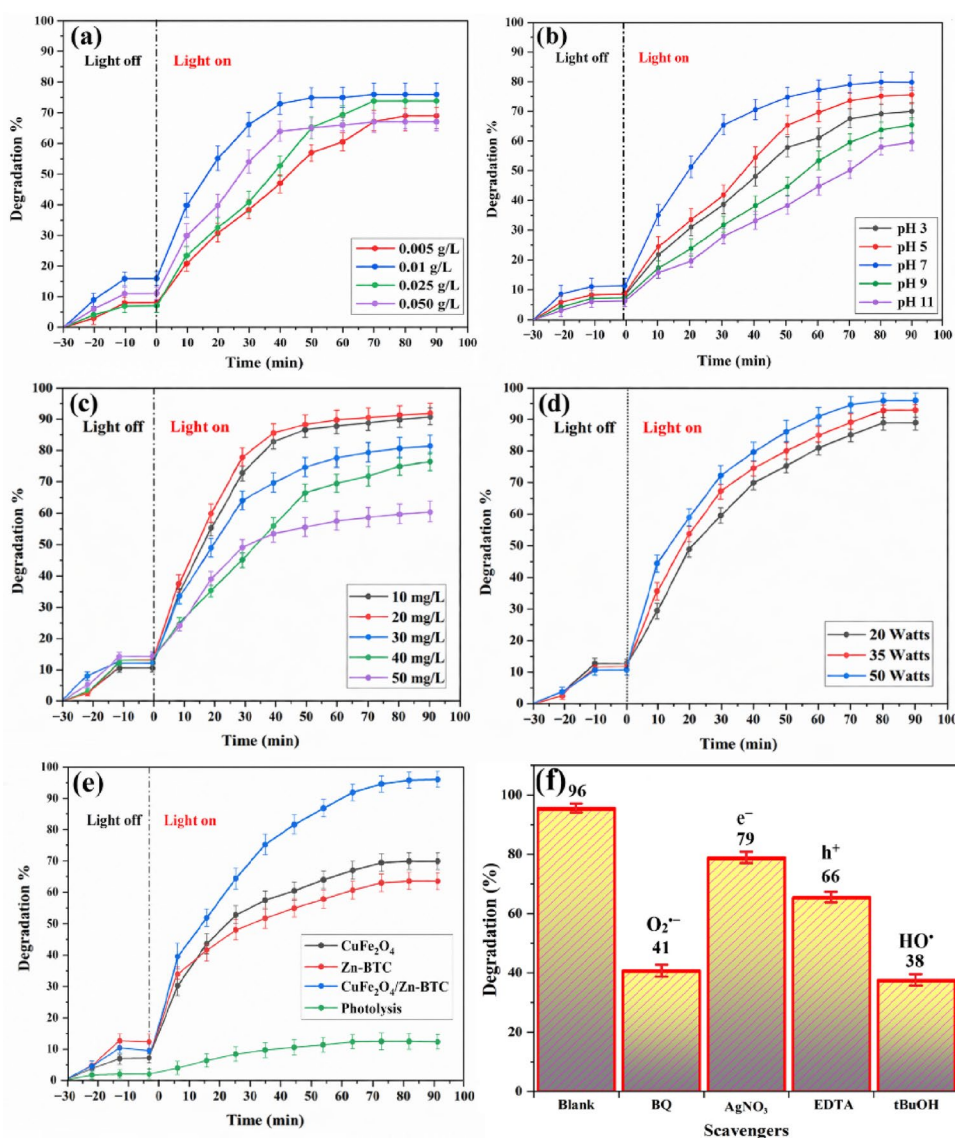
against CBF. Composite showed the 77% degradation of CBF in 90 min, whereas bare CuFe₂O₄ gave 62% and Zn-BTC 55% efficiency with baseline operating conditions 10 mg/L CBF, 0.01 g/L catalyst dosage, 20 W LED irradiation, and pH 7, as shown in Fig. S3. Due to the superior performance of the CuFe₂O₄/Zn-BTC composite, it was selected for further optimization.

The impact of CuFe₂O₄/Zn-BTC dosage (0.005–0.05 g/L) on the degradation of CBF was investigated methodically (Fig. 4a). Degradation increased from 69% to 78% when the dosage was increased from 0.005 to 0.01 g/L due to the accessibility of more active sites and dropped to 74% at 0.05 g/L, happened probably due to particle aggregation that decreases the effective surface area, enhances solution turbidity [22]. Therefore, a 0.01 g/L catalyst loading was employed in all subsequent experiments.

Solution pH and catalyst surface have a considerable impact on CBF degradation (Fig. 4b). The most pronounced degradation (83%) was observed at pH 7, near the composite's PZC (6.30), where the surface is neutral and promotes absorption. At acidic pH (< 6.30), the catalyst surface is positively charged, so CBF protonation occurs that resulted in electrostatic repulsion, reducing performance (70% at pH 3). Under alkaline conditions (> 6.30), both the catalyst and deprotonated CBF (phenoxide anions) are negatively charged, again causing repulsion and reducing degradation (66% at pH 9, 61% at pH 11). These results show the critical role of pH-dependent electrostatic interactions in photocatalytic performance [16].

Degradation efficiency was also greatly influenced by the initial CBF concentration (Fig. 4c). As the concentration increased from 10 to 50 mg/L, efficiency decreased

Fig. 4 Photocatalytic degradation of CBF over $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ within 90 min reaction time: **a** Catalyst dosage (0.005–0.05 g/L) under fixed conditions of 10 mg/L CBF, pH 7, 20 W LED; **b** Solution pH (3–11) at 0.01 g/L catalyst, 10 mg/L CBF, 20 W LED; **c** Initial CBF concentration (10–50 mg/L) at 0.01 g/L catalyst, 20 W LED, pH 7; **d** Visible light intensity (20–50 W LED) at 0.01 g/L catalyst, 20 mg/L CBF, pH 7; **e** Comparative performance of different photocatalysts under optimized conditions; **f** Role of scavengers in CBF degradation over $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ under optimized conditions (20 mg/L CBF, 0.01 g/L catalyst, 50 W LED, pH 7)



from 91% to 60%, with a maximum of 93% at 20 mg/L [9]. Higher pollutant concentrations cause active sites to become saturated and restrict CBF adsorption onto the catalyst surface. The formation of active species may be further reduced by the increased concentration of organic molecules, which may also prevent light from penetrating the catalyst surface [12].

Photocatalytic activity was significantly impacted by the intensity of light (Fig. 4d). When light intensity increased from 20 to 50 W, the degradation performance improved from 89% to 96%. Increased electron-hole pair formation is encouraged at higher intensity, which raises the production of ROS for the degradation of pollutants [40, 41]. The apparent pseudo-first-order rate constants (k_{app}) under different conditions are shown in Fig. S4.

3.3 Comparative Photocatalytic Performance and Mechanistic Study of CBF Degradation

Photocatalytic degradation of CBF was studied under different conditions, comparing four systems: visible light alone, CuFe_2O_4 , Zn-BTC, and the $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ nanocomposite (Fig. 4e). Visible light without a catalyst eliminated less than 12% of CBF in 90 min, which indicated that catalytic ROS production is required for efficient degradation. CuFe_2O_4 exhibited a narrower bandgap (1.86 eV) for visible light absorption, which led to higher removal (69%) than Zn-BTC (63%). The efficiency was limited by rapid charge recombination and a small surface area ($125.4 \text{ m}^2/\text{g}$). The $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ nanocomposite showed the highest CBF degradation (96%), demonstrating the synergistic effect and enhanced performance of the heterostructure compared to the individual components.

Table 2 shows a performance comparison of the $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ composite with previously reported photocatalysts for CBF degradation. While WO_3/ZrO_2 achieved complete removal, it needed a significantly higher catalyst dose (1 g/L) and higher power (150 W) with a longer reaction time of 240 min. Similarly, CdS@MIL-125(Ti) and $\text{NaNbO}_3\text{-Au-Sn}_3\text{O}_4$ required intense light powers (400 and 300 W, respectively), yet achieved lower efficiencies (73% and 83%). Efficient systems like $\text{g-C}_3\text{N}_4/\text{BiOCl}$ achieved 95% removal under 250 W and 120 min, but needed more light energy, and the $\text{Fe}_3\text{O}_4\text{-SnO}_2\text{-gC}_3\text{N}_4$ achieved 89% removal (30 W, 150 min), but required longer treatment times. In contrast, the $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ composite achieved 96% removal within only 90 min under a lower light power of 50 W and a reduced catalyst dose (0.01 g/L), demonstrating faster kinetics and greater energy efficiency, demonstrating superior reaction kinetics, high energy efficiency, and strong potential for practical wastewater treatment applications.

Radical scavenging experiments (Fig. 4f) were systematically performed to identify the active species governing the photocatalytic degradation of CBF. The efficiency dropped to 38% when 10 mmol/L of $t\text{-BuOH}$ ($\cdot\text{OH}$ scavenger) was used, clearly illustrating the crucial role of hydroxyl. In the same way, BQ ($\cdot\text{O}_2$ scavenger) reduced efficiency to 41%, indicating significant participation of superoxide radicals. The relatively small efficiency losses found with AgNO_3 (79%, electron scavenger) and EDTA (66%, hole scavenger) indicate the fact that only minor contributions of the photogenerated charge carriers are involved [8, 28].

The degradation kinetics (Fig. 5a) revealed pseudo-first-order behavior with $R^2 > 0.92$ [30, 39]. As can be seen from Table 3, the rate constant k significantly decreased from 0.0261 min^{-1} to 0.0026 min^{-1} with the increase in CBF concentration from 10 to 50 mg/L. This decrease is due to competitive adsorption of CBF molecules with their intermediates on the catalyst active sites and due to the scavenging of $\cdot\text{OH}$ by the byproduct accumulation. Therefore, the composite is effective at low concentrations of CBF, but is increasingly restricted at higher concentrations of pollutants.

3.4 Mineralization and Biodegradability Study

The photocatalytic degradation of CBF was tested in real wastewater from a pesticide plant in Multan, Punjab, and the important parameters of the wastewater are presented in Table 4. Poor biodegradability and presence of refractory contaminants were quantified by the low BOD_5/COD ratio of 0.32. As shown in Fig. 5b, the TOC reduction was still less than 50% after 30 min and intermediate products production was shown. The treatment time was increased to 120 min, and the TOC reduction was found to be 69% indicating that the refractory intermediates need longer irradiation time for degradation.

Pesticide wastewater is more challenging to treat than model solutions because it contains a high concentration of toxic chemicals, is complex and poorly biodegradable. The initial value of COD and TOC were 1370 mg/L and 1840 mg/L respectively and during treatment, the COD and TOC were monitored. After 2 h, the composite reduced COD by 77% (to 315 mg/L; Fig. 5c) and TOC by 69% (to 570 mg/L; Fig. 5d) and Fig. 5e depicts these reduction ratios for TOC and COD. It can be seen from the results that the composite can remove a significant amount of organic contaminants from complex wastewater.

Biodegradability enhancement was assessed by calculating the average oxidation state (AOS) and carbon oxidation state (COS) using Eqs. (7) and (8) [30];

$$\text{AOS} = 4 - 1.5 \times \frac{\text{COD}}{\text{TOC}} \quad (7)$$

$$\text{COS} = 4 - 1.5 \times \frac{\text{COD}}{\text{TOC}_0} \quad (8)$$

The initial AOS and COS values of 0.74 reflect poor wastewater biodegradability. Following photocatalytic treatment, these values increased AOS to 1.5 and COS to 3.0. This showed the successful conversion of refractory organic compounds into more biodegradable forms (Fig. 5f). This transformation suggests that photocatalysis not only degrades pollutants but also modifies their chemical nature for further biological treatment.

Table 2 Comparative study of the synthesized catalyst with respect to other materials

Sr. No.	Catalysts	CBF concentration (mg/L)	Catalyst dose (g/L)	Light intensity (W)	Reaction time (min)	CBF removal (%)	References
1.	$\text{NaNbO}_3\text{-Au-Sn}_3\text{O}_4$	0.1	0.4	300	120	73%	[42]
2.	$\text{Fe}_3\text{O}_4\text{-SnO}_2\text{-gC}_3\text{N}_4$	1.5	0.0035	30	150	89%	[43]
3.	WO_3/ZrO_2	20	1	150	240	100%	[44]
5.	CdS@MIL-125(Ti)	10	0.5	400	120	83%	[45]
6.	$\text{InVO}_4/\text{In}_2\text{S}_3$	10	0.15	300	60	82%	[46]
7.	$\text{gC}_3\text{N}_4/\text{BiOCl}$	5	0.25	250	120	95%	[22]
8.	$\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$	20	0.01	50	90	96%	Present study

Fig. 5 Degradation and mineralization studies: **a** CBF degradation kinetics, **b** TOC reduction, **c** COD variation, **d** TOC variation in real wastewater, **e** overall COD/TOC reduction, **f** biodegradability improvement

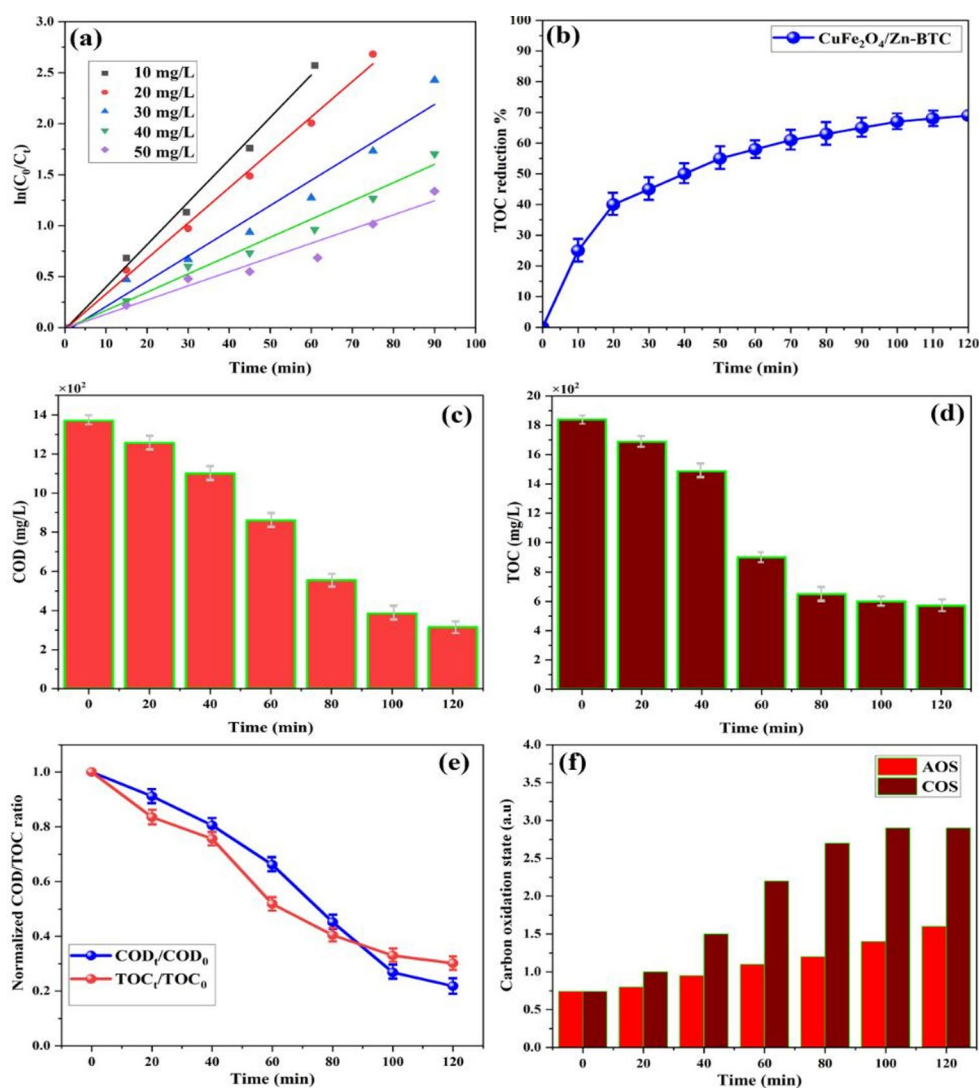


Table 3 First-order kinetic parameters for various CBF concentrations

Initial CBF concentration (mg/L)	Regression coefficient (R^2)	Rate constant k (min^{-1})	Equation
10	0.9844	0.0259	$y = 0.0259x + 1.0355$
20	0.9846	0.0160	$y = 0.0160x + 0.9800$
30	0.9413	0.0124	$y = 0.0124x + 0.6824$
40	0.9284	0.0048	$y = 0.0048x + 0.4412$
50	0.9184	0.0025	$y = 0.0025x + 0.2108$

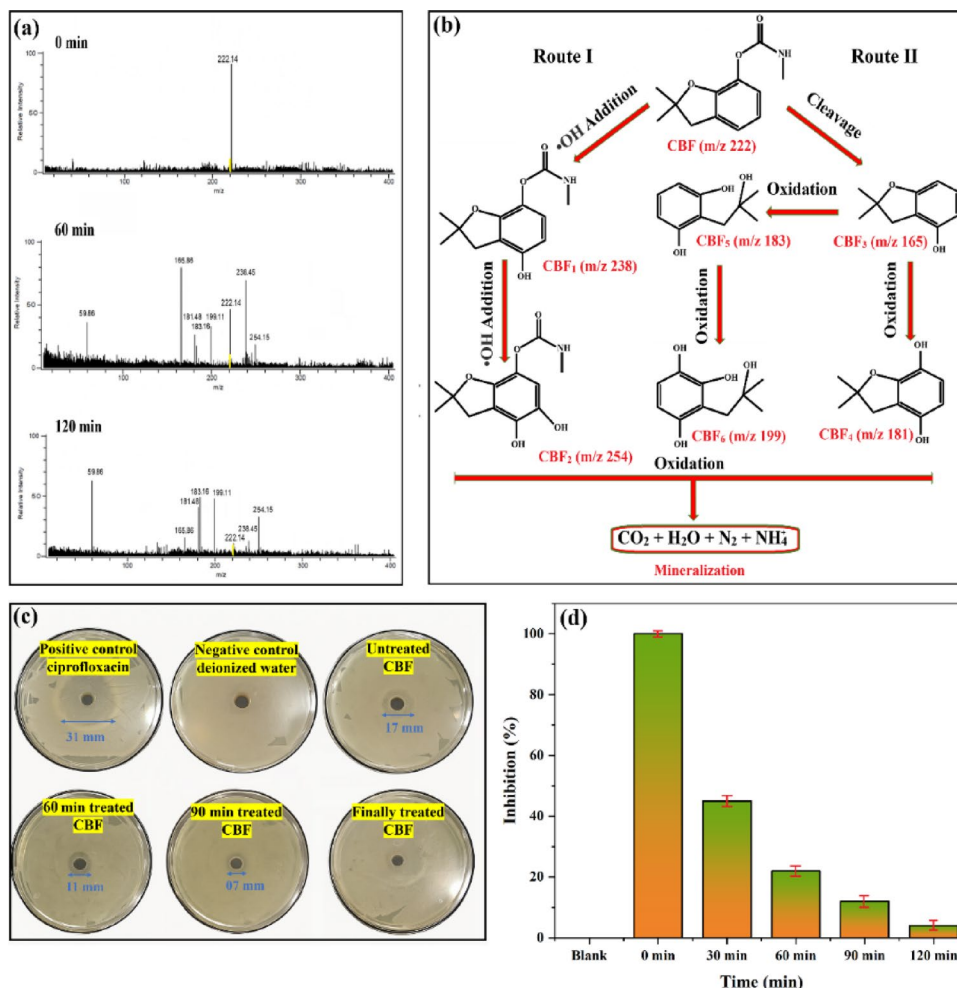
Table 4 Water quality parameters of wastewater samples used in this work

Parameters	Pesticide industry wastewater
pH	6.92
COD (mg/L)	1370
BOD ₅ (mg/L)	450
BOD ₅ /COD	0.32
TOC (mg/L)	1840

3.5 Possible Degradation Pathway of CBF

LC-MS analysis was employed to identify the degradation mechanism of CBF during the photocatalytic process [22]. Structural properties were evaluated from mass spectra and cross-referenced with existing data, which allows us to propose potential degradation pathways (Fig. 6a). Figure 6b shows the LC-MS spectra of intermediate generation under visible-light-driven CuFe₂O₄/Zn-BTC. The first process involves $\cdot\text{OH}$ radicals attacking the benzene ring of CBF ($m/z = 222$), which resulted in hydroxylated CBF₁ ($m/z = 238$). A subsequent addition of $\cdot\text{OH}$ results in CBF₂ ($m/z = 254$). Alternatively, cleaving the C-O bond in the carbamate moiety produces CBF₃ ($m/z = 165$) [47]. Oxidation of CBF₃, accompanied by furan ring opening, leads to CBF₅ ($m/z = 183$), which may undergo further oxidation by ROS or photogenerated holes (h^+) to form CBF₆ ($m/z = 199$). Hydroxylation of the furan ring in CBF₃ can also produce CBF₄ ($m/z = 181$) [48]. Eventually, these intermediates are degraded

Fig. 6 Degradation pathway and antibacterial evaluation: **a** Mass spectra of CBF photodegradation intermediates at different time intervals, **b** Proposed degradation pathway of CBF, **c** Antibacterial activity of initial and treated CBF solutions against *E. coli* via agar well diffusion (controls: ciprofloxacin positive, deionized water negative), and **d** *E. coli* growth inhibition (%)



through successive reactions with ROS and valence band holes, mineralizing to CO₂, H₂O, and NH₄⁺ [22].

3.6 Toxicity of CBF and Its Degradation Intermediates

The toxic effects of CBF and its degradation intermediates were assessed by an agar well diffusion method using *E. coli* (ATCC 8739) as the test organism. Ciprofloxacin was used as a positive control, and deionized water as a negative control to ensure effects were solely from the tested samples. The positive control produced a 31 mm inhibition zone, while the untreated CBF sample showed a 17 mm inhibition zone (Fig. 6c). After 60 min of visible-light irradiation, the inhibition zone for partially degraded CBF was reduced to 11 mm, further shrinking to 7 mm after 90 min of degradation. In contrast, neither the negative control nor the fully degraded CBF sample displayed any inhibitory activity [22, 49]. A supplemental evaluation (Fig. 6b) measured *E. coli* growth using absorbance in cultures exposed to degradation products collected at various irradiation periods. Bacterial growth was completely inhibited in the untreated

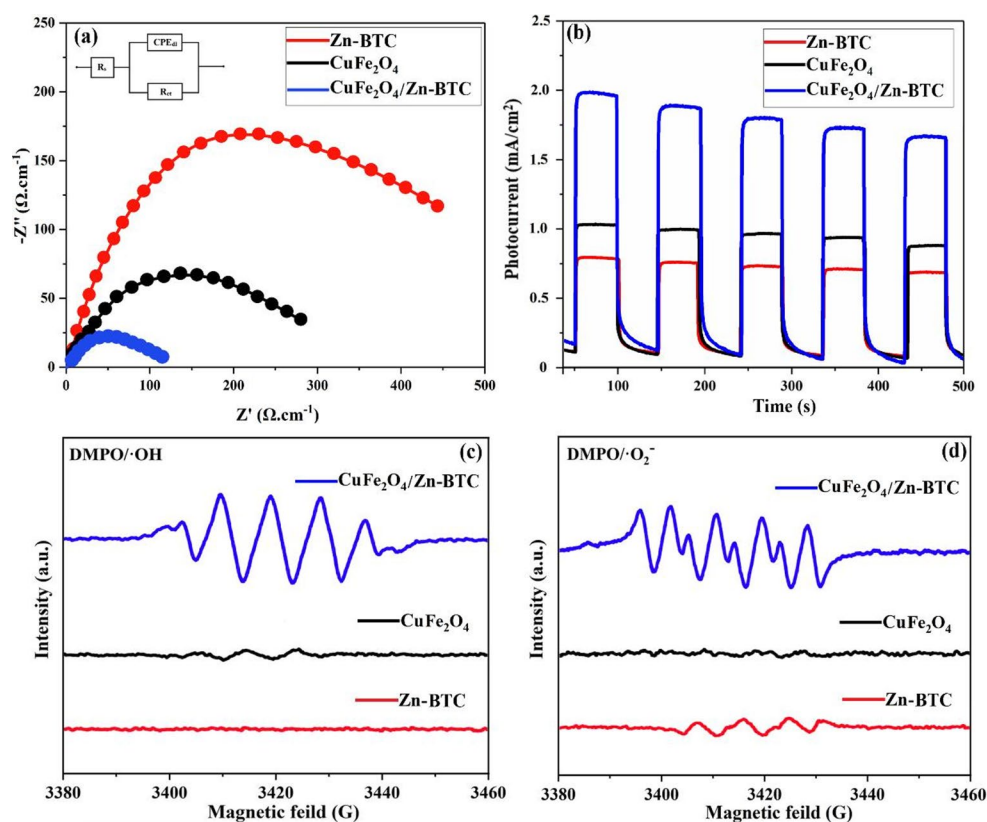
CBF sample (0 min). After 30–90 min of light exposure, inhibition decreased to around 13% that showed significant CBF breakdown. After 120 min, *E. coli* growth returned to around 4%, similar to the blank control [50]. These results indicate that photocatalytic treatment effectively neutralized the antimicrobial activity of CBF and that its degradation products were likely non-toxic.

3.7 Electrochemical Analysis and Proposed Photocatalytic Mechanism

Electrochemical impedance spectra (EIS) for Zn-BTC and CuFe₂O₄ and CuFe₂O₄/Zn-BTC composite are shown in Fig. 7a. The Nyquist plot for the composite has a much smaller semicircular diameter than the other materials, indicating significantly decreased charge transfer resistance (R_{ct}) and enhanced carrier transport across the interface [51]. This improved charge transfer is consistent with the experimentally observed increase in photocatalytic activity [30].

Transient photocurrent responses for Zn-BTC and CuFe₂O₄ and CuFe₂O₄/Zn-BTC composite under xenon light irradiation are shown in Fig. 7b. Higher photocurrent

Fig. 7 Electrochemical and radical detection analysis: **a** EIS Nyquist plots, **b** Transient photocurrent responses, **c** ESR spectra of DMPO/ $\cdot$ OH, **d** ESR spectra of DMPO/ $\cdot$ O₂⁻ for Zn-BTC and CuFe₂O₄ and CuFe₂O₄/Zn-BTC



density reflects a greater number of photoinduced charge carriers on the catalyst surface [52, 53]. The CuFe₂O₄/Zn-BTC composite achieved significantly higher photocurrent density (1.9 mA cm⁻¹) compared to pristine Zn-BTC (0.7 μA cm⁻¹) and CuFe₂O₄ (1.1 mA cm⁻¹), which indicates more efficient separation of photogenerated electron-hole pairs. The stable photocurrent across repeated on/off cycles confirms the composite's robust photostability and superior photoelectrochemical performance [42].

The photoluminescence (PL) spectra were obtained to evaluate charge separation and transfer efficiency [52]. A lower PL intensity means fewer charge carriers recombine, which is better for photocatalysis. As shown in Fig S3, the PL intensity decreases in the order: Zn-BTC > CuFe₂O₄ > CuFe₂O₄/Zn-BTC. The composite shows the weakest PL signal, proving that it achieves the most efficient charge separation due to strong coupling and the formation of an internal electric field [46].

An electron paramagnetic resonance (EPR) with DMPO as a spin trap identified ROS generated during photodegradation [54]. Under illumination, CuFe₂O₄ and Zn MOF exhibited relatively weak or negligible signals. However, the CuFe₂O₄/Zn MOF composite produced clear peaks for the DMPO- $\cdot$ O₂⁻ adduct (Fig. 7c), confirming the photoinduced superoxide radicals ($\cdot$ O₂⁻) production and showing that CB electrons effectively reduce dissolved oxygen, triggering oxidative degradation. Similarly, distinct DMPO- $\cdot$ OH

adduct signals were observed for the composite (Fig. 7d), while the individual components had negligible responses. Therefore, the generation of $\cdot$ OH radicals by VB holes oxidizing water or hydroxide ions plays a key role in pollutant degradation.

Mott-Schottky plots (Fig. 8a) showed flat band potentials of + 0.26 V and - 1.28 V (vs. SCE) for CuFe₂O₄ and Zn-BTC, respectively [51]. The negative slopes confirm their n-type semiconducting character [30, 55]. The difference in flat band positions shows an accurately oriented heterostructure that promotes directional charge migration. Converting the flat band potentials to the NHE scale using Eq. (9) [56].

$$E \text{ (vs. NHE)} = E \text{ (vs. SCE)} + 0.24 \text{ V} \quad (9)$$

yields values of + 0.50 V (CuFe₂O₄) and - 1.04 V (Zn-BTC). Since the CB edge of n-type semiconductors typically lies 0.10 eV more negative than the flat band potential. The CB edge positions were corrected to be + 40 eV for CuFe₂O₄ and - 1.14 eV for Zn-BTC. The VB edges positions were then calculated using Eq. (10) [57].

$$E_{VB} = E_{CB} + E_g \quad (10)$$

giving + 2.26 eV for CuFe₂O₄ and + 2.15 eV for Zn-BTC.

The work function (ϕ) is an important electronic parameter representing the energy required to remove an electron from

Fig. 8 Band structure characterization: **a** Mott-Schottky plots, **b** UPS spectra, **c** Band alignment before and after contact of Zn-BTC and CuFe_2O_4

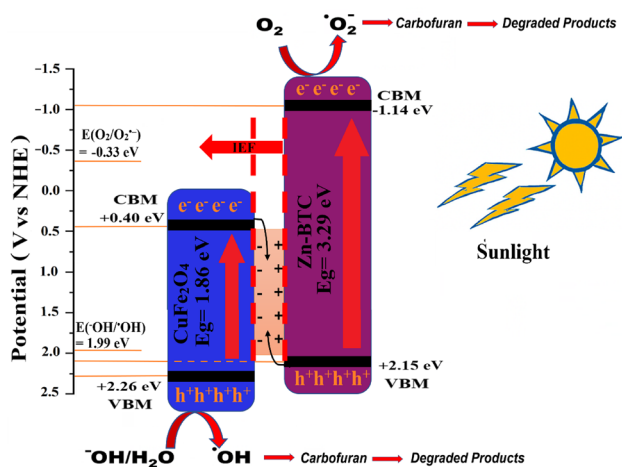
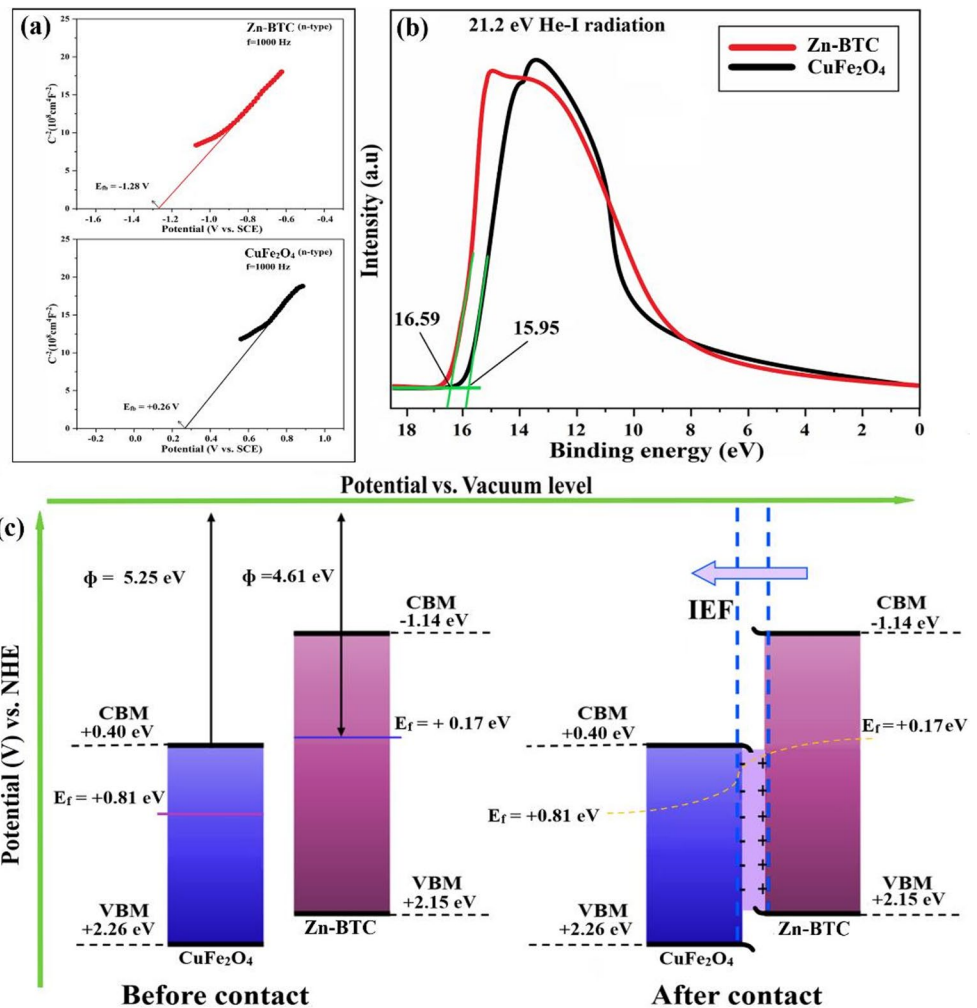


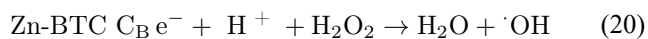
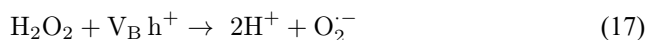
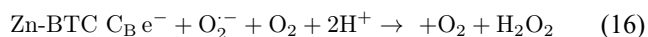
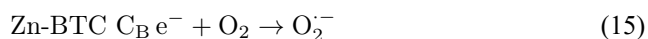
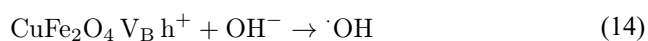
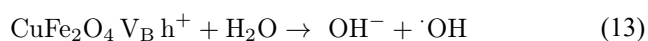
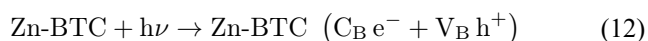
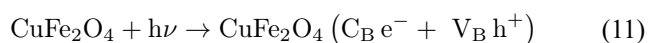
Fig. 9 Proposed S-scheme charge transfer mechanism of $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ composite for CBF degradation, showing electron-hole separation, interfacial charge migration, and ROS generation

the Fermi level (E_f) to the vacuum level [58]. To explain the charge transfer mechanism in the $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ heterostructure, ultraviolet photoelectron spectroscopy (UPS) analysis was carried out (Fig. 8b). The secondary cutoff energies were measured to be 15.95 eV for CuFe_2O_4 and 16.59 eV for Zn-BTC. Applying the relation ($\phi = h\nu - E_{\text{cutoff}}$), these values yield work functions of 5.25 eV and 4.61 eV, respectively. The Fermi levels on the NHE scale ($E_f = \phi - 4.44$) are + 0.81 eV (CuFe_2O_4) and + 0.17 eV (Zn-BTC) vs. NHE (Fig. 8c). CuFe_2O_4 has a deeper E_f and a larger work function so act as an electron acceptor, while Zn-BTC has a shallower E_f and donates electrons. After coupling these two materials, electrons drift from Zn-BTC to CuFe_2O_4 till equilibrium and an internal electric field (IEF) across the interface is established that drives charge separation.

The combined evidence from optical characterization, electrochemical measurements, radical scavenger experiments, and EPR analysis supports an S-scheme charge-transfer mechanism for the $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ composite (Fig. 9). Both materials generate electron-hole pairs in their respective CB and VB when exposed to visible light [22].

Upon contact, the E_f equilibration induces an internal electric field (IEF) and band bending at the interface. This IEF causes low-energy electrons from the CB of CuFe₂O₄ to recombine with low-energy holes in the VB of Zn-BTC after exposure to visible light. This S-scheme spatial separation maintains the high-reduction potential electrons in the CB of Zn-BTC and the high-oxidation potential holes in VB of CuFe₂O₄ [56, 59]. This configuration is favorable because it eliminates lower-energy charged carriers while retaining the highly reducing electrons (e^-) in the CB of Zn-BTC and the highly oxidative holes (h^+) in the VB of CuFe₂O₄. The residual charges with strong redox potential produce $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ which drive oxidation of CBF and produce ROS that actively contribute to the degradation of CBF [60].

Equation (11) to (21) describe the main reactions that control CBF degradation through the S-scheme mechanism.



Photogenerated electrons in the CB of Zn-BTC reduce O_2 to $\text{O}_2^{\cdot-}$, which reacts further to produce hydrogen peroxide (H_2O_2) and hydroperoxyl radicals ($\text{OH}_2^{\cdot}$). These species decompose to yield $\text{OH}^{\cdot}$ radicals. Simultaneously, VB holes in CuFe₂O₄ oxidize H_2O or OH^- to $\text{OH}^{\cdot}$ radicals [30]. The combined effect of ROS, such as $\text{OH}^{\cdot}$ and $\text{O}_2^{\cdot-}$ and $\text{OH}_2^{\cdot}$ drives systematic attack on CBF molecules, transforming to CO_2 and H_2O through successive oxidation, dehalogenation, and mineralization steps [57].

3.8 Reusability and Stability

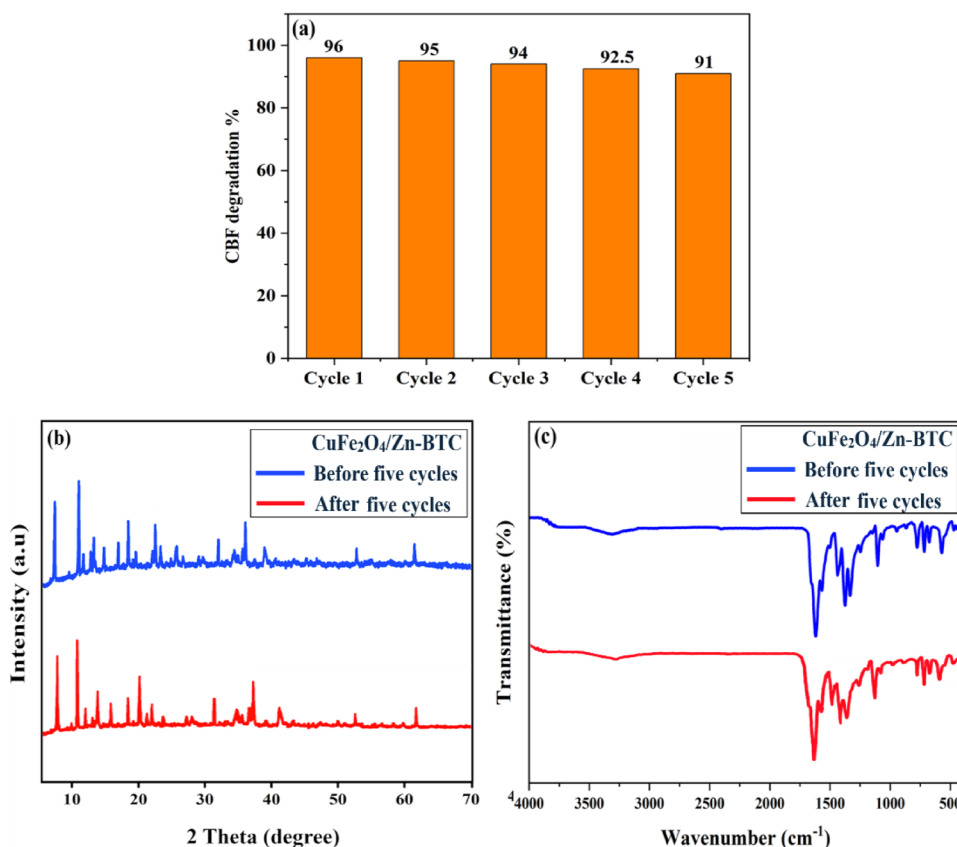
The CuFe₂O₄/Zn-BTC photocatalyst was subjected to five consecutive degradation cycles, during which its efficiency declined only marginally from 96 to 91% (Fig. 10a), highlighting its suitability for repeated wastewater treatment. Post XRD measurements (Fig. 10b) showed that the crystal structure and chemical composition of the composite remained intact even though there was a slight shift in some diffraction peaks. All major functional groups were retained with only a small loss in the intensity of the bands, as evidenced by post FTIR spectra (Fig. 10c).

In this study, ICP-MS analysis was not used, but the results on reusability and stability suggest that leaching of metal ions was not relevant. This was substantiated by the VSM analysis and the catalyst was found to have over 97% recovery efficiency. Furthermore, literature reported in a similar system, Cu and Zn leaching below 0.2 mg/L (well below the MIC for *E. coli* (> 5 mg/L)) [61] indicated that the effect of dissolved metal ions on the observed photocatalytic activity was insignificant. In the case of the antimicrobial effect of CBF, the results further confirm that detoxification is not by leached metals but, rather, by photocatalytic degradation. In future work, however, 3D-EEM fluorescence spectroscopy will be added to the research to elucidate the degradation pathway, and ICP-MS will be used to systematically study the leaching of metal ions to guarantee environmental safety and operating reliability.

4 Conclusion

This study reports the successful hydrothermal synthesis of CuFe₂O₄/Zn-BTC nanocomposite and demonstrates its effective application for the degradation of carbofuran under visible light. Structural, morphological, and textural analysis indicated that CuFe₂O₄ was well integrated into the Zn-BTC framework without sacrificing the crystallinity of either constituent. Upon formation of an S-scheme heterojunction, charge separation and visible-light absorption were improved, and the bandgap was reduced to 2.14 eV when compared to pristine materials. Following first-order kinetics, the CuFe₂O₄/Zn-BTC photocatalyst achieved 96% degradation of carbofuran under optimized conditions. LC-MS profiling identified the degradation intermediates along with possible transformation routes. Mineralization investigation based on COD/TOC reduction confirmed substantial degradation of organic content in the real wastewater sample. Moreover, *E. coli*-based ecotoxicity tests verified a marked reduction in toxicity after treatment, which shows the environmental compatibility of the process. After five reuse cycles, the composite maintained excellent structural robustness, photocatalytic performance, and durability. The

Fig. 10 Catalyst stability and reusability of $\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ composite: **a** Reusability study, **b** Post-XRD, and **c** Post-FTIR of reused catalyst



$\text{CuFe}_2\text{O}_4/\text{Zn-BTC}$ nanocomposite as a whole offers a reliable, magnetically recyclable framework for the removal of pesticides from contaminated water systems.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10562-026-05418-0>.

Acknowledgements The authors express their gratitude to Princess Nourah bint Abdulrahman University Researchers Supporting Project number (PNURSP2026R61), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia.

Author Contributions The manuscript was written with the contributions of all authors. All authors have approved the final version of the manuscript.

Funding Princess Nourah bint Abdulrahman University Researchers Supporting Project number (PNURSP2026R61), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia.

Data Availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare no competing interests.

Ethical Approval Not Applicable.

Consent to Participate Not Applicable.

Consent for Publication Not Applicable.

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