



A CuO/ZnFe₂O₄ heterostructure as an efficient catalyst for NaBH₄-assisted reduction of chloramphenicol

Le Thi Hoa¹, Nguyen Thi Thu Huong¹, Le Quoc Viet¹, Trinh Ngoc Dat²,
Nguyen Duc Cuong³, Le Thi Thanh Nhi^{*4,5} and Tran Thai Hoa^{*1}

Full Research Paper

[Open Access](#)

Address:

¹University of Sciences, Hue University, Hue City 530000, Vietnam, ²The University of Danang, University of Science and Education, Danang City, 550000, Vietnam, ³University of Education, Hue University, Hue City 530000, Vietnam, ⁴Center for Advanced Chemistry, Institute of Research and Development, Duy Tan University, 03 Quang Trung, Danang city, 550000, Vietnam and ⁵Faculty of Natural Sciences, Duy Tan University, 03 Quang Trung, Danang city, 550000, Vietnam

Email:

Le Thi Thanh Nhi^{*} - letthanhnh1@duytan.edu.vn;
Tran Thai Hoa^{*} - tthaihoa@hueuni.edu.vn

^{*} Corresponding author

Keywords:

catalysis; chloramphenicol; CuO; NaBH₄; reduction; ZnFe₂O₄

Beilstein J. Nanotechnol. **2026**, *17*, 1396–1409.
<https://doi.org/10.3762/bjnano.17.97>

Received: 26 June 2026

Accepted: 02 October 2026

Published: 16 October 2026

Associate Editor: C. T. Yavuz



© 2026 Hoa et al.; licensee Beilstein-Institut.
License and terms: see end of document.

Abstract

In this study, a CuO/ZnFe₂O₄ heterostructure in the form of a flower, consisting of rod-like surface features associated with CuO on ZnFe₂O₄ microspheres, was successfully synthesized and evaluated for its catalytic reduction of chloramphenicol (CAP) in the presence of NaBH₄. Structural and morphological analysis confirmed the successful formation of the heterostructure with enhanced contact between ZnFe₂O₄ and CuO. Compared to pure ZnFe₂O₄, the CuO/ZnFe₂O₄ catalyst exhibited significantly improved catalytic activity for CAP reduction. Reaction conditions strongly influenced reduction efficiency, with optimal performance at pH 6, a catalyst dosage of 2.5 g·L⁻¹, and a short reaction time of 20 min. The enhanced catalytic performance under mild, environmentally friendly conditions highlights CuO's crucial role in promoting surface electron transfer and facilitating reduction. Kinetic analysis at room temperature indicated a change in apparent kinetic behavior during the reaction, with pseudo-first-order behavior in the initial stage and a tendency toward zeroth-order behavior at later times. This evolution is consistent with the involvement of surface-mediated catalytic processes. Overall, the CuO/ZnFe₂O₄ heterostructure shows significant potential as an efficient catalyst for rapid CAP reduction under near-neutral conditions, offering a promising strategy for wastewater treatment.

Introduction

The rapid expansion of agro-industrial sectors, including textile, chemical, fertilizer, pesticide, and pharmaceutical industries, has led to the continuous discharge of large amounts of organic

pollutants into aquatic environments. Among these, antibiotic residues are of particular concern due to their persistence and resistance to conventional biological treatment processes. These

compounds are often only partially removed, remaining either in treated effluents or temporarily retained in activated sludge, from which they can subsequently be released back into the environment [1]. Chloramphenicol (CAP), a broad-spectrum antibiotic effective against both Gram-positive and Gram-negative bacteria, has been widely used in medical and veterinary applications. However, its presence in water systems poses serious health risks, as CAP has been associated with severe toxic effects in humans, including bone marrow suppression and, in extreme cases, fatal aplastic anemia [2]. Therefore, the effective removal of these contaminants from water bodies is critical.

Various treatment technologies have been developed to address organic pollutants, including membrane separation, biodegradation, adsorption, and catalytic processes. Among these methods, catalytic reduction has attracted considerable attention due to its operational simplicity, cost-effectiveness, high efficiency, and ease of scaling from laboratory studies to practical applications. In recent years, organic pollutants containing nitro groups have received much attention in this field, as the nitro ($-\text{NO}_2$) functional group can be selectively reduced to less toxic amino derivatives. In this context, sodium borohydride (NaBH_4) has been widely used as a strong hydrogen donor for reduction conversions [3]. However, in the absence of a catalyst, the reduction process is kinetically unfavorable. Therefore, catalytic surfaces, especially those based on metal nanostructures or metal oxides, play a crucial role in facilitating electron transfer and enabling the efficient delivery of active hydrogen species from BH_4^- to pollutant molecules [4].

Magnetic nanoparticles (MNPs) are one of the magnetic metal nanoparticles widely used in catalysis for environmental treatment. MNPs can be synthesized with different compositions and phases, including pure metals such as Fe, Co, and Ni, metal oxides such as Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, ferrites such as MFe_2O_4 ($\text{M} = \text{Cu}, \text{Ni}, \text{Mn}, \text{Mg}$), and metal alloys such as FePt and CoPt [5]. Among them, ZnFe_2O_4 is considered a magnetic semiconductor that can act catalytically in the visible-light region because it has a narrow bandgap energy ($E_g = 1.92 \text{ eV}$) with an electric potential (valence band (VB) at 0.38 V , and conduction band (CB) at -1.54 V) [6]. ZnFe_2O_4 has a spinel structure with Zn^{2+} occupying tetrahedral positions, and Fe^{3+} ions occupying octahedral positions in the crystal lattice. The exact distribution between cations at these two positions significantly impacts the electronic, magnetic, and catalytic properties of ZnFe_2O_4 . In general, ZnFe_2O_4 has many outstanding characteristics, such as magnetism, optical properties, non-toxicity, and stability in many different environments [7]. However, at the nanoscale, ZnFe_2O_4 is often unstable due to its tendency to aggregate and undergo surface oxidation, which can reduce its dispersibility

and magnetic performance over time. To overcome these limitations, various surface functionalization and structural modification strategies have been developed to improve stability and dispersibility, thereby enhancing catalytic efficiency. Based on these considerations, the development of efficient and stable catalysts based on ZnFe_2O_4 spinel ferrite coupled with transition-metal oxides is a potential approach to overcome existing limitations. Among the latter, CuO is a p-type semiconductor with a narrow bandgap ($1.2\text{--}2.1 \text{ eV}$), high stability, good conductivity, low cost, and relatively low toxicity [8]; it has proven effective in applications such as energy storage, antimicrobial applications, and photocatalysis [9]. Therefore, the combination of ZnFe_2O_4 and CuO is expected to improve catalytic activity by enhancing surface reactivity and promoting electron transfer. In this study, a $\text{CuO}/\text{ZnFe}_2\text{O}_4$ heterostructure was designed and synthesized to enhance the catalytic reduction efficiency of CAP in the presence of NaBH_4 . The influence of key reaction parameters, including pH, catalyst dosage, and reaction time, was systematically investigated to evaluate the efficiency of treating nitro-containing organic compounds.

Experimental Materials

Chloramphenicol (CAP, $\text{C}_{11}\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_5$), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), ZnCl_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, N,N' -dimethylformamide (DMF), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, urea (CON_2H_4), NaCl , and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) were purchased from Merck (Germany). No additional purification was performed on the analytical reagents before use, and all experimental procedures used deionized water.

Synthesis of ZnFe_2O_4 NPs

ZnFe_2O_4 was synthesized by the hydrothermal method. A mixture of ethylene glycol (60 mL), ZnCl_2 (0.28 g), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.08 g), urea (2 g), and citric acid (0.5 g) was transferred to a 100 mL Teflon-lined stainless-steel autoclave and heated for 24 h at 160°C . After cooling to room temperature, the resulting solid was filtered, washed with deionized water, and dried in an oven for 6 h at 60°C . The resulting solid was transferred to a muffle furnace at 400°C for 2 h, and the sample was further washed and dried for 6 h at 60°C [10].

Synthesis of $\text{CuO}/\text{ZnFe}_2\text{O}_4$

ZnFe_2O_4 (600 mg) was added to a solution containing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (540 mg) and urea (1.0 g) dissolved in DMF (60 mL). The mixture was homogenized using an ultrasonic device for 10 min. Then, this homogeneous solution was transferred to a heat-resistant vessel in an autoclave and heated at 85°C for 24 h. The product collected by centrifugation (10,000 rpm, 5 min) was washed with DMF and acetone several times. Finally, $\text{CuO}/\text{ZnFe}_2\text{O}_4$ was dried overnight at room temperature.

Characterization

The crystal structure of the composite materials was analyzed by X-ray diffraction (XRD; Bruker AXS, Germany) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over the 2θ range of $10\text{--}80^\circ$. Before analysis, the powder samples were lightly ground and spread evenly on a sample holder to ensure a flat and uniform surface. Surface morphology and microstructure of the samples were examined by scanning electron microscopy (SEM, Hitachi S-4800, Japan). The surface chemical composition and elemental state were studied using X-ray photoelectron spectroscopy (XPS; K-Alpha, Thermo VG, United Kingdom) with monochromated Al K α radiation as the excitation source. Nitrogen adsorption measurements were performed to evaluate the textural properties of ZnFe₂O₄ and CuO/ZnFe₂O₄. We calculated the specific surface area using the Brunauer–Emmett–Teller (BET) method and evaluated pore volume and pore width from the adsorption data, including the Barrett–Joyner–Halenda (BJH) analysis.

Catalytic experiments

In the catalytic reduction experiment, 40 mL of CAP solution ($30 \text{ mg}\cdot\text{L}^{-1}$) at a set pH was mixed with a specified amount of catalyst. Next, 5 mL of NaBH₄ solution (60 mM) was added, and distilled water was added to reach a total volume of 100 mL. Consequently, the initial CAP concentration (C_0) in the reaction system was $12 \text{ mg}\cdot\text{L}^{-1}$, while the NaBH₄ concentration was 3 mM. The mixture was stirred at 150 rpm. After every 2 min, the solids were magnetically separated, and 2.5 mL of supernatant was collected for CAP concentration measurement. The removal efficiency was evaluated using the ratio C/C_0 , decreasing from 1 to 0 as efficiency increased. The effects of time (5–50 min), pH (4–10), catalyst dosage (2.0, 2.5, and $3.0 \text{ g}\cdot\text{L}^{-1}$), and ionic strength with NaCl concentration (0.1–0.4 M), on removal efficiency were systematically studied to find optimal conditions. All catalytic reduction experiments were conducted under normal laboratory ambient light without light shielding. All experiments were performed under identical ambient-light conditions and with identical reaction-vessel configurations to ensure consistency.

The simulated wastewater matrix was prepared using representative inorganic ions and natural organic matter, as commonly included in synthetic wastewater formulations in previous studies [11,12]. The matrix comprised CAP ($12 \text{ mg}\cdot\text{L}^{-1}$), NaCl ($25 \text{ mg}\cdot\text{L}^{-1}$), NaHCO₃ ($40 \text{ mg}\cdot\text{L}^{-1}$), Na₂SO₄ ($25 \text{ mg}\cdot\text{L}^{-1}$), NaH₂PO₄·H₂O ($7 \text{ mg}\cdot\text{L}^{-1}$), and sodium humate ($2 \text{ mg}\cdot\text{L}^{-1}$). These constituents were chosen to reflect the typical levels of chloride, bicarbonate, sulfate, phosphate, and dissolved organic matter found in complex wastewater matrices. The CuO/ZnFe₂O₄ catalyst and NaBH₄ were then introduced under the same conditions used in the catalytic reduction experiments.

For the recycling experiments, the CuO/ZnFe₂O₄ catalyst was magnetically recovered after each catalytic cycle, washed with deionized water, dried, and reused under the same reaction conditions for five consecutive cycles. After each cycle, the separated liquid phase was analyzed by atomic absorption spectroscopy (AAS) to determine the concentrations of dissolved Fe, Cu, and Zn. We further characterized the catalyst recovered after the fifth cycle by XRD and XPS.

Results and Discussion

Characterization

Crystal structure and phase composition of ZnFe₂O₄ and CuO/ZnFe₂O₄ were studied by X-ray diffraction (XRD). As shown in Figure 1, the diffraction peaks of pure ZnFe₂O₄ located at $2\theta = 29.9^\circ, 35.2^\circ, 42.9^\circ, 53.8^\circ, 57.0^\circ$, and 62.2° can be identified as the (220), (311), (400), (422), (511), and (440) planes of cubic ZnFe₂O₄ spinel (PDF#22-1012), indicating the successful formation of well-crystallized ZnFe₂O₄ [13,14]. For the CuO/ZnFe₂O₄ composite material, all characteristic diffraction peaks of ZnFe₂O₄ appear, meaning the spinel structure of ZnFe₂O₄ remains intact after the formation of the composite material. Several new diffraction peaks appear at $2\theta = 36.1^\circ, 38.9^\circ, 52.9^\circ, 61.7^\circ$, and 66.2° , assigned to the planes (002), (111), (020), (113), and (311) of monoclinic CuO (PDF#48-1548), respectively [15,16]. The coexistence of ZnFe₂O₄ and CuO diffraction features confirms the successful construction of the CuO/ZnFe₂O₄ heterostructure, in which CuO is effectively incorporated without disrupting the ZnFe₂O₄ crystal framework.

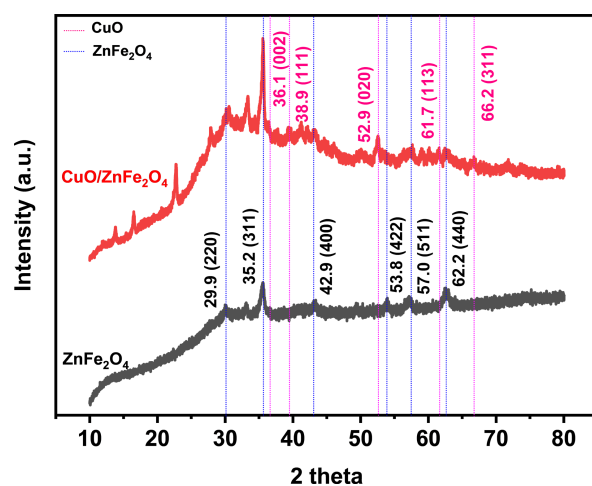


Figure 1: XRD patterns of ZnFe₂O₄ and CuO/ZnFe₂O₄.

While XRD analysis confirmed the phase composition and crystal structure of the ZnFe₂O₄ and CuO/ZnFe₂O₄ samples, XPS analysis clarified the surface elemental composition,

chemical states, and electronic interactions at the interface between ZnFe_2O_4 and CuO . The survey XPS spectra of ZnFe_2O_4 and $\text{CuO/ZnFe}_2\text{O}_4$ (Figure 2a) show Zn, Fe, and O in pristine

ZnFe_2O_4 and, additionally, a clear Cu signal in the heterostructure, confirming the surface incorporation of the Cu-containing component. The high-resolution Zn 2p spectra (Figure 2b) ex-

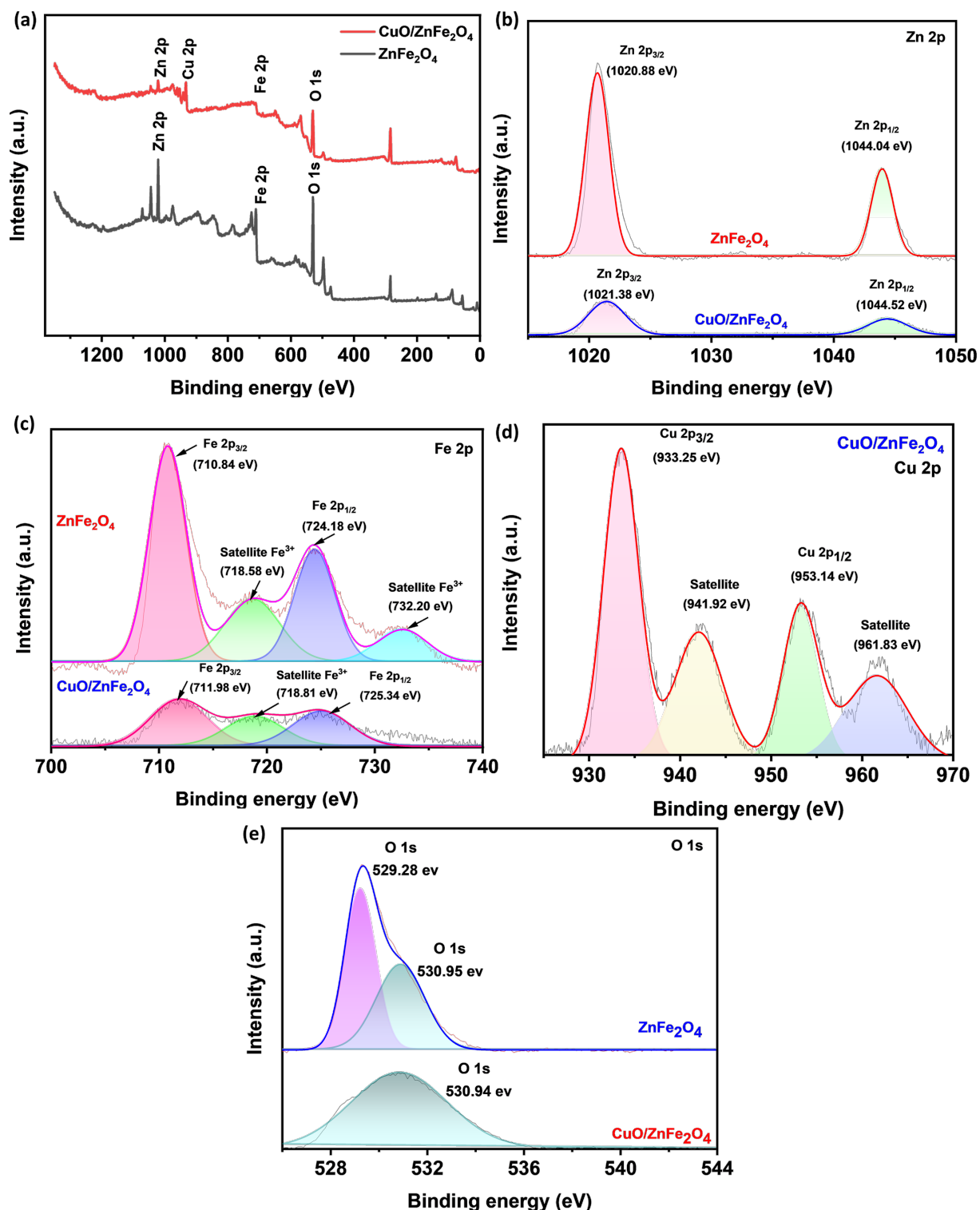


Figure 2: XPS spectra. (a) Survey spectrum, (b) Zn 2p and (c) Fe 2p for ZnFe_2O_4 and $\text{CuO/ZnFe}_2\text{O}_4$, (d) Cu 2p for $\text{CuO/ZnFe}_2\text{O}_4$ and (e) O 1s for ZnFe_2O_4 and $\text{CuO/ZnFe}_2\text{O}_4$.

hibit Zn 2p_{3/2} and Zn 2p_{1/2} components at approximately 1021 and 1044 eV, respectively, consistent with Zn²⁺ in the spinel ferrite structure [17,18]. The Fe 2p spectra were re-evaluated by considering the characteristic multiplet and shake-up satellite structure of Fe in iron oxides rather than assigning a single unconstrained peak to each formal oxidation state. For ZnFe₂O₄, the Fe 2p_{3/2} and Fe 2p_{1/2} envelopes occur at approximately 710.84 and 724.18 eV, together with satellite features at approximately 718.58 and 732.20 eV (Figure 2c). In CuO/ZnFe₂O₄, the corresponding Fe 2p features remain in the Fe(III)-characteristic binding-energy region, with a satellite near 718.81 eV. These spectral features indicate that Fe(III) is the predominant iron oxidation state, consistent with the Zn²⁺Fe³⁺O₄ spinel structure identified independently by XRD. No distinct additional Fe(I) or Fe(II) components could be reliably resolved from the experimental spectra; therefore, such components were not artificially introduced into the fitting. For Cu 2p (Figure 2d), the main Cu 2p_{3/2} and Cu 2p_{1/2} peaks are located at 933.25 and 953.14 eV, respectively, with a spin–orbit separation of approximately 19.9 eV. Pronounced shake-up satellite features at approximately 941.92 and 961.83 eV are characteristic of Cu(II) and support CuO as the predominant Cu-containing phase, in agreement with XRD [19]. Accordingly, the Cu 2p analysis was assigned to the experimentally resolved Cu(II) doublet and its characteristic shake-up satellite contributions. Distinct Cu(I) or Cu(III) components were not resolved and were therefore not introduced artificially into the deconvolution. The O 1s spectra (Figure 2e) were interpreted according to oxygen chemical environments rather than formal metal oxidation states. In ZnFe₂O₄, the lower-binding-energy contribution at approximately 529.28 eV is assigned primarily to lattice O^{2−} in metal–oxygen bonds, whereas the higher-binding-energy contribution near 530.94 eV is associated with

surface/defect-related and hydroxy/adsorbed oxygen species [17]. In the CuO/ZnFe₂O₄ heterostructure, the broadened O 1s envelope reflects overlapping oxygen environments associated with the ZnFe₂O₄ and CuO lattices and surface-related oxygen species. Because these contributions overlap strongly, the O 1s spectrum is discussed in terms of chemically plausible oxygen environments without overassigning individual components. Overall, the revised XPS analysis supports Zn²⁺, predominantly Fe³⁺, and predominantly Cu²⁺ as the resolved cationic states in the CuO/ZnFe₂O₄ heterostructure, consistent with the ZnFe₂O₄ and CuO phases independently identified by [17–22].

N₂ adsorption measurements were performed to assess the textural properties of ZnFe₂O₄ and CuO/ZnFe₂O₄. The BET specific surface area decreased from 56.89 m²·g^{−1} for ZnFe₂O₄ to 49.27 m²·g^{−1} for CuO/ZnFe₂O₄, showing that CuO incorporation did not enlarge the specific surface area. In contrast, the total pore volume increased from 0.1653 to 0.1825 cm³·g^{−1}, while the average pore width (4V/A by BET) increased from 11.62 to 14.82 nm. The BJH adsorption average pore width likewise increased from 11.06 to 13.45 nm. These results indicate that CuO incorporation modifies the pore architecture of ZnFe₂O₄ rather than simply increasing its specific surface area. The moderate decrease in BET surface area may be associated with partial coverage or blockage of accessible ZnFe₂O₄ surface sites by the deposited CuO component, whereas the increased pore volume and average pore width suggest larger accessible pore/interparticle void dimensions in the heterostructure. While XPS provided strong evidence for the chemical states and confirmed the successful formation of the CuO/ZnFe₂O₄ composite, SEM was employed to further elucidate the surface morphology and assess the spatial distribution of the CuO phase on the ZnFe₂O₄ matrix. As illustrated in Figure 3,

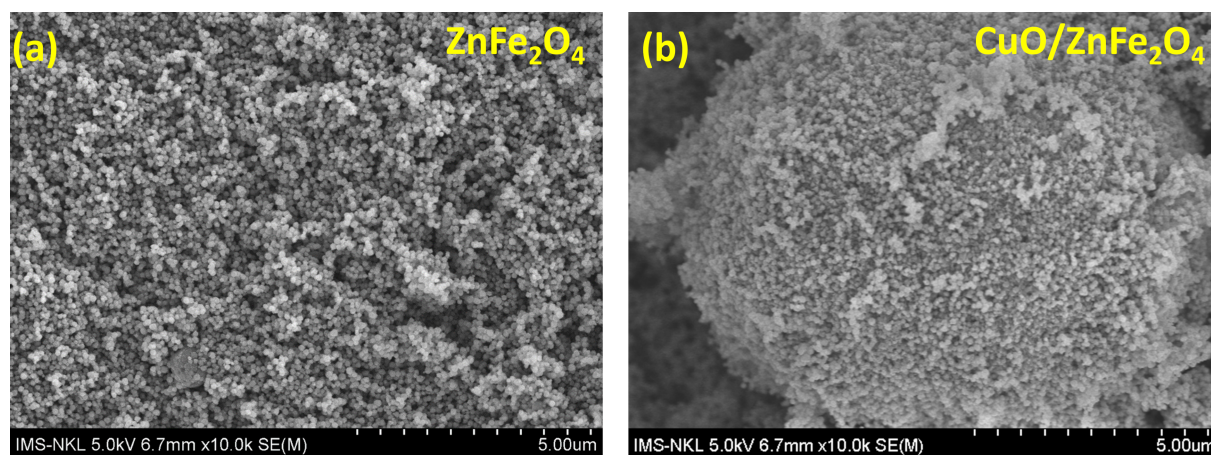


Figure 3: The SEM images of ZnFe₂O₄ (a) and CuO/ZnFe₂O₄ (b). The scale bar is 5 μm for both images.

the CuO/ZnFe₂O₄ material exhibits flower-like hierarchical microstructures with characteristic dimensions of approximately 4 μm , as estimated from the SEM images. These structures are formed by the assembly of densely packed rod-like surface features radiating outward, resulting in a rough and highly textured morphology. Compared with ZnFe₂O₄ (inset), which displays a relatively compact, granular surface, the incorporation of CuO significantly alters the surface architecture, increasing surface roughness. Such hierarchical heterostructures are expected to provide more accessible active sites and facilitate interfacial electron transfer [23] during catalytic reaction.

Catalytic activity

The catalytic reduction of CAP was examined using NaBH₄ as the electron donor and both ZnFe₂O₄ and CuO/ZnFe₂O₄ as heterogeneous catalysts. The reaction progress was monitored by observing UV–vis spectral changes of CAP under various conditions: CAP alone, CAP with NaBH₄, CAP with ZnFe₂O₄, CAP with CuO/ZnFe₂O₄, CAP with NaBH₄ and ZnFe₂O₄, and CAP with NaBH₄ and CuO/ZnFe₂O₄, as illustrated in Figure 4a. These control experiments were performed to assess the possible contribution of adsorption and to distinguish it from the NaBH₄-assisted catalytic conversion of CAP. In the absence of NaBH₄, the absorption intensity of CAP remained nearly constant in the presence of both ZnFe₂O₄ and CuO/ZnFe₂O₄, indicating that adsorption alone contributed minimally to CAP removal under the tested conditions. Similarly, NaBH₄ alone did not significantly alter the absorption spectrum of CAP, demonstrating the kinetic limitation of direct reduction. When ZnFe₂O₄ was combined with NaBH₄, only a slight decrease in CAP absorption intensity at approximately 280 nm was observed, without the emergence of a new absorp-

tion band, suggesting limited catalytic conversion. In contrast, the CuO/ZnFe₂O₄-NaBH₄ system showed a substantial decrease in the characteristic CAP absorption band at approximately 280 nm, along with the appearance and growth of a new absorption feature at around 236 nm. These spectral changes suggest that the enhanced CAP removal in the CuO/ZnFe₂O₄-NaBH₄ system is primarily due to catalytic transformation promoted by NaBH₄, rather than adsorption. The improved catalytic performance is likely related to the incorporation of CuO, which may facilitate interfacial electron transfer and promote CAP conversion, while ZnFe₂O₄ provides a supporting surface and contributes to the overall catalytic process. Although the detailed reaction pathway remains to be elucidated, the comparative results in Figure 4a demonstrate that the CuO/ZnFe₂O₄ composite plays a more significant role in the NaBH₄-assisted conversion of CAP than ZnFe₂O₄ [24,25]. The kinetic change of the reduction process is more clearly shown in Figure 4b, which depicts the decrease in the absorption intensity of CAP at 280 nm over reaction time after the addition of CuO/ZnFe₂O₄ in the presence of NaBH₄. The absorption intensity decreases continuously throughout the reaction period, indicating that CAP is efficiently converted under these catalytic conditions. These results confirm that the CuO/ZnFe₂O₄ system exhibits superior catalytic activity compared to ZnFe₂O₄ alone and highlight the role of CuO in enhancing the CAP reduction efficiency in the NaBH₄ system.

The results of the pH effect survey (Figure 5) show that catalytic reduction activity strongly depends on the reaction environment and the material's surface. For ZnFe₂O₄, the absorption spectrum changed only slightly over time within the investigated pH range (pH 4, 6, and 10), indicating limited CAP removal

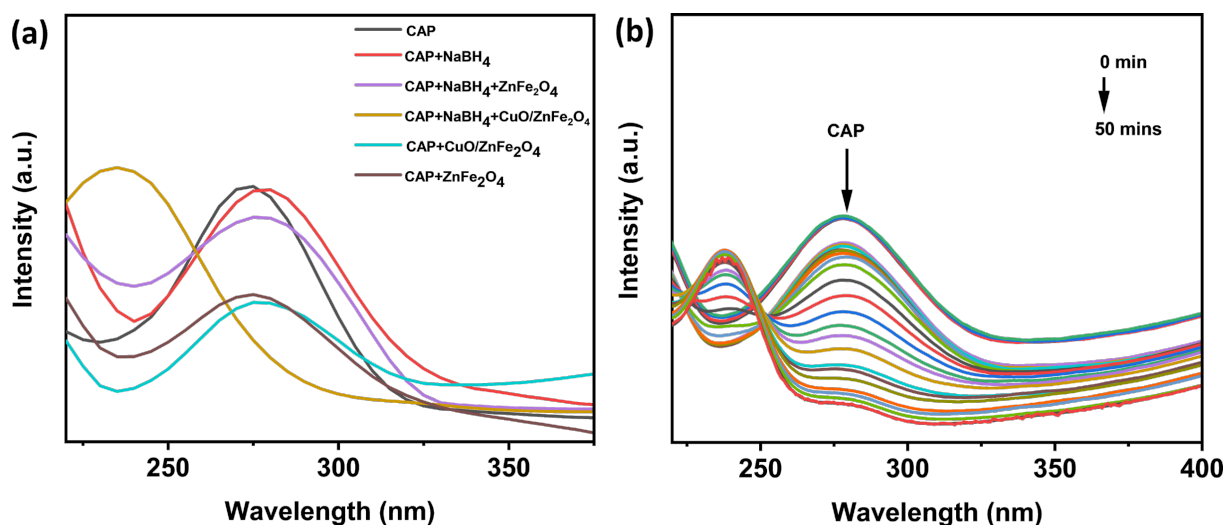


Figure 4: UV–vis spectra of the CAP solution before and after the removal processes (a) all samples; (b) CuO/ZnFe₂O₄ over 50 min of reaction time.

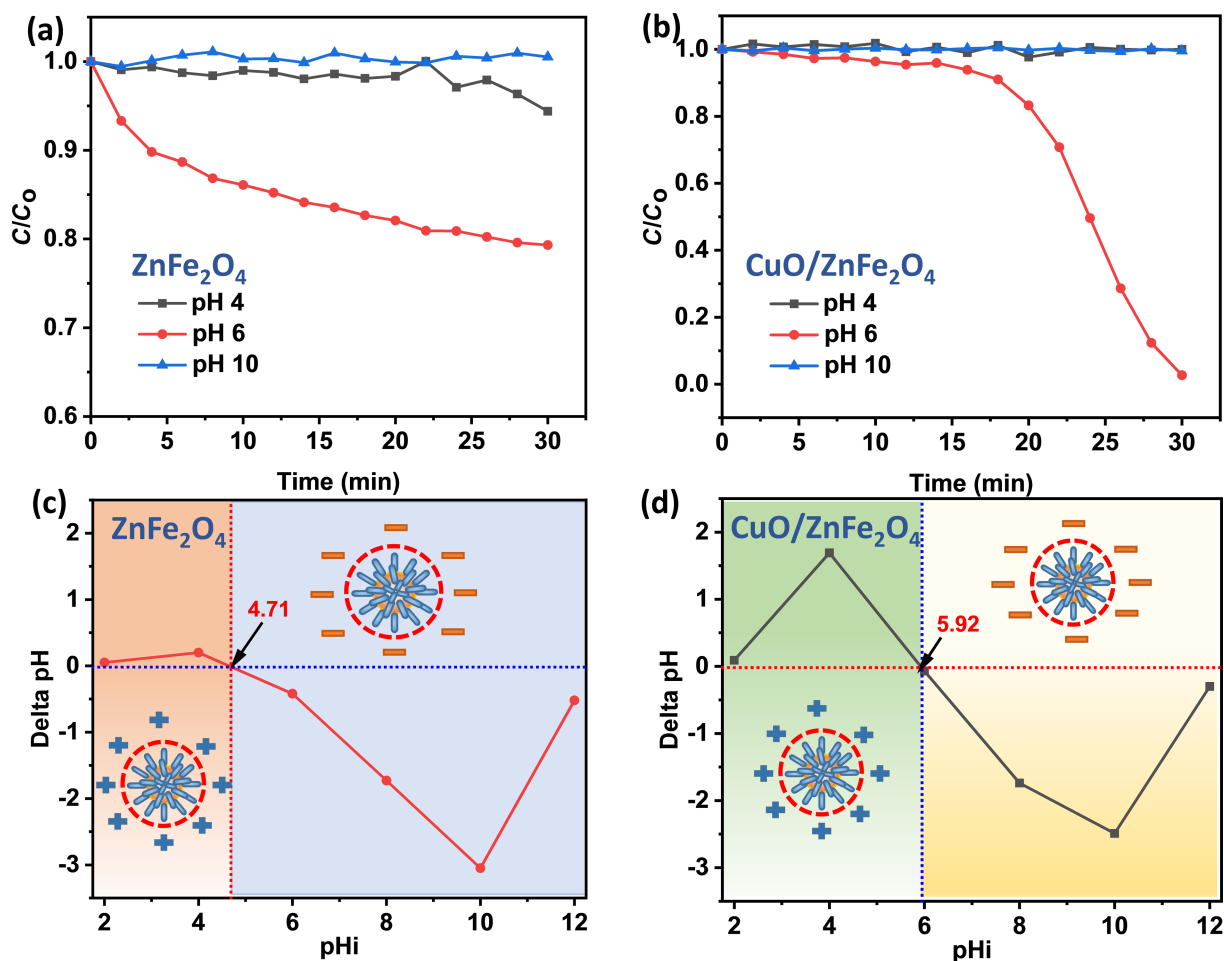
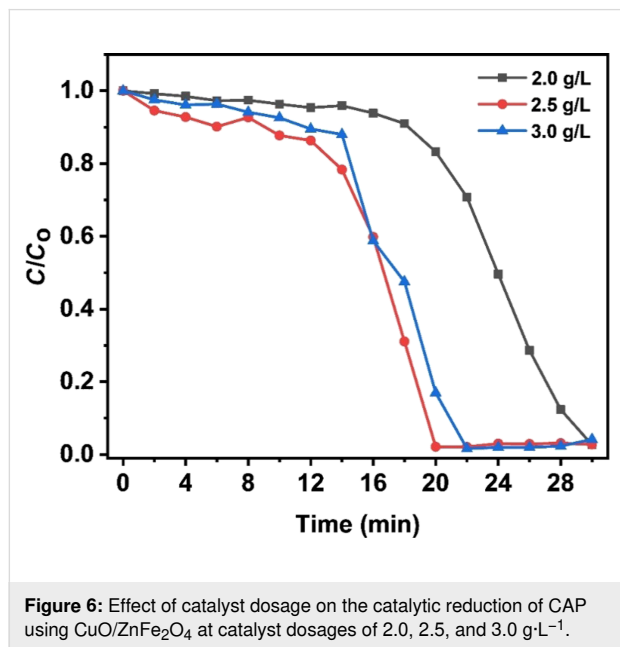


Figure 5: (a, b) Effect of pH on the reduction of CAP; pH_{PZC} of (c) ZnFe₂O₄ and (d) CuO/ZnFe₂O₄.

under these conditions. Together with the control experiments in Figure 4a, which showed minimal adsorption in the absence of NaBH₄, these results indicate that pristine ZnFe₂O₄ exhibits limited catalytic activity in the NaBH₄-assisted system compared with the CuO/ZnFe₂O₄ heterostructure [26]. Conversely, the CuO/ZnFe₂O₄ system exhibits a significant pH dependence, with the highest catalytic performance observed at pH 6. Under this condition, the C/C_0 ratio decreases markedly, indicating rapid CAP conversion. The enhanced activity near pH 6 may reflect a favorable balance between catalyst surface charge, CAP–surface interactions, and the availability of BH₄[−]-derived reducing species, thereby facilitating interfacial electron transfer [27]. At more acidic or alkaline pH, less favorable surface interactions may reduce the catalytic performance. Furthermore, the incorporation of CuO provides redox-active surface sites that may facilitate electron transfer [28], which may explain the enhanced catalytic performance of CuO/ZnFe₂O₄ compared with ZnFe₂O₄.

Figure 6 illustrates the effect of catalyst dosage (2.0, 2.5, and 3.0 g·L^{−1}) on the catalytic removal efficiency of CAP in the presence of NaBH₄. Compared with the dosage of 2.0 g·L^{−1}, increasing the CuO/ZnFe₂O₄ loading to 2.5 and 3.0 g·L^{−1} significantly enhanced both the removal efficiency and the reaction rate throughout the catalytic process. Specifically, the system containing 2.0 g·L^{−1} of catalyst required approximately 30 min to achieve high CAP removal efficiency, whereas the reaction time was shortened to 20 min and 22 min for catalyst dosages of 2.5 and 3.0 g·L^{−1}, respectively. The improved catalytic performance at higher catalyst loadings can be attributed primarily to the increased availability of CuO-containing active sites, which facilitate interactions among BH₄[−], CAP, and the catalyst surface and promote interfacial electron transfer [28]. However, when the catalyst dosage exceeded 2.5 g·L^{−1}, the catalytic activity enhancement became insignificant and even declined slightly. This behavior is likely associated with the limited amount of NaBH₄ in the reaction system, which restricts the

generation of active hydrogen species and the transfer of electrons required for the reduction reaction [29]. Therefore, a catalyst dosage of $2.5 \text{ g}\cdot\text{L}^{-1}$ was selected as the optimal condition for subsequent experiments.



Kinetic analysis results (Figure 7) at catalyst dosages of 2.0, 2.5, and $3.0 \text{ g}\cdot\text{L}^{-1}$ at room temperature indicate that the CAP reduction on CuO/ZnFe₂O₄ cannot be adequately interpreted as a single kinetic regime over the entire reaction period. The transition between the two apparent kinetic regions was assigned from the observed change in linearity of the kinetic profiles, which occurred after approximately 12–14 min. Accordingly, the 0–12 min interval was used to describe the initial apparent regime and the 14–22 min interval to evaluate the later regime. For 0–12 min, the $\ln(C/C_0)$ versus time plots showed good linearity with the pseudo-first-order model (Figure 7a,c,e). At later times, the profiles deviated from the initial pseudo-first-order behavior and showed a tendency toward zeroth-order behavior (Figure 7b,d,f). These kinetic assignments should therefore be regarded as apparent descriptions of different portions of the reaction profile rather than as proof of a sharp mechanistic transition at a single time point. The apparent rate constants also showed a non-monotonic dependence on catalyst dosage. In particular, k_1 decreased from 0.01106 min^{-1} at $2.5 \text{ g}\cdot\text{L}^{-1}$ to 0.00805 min^{-1} at $3.0 \text{ g}\cdot\text{L}^{-1}$, whereas the later-stage k_0 increased from 0.2627 to $0.3218 \text{ mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$. This difference is not a direct contradiction because k_1 and k_0 describe different apparent kinetic regions and have different dimensions; they should therefore not be compared as a single dose-dependent rate parameter. The results instead indicate that increasing the nominal catalyst dosage beyond $2.5 \text{ g}\cdot\text{L}^{-1}$ does not produce a

proportional improvement in the apparent reaction rate in all stages of the process, consistent with the small decrease in overall catalytic performance observed at $3.0 \text{ g}\cdot\text{L}^{-1}$. The kinetic profiles presented here were obtained from individual experimental runs rather than replicate kinetic measurements; therefore, statistically meaningful standard deviations and error bars cannot be calculated retrospectively. The kinetic interpretation is consequently limited to the measured profiles and their apparent fitting behavior, without assigning statistical significance to differences between fitted parameters. The observed evolution in kinetic behavior may reflect changes in surface coverage by CAP, reaction intermediates, BH₄⁻-derived species, or borate products as the reaction proceeds. Such behavior is qualitatively consistent with a surface-mediated Langmuir–Hinshelwood-type process, but the present kinetic data alone do not establish a unique mechanistic model [30,31]. Among the investigated catalyst dosages, $2.5 \text{ g}\cdot\text{L}^{-1}$ provided the best overall CAP removal performance within 20 min and was therefore selected as the optimum dosage.

Different concentrations of NaCl were added to the CAP solution to evaluate the effect of ionic strength on the catalytic activity of CuO/ZnFe₂O₄. As shown in Figure 8a, both the decomposition efficiency and the rate of CAP reduction were strongly affected by ionic strength. As the NaCl concentration increased from 0.1 to 0.4 M, the reduction process became slower, requiring a longer reaction time to achieve equivalent removal efficiency. At relatively low ionic strengths, the electrolyte had only a minor effect on the catalytic reduction of CAP; however, a pronounced inhibitory effect was observed at higher ionic strengths, especially at 0.4 M. This phenomenon suggests that excess ions in solution may hinder the interaction among BH₄⁻, CAP, and the CuO/ZnFe₂O₄ surface, thus inhibiting adsorption and electron transfer through the surface during catalysis, affecting catalytic efficiency [32]. Overall, these results indicate that the CuO/ZnFe₂O₄ heterostructure exhibits more favorable catalytic performance under conditions of low ionic strength. To further evaluate the performance of CuO/ZnFe₂O₄ in a more complex aqueous environment, a simulated wastewater system containing typical inorganic salts and sodium humate, as commonly used in synthetic wastewater formulations reported in previous studies [11,12], was investigated. Under simulated wastewater conditions, the CAP removal efficiency (Figure 8b) decreased relative to that observed in deionized water, yet remained notably high at 86.25%. The observed reduction aligns with the inhibitory trend observed in experiments on NaCl ionic strength (Figure 8a), although the current experiments could not isolate the individual contributions of each component in the simulated wastewater. Nevertheless, maintaining a CAP removal efficiency of 86.25% in the simulated wastewater environment demonstrates that the CuO/

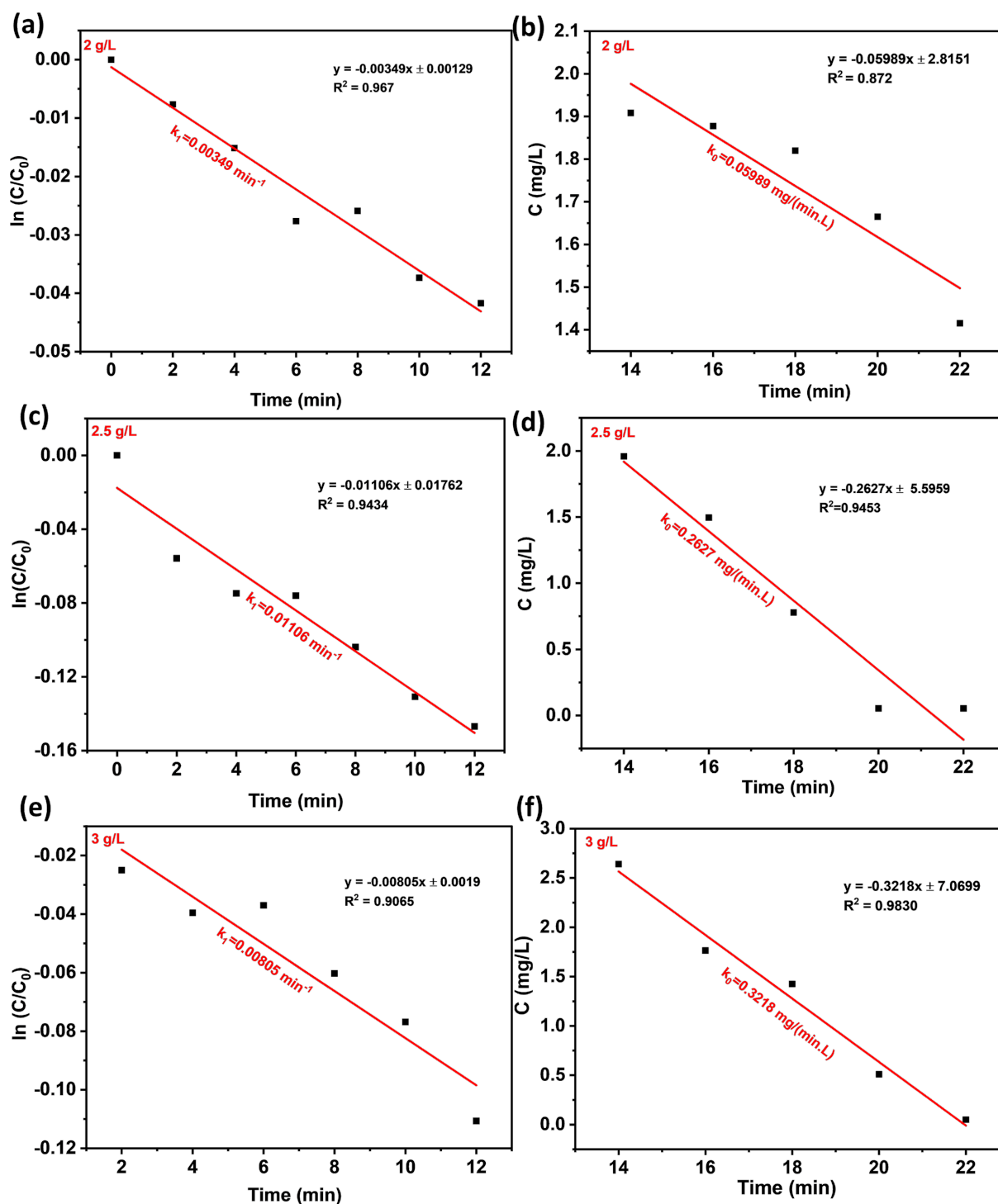
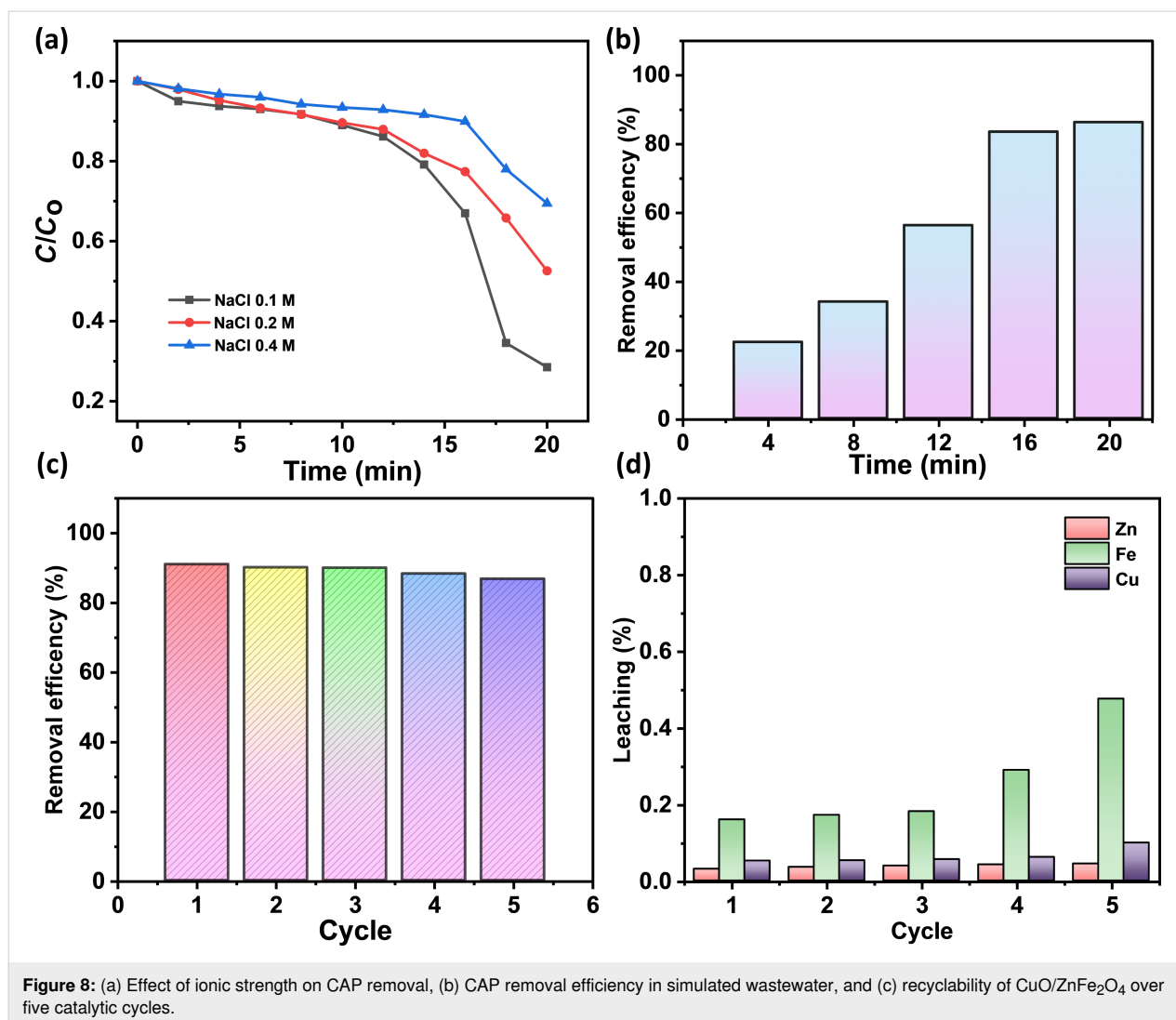


Figure 7: Kinetic analysis of CAP reduction of CuO/ZnFe₂O₄ at different dose of 2 g/L (a, b), 2.5 g/L (c, d) and 3 g/L (e, f) at room temperature.

ZnFe₂O₄–NaBH₄ system retains significant catalytic activity under more complex water conditions.

The reusability of the CuO/ZnFe₂O₄ catalyst for CAP reduction in the presence of NaBH₄ was evaluated over five consecu-

tive reaction cycles. As shown in Figure 8c, the CAP removal efficiency decreased only modestly from 91.0% in the first cycle to 86.8% after the fifth cycle, indicating that the catalyst retained substantial catalytic activity during repeated use. The modest performance loss may reflect a combination of catalyst



loss during recovery, surface modification, accumulation of surface-bound species, and metal leaching during repeated operation. AAS analysis (Supporting Information File 1, Table S1) of the liquid phase after each catalytic cycle confirmed measurable Fe, Cu, and Zn leaching. These results indicate that, although the catalyst retains substantial catalytic activity over five cycles, metal release occurs under the investigated reaction conditions and limits the present catalyst system. To further assess the catalyst after repeated use, the material recovered after the fifth catalytic cycle was characterized by XRD and XPS (Figure 9).

After five consecutive catalytic cycles, the XRD pattern of the recovered catalyst still showed the main diffraction features of the CuO/ZnFe₂O₄ heterostructure (Figure 9a). This result indicates that the major crystalline framework remained detectable after repeated use. The XPS spectra taken after the reaction provided more information about the catalyst's surface chemical

states. The Zn 2p and Fe 2p signals remained (Figure 9b,c), indicating that Zn and Fe components persisted after five cycles. The Zn 2p_{3/2} and Zn 2p_{1/2} peaks were found at about 1020.65 and 1043.89 eV, and the Fe 2p_{3/2} and Fe 2p_{1/2} signals appear at approximately 710.50 and 724.09 eV, respectively, accompanied by an Fe(III)-related satellite peak at approximately 716.98 eV. In the Cu 2p region, the Cu 2p_{3/2} and Cu 2p_{1/2} peaks were seen at about 932.22 and 952.17 eV (Figure 9d). These lower Cu 2p binding energies match the presence of reduced Cu species on the catalyst surface after repeated exposure to NaBH₄. However, because the Cu 2p binding-energy regions for Cu(I) and Cu(0) overlap, it is not possible to clearly identify the post-reaction Cu species as either Cu₂O or metallic Cu based only on the Cu 2p spectrum. Overall, the XRD and XPS results after the reaction show that the main crystalline framework remains stable after five cycles, while the Cu-containing surface changes chemically under reaction conditions involving NaBH₄. Together with AAS evidence of metal

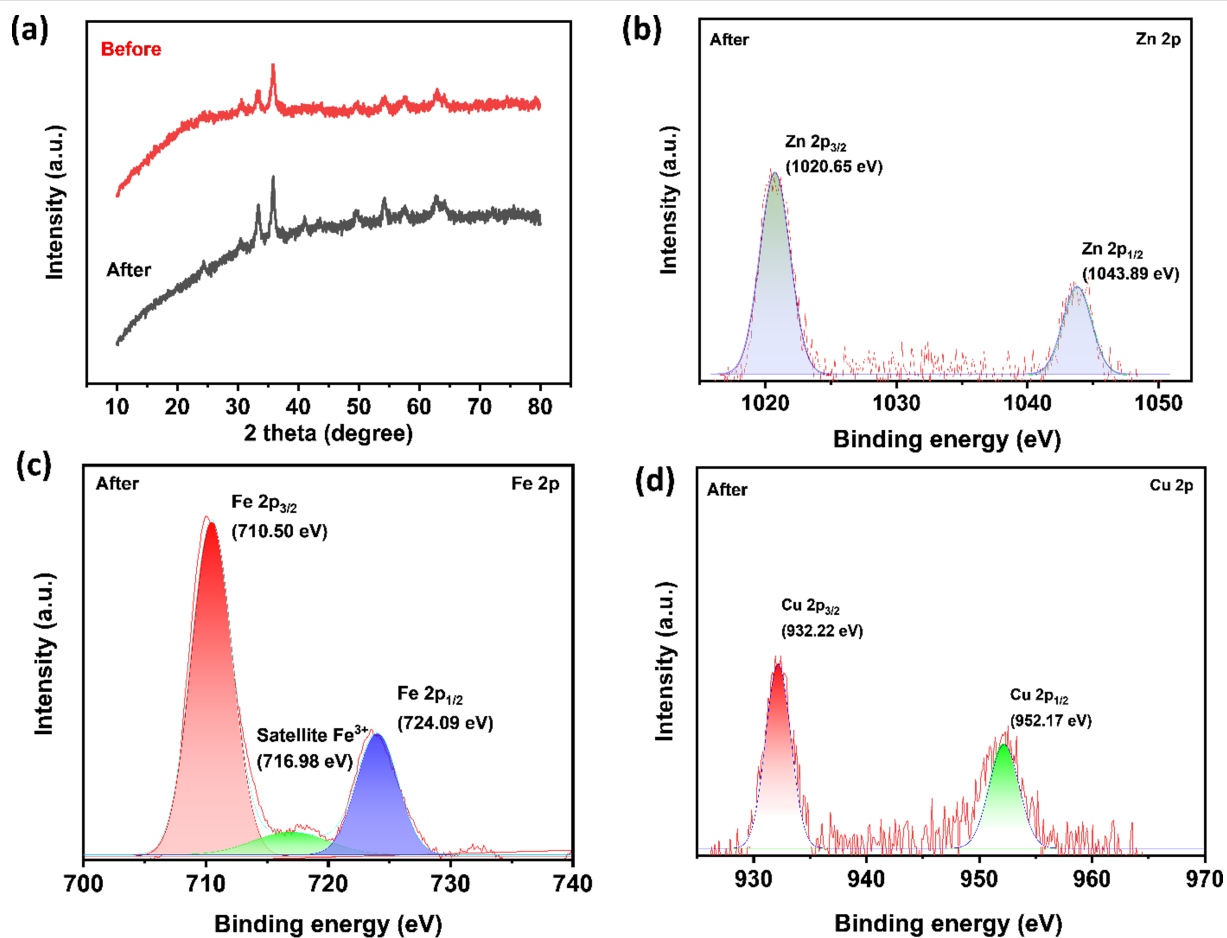


Figure 9: Post-reaction characterization of CuO/ZnFe₂O₄ recovered after five catalytic cycles: (a) XRD pattern, (b) Zn 2p, (c) Fe 2p, and (d) Cu 2p high-resolution XPS spectra.

leaching, these results suggest that improving the structural and chemical stability of the CuO/ZnFe₂O₄ heterostructure, especially at the CuO-ZnFe₂O₄ interface, is an important area for future work.

According to Table 1, the CuO/ZnFe₂O₄ system achieves a significantly shorter reaction time of only 20 min, demonstrating rapid reduction under near-neutral conditions. Photocatalytic systems like Ce(MoO₄)₂/graphene oxide (GO) and Ag/TiO₂

require longer reaction times and depend on external light irradiation. MOF-based (Al-MIL) and nano zero-valent iron (nZVI)/GO systems, though efficient, often need higher catalyst dosages or extended processing times. CuO/ZnFe₂O₄ stands out due to its fast kinetics, near-neutral pH operation, and operation without controlled external light irradiation, making it promising for practical NaBH₄-assisted reduction. The initial CAP concentration of 12 mg·L^{−1} used in this study is much higher than that typically found in aquatic environments, where

Table 1: Comparison of CAP removal using different catalytic systems.

Material	Conditions	Catalytic	Light source	Reference
Ce(MoO ₄) ₂ /GO	pH 5; C _{CAP} = 20 mg·L ^{−1} ; t = 50 min	photocatalytic	visible	[34]
Ag/TiO ₂	pH 6.5; C _{CAP} = 20 mg·L ^{−1} ; t = 120 min	photocatalytic	UV-C	[2]
persulfate	pH 3; C _{CAP} = 0.03 mM; t = 120 min	UV-activated persulfate oxidation	UV	[35]
Al-MIL	pH 5.4; C _{CAP} = 80 mg·L ^{−1} ; t = 120 min	persulfate oxidation	—	[36]
nZVI/GO	pH 5; C _{CAP} = 100 mg·L ^{−1} ; t = 180 min	photocatalytic	—	[37]
CuO/ZnFe ₂ O ₄	pH 6; C _{CAP} = 12 mg·L ^{−1} ; t = 20 min	NaBH ₄ reduction	—	this study

levels are typically in the nanogram per liter to low-microgram per liter range [33]. Therefore, further studies using environmentally relevant CAP concentrations are required to more comprehensively assess the practical applicability of the CuO/ZnFe₂O₄ catalytic system.

Mechanism

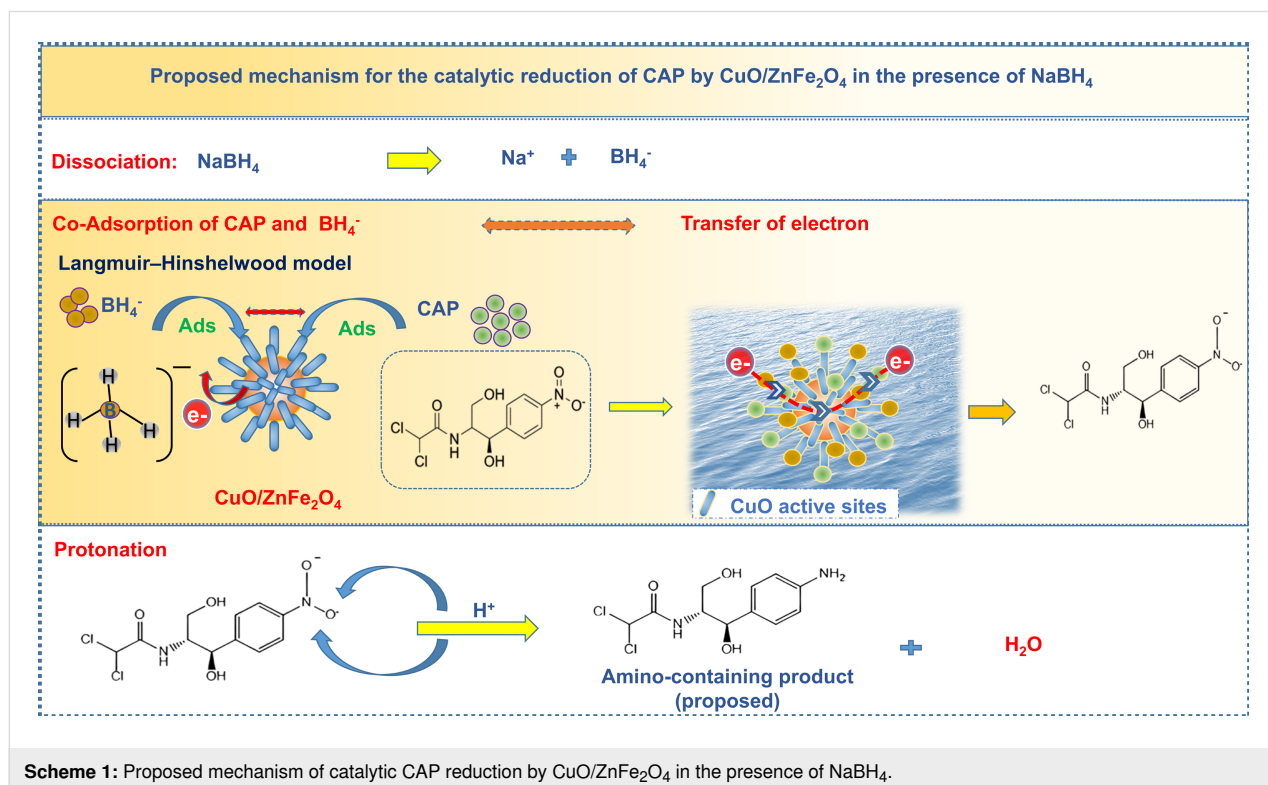
Previous studies have demonstrated that aromatic nitro compounds can be reduced to their corresponding amino derivatives using NaBH₄ [38,39]. Based on these findings, Scheme 1 illustrates the proposed CAP reduction pathway on the CuO/ZnFe₂O₄ heterostructure. Initially, NaBH₄ dissociates in aqueous solution to release BH₄[−] ions, which may interact with the catalyst surface and facilitate electron transfer and the formation of reactive hydrogen species involved in CAP reduction. Simultaneously, CAP molecules are adsorbed onto the CuO/ZnFe₂O₄ surface, which could facilitate electron transfer between interfaces and subsequent reduction processes. As illustrated in Scheme 1, the nitro group of the CAP is proposed to undergo stepwise electron/proton transfer, leading to the formation of products consistent with the corresponding amino derivative (−NH₂) and H₂O.

Kinetic analysis indicated pseudo-first-order behavior during the initial reaction stage and a tendency toward zeroth-order behavior at later times. This shift in apparent kinetics may reflect progressive changes in surface coverage by CAP, reaction inter-

mediates, BH₄[−]-derived species, or borate products. The observations are qualitatively consistent with a surface-mediated Langmuir–Hinshelwood-type process in which adsorption and interfacial electron transfer contribute to CAP reduction; however, the kinetic data alone do not establish a unique mechanistic pathway. Overall, the CuO/ZnFe₂O₄ heterostructure provides favorable interfacial sites for adsorption and electron transfer in the NaBH₄-assisted catalytic system. The proposed pathway is consistent with previously reported catalytic reduction processes for nitro-containing organic compounds [40].

Conclusion

A CuO/ZnFe₂O₄ heterostructure was synthesized with a flower-like morphology composed of rod-like surface features associated with the CuO-containing component on the ZnFe₂O₄ surface. In the presence of NaBH₄, the CuO/ZnFe₂O₄ system displayed markedly enhanced catalytic reduction efficiency for CAP compared to pristine ZnFe₂O₄, reaching maximum performance at pH 6, a catalyst loading of 2.5 g·L^{−1}, and a reaction period of 20 min. The enhanced catalytic performance is attributed to the formation of the CuO/ZnFe₂O₄ heterostructure, which provides CuO-containing active sites and favorable interfacial interactions for reduction. Kinetic analysis indicated a change in apparent kinetic behavior during the reaction, with pseudo-first-order behavior in the initial stage and a tendency toward zeroth-order behavior at later times. This



evolution is consistent with surface-mediated processes, although the present kinetic data do not establish a unique Langmuir–Hinshelwood mechanism. Reusability tests showed that CAP removal decreased only modestly from 91.0% in the first cycle to 86.8% after the fifth cycle. Post-reaction XRD showed that the major crystalline features of the heterostructure remained detectable after five cycles, while XPS indicated the presence of reduced Cu surface species, consistent with modification of the Cu-containing surface during repeated exposure to NaBH_4 . AAS analysis confirmed measurable Fe, Cu, and Zn leaching during repeated operation, identifying metal retention as a limitation of the present catalyst system. Overall, the $\text{CuO}/\text{ZnFe}_2\text{O}_4$ heterostructure demonstrates rapid NaBH_4 -assisted CAP reduction and substantial activity retention under simulated-wastewater and repeated-use conditions. Further development should focus on improving the heterostructure's structural and chemical stability, particularly by strengthening the CuO – ZnFe_2O_4 interfacial interaction and suppressing metal leaching while preserving catalytic activity.

Supporting Information

Supporting Information File 1

AAS measurements of dissolved metal ions.

[<https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-17-97-S1.pdf>]

Acknowledgements

The authors gratefully acknowledge IMS-NKL for assistance with SEM measurements and the facilities that supported XRD, XPS, and BET characterization in this study.

Funding

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.06-2021.60.

Conflict of Interest

The authors declare no potential conflicts of interest.

Author Contributions

Le Thi Hoa: conceptualization; writing – original draft. Nguyen Thi Thu Huong: data curation; methodology; visualization. Le Quoc Viet: conceptualization; data curation; methodology. Trinh Ngoc Dat: data curation; methodology. Nguyen Duc Cuong: conceptualization; writing – original draft. Le Thi Thanh Nhi: methodology; validation; writing – original draft. Tran Thai Hoa: conceptualization; supervision; validation; writing – review & editing.

ORCID® iDs

Le Thi Hoa - <https://orcid.org/0000-0002-1359-187X>

Le Thi Thanh Nhi - <https://orcid.org/0009-0007-5078-6151>

Tran Thai Hoa - <https://orcid.org/0000-0003-4814-4364>

Data Availability Statement

Data generated and analyzed during this study is available from the corresponding author upon reasonable request.

Preprint

A non-peer-reviewed version of this article has been previously published as a preprint: <https://doi.org/10.3762/bxiv.2026.20.v1>

References

- Elmolla, E. S.; Chaudhuri, M. *Desalination* **2010**, *252*, 46–52. doi:10.1016/j.desal.2009.11.003
- Jodat, A.; Jodat, A. *Desalin. Water Treat.* **2014**, *52*, 2668–2677. doi:10.1080/19443994.2013.794115
- Ravikumar, K. V. G.; Dubey, S.; Pulimi, M.; Chandrasekaran, N.; Mukherjee, A. *J. Mol. Liq.* **2016**, *224*, 589–598. doi:10.1016/j.molliq.2016.10.040
- Ecevit, H.; Altun, T. *J. Water Process Eng.* **2025**, *76*, 108177. doi:10.1016/j.jwpe.2025.108177
- Aghayi-Anaraki, M.; Safarifar, V. *Eur. J. Inorg. Chem.* **2020**, *2020*, 1916–1937. doi:10.1002/ejic.202000012
- Tao, R.; Zhao, C.; Shao, C.; Li, X.; Li, X.; Zhang, J.; Yang, S.; Liu, Y. *Mater. Res. Bull.* **2018**, *104*, 124–133. doi:10.1016/j.materresbull.2018.03.041
- Liu, Z.; Fan, T.; Zhou, H.; Zhang, D.; Gong, X.; Guo, Q.; Ogawa, H. *Bioinspiration Biomimetics* **2007**, *2*, 30–35. doi:10.1088/1748-3182/2/1/004
- Li, L.; Chen, X.; Quan, X.; Qiu, F.; Zhang, X. *ACS Omega* **2023**, *8*, 2723–2732. doi:10.1021/acsomega.2c07364
- Singh, J.; Soni, R. K. *Appl. Surf. Sci.* **2020**, *521*, 146420. doi:10.1016/j.apsusc.2020.146420
- Niaki, Z. M.; Ghorbani, M.; Ghoreishi, S. A. *J. Environ. Health Sci. Eng.* **2021**, *19*, 1583–1596. doi:10.1007/s40201-021-00713-x
- Zhao, Z.; Ma, X.; Wang, X.; Ma, Y.; Liu, C.; Hang, H.; Zhang, Y.; Du, Y.; Ye, W. *Appl. Surf. Sci.* **2018**, *457*, 1009–1017. doi:10.1016/j.apsusc.2018.06.285
- Venancio, W. A. L.; Rodrigues-Silva, C.; Maniero, M. G.; Guimarães, J. R. *Water Sci. Technol.* **2018**, *78*, 1668–1678. doi:10.2166/wst.2018.443
- Wang, K.; Chen, Q.; Xie, H.; Wang, M.; Kong, X.; Cheng, K.; Jin, Z. *Catal. Lett.* **2024**, *154*, 6227–6240. doi:10.1007/s10562-024-04830-8
- Huerta-Aguilar, C. A.; Diaz-Puerto, Z. J.; Tecuapa-Flores, E. D.; Thangarasu, P. *ACS Omega* **2022**, *7*, 33985–34001. doi:10.1021/acsomega.2c03153
- Wang, X.; Han, Q.; Cai, S.; Wang, T.; Qi, C.; Yang, R.; Wang, C. *Analyst* **2017**, *142*, 2500–2506. doi:10.1039/c7an00589j
- Zhu, D.; Wang, L.; Yu, W.; Xie, H. *Sci. Rep.* **2018**, *8*, 5282. doi:10.1038/s41598-018-23174-z
- Nikolic, M. V.; Vasiljevic, Z. Z.; Lukovic, M. D.; Pavlovic, V. P.; Krstic, J. B.; Vujanecic, J.; Tadic, N.; Vlahovic, B.; Pavlovic, V. B. *Int. J. Appl. Ceram. Technol.* **2019**, *16*, 981–993. doi:10.1111/ijac.13190

18. Xu, Y.; Wu, S.; Li, X.; Huang, Y.; Wang, Z.; Han, Y.; Wu, J.; Meng, H.; Zhang, X. *New J. Chem.* **2017**, *41*, 15433–15438. doi:10.1039/c7nj03373g
19. Boruban, C.; Esenturk, E. N. *J. Nanopart. Res.* **2018**, *20*, 59. doi:10.1007/s11051-018-4139-0
20. Chen, H.; Liu, W.; Qin, Z. *Catal. Sci. Technol.* **2017**, *7*, 2236–2244. doi:10.1039/c7cy00308k
21. Zhou, X.; Li, X.; Sun, H.; Sun, P.; Liang, X.; Liu, F.; Hu, X.; Lu, G. *ACS Appl. Mater. Interfaces* **2015**, *7*, 15414–15421. doi:10.1021/acsami.5b03537
22. Thekkae Padil, V. V.; Černík, M. *Int. J. Nanomed.* **2013**, *8*, 889–898. doi:10.2147/ijn.s40599
23. Solanki, K.; Sharma, S.; Yadav, S.; Kaushik, B.; Rana, P.; Dixit, R.; Sharma, R. K. *Small* **2023**, *19*, 2300394. doi:10.1002/sml.202300394
24. Guo, W.; Zheng, Y.; Xiang, W.; Zhang, Y. *RSC Sustainability* **2025**, *3*, 243–254. doi:10.1039/d4su00531g
25. Nachaichot, A.; Kenvised, O.; Choram, S.; Nijpanich, S.; Budsombat, S. *RSC Adv.* **2025**, *15*, 6974–6983. doi:10.1039/d5ra00081e
26. Zhang, K.; Suh, J. M.; Choi, J.-W.; Jang, H. W.; Shokouhimehr, M.; Varma, R. S. *ACS Omega* **2019**, *4*, 483–495. doi:10.1021/acsomega.8b03051
27. Mohd Din, A. T.; Ahmad, M. A.; Hameed, B. H. *Chem. Eng. J.* **2015**, *260*, 730–739. doi:10.1016/j.cej.2014.09.010
28. Li, Y.; Wang, Y.; Lu, H.; Li, X. *Int. J. Hydrogen Energy* **2020**, *45*, 16080–16093. doi:10.1016/j.ijhydene.2020.04.002
29. Mirshafiee, F.; Rezaei, M. *Sci. Rep.* **2024**, *14*, 9659. doi:10.1038/s41598-024-60428-5
30. Wunder, S.; Polzer, F.; Lu, Y.; Mei, Y.; Ballauff, M. *J. Phys. Chem. C* **2010**, *114*, 8814–8820. doi:10.1021/jp101125j
31. Andrieux, J.; Demirci, U. B.; Miele, P. *Catal. Today* **2011**, *170*, 13–19. doi:10.1016/j.cattod.2011.01.019
32. Kottappara, R.; Pillai, S. C.; Kizhakkekilkoodayil Vijayan, B. *Inorg. Chem. Commun.* **2020**, *121*, 108181. doi:10.1016/j.inoche.2020.108181
33. Nguyen, L. M.; Nguyen, N. T. T.; Nguyen, T. T. T.; Nguyen, T. T.; Nguyen, D. T. C.; Tran, T. V. *Environ. Chem. Lett.* **2022**, *20*, 1929–1963. doi:10.1007/s10311-022-01416-x
34. Karthik, R.; Vinoth Kumar, J.; Chen, S.-M.; Karuppiyah, C.; Cheng, Y.-H.; Muthuraj, V. *ACS Appl. Mater. Interfaces* **2017**, *9*, 6547–6559. doi:10.1021/acsami.6b14242
35. Tan, C.; Fu, D.; Gao, N.; Qin, Q.; Xu, Y.; Xiang, H. *J. Photochem. Photobiol., A* **2017**, *332*, 406–412. doi:10.1016/j.jphotochem.2016.09.021
36. Geçgel, C.; Görmez, Ö.; Gözmen, B.; Turabik, M.; Kalderis, D. *Chemosphere* **2022**, *308*, 136411. doi:10.1016/j.chemosphere.2022.136411
37. Idham, M. F.; Falyouna, O.; Eljamal, R.; Maamoun, I.; Eljamal, O. *J. Water Process Eng.* **2022**, *50*, 103289. doi:10.1016/j.jwpe.2022.103289
38. Colón, D.; Weber, E. J.; Anderson, J. L.; Winget, P.; Suárez, L. A. *Environ. Sci. Technol.* **2006**, *40*, 4449–4454. doi:10.1021/es0600429
39. Zeynizadeh, B.; Mohammadzadeh, I.; Shokri, Z.; Ali Hosseini, S. *J. Colloid Interface Sci.* **2017**, *500*, 285–293. doi:10.1016/j.jcis.2017.03.030
40. Edebalı, S. *Appl. Surf. Sci. Adv.* **2023**, *18*, 100496. doi:10.1016/j.apsadv.2023.100496

License and Terms

This is an open access article licensed under the terms of the Beilstein-Institut Open Access License Agreement (<https://www.beilstein-journals.org/bjnano/terms>), which is identical to the Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0>). The reuse of material under this license requires that the author(s), source and license are credited. Third-party material in this article could be subject to other licenses (typically indicated in the credit line), and in this case, users are required to obtain permission from the license holder to reuse the material.

The definitive version of this article is the electronic one which can be found at:
<https://doi.org/10.3762/bjnano.17.97>