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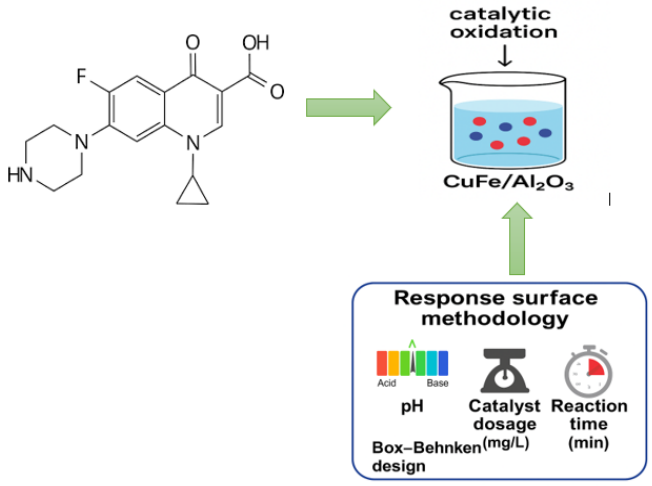
Heterogeneous catalytic oxidation of ciprofloxacin over $CuFe/Al_2O_3$: Multi-variable optimization by Box Behnken design and kinetic interpretation

Neha Kulshreshtha, Vishal Kumar Sandhwar*, Alok Tiwari, Shivendu Saxena, Ashish Mishra

Department of Chemical Engineering, Parul Institute of Technology, Faculty of Engineering & Technology, Parul University, Vadodara, Gujarat, India.

GRAPHICAL ABSTRACT



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ABSTRACT

Ciprofloxacin (CIP), as a commonly used fluoroquinolone antibiotic, is frequently detected in pharmaceutical effluents and aquatic environments and poses significant microbiological hazards due to low biodegradability and high stability. In this study, heterogeneous catalytic oxidation of ciprofloxacin was explored using a bimetallic $CuFe/Al_2O_3$ catalyst synthesized by wet impregnation method. FTIR, XRD, SEM, and BET analyses characterized the catalyst, showing Cu and Fe oxides uniformly distributed on the Al_2O_3 support and a mesoporous structure with a specific surface area of 91.9 $m^2\ g^{-1}$. Subsequently, batch oxidization experiments determined the influence of operating parameters (catalyst dosage, initial pH and reaction time) on ciprofloxacin removal efficiency. Box–Behnken Design (BBD)of Response Surface Methodology (RSM) verified process optimum and variable interaction analysis. Maximum CIP degradation of 80.66 % was observed in aqueous solution at optimal operating conditions. Kinetic studies showed pseudo-first-order kinetics ($k = 0.0191\ min^{-1}$ ($R^2 = 0.9911$); $t_1/_2 = 36.3$ min) confirmed rapid oxidation. $CuFe/Al_2O_3$ showed superior performance due to the redox cycle of Cu^{2+}/Cu^{+} and Fe^{3+}/Fe^{2+} species, advantageous generation of hydroxyl radicals from heterogeneous Fenton-like reactions. Therefore, the results support that $CuFe/Al_2O_3$ catalyst is a worthwhile and stable catalyst for antibiotic breakdown via advanced oxidation for sustainable pharmaceutical wastewater treatment.

1. Introduction

The global occurrence of pharmaceutical contaminants in aquatic environments is a concern for governments and public health organizations as they bioaccumulate and exert negative externalities on ecosystems and human populations. Pharmaceuticals like antibiotics (e.g., ciprofloxacin (CIP)) remain bioactive during their unintended release and can promote antibiotic resistance over time (Hou *et al.* 2019). As a fluoroquinolone antibiotic to treat bacterial infections, ciprofloxacin is frequently found in hospital discharges, municipal wastewater, and surface water at ng/L to mg/L concentrations. Its persistence against biologically mediated treatment means that state-of-the-art treatment technologies are required to reduce environmental complications (Giri *et al.* 2014, Imam *et al.* 2019, Imam *et al.* 2020, Malakootian *et al.* 2019, Wang *et al.* 2024)

Advanced oxidation processes (AOPs) are emerging treatment technologies that generate hydroxyl radicals (- OH) with the ability to mineralize recalcitrant organic micropollutants through non-selective

*Corresponding author Email: vishal.sandhwar8850@paruluniversity.ac.in

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oxidative degradation (Brillas *et al*. 2023, Dindaş *et al*. 2024, Wang *et al*. 2023). Of the AOPs, catalytic oxidation is a promising tool against pharmaceutical micropollutants because of its increased effectiveness, reduced energy requirements, and catalyst recycling capacity (Adnan *et al*. 2021, Garrido-Cardenas *et al*. 2020). Heterogeneous catalytic oxidation systems, involving transition metal catalysts supported on solid carriers, are garnering significant attention in wastewater treatment applications, primarily because they are more stable than their homogeneous counterparts, easier to separate, and create less sludge. Copper-iron bimetallic catalysts supported on alumina supports ($CuFe/Al_2O_3$) are effective under heterogeneous catalytic oxidation conditions due to their synergistic redox reactions, which generate reactive oxygen species upon oxidant activation (e.g., H_2O_2) through a Fenton-like mechanism (Adnan *et al*. 2021, Ahmed *et al*. 2025, Peng *et al*. 2025). Cu and Fe combinations provide better electron transfer rates, higher availability of active catalytic sites, and stronger fouling/ leaching resistance all beneficial for longer activity times in waters. Alumina (Al_2O_3) boasts a high surface area and chemically nonreactive support that enables active metals to disperse evenly, increases catalyst surface area, and boosts mechanical strength. Prior research notes good removal efficiencies of dyes, phenols, and other pharmaceuticals under Fenton-like oxidation conditions with $CuFe/Al_2O_3$ catalysts (Jia *et al*. 2025).

However, to optimize degradation efficiency (and thereby better reduce oxidant/catalyst requirements), essential parameters must be determined for implementation. Compound relationships exist with the interlinked behaviour of catalyst dosage, pH and reaction time which impact catalytic efficiency, reaction kinetics, and overall process economics. The standard method of investigation for such factors is to vary one while holding the other constant (Sarrai *et al*. 2016, Madjene *et al*. 2021). This requires excessive time and energy since such a method fails to adequately tease apart the interactions between any combinations of the three. Therefore, a wealth of literature suggests more effective statistical experimental design approaches where multiple factor variables can be assessed and optimized through box behnken design (BBD) (Mauna *et al*. 2025, Singh *et al*. 2015). BBD allows the researcher to assess a wide parametric space in a systematic step manner to understand which factors are most impactful in substantive ways predicted through empirical models with limited follow-up runs (Poozesh *et al*. 2025, Sandhwar & Prasad 2017). Furthermore, BBD reveals the interaction effects of factors and any quadratic response which matters for scale-up and operational handling (Buenaño *et al*. 2024). Of increasing importance, however, is the role of kinetic interpretation for both enhancement and degradation mechanism/rate limiting step insights which inform oxidation by heterogeneous catalysts like $CuFe/Al_2O_3$. For example, kinetic modeling provides understanding of the adsorption kinetics, movements of reactive species, and surface interactions which occur under varying conditions which all facilitate optimization study for further understanding of future catalytic studies for chemical design (Giri *et al*. 2014, Sun *et al*. 2009). Pseudo-first-order kinetic has been applied in antibiotic degradation systems to support catalyst performance.

However, with the growing importance of ciprofloxacin treatment in aqueous matrices, this study presents the heterogenous catalytic oxidation of ciprofloxacin over $CuFe/Al_2O_3$ in Fenton-like conditions as well as approaches BBD to assess catalyst dosage, pH and reaction time as critical parameters for enhanced degradation efficiency while minimizing oxidant/catalyst use from optimal design parameters to better facilitate future treatment. In addition, kinetics will be assessed to deduce mechanisms of degradation as well as provide comparative quantification for the general catalytic process. Such information would benefit the implementation of $CuFe/Al_2O_3$ catalysts in pharmaceutical wastewater treatment for future scale-up and industrial application (Jalali *et al*., 2025, Liu *et al*., 2022).

The development of heterogeneous Fenton-like oxidation of ciprofloxacin (CIP) utilizing Cu-Fe bimetallic catalysis has previously been demonstrated through a variety of means including; $CuFe_2O_4$@biochar composite materials that have exhibited PMS activated removal under acidic conditions (Zeng *et al*., 2023), zeolites loaded with copper that are capable of removing CIP at a neutral pH (Guo *et al*., 2023); however, both were conducted in the absence of a multi-variable optimization strategy, hematite/MOF nanocomposites that have shown activity up to pH 3–4 through single-factor studies (Hashemzadeh *et al*., 2021), and Fe-Cu/γ-Al_2O_3 systems that have utilized a different type of pollutant than an antibiotic such as nitrobenzene (Jiang *et al*., 2026). This research fills the noted gaps in the field by creating a highly active and durable $CuFe/Al_2O_3$ catalyst via incipient-wetness co-impregnation method that is able to remove CIP (10 mg/L) at a nearly neutral pH. The novelty of this approach lies in the enhanced generation of •OH radicals on a high surface area Al_2O_3 support due to the synergistic Cu-Fe interaction, thus minimizing leaching while allowing for operation over a broad pH range, unlike the pH limited or leaching prone systems noted above. In addition, the use of a BBD optimization strategy for the three independent variables (pH, catalyst amount, reaction time) resulted in a robust quadratic model (R^2 = 0.9999, confirmed by additional validation experiments) that revealed interactions between the variables (i.e., pH and catalyst synergism) that were not apparent when applying single-factor strategies to CIP, along with kinetic models of the catalyst performance and detailed characterization of the catalyst (FTIR/XRD/SEM). Overall, these advancements position $CuFe/Al_2O_3$ as a viable catalyst system for the treatment of actual pharmaceutical wastewaters, and extend the application of Fe-Cu/Al_2O_3 systems beyond the removal of CIP to other types of pollutants. This study fills knowledge gaps in this field by (i) synthesizing and characterizing $CuFe/Al_2O_3$ for optimized oxidation of ciprofloxacin; (ii) applying multi-variable assessment through statistical optimization via BBD; (iii) performing an investigative kinetic analysis to better understand the mechanism underlying the reactions. Ultimately findings will support future sustainable treatment technologies targeting emerging pharmaceuticals as contaminants of concern while also promoting knowledge of heterogeneous catalytic oxidation processes.

2. Materials and methods

2.1. Materials

All chemicals and reagents used in this study, including ciprofloxacin (CIP, analytical grade), copper nitrate, ferric nitrate, and aluminum oxide (Al_2O_3) support, were purchased from reputable suppliers and used without further purification.

2.2. Wastewater Sampling

A synthetic solution of ciprofloxacin was prepared for experiment by dissolving CIP in ultrapure deionized water at a concentration of 10 mg/L. All solutions were prepared at room temperature in the laboratory and away from sunlight to reduce ciprofloxacin photodegradation. Prepared synthetic wastewater were kept in glass bottles at 4°C for chemical stability until their application in catalytic degradation. To ensure validity, UV-vis analysis was performed on the solutions before degradation to check CIP concentration at its peak wavelength, assisted by a previously made calibration curve. Thus, this made-up solution served as a constant between experiments to simulate pharmaceutical wastewater conditions necessary for process optimization and kinetic experiments with the $CuFe/Al_2O_3$ catalyst.

2.3. Synthesis of catalyst

The $CuFe/Al_2O_3$ catalyst used for heterogeneous catalytic oxidation of ciprofloxacin was prepared by the incipient wetness co-impregnation method under the assumption of a homogeneously dispersed active metal species and a strong attachment to the Al_2O_3 support (Zumbar *et al*. 2023, Vandevyvere *et al*. 2023, Munnik *et al*. 2015). Copper(II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) and iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) of analytical grade were used as precursors for metals while γ-Al_2O_3 was relied on as the support due to its highly porous, stable and amphoteric character, favoring both adsorption and redox activity (Jayan *et al*. 2023). γ-Al_2O_3 was first pre-dried at 120 °C for 3 h to eliminate moisture and facilitate effective interaction. The precursors were mixed in an aqueous solution of Cu and Fe in a 1:1 molar ratio to achieve a total weight percent of metal loading at 10 wt%. The precursor solution was slowly added dropwise to the pre-dried Al_2O_3 powder under constant stirring at room temperature until incipient wetness was reached (i.e., pore-filling without excess liquid available) (Gao *et al*. 2018, Tiwari *et al*. 2025). The obtained impregnated material was aged at room temperature for 12 h to ensure uniformity of diffusion of metallic species into the pore structure, and subsequently dried at 105 °C for 12 h to eliminate excess moisture and render the nitrates partially decomposed but still held together in the presence of dry Al_2O_3 at room temperature. The dried material was subsequently calcined in an air atmosphere at 500 °C for 4 h (with a heating ramp of 5 °C min^{-1}) to ensure final decomposition of the nitrates to CuO and Fe_2O_3, as well as to preferentially develop Cu–Fe mixed oxide or spinel-type creations, e.g., $CuFe_2O_4$ at the metal–support interface. The chosen calcination temperature was optimized to ensure complete crystalline conversion but prevent excessive sintering of particles and loss of surface area. The catalyst was washed many times with deionized water to eliminate unwanted nitrate residue, dried again at 110 °C for 6 h, ground into powder (Arvind *et al*. 2021).

2.4. Characterization of synthesized catalyst
2.5. FTIR Analysis

The FTIR spectrum of the $CuFe/Al_2O_3$ synthesized material (Figure 1) contains fundamental absorption peaks which define the materials made under reaction conditions and confirm the presence of surface hydroxyls, metal-oxygen interactions, and the alumina framework. For instance, a broad absorption band located at 3370 cm^{-1} corresponds to stretching vibrations of the -OH bond emerging from adsorbed water and hydroxyls coming from both empty alumina sites and as a result of the formation of metal oxides (Kumar *et al*. 2021, Haneda *et al*. 2001, Moeini & Meshkani 2023). Meanwhile, a weak band detected at 1640 cm^{-1} comes from a bending mode of H_2O which is molecularly absorbent (Al-Abadleh & Grassian 2003). A band at 1380-1400 cm^{-1} also emerges which comes from symmetric and asymmetric stretching of residual nitrates that did not react on the surface and comes from the metal precursors (Hassan *et al*. 2025). This implies that although calcination should have removed these nitrates, they were only minimally removed. However, a very strong absorption band at 1000 cm^{-1} and below corresponds to Cu–O, Fe–O, Al–O metal-oxygen vibrations which indicates that the formation of metal oxides did indeed take place and that Cu and Fe were successfully impregnated on the Al_2O_3 surface (Shaheen *et al*. 2020; Ravi & Thyagarajan 2024). This is important because there are no organic bands observed between 2800-3000 cm^{-1} which show that nitrate and organic components were completely removed through calcination. Thus, it can be confirmed that through co-impregnation followed by calcination, a well-defined bimetallic oxide phase was formed that was strongly attached to the surface of alumina as evidence supports this (Khatamian *et al*. 2024, Mardwita *et al*. 2019, Rezaei & Vione 2018).

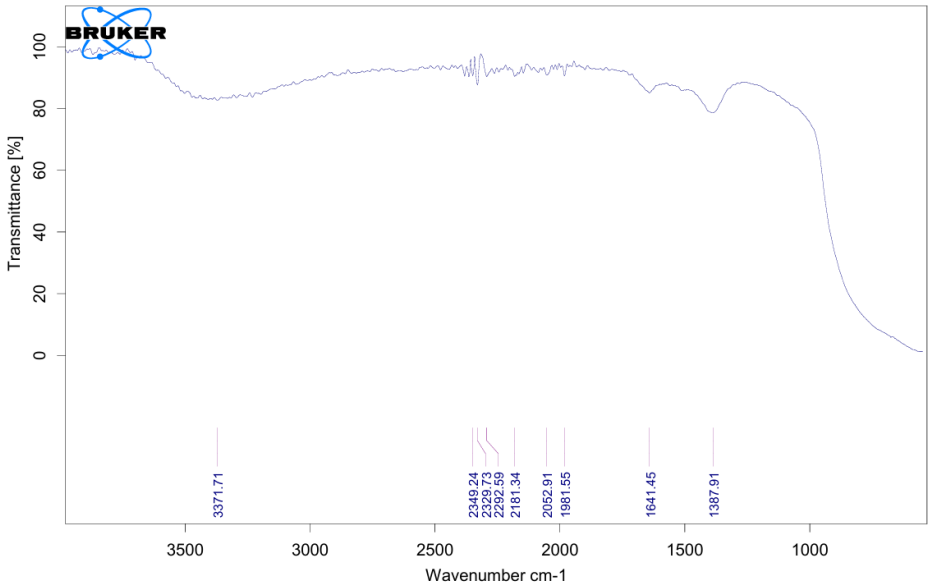

Fig. 1: FTIR spectrum of Cu-Fe/Al_2O_3 catalyst.

2.6. XRD analysis

The X-ray diffraction pattern of $CuFe/Al_2O_3$ was examined (Figure 2) and displays both crystalline characteristics and amorphous characteristics that reveal a mixed-metal oxide supported on alumina (Luo *et al*. 2005, Zhao *et al*. 2018). For instance, peaks approximately at 2θ = 37.2°, 45.9° and 67° correspond to γ-Al_2O_3 where the planes are (311), (400), (440) which implies that the support maintained its crystalline structure throughout impregnation and calcination stages (Horsth *et al*. 2023). Also observed are additional broad peaks appearing at 2θ = 35.6°, 43.2°, and 62.4° which can be assigned to the (111), (200), and (220) reflections of CuO and Fe_2O_3 phases which promotes the construction of CuO and Fe_2O_3 crystallites uniformly dispersed within the alumina matrix. However, since these peaks display slight broadening and slightly less intensity compared to bulk oxides, this means they are dispersed on a nanoscale (Nikam *et al*. 2024, Horsth *et al*., 2023. Additionally, since $CuFe/Al_2O_3$ was synthesized through solid-state methods, this could also indicate the formation of Cu–Fe mixed oxide or spinel ($CuFe_2O_4$) which occurs through partial solid-state diffusion over longer times/at higher temperatures—in this case 500 °C, but this is expected as Cu and Fe compounds were expected to form tight bonds in solid state to create homogenous alloys instead of heterogeneous ones. There were no peaks detected for unreacted nitrates which shows complete decomposition occurred through thermal means. In addition, a lack of other peaks besides alumina confirms that there were no impurities formed in the process nor was there any change in the crystal structure of alumina from impregnation (Faungnawakij *et al*. 2009, Luo *et al*. 2005, Sumathirathne and Euler 2021).

2.7. SEM Analysis

The SEM micrograph shown in Figure 3 provides surface morphology of $CuFe/Al_2O_3$ that denotes a rough, granular structure that does not contain discrete particles but rather assemblages with a range of particle sizes which still presents a non-uniform yet appropriately dispersed feature (Jayan *et al*. 2023, Kumar *et al*. 2021, Abimanyu *et al*. 2008). For example, larger assemblages are found in the 2-10 µm range while smaller assemblages pervade around this particle structure with a finer distribution—presumably due to Cu/Fe oxide nanoparticles embedded within the alumina network (Gao *et al*. 2022, Shaheen *et al*. 2020). Such a rough surface and porous nature is critical for enhanced site access during oxidation when mass transfer occurs, as indicated by Haneda *et al*. 2001 and Franco *et al*. 2017. Furthermore, the textured particles maintain strong adhesion to the support without sintering or aggregation due to calcination, meaning active phase attachment maintains the advantageous properties necessary for catalysis (Zumbar *et al*. 2023, Vandevyvere *et al*. 2023). Therefore, the morphology suggests that co-impregnation has resulted in a bimetallic catalyst on a greater surface area than expected with appropriate heterogeneity properties required for particle dispersion for optimal oxidation in aqueous systems as ciprofloxacin transformed via H_2O attempts to transmute this pharmaceutical into favorable byproducts via catalytic transformation techniques (Khatamian *et al*. 2024, Mardwita *et al*. 2019).

2.8. BET surface area analysis

Catalyst $CuFe/Al_2O_3$ was characterized by Brunauer–Emmett–Teller (BET) who assessed a specific surface area of 91.9 $m^2\ g^{-1}$ to indicate a mesoporous structure with substantial levels of textural porosity suitable for heterogeneous catalysis (Jayan *et al*. 2023, Kumar *et al*. 2021). This moderately high specific surface area is due to mesoporous γ-Al_2O_3 support where metal impregnation and the calcination step do not destroy the porous structure and allow for even distribution of Cu and Fe oxide species at the catalyst surface (Gao *et al*. 2022, Shaheen *et al*. 2020). This distribution did decrease the specific surface area as compared to the virgin alumina support, albeit slightly, indicating that pore blocking does occur due to active metal phases, yet not significantly to impede mass transfer or active site accessibility required during catalytic oxidation (Haneda *et al*. 2001, Franco *et al*. 2017). The mesoporous structure ensures nanoscale active phase distribution whereby an optimal size exists to balance effective surface area with active phase stability. This is crucial for hydroxyl radical production

during ciprofloxacin degradation under heterogeneous conditions creating a Fenton-like process (Khatamian *et al*. 2024, Mardwita *et al*. 2019, Rezaei and Vione 2018).

2.9. Experimental procedure

Batch oxidation experiments were performed in a 250 mL glass reactor equipped with magnetic stirring for homogenous mixing. An aliquot of ciprofloxacin solution (100 mL) with a known initial concentration (10 mg L^{-1}) was added to the reaction vessel, along with a predetermined dose of $CuFe/Al_2O_3$ catalyst and fixed H_2O_2 concentration (10 mM). The pH was adjusted to a required pH via 1 M HCl or NaOH when applicable and before commencing the reaction. The reaction occurred at room temperature under atmospheric pressure and stirring (generally at 300 rpm) to avoid any external mass-transfer limitations. At certain times of reactions, aliquots were withdrawn with a glass syringe, and filtered with a 0.22 µm syringe filter to remove catalyst particles. The remaining concentration of ciprofloxacin in each aliquot was determined via UV–Visible spectrophotometry at 276 nm. All experiments were conducted in duplicates, the mean values were statistically treated, and the percentage removal of ciprofloxacin was calculated based on initial versus final concentrations. This data was used for catalyst dosage, initial pH, and reaction time to determine values needing optimization. The BBD model's values were ultimately applied toward kinetic studies for further interpretation of the degradation process as well as the determination of apparent rate constants.

$$\% \text{ CIP removal} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where, C_0 & C_t are initial and final concentration of CIP.

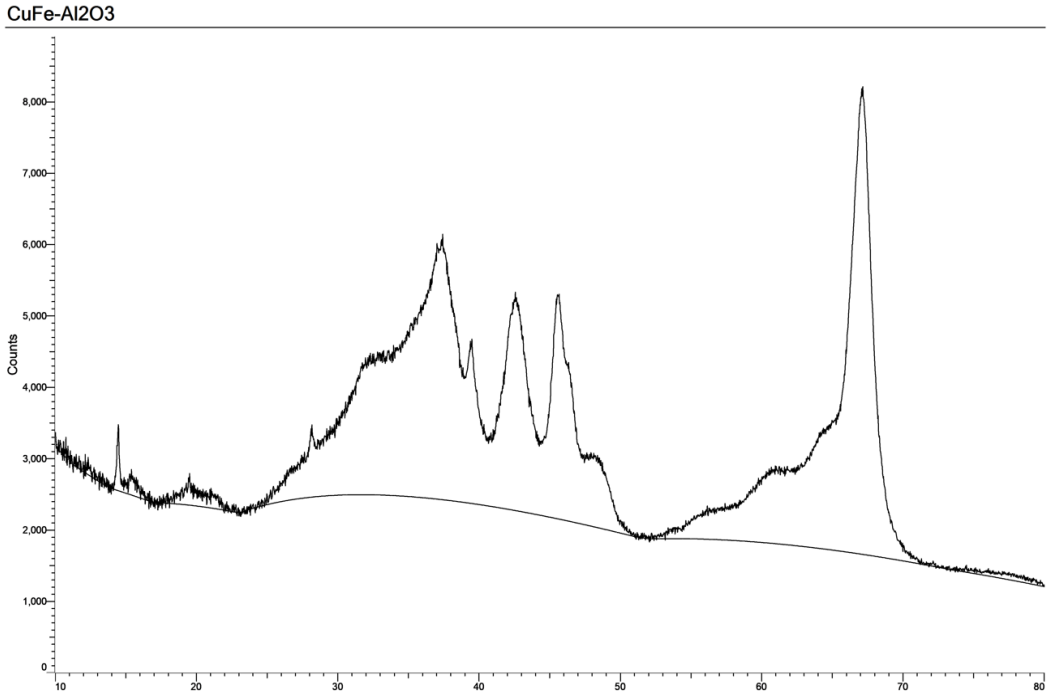

Fig. 2: XRD spectrum of $Cu\text{-}Fe/Al_2O_3$ catalyst.

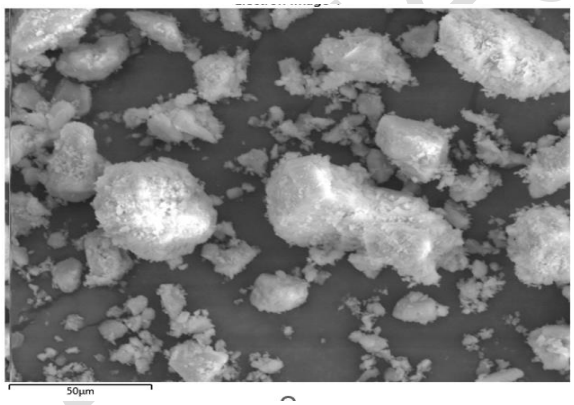

Fig. 3: SEM image of $Cu\text{-}Fe/Al_2O_3$ catalyst.

2.10. Box–Behnken Design study

The multi-variable optimization of ciprofloxacin (CIP) degradation over $CuFe/Al_2O_3$ catalyst was performed using a Box–Behnken Design (BBD) based on response surface methodology (RSM), which is a valuable method for exploring multiple variable interactions with fewer experiments. Three factors were chosen as independent variables—catalyst dosage (g/L), solution pH, and reaction time (min)—and assessed at three levels (low, medium, high). The response variable was the percentage removal of CIP. A total of 17 runs were performed, including five center points, in order to assess experimental error and confirm the model. The experimental data were correlated to a second order polynomial equation. Variables and their levels are presented in Table 1. Predicted set of experimental runs is shown in Table 2.

Table 1: Operating parameters and their levels.

Box Behnken design characteristics			
	Parameters (Range)		
	A	B	C
Levels	Catalyst dosage (40-120 mg/L)	pH (3-9)	Time (30-90 min)
-1	40	3	30
0	80	6	60
+1	120	9	90

Table 2: BBD predicted set of runs.

Run No.	A	B	C
1	80	9	90
2	80	3	90
3	120	6	90
4	80	6	60
5	80	6	60
6	40	6	90
7	80	6	60
8	80	6	60
9	80	6	60
10	120	6	30
11	40	3	60
12	80	9	30
13	40	6	30
14	120	3	60
15	40	9	60
16	120	9	60
17	80	3	30

3. Results and discussion

The interactive influence of catalyst dosage, pH, and reaction time on the percentage removal of ciprofloxacin (CIP) by $CuFe/Al_2O_3$ catalyst was investigated by three-dimensional response surface and contour plots using Box–Behnken Design (BBD) (Figures 4 (a-c)). According to the statistical prediction of the model, the maximum value of CIP removal efficiency is forecasted to be 80.66% at the optimum experimental conditions of catalyst dosage = 91.77 mg L^{-1}, pH = 6.57, and reaction time = 63.91 min.

3.1. Effect of catalyst dosage

As seen in Figs.4 a and b, CIP removal efficiency increased with an increase in catalyst dosage up to around 90–100 mg/L. This is because a larger number of active sites were available for CIP to react, and an increasing quantity of Cu and Fe redox couples on the $CuFe/Al_2O_3$ surface emerged to produce reactive oxygen species (ROS) for oxidative degradation of CIP molecules, especially hydroxyl radicals (•OH) (Kumar *et al*. 2021; Abimanyu *et al*. 2008, Adnan *et al*. 2021). However, beyond the optimum dosage, increases in catalyst removal efficiency reached a plateau. This is likely attributed to the agglomeration of catalyst particles at high concentrations and a decrease in surface area availability as well as potential radical recombination (Hassan *et al.* 2025). Therefore, an optimum catalyst dosage of 91.77 mg/L keeps a relevant quantity of ROS producers without wasteful excess due to hindered access as a result of physical grouping (Shaheen *et al*. 2020).

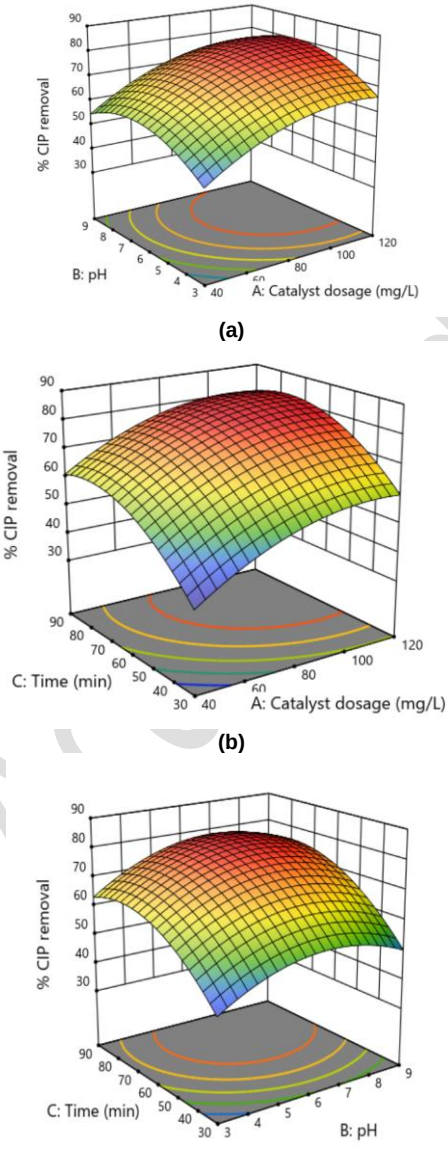

Fig. 4: Effect of (a) catalyst dosage a pH (b) catalyst dosage and time (c) pH and time on % CIP removal.

3.2. Effect of pH

The pH can directly influence heterogeneous catalytic oxidation since it affects the charge of the surface of the catalyst, metal redox potentials and acidic/base equilibrium. As illustrated in 4 (a) and (c), CIP removal increased parabolically with respect to pH: reaction rates increased from strongly acidic conditions (pH ≈ 3) to an optimal area around pH 6.5 and decreased again beyond neutral into more alkaline conditions (Sun *et al*. 2009, Jalali *et al*. 2025. It can be suggested that during strong acidic conditions, too many H^+ ions were scavenging hydroxyl radicals necessary for oxidative participation. On the contrary, at higher pH (> 7), formation precipitations of metal hydroxides deactivating catalytic sites with limited formation of hydroxyl radicals (Giri *et al*., 2014). The optimum pH = 6.57 highlights that neutral conditions favour both stability of $CuFe/Al_2O_3$ and preferred equilibrium for redox cycling (Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu^{+}), leading to enhanced CIP degradation (Khatamian *et al*. 2024).

3.3. Effect of reaction time

The effect of reaction time on CIP removal is recorded in Figs. 4 a and b, over a gradual correlation, where removal efficiency increased with time until around 60–70 min, where it plateaued. When it comes to the immediate presence of CIP molecules in solution, sufficient ROS could be generated to produce high degradation rates as quickly as possible. However, once the reaction started to occur, less CIP was available, and created radicals could either be depleted or scavenged by intermediate species occurred from early degradation (Sarrai *et al*. 2016). The optimal time predicted by the model was 63.91 min which indicates the majority of degradable fraction of CIP could be oxidized within this time frame to adequately oxidize particles without excessively lengthening reaction time. Interactive nature between parameters observed through curvature response surfaces. For instance, under such optimal conditions (catalyst dosage ≈ 92 mg L^{-1}, pH ≈ 6.6, time ≈ 64 min), this is a number of active sites sufficiently facing an interdependent surface charge with prolonged ROS viability that can justify such effective removal efficiency (80.66%) documented (Kumar *et al*. 2021). This means that the interaction catalyst dosage-time was positively related since sufficient time would allow for degradation to take place at a greater extent with enough time (Hassan *et al*., 2025, Shaheen *et al*. 2020). The pH-catalyst dosage interaction relative to removal efficiency increased as performance was most positive in neutral pH levels where even promoted catalyzation was reported (Adnan *et al.* 2021).

Compared to the ciprofloxacin (CIP) removal systems reported as shown in Table 3, the $CuFe/Al_2O_3$ catalyst achieves a competitive removal efficiency (77.08% experimental; 80.66% BBD-predicted) under nearly neutral pH and modest catalyst dosage as well as interference from other heterogeneous Fenton catalysts at comparable pH and catalyst dosage. Thus, the proposed system matches systems that have already been implemented in effectiveness. Furthermore, not all systems that have been implemented so far use such a low catalyst dosage and such an effective yet green pH level, which makes it feasible for real-world implementation.

3.4. Optimization and ANOVA study

Box–Behnken optimization suggests that every parameter—catalyst dosage, pH and reaction time—has a statistically significant influence on CIP removal with an observed non-linear trend (Madjene *et al*. 2021, Singh *et al.* 2015). The maximum experimental conditions based on predicted efficacy (91.77 mg L^{-1}, pH 6.57, 63.91 min) reached an even higher removal efficiency of 80.66% as noted in Table 4 for the lowest catalyst applied in situ and acceptable reaction time indicating $CuFe/Al_{23}$ is an effective heterogeneous catalyst for pharmaceutical wastewater treatment at such lower levels. Box–Behnken design and ANOVA results (shown in Table 5) also confirmed the effectiveness of the quadratic response surface model generated for the catalytic oxidation process by successful fitting of the response surface model. In fact, the model revealed a standard deviation of 0.24 and a mean response of 64.41, where the subsequent coefficient of variation (C.V.) of 0.37% is extremely low, implying accurate predictions with minimal experimental error (Mauna *et al*. 2025). In addition, the coefficient of determination (R^2 = 0.9999) denotes a virtually perfect correlation between the experimental and predicted values over the adjusted R^2 (0.9997) and predicted R^2 (0.9990) values, which are very similar (Chacker *et al*. 2021). Finally, a subsequent adequate precision value of 224.07, comfortably higher than the cutoff of 4, reveals that there is excellent signal-to-noise ratio, confirming that the developed model has regional integrity within the assessed experimental space (Madjene *et al.* 2021). Therefore, these parameters justify that the relationship

created by the three operating parameters pH, catalyst dosage and reaction time on the response (% CIP removal) are appropriately modelled by the quadratic equation and thus, BBD-based optimization successfully assessed significant parameters and their interactions with acceptable levels of prediction for catalytic oxidation treatment of pharmaceutical wastewater (Singh *et al*. 2015). Eq. 2 represents the output (% CIP removal) in terms of coded factor.

% CIP removal (Ni-Co/Al2O3) = 76.51+10.21A +4.32B +10.77C +0.2700AB -0.7075AC +1.24BC−6.98A2−8.94B2−9.77C2 (2)

The coding regression model applied to % CIP removal using the Cu–Fe/Al_2O_3 catalyst is represented in Eq. 2. The strong influence of catalyst dosage (A, +10.21) and reaction time (C, +10.77) on CIP removal as linear positive coefficients suggests that within the range observed, the more catalyst and more reaction time the better for CIP removal; pH (B, +4.32) is a smaller linear positive influence but still positive (El Salam & El-Fawal 2024, Assassi *et al*. 2023). Interaction effects were determined to be smaller, with some positive and some negative; catalyst dosage × pH (AB = +0.27) is slightly synergetic, pH × reaction time (BC = +1.24) is a mildly synergetic influence while catalyst dosage × reaction time (AC = −0.7075) is a weak antagonist (Mardwita *et al*. 2019, Nascimento *et al*. 2024). The negative quadratic coefficients suggest curvature in the response surface (A^2, B^2 and C^2 at −6.98, −8.94 and −9.77, respectively) which confirms that when a factor has a significant (peak) value, the response will decrease when increasingly high levels of that factor are applied (El Salam & El-Fawal 2024).

Overall, Equation (2) confirms that dosage and reaction time are overwhelmingly positive at their lower levels with much to gain from increases in CIP removal but the nonlinearity and interactions suggest less than obvious findings. ANOVA yielded a statistically validated effective model (R^2 high and adequate for prediction and tested) that suggests an accurate prediction for the best operative values for catalytic oxidation (Haque *et al*., 2023; Assassi *et al*., 2023).

Table 3. Data reported by various authors for CIP wastewater treatment.

Catalyst system	CIP, mg/L	pH	Catalyst dosage	Oxidant (dosage)	Time, min	CIP removal, %	Ref.
$CuFe_2O_4$@biochar	10	Neutral and weak alkali condition	0.1 g/L	Peroxymonosulfate (2.5 mM)	30	≈97	Zeng *et al.* 2023
Cu-loaded biochar	20	pH = 9.95 and 11.95	0.2 g/L	Peroxymonosulfate (0.3 g/L)	40	>99	Guo *et al.* 2023
Hematite/MOF nanocomposite	20	-	0.1 g/L	Peroxymonosulfate (0.2 g/L)	30	100	Hashemzadeh *et al.* 2021
δ-FeOOH/MWCNTs nanocomposite	10	5.3	23.5 mg	H_2O_2 (20.6 mM)	131.6	86.9	Salari *et al.* 2021
Corncob Biochar-Based Magnetic Iron–Copper Bimetallic Nanomaterial	20	6.4	0.6 g/L	H_2O_2 (10 mM)	360	93.6	Liu *et al.* 2022
$CuFe/Al_2O_3$	10	6.57	91.77 mg/L	H_2O_2 (10 mM)	63.91	77.08 (exp.) /80.66 (BBD)	This study

3.5. Kinetic study

Ciprofloxacin degradation kinetics over $CuFe/Al_2O_3$ catalyst was studied to determine the reaction mechanism and the rate-limiting step of the heterogeneous Fenton-like oxidation process. The kinetic data were fitted to the pseudo-first-order kinetic model expressed as $\ln(C_0/C_t) = k \cdot t$ where C_0 and C_t are the ciprofloxacin concentrations at time zero and at time t, respectively, and k is the apparent rate constant (min^{-1}). A linear relationship (Fig. 5) was established between $\ln(C_0/C_t)$ and reaction time, signifying the adherence to pseudo-first-order kinetics. The rate constant (k) was calculated to be 0.0191 min^{-1} with an excellent regression coefficient (R^2 = 0.9911) obtained. These findings support that ciprofloxacin degradation occurs with pseudo-first-order kinetics relative to its concentration (assuming excess oxidant, as $CuFe/Al_2O_3$ is a good catalyst and H_2O_2 is readily activated and decomposed into reactive hydroxyl radicals (Kumar *et al.* 2021, Pratiwi *et al*. 2024). In addition, the proximity of the data supports consistent availability of active sites over the course of the reaction, as catalytic performance was similar throughout. Such findings are consistent with reports in transitional metal-based heterogeneous Fenton systems where radical generation and surface-mediated adsorption–reaction kinetics predominantly influence the overall degradation rate. Therefore, $CuFe/Al_2O_3$ is a stable and effective catalyst for ciprofloxacin oxidation under optimal conditions (Khatamian *et al*. 2024). For a first-order reaction, the half-life ($t_1/_2$) is calculated using Eq. 3.

$$t_{1/2} = \frac{0.693147}{k} = \frac{0.693147}{0.0191} = 36.29 \text{ min} \quad (3)$$

Therefore, with the associated conditions, ciprofloxacin will decrease to 50% of its initial concentration in about 36.3 minutes.

3.6. Catalyst recyclability study

To check the recyclability of the catalyst as a factor of its feasibility and economic effectiveness of heterogeneous Fenton-like application, $CuFe/Al_2O_3$ catalysts recyclability experiments were performed under optimized operating conditions (catalyst dosage: 91.77 mg/L; pH: 6.57, Time: 63.91 min). As CIP removal (77.08 % based on the test run) confirmed, the first cycle of the catalyst was performed with the most potent performance, possessing all active sites accessible. The catalyst was recovered through centrifugation after each cycle, adsorbed residues were extensively washed with distilled water, dried, and then applied to the subsequent cycle without any additional treatment. Over four successive cycles, catalytic activity was reduced. CIP removal in Cycle 2 was 70.34 %, Cycle 3 was 63.11%, and Cycle 4 was 59.23 %. Such reductions are in accordance with findings from comparative literature deactivation mechanisms where they suggest that (i) leaching of active Fe/Cu species occurs due to the partial re-application of active sites due to no covalent bond formation at this level to limit Fe^{3+}/Cu^{2+} sites from returning to Fe^{2+}/Cu^{+} or maintaining itself at one site; and (ii) surface carbonaceous deposition because hydroxyl radical generation is inhibited by catalytic surfaces being blocked by other non-related byproducts accumulation.

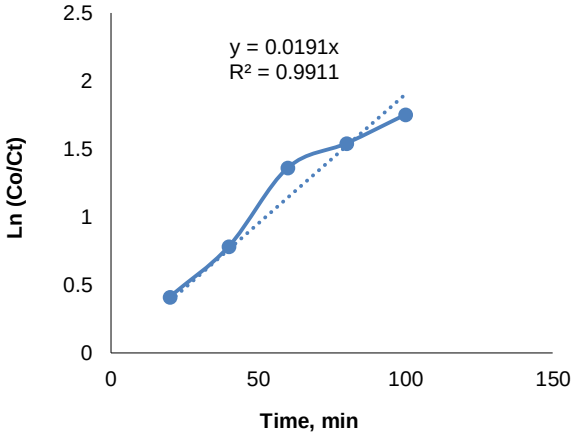

Fig. 5: Pseudo first-order kinetics analysis of CIP removal.

Similar observations have been made in other heterogeneous Fenton systems. For example, the performance of Fe-loaded coal fly ash was reduced in cycles because of Fe leaching and surface blocking

(Arvind *et al.* 2021). In addition, the Fe-Cu/γ-Al_2O_3 system found in the literature has a reduced TOC removal efficiency compared to the first cycle at 50.15% about 41.29% in cycle 2; the performance reduced gradually in subsequent cycles to a stable value of about 34% (Jiang *et al.* 2026). In addition, compared to the advanced catalytic systems of Cu-MOFs-800/H_2O_2 (Chen *et al*., 2020) which could effectively degrade methyl orange for four cycles; the Fe_2O_3@Cu-MOFs/H_2O_2 (Li *et al*., 2019), which could effectively remove rhodamine B for four cycles; and α-Fe_2O_3@SiO_2/H_2O_2 (Wu *et al* ., 2014) which could effectively operate for five cycles without reduced efficiency, the CuFe/Al_2O_3 in this work had comparable or better reusability which is critical for real water treatment applications. It can be qualitatively suggested that the catalyst did not show significant physical structure weakening or sludge formation and operated with substantial activity for several subsequent cycles leading to determined reliable recyclability and operational stability, supporting heterogeneous catalytic oxidation.

4. Conclusions

The results of this research indicate that ciprofloxacin heterogeneous catalytic oxidation with bimetallic CuFe/Al_2O_3 is an efficient process at specific operating ranges. Box–Behnken Design facilitated batch experiments where catalyst doses (40–120 mg/L), pH levels (3–9), and reaction times (30–90 min) were assessed to obtain the greatest advanced oxidation. The optimum conditions were determined to be catalyst dosage of 91.77 mg/L, 6.57 pH and 63.91 min reaction time which resulted in ciprofloxacin removal of 80.7% (actual result was 77.1%) which indicates that there is strong correlation between predicted and laboratory-derived values. Kinetic studies demonstrated pseudo-first order with k = 0.0191 min^{-1} which implies the reaction occurs rapidly and effectively when exposed to the catalyst conditions. Such efficacy can be explained by the redox cycling of Cu^{2+}/Cu^{+} and Fe^{3+}/Fe^{2+} over the high surface area alumina responsible for intensive hydroxyl radical production. Throughout a majority of the tested ranges, the catalyst operates with no inhibition and through a high stability which implies that it is applicable for large scale treatment of pharmaceutical industrial wastewater. Thus, this work confirms that statistical optimization through multiple variable adjustment can effectively develop bioactive systems to remove recalcitrant antibiotics in engineered systems for water treatment.

Author Contributions

Neha Kulshreshtha: Writing, Validation, Formal analysis
Vishal Kumar Sandhwar: Supervision, Conceptualization, Writing-review and editing
Alok Tiwari: Formal analysis
Shivendu Saxena: Validation
Ashish Mishra: Writing—review and editing

Conflicts of Interest

There are no conflicts to declare.

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