

Article

Cyclodextrin Polymer-Supported Cu-Fe Nanoparticles Enhanced the Degradation of 4-Chlorophenol by Citric Acid Complexation

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Abstract

4-Chlorophenol (4-CP) is a persistent and highly toxic pollutant commonly found in groundwater. However, its efficient degradation remains challenging due to the rapid agglomeration of conventional zero-valent iron (ZVI) nanoparticles, their narrow pH operating range, and the environmental risks associated with synthetic chelating agents. To address these limitations, this study presents a rationally designed catalytic system integrating cyclodextrin polymer (CDP)-supported bimetallic Cu-Fe nanoparticles (Cu-Fe-CDP) with citric acid (CA) as a green complexing agent. The porous CDP matrix effectively mitigates nanoparticle agglomeration and provides abundant active sites, while the Fe-Cu bimetallic coupling accelerates electron transfer and iron corrosion. Critically, CA acts as a biocompatible ligand that sustains Fe(II)/Fe(III) redox cycling, expands the effective pH range, and enhances hydroxyl radical ($\cdot\text{OH}$) generation. The system achieves 92.13% degradation of 4-CP within 80 min at pH 9.0 and nearly complete removal at pH values between 3.0 and 7.0. Mechanistic studies, including electron paramagnetic resonance (EPR) spectroscopy and radical quenching tests, confirm the dominance of $\cdot\text{OH}$ radicals (82.67% inhibition by TBA) and the essential role of surface Fe(II)/Fe(III) cycling. The catalyst exhibits excellent reusability, broad-spectrum activity toward multiple pollutants, and sustained performance in real water matrices and long-term column tests with minimal metal leaching. This work demonstrates a chemically robust strategy for chlorophenol remediation using green citric acid and biodegradable CDP without exogenous oxidant addition, showing promise for further development toward practical applications.

Keywords: 4-chlorophenol; iron; citric acid; degradation; cyclodextrin polymer



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1. Introduction

4-Chlorophenol (4-CP), extensively used as an industrial raw material and synthetic intermediate, poses severe threats to human health due to its acute toxicity and environmental recalcitrance [1]. Recognized as a priority pollutant by the World Health Organization and the International Agency for Research on Cancer, chlorophenols exhibit high solubility and thermal stability, facilitating their migration into soil and groundwater systems, where they pose long-term ecological risks [2,3].

Zero-valent iron (ZVI) has demonstrated efficacy in reductive dechlorination of halogenated organics via electron transfer mechanisms [4]. However, its application for chlorophenol remediation remains constrained by slow kinetics and incomplete degradation [5,6]. To address this, bimetallic materials prepared by deposition of secondary metals on ZVI surfaces can significantly enhance dechlorination. Metals such as Pd, Ag, Ni, Al, or Cu possess high standard redox potentials that promote chemical reactions via hydrogenation and accelerated corrosion [4,7,8]. While Fe-Pd exhibits superior properties due to palladium's excellent hydrogenation activity, its high cost greatly restricts widespread application [9]. In contrast, the cheap and readily available Fe/Cu system offers greater potential for industrial waste treatment [8].

Although bimetallic systems can improve the reductive dechlorination ability of ZVI, they remain constrained by challenges such as rapid particle agglomeration and susceptibility to passivation. To overcome these limitations, porous materials including bentonite, montmorillonite, and activated carbon have been used as supporting matrices to improve nanoparticle dispersion and facilitate electron transfer [10–12]. In addition to traditional supports, water-soluble supramolecular receptors such as cyclodextrins have garnered increasing attention due to their exceptional molecular recognition properties. Cyclodextrin polymers are naturally occurring, nontoxic, inexpensive cyclic oligosaccharides derived from starch [13]. Recent studies have used β -cyclodextrin (β -CD) to synthesize porous carbon adsorbents with high specific surface areas [14–16]. Furthermore, water-insoluble β -CD-based polymers can serve as suitable carbon sources and maintain long-term catalyst efficiency in groundwater and soil [15]. The unique cavity structure of CDP not only disperses and stabilizes metal nanoparticles but also selectively concentrates organic pollutants through inclusion complexation, potentially enhancing degradation efficiency.

To further improve the utilization efficiency of nanoscale ZVI (nZVI), researchers have conducted numerous experimental studies. Acidic conditions have been found beneficial for 4-CP degradation, as Fe(III) precipitation and H_2O_2 decomposition at higher pH reduce treatment efficiency [17]. Consequently, the introduction of ligands into nZVI reaction systems has been widely explored as a strategy to optimize performance. Ethylenediaminetetraacetic acid and nitrilotriacetic acid have been widely reported. However, these synthetic chelating agents pose potential environmental risks due to their persistence and toxicity [18]. In response, recent studies have shifted focus toward environmentally benign, naturally occurring reagents [19]. Among various organic acids including tartaric acid, formic acid, and oxalic acid, systematic studies have demonstrated that citric acid and oxalic acid are most effective in accelerating the iron redox cycle and $\cdot OH$ generation in Fenton-based systems [20]. Citric acid (CA) is a common chelating agent found in citrus fruits and possesses multiple reaction sites and a wide pH range [21]. Compared with oxalic acid, which exhibits stronger corrosivity and higher toxicity, CA offers superior biocompatibility and environmental safety, making it a more sustainable choice for remediation applications. Previous research has demonstrated that introducing CA into nZVI systems can greatly increase the degradation rate of 4-CP by accelerating ferrous iron oxidation, thereby increasing reactive oxygen species (ROS) generation [22]. However, the influence of CA on promoting the Cu-Fe-CDP systems remains unexplored.

In this study, we present a chemically integrated strategy to address the persistent challenges in 4-CP remediation through three synergistic design elements. First, the cyclodextrin polymer is employed as a green support matrix that not only disperses and stabilizes Cu-Fe nanoparticles to prevent agglomeration but also pre-concentrates 4-CP through host–guest inclusion, enhancing local pollutant availability. Second, the bimetallic Fe-Cu coupling accelerates electron transfer and iron corrosion, overcoming the kinetic limitations of monometallic ZVI systems. Third, citric acid is introduced as a natural com-

plexing agent that sustains Fe(II)/Fe(III) redox cycling, expands the effective pH range, and enhances hydroxyl radical generation while avoiding the environmental risks associated with synthetic chelators. The composite of cyclodextrin polymer-supported Fe/Cu bimetallic nanoparticles (Cu-Fe-CDP) was synthesized for the removal of 4-CP. The structural and physicochemical properties of the composite were characterized through multiple techniques. To evaluate the enhancing role of citric acid, the 4-CP removal efficiency of the Cu-Fe-CDP system was compared with that of the CA-modified system. Key operational parameters were comprehensively optimized to assess their impacts on degradation kinetics. ROS were identified using radical scavengers. Based on ROS detection and intermediate analysis, two plausible degradation pathways for 4-CP were proposed. In conclusion, the developed CA/Cu-Fe-CDP system demonstrates notable environmental compatibility and sustainability, offering a promising strategy for advancing remediation technologies in contaminated soil and groundwater systems.

2. Materials and Methods

2.1. Chemical Reagents

Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), copper sulfate (CuSO_4), citric acid, phenol ($\text{C}_6\text{H}_6\text{O}$) and cyclodextrin polymer were all purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 4-Chlorophenol ($\text{C}_6\text{H}_5\text{ClO}$, 4-CP), sodium borohydride (NaBH_4), nitric acid (HNO_3), sodium hydroxide (NaOH), potassium dihydrogen phosphate (KH_2PO_4), Rhodamine B (RhB, $\geq 95\%$), tetracycline (TC, $\geq 98\%$), sulfamethoxazole (SMX, $\geq 98\%$), 2,2'-bipyridine (BPY), tert-Butyl alcohol (TBA), p-benzoquinone (p-BQ), 5,5-dimethyl-1-pyrroline N-oxide (DMPO), and methanol (HPLC grade) were purchased from Shanghai Maclean Biochemical Technology Co., Ltd. (Shanghai, China). Other biomacromolecular polymers, such as guar gum (viscosity: 5000–5500 mPa·s, 200 mesh), sodium carboxymethyl cellulose (USP grade) and carboxymethyl chitosan (substitution degree $\geq 80\%$), were also purchased from Shanghai Maclean Biochemical Technology Co. Ltd. All chemicals were of analytical grade.

2.2. Preparation of Materials

2.2.1. Preparation of CDP

As shown in Figure 1a, initially, 12.00 g of β -cyclodextrin (β -CD), 6.09 g of citric acid (CA), 3.00 g of KH_2PO_4 and 40 mL of deionized water were mixed in a beaker. The mixture was homogenized using a magnetic stirrer and ultrasonication. Subsequently, it was heated at 100 °C under continuous stirring for approximately 1 h. The resulting solution was then transferred to a Petri dish and subjected to thermal cross-linking in a vacuum drying oven at 150 °C for 2 h. After complete cross-linking, the composite material was thoroughly rinsed with deionized water to remove the unreacted reagents. The CDP solution was completely dried in an oven at 60 °C for several hours and subsequently ground into a powder to obtain the CDP polymer.

2.2.2. Preparation of Cu-Fe-CDP

The Cu-Fe-CDP composite was synthesized using a liquid phase reduction method, in which ferrous ions (Fe^{2+}) were reduced by borohydride (BH_4^-) to generate nanoscale zero-valent iron (nZVI). First, 0.9928 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.0057 g of CuSO_4 (nFe: nCu = 50:1), 0.2000 g of CDP and 30 mL of water were added sequentially to a 250 mL three-necked flask. The mixture was homogenized using a mechanical stirrer at 500 rpm. Separately, 0.4100 g of sodium borohydride (NaBH_4) was dissolved in 10 mL of deionized water and introduced into the flask via a constant-pressure funnel at a controlled rate of 3 mL/min. Following the addition of the NaBH_4 solution, the resulting suspension was transferred to

a 50 mL anaerobic headspace bottle, aerated with nitrogen gas for 5 min to remove residual hydrogen (H_2), and then sealed under anaerobic conditions.

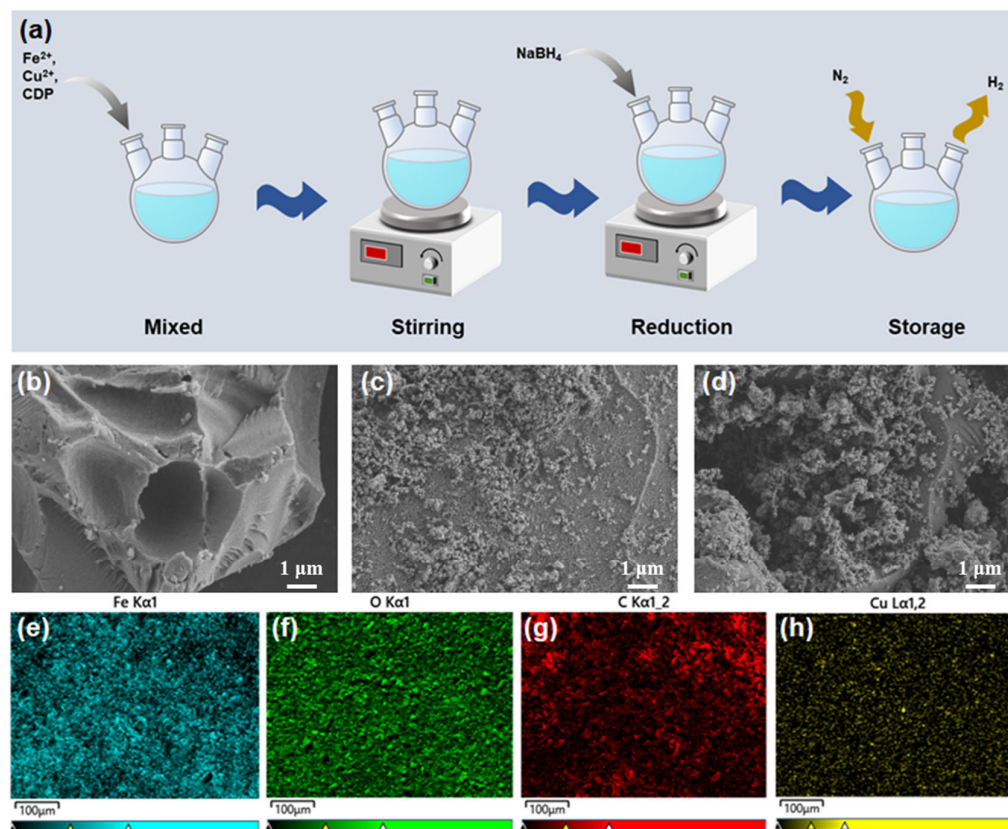
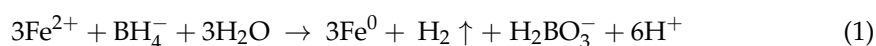


Figure 1. (a) Schematic illustrating the preparation process of CA/Cu-Fe-CDP; SEM images of (b) CDP, (c) original Cu-Fe NPs, (d) Cu-Fe-CDP at a magnification of 10,000 $\times$ and (e–h) EDS mapping images of the Cu-Fe-CDP surface.

2.3. Characterization

The morphological features and elemental distribution of the samples were analyzed using a scanning electron microscope (SEM, ZEISS Gemini 300, ZEISS, Oberkochen, Germany) equipped with an SE2 secondary electron detector, operated at an acceleration voltage of 3 kV. Energy-dispersive spectroscopy (EDS) mapping was concurrently performed to assess spatial elemental composition. The specific surface area (SSA) was quantified via the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption–desorption isotherms (Micromeritics ASAP 2460, Norcross, GA, USA). The surface functional groups on the materials were identified by Fourier-transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet iS5, Waltham, MA, USA) across a wavenumber range of 4000–400 cm^{-1} , the scan number was 32, and the resolution was 4 cm^{-1} . Crystallographic phases were determined by X-ray diffraction (XRD, Rigaku SmartLab SE, Tokyo, Japan) using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) over a 2θ range of 10–90°. Chemical states and surface elemental composition were further characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Waltham, MA, USA). All XPS spectra were charge-corrected using the adventitious carbon (C 1s) peak at a binding energy of 284.80 eV.

2.4. Degradation Experiments of 4-CP

In this study, four macromolecular polymers were selected to support the Cu-Fe nanoparticles: Cu-Fe-GG (0.20 g guar gum), Cu-Fe-CC (0.1 g carboxymethyl chitosan), Cu-Fe-SCC (0.1 g sodium carboxymethyl cellulose), and Cu-Fe-CDP (0.2 g cyclodextrin polymer). Five milliliters of each of the above materials was added to 50 mL 20 mg/L 4-CP solution, and the changes in the 4-CP concentration were analyzed. The degradation kinetics of 4-CP were fitted using a pseudo-first-order model [23]:

$$\ln(C/C_0) = k_{\text{obs}} \cdot t$$

where C_0 and C_t are the 4-CP concentrations at time 0 min and t (min), respectively, and k_{obs} is the apparent rate constant (min^{-1}). The k_{obs} values were obtained from the slope of linear regression of $\ln(C_0/C_t)$ versus reaction time.

To optimize the Fe/CA molar ratio for 4-CP degradation, five ratios were investigated [24]: 1:1, 1:1.2, 1:1.5, 1:1.7, and 1:2.0.

The specific experimental steps were as follows: 0.6860 g CA, 0.2 g CDP and 30 mL water were added to a 250 mL three-necked flask successively, and then, precise quantities of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and CuSO_4 were added to adjust the Fe/CA ratios. The mixture was homogenized using a mechanical stirrer at 500 rpm. NaBH_4 was dissolved in 10 mL of water and then added dropwise (3 mL/min) through a constant pressure funnel to the three-neck flask. After the addition of the NaBH_4 solution, the suspension was transferred to a 50 mL anaerobic headspace bottle, aerated with nitrogen for 10 min to remove residual H_2 , and anaerobically sealed. The synthetic material was a black suspension, in which CA/Cu-Fe-CDP and Fe^0 slowly dissolved and H_2 bubbles were generated, which was unstable during storage and needed to be used within 6 h. Then, 5 mL of each suspension was added to 50 mL of 10 mg/L 4-CP solution at initial pH 6.0, and the residual 4-CP concentration was measured at 1, 3, 5, 10, 20, 30, 50 and 80 min.

In the investigation of initial pH effect on the degradation of 4-CP, 1 M NaOH and HNO_3 solutions were used to adjust the pH of the reaction system ($[4\text{-CP}] = 10 \text{ mg/L}$, $V_0 = 50 \text{ mL}$, $[\text{Cu-Fe-CDP}] = 2 \text{ g/L}$, $n_{\text{Fe}}:n_{\text{CA}} = 1:1$) to 3, 5, 7 and 9. The 4-CP concentration and solution pH were measured during 80 min.

In the investigation of optimal CA/Cu-Fe-CDP dosage, different dose (0.5, 1, 2, 4, 5 g/L) of CA/Cu-Fe-CDP was added in 4-CP solution under certain conditions ($[4\text{-CP}] = 5 \text{ mg/L}$, $V_0 = 50 \text{ mL}$, $n_{\text{Fe}}:n_{\text{CA}} = 1:1.7$, initial pH = 5.2), and the residual 4-CP concentration was measured at 1, 3, 5, 10, 20, 30, 50 and 80 min.

2.5. Analysis of Contaminant Concentrations

4-CP, TC and SMX were detected by Agilent 1260 high-performance liquid chromatography (HPLC) on a $4.6 \times 150 \text{ mm}$ Eclipse XDB- C_{18} column. An ultraviolet detector with a wavelength of 270 nm for 4-CP, 355 nm for TC 270 nm for SMX, and a volume ratio of 70:30 methanol to pure water as the mobile phase was used to detect 4-CP. At a flow rate of 0.6 mL min^{-1} , the injection volume was 40 μL , the column temperature was 25°C , and the retention time was 4.7 min. The concentrations of RhB were determined by UV-vis spectrophotometry (RhB, $\lambda = 554 \text{ nm}$).

2.6. p-HBA Analysis

To investigate the mechanism of 4-CP degradation by the Cu-Fe-CDP catalytic oxidation system, sodium benzoate was used as a trapping agent to study the reaction product of p-hydroxybenzoic acid (p-HBA) with a hydroxyl radical ($\cdot\text{OH}$) [25]. An Agilent 1260 high-performance liquid chromatograph was used to detect p-HBA in the product. The detection conditions were as follows: determination was performed on a $4.6 \times 150 \text{ mm}$

Eclipse XDB-C18 column with an ultraviolet detector. The detection wavelength was 255 nm, and the volume ratio of the methanol and water phases (including 1% acetic acid) was 30:70 as the mobile phase. The flow rate was 0.8 mL min^{-1} , the sample size was $20 \text{ }\mu\text{L}$, the column temperature was $30 \text{ }^{\circ}\text{C}$, and the retention time was 3.5 min.

2.7. Radical Identification Experiments

Radical quenching experiments were performed using tert-butyl alcohol (TBA) for $\cdot\text{OH}$ and p-benzoquinone (p-BQ) for $\text{O}_2^{\cdot-}$ scavenging. In each test, 2 g/L of CA/Cu-Fe-CDP suspension was added to 50 mL of 10 mg/L 4-CP solution ($\text{pH } 7.0$) containing 50 mM TBA or 50 mM p-BQ. Degradation efficiency was monitored over 80 min , and the inhibition rate was calculated relative to scavenger-free controls. Hydrogen peroxide (H_2O_2) concentrations were determined using the titanium oxalate spectrophotometric method at 400 nm [26]. To verify radical generation, electron paramagnetic resonance (EPR) spectroscopy was conducted using DMPO as a spin-trapping agent. Briefly, $100 \text{ }\mu\text{L}$ of the reaction suspension was mixed with $10 \text{ }\mu\text{L}$ of 100 mM DMPO, and spectra were recorded on a Bruker EMXplus spectrometer (X-band, 9.8 GHz , 20 mW). The characteristic 1:2:2:1 quartet signal was monitored to confirm DMPO- $\cdot\text{OH}$ adduct formation.

2.8. Statistical Analysis

All experiments were performed in triplicate ($n = 3$), and data are expressed as mean $\pm$ standard deviation (SD). Statistical significance between groups was evaluated using a two-tailed Student's *t*-test ($p < 0.05$) for two-group comparisons and one-way ANOVA with Tukey's post hoc test for multiple-group comparisons.

3. Results and Discussion

3.1. Characterization of Cu-Fe-CDP

The synthesized CDP, pristine Cu-Fe NPs and CA/Cu-Fe-CDP were characterized by scanning electron microscopy (SEM). As shown in Figure 1b, CDP exhibited a porous morphology with prominent surface grooves, providing abundant anchoring sites for Cu-Fe NPs. The pristine Cu-Fe NPs appeared as uniformly spherical particles ($20\text{--}100 \text{ nm}$ diameter) but displayed significant agglomeration (Figure 1c). Upon CDP support, the particle size and morphology remained largely unchanged, while interparticle dispersion markedly improved (Figure 1d). In addition, the distribution of elements on the surface of the Cu-Fe-CDP nanoparticles was further confirmed that the surface of the Cu-Fe-CDP nanoparticles was evenly distributed (Table S1 and Figure 1d). Notably, the oxygen content (14.39% higher than iron), which was due to the oxidation of Fe^0 on the surface of the Cu-Fe-CDP composite [27].

The XRD patterns in Figure 2a reveal distinct crystallographic differences among the samples. Pristine Cu-Fe nanoparticles exhibit sharper diffraction peaks compared to CDP and Cu-Fe-CDP, predominantly corresponding to metallic Fe^0 (PDF#99-0064) and Fe_3O_4 phases. The characteristic peaks of Fe^0 all appeared at $2\theta = 44.5^{\circ}$. After CDP loading, the Fe^0 intensity of the Cu-Fe surface decreased, suggesting effective encapsulation of Cu-Fe nanoparticles within CDP's amorphous matrix [28]. Critically, the stronger iron oxide signatures in pristine Cu-Fe compared to Cu-Fe-CDP indicate that CDP plays a protective role in mitigating surface oxidation, thereby enhancing material stability for prolonged environmental application [29]. The FTIR spectra of CDP, pristine Cu-Fe NPs, and Cu-Fe-CDP are presented in Figure 2b. The characteristic C-O stretching vibration at 1035 cm^{-1} in both Cu-Fe-CDP and CDP confirms the presence of CDP immobilization on the nanoparticle surface [30], which was consistent with previous EDX analyses. The broad absorption band at 3390 cm^{-1} could be attributed to the stretching vibration of $\cdot\text{OH}$, and

the peak strength of Cu-Fe increased after the CDP loading [31]. Notably, the presence of a distinct peak at 2936 cm^{-1} corresponded to $-\text{CH}_2$ symmetric stretching, which was absent from the pristine Cu-Fe nanoparticles. In addition, the characteristic absorption bands at 1693 cm^{-1} (attributed to $\text{C}=\text{O}$ and $\text{C}=\text{C}$ stretching), the increased intensity increased, and the shifting position in the Cu-Fe-CDP demonstrate altered electronic environments in Cu-Fe-CDP [32]. Collectively, these spectral features verify effective immobilization of Cu-Fe nanoparticles onto the CDP matrix. The surface chemical states of Fe, C and Cu on the Cu-Fe NPs and Cu-Fe-CDP were analyzed by X-ray photoelectron spectroscopy (XPS) (Figure 2c–h). Deconvolution of the Fe 2p spectra revealed peaks at 713.4, 712.5, and 710.5 eV assigned to Fe(II) species, while the characteristic Fe^0 peak appeared at 706.5 eV [33]. Notably, Cu-Fe-CDP exhibited higher Fe^0 content than pristine Cu-Fe NPs, indicating suppressed surface oxidation (Tables S2 and S3). This likely stems from CDP's spatial confinement effect: its porous structure reduces nanoparticle exposure by providing abundant adsorption sites, thereby minimizing oxidative degradation [34,35].

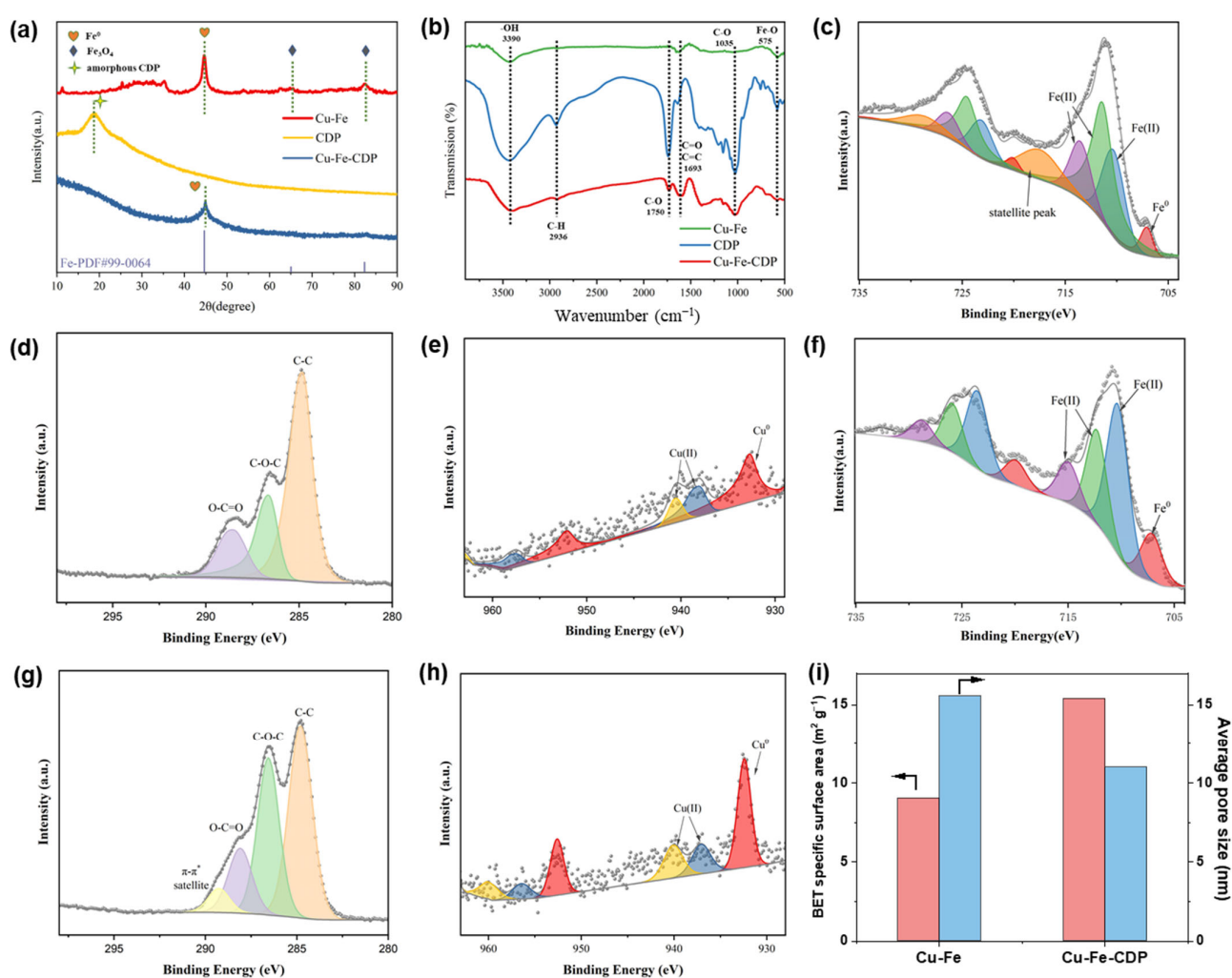


Figure 2. (a) XRD patterns; (b) FTIR patterns; XPS data for the original Cu-Fe NPs (c–e) and Cu-Fe-CDP (f–h) at Fe 2p (a,d), C 1s (b,e) and Cu 2p (e,f); (i) BET specific surface area and average pore diameter of Cu-Fe and Cu-Fe-CDP.

The C 1s spectra were fitted into three components: $\text{O}=\text{C}-\text{O}$ (288.8 eV), $\text{C}-\text{O}-\text{C}$ (286.2 eV), and $\text{C}-\text{C}$ (284.8 eV). Compared to Cu-Fe NPs, Cu-Fe-CDP showed intensified $\text{C}-\text{O}-\text{C}$ signals (287 eV) and diminished $\text{O}=\text{C}=\text{O}$ contributions, consistent with CDP's hydroxyl/carboxyl groups ($-\text{OH}/-\text{COOH}$) participating in nanoparticle immobilization [36].

The most prominent peaks in the Cu 2p spectra of the Cu-Fe NPs were observed at 933.56 eV for Cu⁰ and 938–941 eV for Cu²⁺. The signal strength of Cu⁰ in Cu-Fe-CDP was greater than that of the original Cu-Fe NPs, which might promote the reduction effect on pollutants [37]. The Brunauer–Emmett–Teller (BET) specific surface area and pore size of Cu-Fe and Cu-Fe-CDP were characterized, with results summarized in Figure 2i. Significant alterations in physicochemical properties were observed upon CDP support: the specific surface area increased from 8.03 m²/g to 15.41 m²/g, while the average pore size decreased from 15.56 nm to 10.97 nm. These structural changes—indicative of a hierarchical porous architecture—align with SEM observations. Notably, although the BET increase is modest, the primary structural benefit of CDP support lies in its three-dimensional porous network, which provides abundant anchoring sites, prevents nanoparticle agglomeration, and ensures better accessibility of active sites. This might be due to the dispersion effect of CDP on the Cu-Fe nanoparticles, which inhibited the agglomeration behavior among the particles [38].

3.2. Performance of CA/Cu-Fe-CDP in the Degradation of 4-CP

Figure 3a compares the degradation efficiencies of 4-CP by Cu-Fe nanomaterials supported by four distinct macromolecular polymers: Cu-Fe-GG (0.20 g guar gum), Cu-Fe-CC (0.1 g carboxymethyl chitosan), Cu-Fe-SCC (0.1 g sodium carboxymethyl cellulose), and Cu-Fe-CDP (0.2 g cyclodextrin polymer). Among them, the Cu-Fe-CDP composite had the best degradation effect on 4-CP, and the degradation efficiency reached 58.32% after 120 min, which was 44.32% greater than that of the unmodified Cu-Fe particles. Kinetic analysis revealed that Cu-Fe-CDP achieved the optimal balance between degradation rate and removal efficiency among the four polymer-supported Cu-Fe materials, exhibiting the highest apparent rate constant (k_{obs}) and the greatest 4-CP removal efficiency (Figure S1, Table S4). Previous studies have shown that nZVI coated with CDP retains the network structure of CDP, primarily trapping nZVI particles 40–80 nm in size internally and coating with iron particles 300 nm in size, resulting in high adsorption selectivity for organic pollutants in groundwater [13]. The composite material shows high stability, possibly because CDP entraps nZVI through molecular recognition and size matching, and the internal porous network structure selectively adsorbs 4-CP [39].

To elucidate the origin of the superior degradation performance of Cu-Fe-CDP over other polymer-supported materials, chronoamperometry was employed to evaluate the electron transfer capability of each composite. As shown in Figure S2, the maximum current response of the four Cu-Fe-polymer electrodes followed the order: Cu-Fe-CDP (31.7 μ A) > Cu-Fe-GG (17.9 μ A) > Cu-Fe-CC (14.8 μ A) > Cu-Fe-SCC (9.9 μ A). The highest current response of Cu-Fe-CDP indicates its superior electron transfer capability, which can be attributed to the porous structure of CDP that facilitates electrolyte penetration and provides abundant accessible active sites for electron exchange. Although the instantaneous current values exhibited minor fluctuations during the measurement, this relative ranking remained consistent throughout the entire testing period, confirming the intrinsically superior electron transfer capability of the CDP-supported composite. The superior electron transfer capability of the CDP support can be attributed to three key factors. First, the porous three-dimensional network of CDP facilitates electrolyte penetration and provides abundant accessible active sites for interfacial electron exchange [40], whereas the dense or film-forming structures of guar gum, carboxymethyl chitosan, and sodium carboxymethyl cellulose tend to impede ion diffusion and increase charge-transfer resistance. Second, the hydrophilic hydroxyl-rich surface of CDP promotes better dispersion of Cu-Fe nanoparticles, minimizing agglomeration and preserving a larger electrochemically active surface area [41]. Third, the hydrophobic cavity of CDP enables molecular recognition and pre-concentration of 4-CP through host–guest inclusion

complexation, which shortens the diffusion path for electron transfer and enhances the local pollutant concentration available for radical attack [42]. This synergistic effect, involving superior electron transfer, effective nanoparticle stabilization, and pollutant pre-concentration, collectively accounts for the highest degradation performance of Cu-Fe-CDP among the four polymer-supported systems.

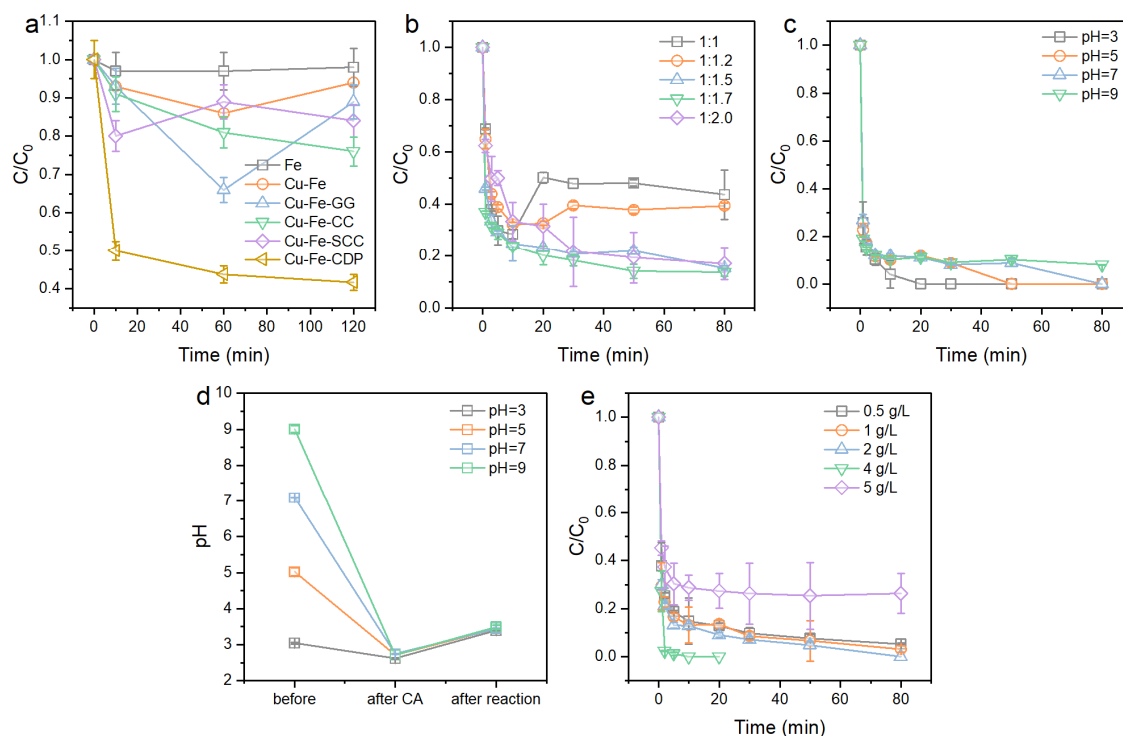


Figure 3. (a) Comparison of 4-CP degradation efficiency using different Cu-Fe materials stabilized by four macromolecular polymers; (b) effects of different Fe/CA ratios (1:1, 1:1.2, 1:1.5, 1:1.7 and 1:2.0) on the degradation of 4-CP (4-CP = 10 mg/L, V_{4-CP} = 50 mL, [Cu-Fe-CDP] = 2 g/L, pH = 6); (c) degradation effects of Cu-Fe-CDP on 4-CP at different pH values; (d) changes in pH during the reaction; (e) degradation efficiencies of CA/Cu-Fe-CDP to 4-CP at different dosages (0.5, 1, 2, 4, and 5 g/L). Error bars represent standard deviation ($n = 3$).

In addition, the degradation of 4-CP by the original Fe particles did not change significantly from 0 to 120 min. Control experiments showed that CA alone, CDP alone, Cu-CDP, and Fe-CDP achieved only 6.00%, 4.83%, 15.41%, and 47.13% removal (Figure S3), respectively, confirming the essential synergy among all components. Consequently, Cu-Fe-CDP was selected for the subsequent experiments, and the degradation effects of the ZVI suspension and the Cu-Fe-CDP solid on 4-CP were similar (Figure S4). Preliminary studies (Figures S5 and S6) confirmed that citric acid (CA) significantly enhances 4-CP degradation by solid-phase Cu-Fe-CDP. To systematically evaluate CA's role, our study used four Fe/CA molar ratios (1:1, 1:1.2, 1:1.5, 1:1.7, and 1:2.0). As shown in Figure 3b, the degradation efficiency of 4-CP also significantly depended on the concentration of CA and increased with the Fe/CA ratio (from 1:1 to 1:2.0). It can be attributed to CA-mediated acidic condition, which promotes the generation of Fe(II)/Fe(III) cycling, and accelerated the Fenton reaction [6]. Notably, when the ratio was 1:2.0, the degradation efficiency tended to decline, indicating an optimal threshold. When the reaction was carried out for 80 min, the degradation efficiency of 4-CP by CA/Cu-Fe-CDP (Fe/CA = 1:1.7) was improved from 56% to 87% by CA/Cu-Fe-CDP (Fe/CA = 1:1). A previous study has reported that citrate ions coordinate with Fe(III) to form stable Fe(III)-organic ligand complexes, thus promoting

the Fenton reaction to produce oxidizing free radicals (ROS) and increasing the transfer efficiency to target contaminants [43,44].

The influence of pH on degradation mechanisms was investigated (Figure 3c). The CA/Cu-Fe-CDP exhibited effective pH tolerance (100% 4-CP removal at pH 3.0–7.0), achieving a 4-CP removal efficiency of 92.13% even in the treatment group at pH 9. This reduced efficiency under alkaline conditions likely stems from 4-CP deprotonation: elevated pH converts phenolic groups to anions, inducing electrostatic repulsion with negatively charged Cu-Fe-CDP surfaces and weakening adsorption. Alternatively, the original CDP removes organic compounds (including aromatic compounds) from water by adsorption, which is more favorable at lower pH values. To further confirm the role of CA or low pH, CA was introduced to 4-CP solutions at varying initial pH values. Figure 3d reveals that the pH values of all the treatment groups were at the same level after the reaction and increased CA-amended systems. This pH increase originates from iron oxidation precipitating iron (oxy)hydroxides, confirming CA's role in sustaining optimal acidic conditions for Fenton activity. The CA/Cu-Fe-CDP dosage critically modulates solution pH during dichlorination, resulting in the different degradation efficiency [21]. As shown in Figure 3e, the degradation efficiency of 4-CP exhibited pronounced time- and dose-dependence. Notably, dose-dependent desorption occurred after 10 min in the 1, 2, and 4 g/L systems. When the reaction time reached 80 min, the degradation efficiencies of the 0.5 and 5 g/L treatment groups were 94.7% and 73.7%, respectively. Despite similar endpoint efficiencies, the reaction rate of 0.5 g/L was faster than that of 5 g/L, and equilibrium was reached at 15 min, possibly due to the agglomeration of excess CA/Cu-Fe-CDP in aqueous solution, which reduces the number of adsorption sites and decreases its degradability [44].

Compared with previously reported catalytic systems for 4-CP degradation (Table S5), the CA/Cu-Fe-CDP system achieves complete (100%) removal at near-neutral pH (3.0–7.0) and near-complete removal (92.13%) even under alkaline conditions (pH 9.0), without the addition of any exogenous oxidant such as H₂O₂ or peroxymonosulfate (PMS) [45–49]. This peroxide-free, broad-pH operation, distinguishes our system from most literature reports, which typically require acidic conditions, external oxidants, or noble metal catalysts.

Through concentrated hydrochloric acid digestion and desorption of solid materials in the sample, adsorption data for 0.5 mL, 1 mL and 2 mL suspensions were obtained (Figure 4). The quasi-first-order adsorption kinetics fitting results of the three groups of data are shown in Figure 4b–d, which revealed that the fitting effect was better when the addition amounts were 0.5 and 1 g/L, and the maximum adsorption amounts for 4-CP were 28.55 and 24.61 mg/g CDP, respectively. The fitting results revealed that adsorption was mainly a physical process [50]. When the addition amount was 2 mL, the deviation was too large to fit, and the maximum adsorption amount reached 24.56 mg/g CDP at 10 min, followed by desorption rebound. It was speculated that the passivation of excess zero-valent iron may lead to blockage of the adsorption site [51].

The contributions of adsorption and oxidative degradation to the overall removal of 4-CP were distinguished by investigating the distribution of 4-CP on the catalyst surface and in solution under both air and N₂ atmospheres (Figure S7a,b). Under air atmosphere, CA/Cu-Fe-CDP effectively promoted simultaneous removal of 4-CP from both the solution phase and the catalyst surface, indicating that oxidative degradation actively consumed the adsorbed pollutant. In contrast, under N₂ atmosphere, the concentration of 4-CP in solution reaching a maximum surface loading at 10 min. TOC analysis (Figure S7c) revealed a gradual decline in organic carbon under air conditions, whereas under N₂ atmosphere, the TOC profile closely paralleled the change in solution-phase 4-CP concentration, indicating that adsorption was the dominant interfacial process when O₂ was absent. This interpretation

was further corroborated by the Cl^- release profiles (Figure S7d), which showed substantial dechlorination only under air atmosphere, while no Cl^- was detected under N_2 conditions.

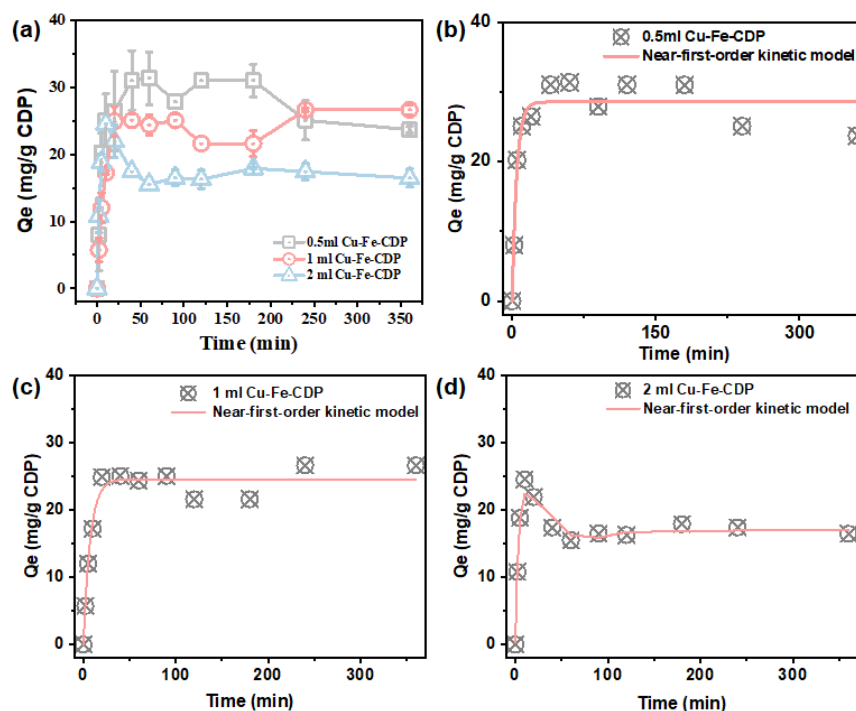


Figure 4. (a) Adsorption capacities of 4-CP ($n = 3$). The quasi-first-order adsorption kinetics of 4-CP were fitted by (b) 0.5, (c) 1 and (d) 2 g/L of CA/Cu-Fe-CDP.

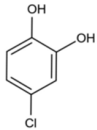
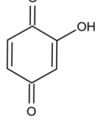
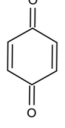
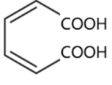
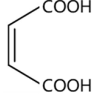
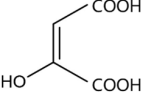
Based on these results, the core mechanism can be summarized as follows: the catalyst exhibits strong adsorption affinity for 4-CP, enabling rapid capture of the pollutant onto the catalyst surface. Once captured, the adsorbed 4-CP is subject to oxidative degradation driven by reactive oxygen species generated from O_2 activation on the catalyst surface. Under aerobic conditions, the continuous consumption of adsorbed 4-CP by oxidative degradation maintains a concentration gradient that drives further adsorption, resulting in sustained removal. Under anaerobic conditions, however, the absence of oxidative degradation leads to surface saturation, after which no further removal occurs. This adsorption-degradation synergy, where CDP pre-concentrates the pollutant and O_2 -derived radicals provide the oxidative driving force, underlies the high efficiency of the CA/Cu-Fe-CDP system.

3.3. Possible Degradation Pathways of 4-CP by CA/Cu-Fe-CDP

Based on mass spectrometry analysis (Text S5), key intermediate products detected of 4-CP by CA/Cu-Fe-CDP were identified in Table 1, and a dual-pathway mechanism was proposed in Figure 5. It can be divided into two paths according to the different oxygenation positions of the benzene ring. Subsequent, active oxygen radicals attack cleave of the C-Cl bond, initiating dechlorination. The resulting intermediates undergo stepwise oxidation to quinones (e.g., p-benzoquinone, m/z 107.0260), followed by ring opening and chain shortening to aliphatic acids (e.g., maleic acid, m/z 114.9353), ultimately mineralizing to CO_2 and H_2O [52]. To evaluate the environmental safety of the degradation process, the toxicities of 4-CP and its identified intermediates were predicted using ECOSAR software (v1.11). The predicted LC_{50} and ChV values for all intermediates were substantially higher than those of pristine 4-CP, indicating a significant reduction in both acute and chronic toxicity after degradation (Figure S10a). This toxicity attenuation confirms that the

CA/Cu-Fe-CDP system not only transforms 4-CP structurally but also effectively reduces its environmental hazard, further supporting the practical applicability of the developed catalytic system. This prediction was further validated by a 7-day wheat seed germination test using 0.22 μm -filtered 4-CP solutions before and after treatment. As shown in Figure S10b, the after-treatment group exhibited significantly higher germination indices from Day 3 onward compared to the before-treatment group ($p < 0.01$ for Days 3–4; $p < 0.001$ for Days 5–7), confirming that the CA/Cu-Fe-CDP system effectively reduces the phytotoxicity of 4-CP and its degradation intermediates.

Table 1. Determination of 4-CP degradation intermediates in the CA/Cu-Fe-CDP system by liquid chromatography-mass spectrometry.

No.	Intermediate Product	Material Structure	Molecular Formula	Theoretical m/z	Measured m/z
P0	4-chloro-catechol		$\text{C}_6\text{H}_5\text{O}_2\text{Cl}$	142.99	142.9925
P1	2-hydroxyp-benzoquinone		$\text{C}_6\text{H}_4\text{O}_3$	123.01	123.0089
P2	p-benzoquinone		$\text{C}_6\text{H}_4\text{O}_2$	107.01	107.0260
P3	2,4-hexadienoic acid		$\text{C}_6\text{H}_6\text{O}_4$	141.02	140.9315
P4	Maleic acid		$\text{C}_4\text{H}_4\text{O}_4$	115.00	114.9353
P5	2-hydroxybutenedioic acid		$\text{C}_4\text{H}_4\text{O}_5$	131.00	130.9930

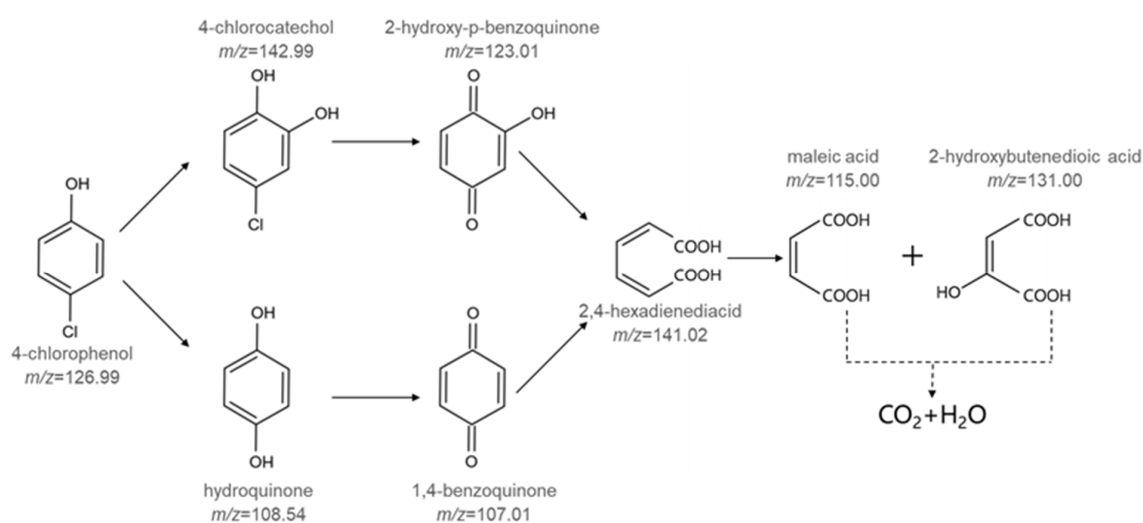
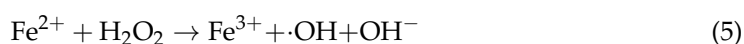
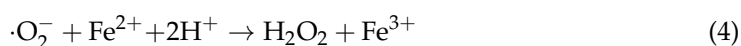
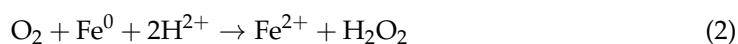


Figure 5. Possible pathways for CA/Cu-Fe-CDP degradation of 4-CP.

3.4. Reaction Mechanism of CA/Cu-Fe-CDP for 4-CP Degradation

Although zero-valent iron (Fe^0) exhibits strong reducing capacity for converting toxic pollutants to less harmful forms, its efficacy is typically limited to anaerobic conditions. Critically, under aerobic environments, Fe^0 facilitates reactive oxygen species (ROS) generation that oxidizes recalcitrant pollutants unreducible by Fe^0 alone [53]. As confirmed by XRD and XPS characterization results shown in Chapter 3.1, Fe^0 in Cu-Fe-CDP was oxidized by O_2 into Fe^{2+} and Fe^{3+} (Equations (2)–(4)), whereas the generated H_2O_2 oxidized Fe^{2+} to produce $\cdot\text{OH}$ (Equation (5)). XPS Fe 2p high-resolution analysis of the spent catalysts further revealed that the Fe(II) content increased from 50.5% in the CA-free system to 53.9% in the CA-amended system, confirming that CA effectively promotes Fe(II) regeneration (Figure S11, Table S3). From a coordination chemistry perspective, citric acid acts as a tridentate ligand that forms stable Fe(III)-citrate complexes ($\log \beta = 11.4$ for Fe(III)Cit and $\log \beta = 25.0$ for Fe(III)Cit_2^{5-}), which prevent Fe(III) precipitation and facilitate its reduction back to Fe(II) via electron transfer from Fe^0 or ligand-to-metal charge transfer pathways [54,55]. BPY selectively binds surface-exposed Fe(II) and prevents its participation in Fenton reactions, thereby interrupting the Fe(II)/Fe(III) redox cycle. Prior to degradation, the CA/Cu-Fe-CDP suspension was pre-incubated with BPY at concentrations of 20 mM and 100 mM for 30 min. As shown in Figure S12, 4-CP degradation was progressively suppressed with increasing BPY concentration. This BPY concentration-dependent inhibition confirms that surface Fe(II)/Fe(III) cycling is essential for sustaining $\cdot\text{OH}$ generation and subsequent 4-CP oxidation. To identify the contribution of Cu species, Cu^{2+} ions at 1.0 mM and 5.0 mM were introduced into the CA/Fe-CDP system (Figure S13). The degradation efficiency increased from 45.5% (without Cu^{2+}) to 65.5% and 82.9%, respectively, confirming that Cu species promote the Fe(II)/Fe(III) redox cycle by facilitating electron transfer and accelerating Fe^0 corrosion for sustained $\cdot\text{OH}$ generation. In this study, the concentration of $\cdot\text{OH}$ was obtained from the concentration of p-hydroxybenzoic acid (p-HBA) from benzoate trapping (from Cu-Fe-CDP) (Equation (6)) [53].



To identify the dominant reactive oxygen species (ROS) involved in the CA/Cu-Fe-CDP system, radical quenching experiments were conducted using tert-butyl alcohol (TBA) as a $\cdot\text{OH}$ scavenger and p-benzoquinone (p-BQ) as an $\text{O}_2\cdot^-$ scavenger. As shown in Figure S14a,b, the addition of TBA suppressed 4-CP degradation by 82.7%, while p-BQ inhibited degradation by 37.1%, indicating that $\cdot\text{OH}$ is the primary reactive species responsible for 4-CP oxidation, with $\text{O}_2\cdot^-$ playing a secondary role. To further verify radical generation, electron paramagnetic resonance (EPR) spectroscopy was performed using DMPO as a spin-trapping agent. As presented in Figure S14c,d, characteristic signals corresponding to DMPO- $\cdot\text{OH}$ adducts (1:2:2:1 quartet) and DMPO- $\text{O}_2\cdot^-$ adducts were clearly detected, confirming the generation of both $\cdot\text{OH}$ and $\text{O}_2\cdot^-$ radicals in the CA/Cu-Fe-CDP system. These results corroborate the proposed radical-mediated degradation pathways. Hydrogen peroxide (H_2O_2) concentration monitoring (Figure S15a) revealed that in the CA-assisted system, H_2O_2 peaked at approximately 650 μM at 20 min and then decreased to a stable level around 550–600 μM . In contrast, without CA addition,

H_2O_2 accumulated to only $32.5\ \mu\text{M}$ at the end of the reaction, approximately 1/20 of that in the CA-amended system. This substantial difference confirms that CA significantly promotes H_2O_2 generation by maintaining iron solubility, sustaining Fe(II)/Fe(III) cycling, and accelerating Fe^0 corrosion [22]. Gas atmosphere experiments confirmed that sufficient O_2 supply is critical for H_2O_2 generation. Under N_2 purging, H_2O_2 production was almost completely suppressed ($<25\ \mu\text{M}$), while under ambient air it reached $1702.8\ \mu\text{M}$ at 20 min (Figure S16). This confirms that H_2O_2 is generated via O_2 reduction (Equations (2)–(4)) driven by Fe–Cu galvanic coupling, rather than from other sources. Moreover, Figure S15b demonstrates the pivotal role of CA by showing the time-dependent changes in $\cdot\text{OH}$ and p-HBA concentrations in the presence and absence of CA. The oxidation efficiency of Cu–Fe–CDP was significantly improved by the presence of CA, and the concentration of $\cdot\text{OH}$ produced reached $335.3\ \mu\text{M}$ at 20 min, followed by a gradual decrease [56]. These results indicated that CA significantly improved the ability of Cu–Fe–CDP to produce $\cdot\text{OH}$ [57]. The relationship between the $\cdot\text{OH}$ and PHBA concentrations is shown in Equation (6).

The mechanism of CA/Cu–Fe–CDP degradation of 4-CP is shown in Figure 6. CDP not only disperses and stabilizes Cu–Fe nanoparticles but also pre-concentrates 4-CP near the reactive sites via host–guest inclusion complexation. Mechanistically, citric acid forms the $\text{Fe(II)}[\text{Cit}]^-$ complex on the iron surface, which serves as the key reactive species [22]. This complex adsorbs onto the Fe^0 surface and accelerates electron transfer from Fe^0 to dissolved O_2 , promoting H_2O_2 generation and subsequent $\cdot\text{OH}$ production. Unlike other organic acids such as formic acid or malonic acid, which exhibit negligible or even inhibitory effects on iron redox cycling [39], CA possesses three carboxyl groups that enable tridentate chelation with Fe ions, forming highly stable complexes that effectively prevent Fe(III) precipitation and sustain the Fe(II)/Fe(III) redox cycle even under alkaline conditions. Cu(0) promoted the electron transfer of Fe(0), accelerated the production of Fe^{2+} and Fe^{3+} , and enhanced the $\cdot\text{OH}$ yield, thereby achieving efficient degradation of 4-CP.

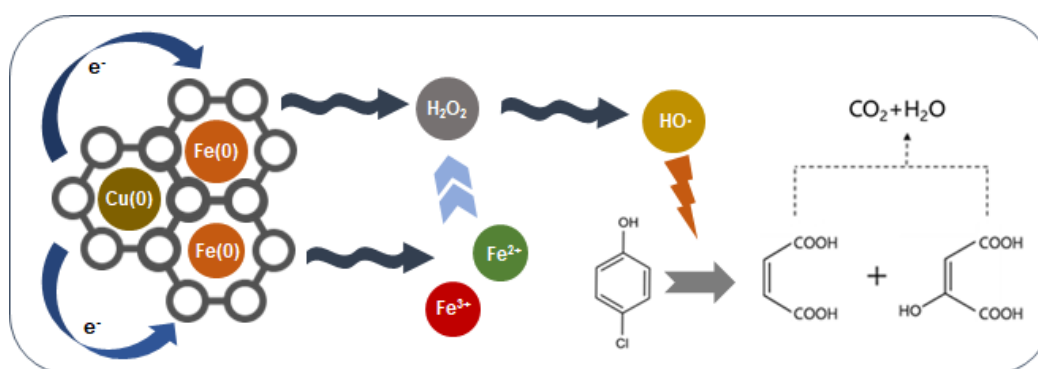


Figure 6. Mechanism for CA/Cu–Fe–CDP degradation of 4-CP.

3.5. Simulated Environmental Application

To evaluate the practical applicability and long-term stability of the CA/Cu–Fe–CDP system, a series of environmental simulation experiments was conducted.

At first, to evaluate the applicability of the CA/Cu–Fe–CDP system under environmentally relevant concentrations, degradation experiments were conducted at 4-CP concentrations of 20, 100, 200, and $1000\ \mu\text{g/L}$. As shown in Figure S17a, 4-CP was rapidly degraded at all tested concentrations, with removal efficiencies exceeding 99%. These results confirm that the system maintains excellent catalytic activity even at trace pollutant levels, demonstrating its practical applicability for in situ groundwater remediation where chlorophenol concentrations are typically in the $\mu\text{g/L}$ range. Furthermore, degradation experiments at higher 4-CP concentrations of 50, 80, and $120\ \text{mg/L}$ (representative of

industrial wastewater levels) achieved removal efficiencies exceeding 95% for all tested concentrations (Figure S17b), confirming the superior catalytic activity of the CA/Cu-Fe-CDP system across a wide concentration spectrum from $\mu\text{g/L}$ to mg/L levels. As shown in Figure 7a, the CA/Cu-Fe-CDP catalyst maintained excellent reusability over six consecutive cycles, with 4-CP removal efficiency remaining as high as 97.1% after the sixth cycle. This remarkable stability indicates that the catalyst retains its catalytic activity without significant deactivation, which can be attributed to the protective role of CDP in mitigating surface oxidation of Fe^0 and the sustained $\text{Fe(II)}/\text{Fe(III)}$ cycling facilitated by citric acid.

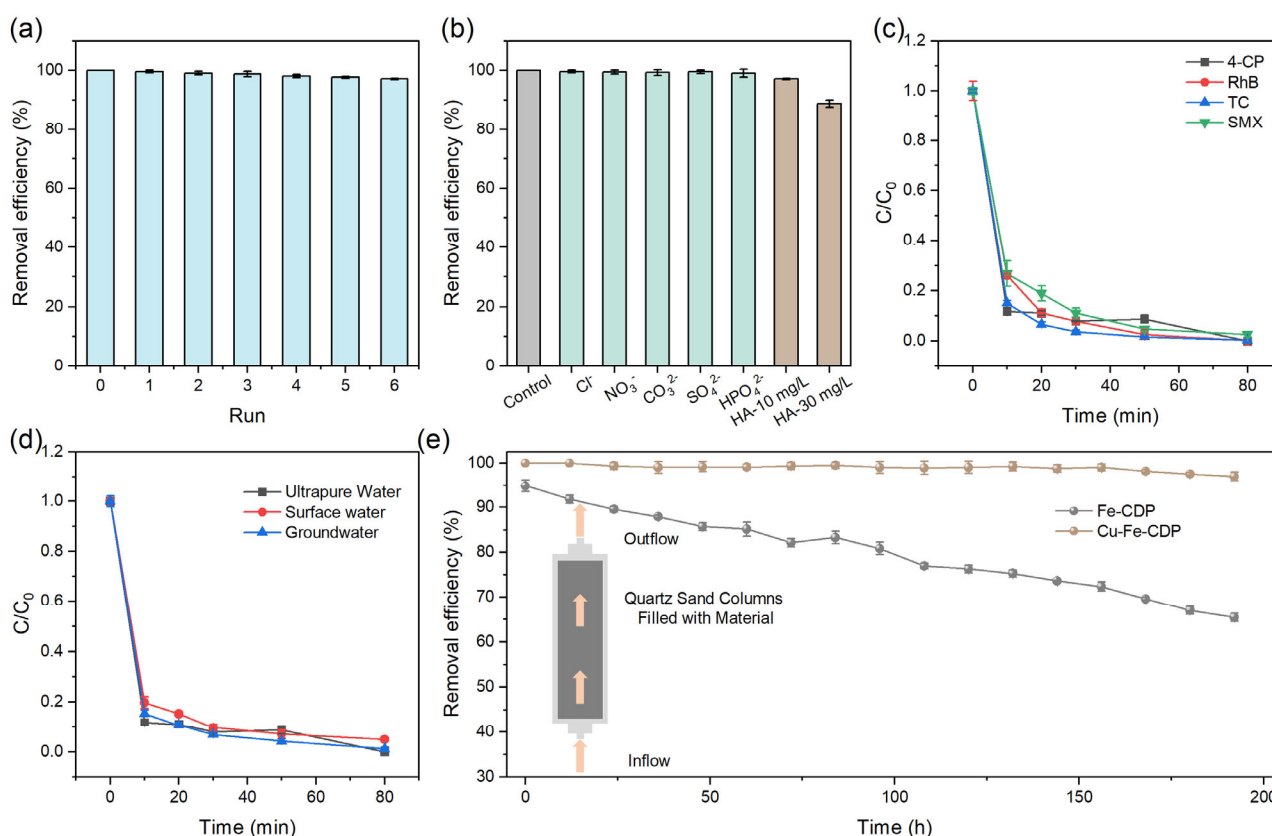


Figure 7. Environmental application performance of the CA/Cu-Fe-CDP system. (a) Reusability over six consecutive cycles; (b) effect of competing ions (10 mM Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , HPO_4^{2-}) and humic acid (HA, 10 and 20 mg/L) on 4-CP degradation; (c) degradation of multiple pollutants (RhB, TC, and SMX); (d) degradation efficiency in different water matrices (deionized water, tap water, surface water, and groundwater); (e) long-term column test (192 h) comparing CA/Cu-Fe-CDP and CA/Fe-CDP (without Cu).

The influence of common anions and humic acid (HA) on 4-CP degradation is presented in Figure 7b. The presence of 10 mM Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , and HPO_4^{2-} exhibited negligible inhibition on 4-CP removal, with degradation efficiencies remaining above 90% in all cases. However, the addition of HA at 10 and 20 mg/L resulted in a slight suppression of degradation efficiency (approximately 10–15% reduction), which is attributable to the competitive consumption of reactive oxygen species (ROS) and competition for active sites on the catalyst surface between HA and 4-CP during the adsorption–degradation process. The strong tolerance to inorganic anions suggests that the CA/Cu-Fe-CDP system is well-suited for application in complex groundwater matrices. The catalytic versatility of the system was evaluated by testing three additional organic pollutants: rhodamine B (RhB, a dye), tetracycline (TC, an antibiotic), and sulfamethoxazole (SMX, a pharmaceutical). As shown in Figure 7c, the CA/Cu-Fe-CDP system achieved degradation efficiencies of 94.6%

for RhB, 88.3% for TC, and 91.7% for SMX within 80 min. These results demonstrate that the catalytic oxidation system is capable of degrading a wide range of organic pollutants, confirming its broad-spectrum applicability in wastewater treatment. The degradation of 4-CP in different water matrices is shown in Figure 7d. Compared with deionized water (control, 87% removal), the CA/Cu-Fe-CDP system achieved 84.6% removal in tap water, 82.1% in surface water, and 86.3% in groundwater. The slightly lower efficiency in surface water is likely due to the presence of natural organic matter and suspended particles that consume ROS or block active sites. Nevertheless, the consistently high removal efficiencies ($\geq 82\%$) across all tested water matrices confirm the excellent stability and robustness of the CA/Cu-Fe-CDP system, demonstrating its promising potential for practical water treatment applications.

To simulate real groundwater remediation scenarios, a continuous-flow column test was conducted over 192 h. As shown in Figure 7e, the CA/Cu-Fe-CDP system maintained a 4-CP removal efficiency of $>97\%$ throughout the entire operation period, indicating exceptional long-term stability. In contrast, the CA/Fe-CDP system (without Cu) showed a gradual decline in removal efficiency from an initial 90.2% to 65.4% by 192 h. This significant difference highlights the critical role of Cu in sustaining catalytic activity: Cu species promote electron transfer from Fe^0 , accelerate Fe^0 corrosion, and regenerate Fe^{2+} from Fe^{3+} , thereby maintaining the Fe(II)/Fe(III) redox cycle and preventing premature catalyst deactivation. The superior long-term performance of the Cu-Fe bimetallic system makes it a promising candidate for long-term in situ groundwater remediation. During the long-term column operation, Fe and Cu leaching were monitored by ICP-OES. As shown in Figure S18, the maximum concentrations of leached Fe and Cu in the effluent were only 29.7 $\mu\text{g/L}$ and 5.0 $\mu\text{g/L}$, respectively, which are far below the Chinese national standard for drinking water (GB 5749–2022 [58]: $\text{Fe} < 0.3 \text{ mg/L}$ and $\text{Cu} < 1.0 \text{ mg/L}$). The extremely low metal leaching confirms the excellent immobilization of Cu-Fe nanoparticles within the CDP matrix and indicates that the CA/Cu-Fe-CDP system poses negligible secondary pollution risks during long-term environmental applications. CDP support effectively stabilizes the nanoparticles, preventing their detachment and release into treated water. The rapid degradation observed at environmentally relevant concentrations, combined with the long-term stability demonstrated in the column test, supports the practical feasibility of the CA/Cu-Fe-CDP system for field-scale groundwater remediation, particularly as a permeable reactive barrier or in situ injection technology for treating chlorophenol-contaminated sites.

4. Sustainability Perspectives and Limitations

The use of earth-abundant and inexpensive metals (Fe and Cu) instead of noble metals (Pd, Ag) substantially reduces material costs, while the biodegradable CDP (derived from starch) and naturally occurring citric acid further minimize the environmental footprint compared to synthetic chelators such as EDTA or NTA. Moreover, unlike conventional Fenton systems that require external addition of H_2O_2 , our system generates H_2O_2 in situ through O_2 activation driven by Fe-Cu galvanic coupling, eliminating the need for exogenous oxidant supply and its associated costs, storage risks, and scavenging effects. Although NaBH_4 is employed as the reducing agent in the synthesis, its quantity is minimal (0.4100 g per batch), and the exceptional reusability (97.1% after six cycles) and long-term stability ($>97\%$ removal over 192 h) significantly reduce the overall material consumption and operational costs per unit volume of treated water. The simple liquid-phase reduction synthesis is readily scalable, and the magnetic recovery of the catalyst facilitates separation and reuse in continuous-flow systems. Regarding secondary pollution risks, metal leaching analysis confirmed that Fe and Cu concentrations in the effluent (29.7 $\mu\text{g/L}$ and 5.0 $\mu\text{g/L}$, respectively) are far below

the Chinese drinking water standards (GB 5749–2022 [58]), while toxicity prediction using ECOSAR software confirmed that the degradation intermediates exhibit significantly lower acute and chronic toxicity than pristine 4-CP. The system operates efficiently across a broad pH range (3.0–9.0), eliminating the need for strong acidification or basification of treated water, which further reduces chemical consumption and waste generation.

Despite the promising results, several limitations should be acknowledged. The synthesis of Cu-Fe nanoparticles relies on NaBH_4 as the reducing agent, which raises sustainability concerns. Future work should explore greener alternatives such as plant extract-mediated reduction or ball milling. Additionally, while the system performed well in spiked environmental water samples, validation using actual industrial wastewater has not been conducted, and a comprehensive techno-economic analysis is still lacking. Although seed germination tests confirmed toxicity reduction, more comprehensive ecotoxicity assessments are needed. Despite these limitations, the exceptional long-term stability (>97% removal over 192 h), minimal metal leaching, and robust performance in complex water matrices position the CA/Cu-Fe-CDP system as a promising platform for in situ groundwater remediation. Future research will focus on green synthesis, pilot-scale validation, and economic assessments to advance practical application.

5. Conclusions

This study successfully developed a citric acid-modified Cu-Fe-CDP composite that addresses the critical challenges in 4-chlorophenol remediation, including nanoparticle agglomeration, narrow pH tolerance, and reliance on synthetic chelators. CDP support significantly improved nanoparticle dispersion and increased specific surface area from 8.03 to 15.41 m^2/g , while stabilizing zero-valent iron against oxidation. The bimetallic Fe-Cu design enhanced electron transfer and iron corrosion kinetics, as confirmed by chronoamperometric analysis showing the highest current response for Cu-Fe-CDP among the polymer-supported materials. Critically, citric acid served as a green complexing agent that sustained Fe(II)/Fe(III) cycling, promoted $\cdot\text{OH}$ generation (confirmed by EPR and radical quenching experiments), and enabled effective degradation across a broad pH range from 3.0 to 9.0. Optimal performance achieving 92.13% degradation within 80 min at pH 9.0 and complete removal at pH 3.0–7.0 was obtained with an Fe/CA molar ratio of 1:1.7. Mechanistic studies confirmed the dominance of hydroxyl radicals (82.67% inhibition by TBA) and the essential role of surface Fe(II)/Fe(III) cycling (validated by BPY chelation), with Cu species further promoting electron transfer and Fe redox cycling (degradation increased from 45.5% to 82.9% upon Cu^{2+} addition). Notably, unlike conventional Fenton systems that rely on external H_2O_2 supply, the CA/Cu-Fe-CDP system generates H_2O_2 in situ through O_2 activation driven by Fe-Cu galvanic coupling, eliminating the need for exogenous oxidants and their associated costs and safety concerns. The system demonstrated excellent reusability (97.1% after six cycles), strong tolerance to competing ions, broad-spectrum activity toward multiple pollutants (RhB, TC, and SMX), and stable performance in real water matrices ($\geq 82\%$ removal). Long-term column tests confirmed sustained >97% removal over 192 h with minimal metal leaching ($\text{Fe} < 29.7 \mu\text{g}/\text{L}$, $\text{Cu} < 5.0 \mu\text{g}/\text{L}$), well below drinking water standards. The CA/Cu-Fe-CDP system thus offers a synergistic integration of dispersion stabilization, bimetallic activation, ligand-enhanced Fenton chemistry, and peroxide-free operation, positioning it as a promising, durable, and environmentally benign platform for long-term in situ groundwater remediation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su18168079/s1>, Figure S1. Pseudo-first-order kinetic fitting of 4-CP degradation by different Cu-Fe-polymer composites (Cu-Fe-GG, Cu-Fe-CC, Cu-Fe-SCC, and Cu-Fe-CDP). Figure S2. Electron transfer between Cu-Fe materials and biomacromolecular polymers

(chronoamperometric current responses of Cu-Fe-GG, Cu-Fe-CC, Cu-Fe-SCC, and Cu-Fe-CDP electrodes). Figure S3. Control experiments for 4-CP degradation under identical conditions: CA alone, CDP alone, Cu-CDP, Fe-CDP, and CA/Cu-Fe-CDP (pH 6.0, [4-CP] = 10 mg/L, [Materials] = 2 g/L, 80 min). Figure S4. Degradation effects on 4-CP in the presence of Cu-Fe-CDP+CA and Cu-Fe-CDP ([4-CP] = 20 mg/L, V_4 -CP = 50 mL, [Cu-Fe-CDP] = 5 g/L, nFe:nCA = 1:1, pH = 6). Figure S5. Degradation effects of ZVI suspensions, Cu-Fe-CDP solids, and Cu-Fe-CDP+CA (4-CP = 10 mg/L, V_4 -CP = 50 mL) on 4-CP. The theoretical Fe^0 concentration in the ZVI suspension was 5 g/L, and a 2 mL suspension was added to the 4-CP solution such that the Fe^0 concentration in the degradation system was consistent with that in the Cu-Fe-CDP suspension (0.2 g/L Fe^0). The addition amount of the Cu-Fe-CDP solid was 20 mg, and the amount of CA was equal to that of the Cu-Fe-CDP+CA, which was 5.4 mM. Figure S6. Degradation effects on 4-CP in the presence of CA (phenol = 10 mg/L, V_4 -CP = 50 mL, [Cu-Fe-CDP] = [Fe-CDP] = 2 g/L, nFe:nCA = 1:1.5). Figure S7. (a) Distribution of 4-CP in solution and on the catalyst surface under air atmosphere; (b) distribution of 4-CP in solution and on the catalyst surface under N_2 atmosphere; (c) TOC removal over time; (d) Cl^- release during the degradation reaction. Reaction conditions: [4-CP] = 10 mg/L, pH 7.0, [CA/Cu-Fe-CDP] = 2 g/L. Error bars represent standard deviation ($n = 3$). Figure S8. Comparison of the degradation effects of Cu-Fe and Cu-Fe-NaAC on 4-CP. Figure S9. Changes in 4-CP concentration before and after desorption under 0.5, 1, and 2 g/L of CA/Cu-Fe-CDP treatment. Figure S10. (a) Biototoxicity of 4-CP degradation intermediates predicted by ECOSAR. (b) Wheat seed germination indices over 7 days for 4-CP solutions before and after treatment by the CA/Cu-Fe-CDP system. ** and *** indicate statistical significance at $p < 0.01$ and $p < 0.001$, respectively. Figure S11. Fe 2p XPS high-resolution spectra of spent catalysts after 80 min reaction. Figure S12. Effect of BPY pre-mixing on 4-CP degradation by the CA/Fe-CDP system (pH 7.0, [4-CP] = 10 mg/L, [CA/Cu-Fe-CDP] = 2 g/L, and 80 min). BPY concentrations: 20 and 100 mM. Figure S13. Effect of Cu^{2+} addition on 4-CP degradation by the CA/Fe-CDP system (pH 6.0, [4-CP] = 10 mg/L, [CA/Cu-Fe-CDP] = 2 g/L, and 80 min). Cu^{2+} concentrations: 0, 1.0, and 5.0 mM. Figure S14. Radical species involved in the CA/Cu-Fe-CDP system. (a) Effect of scavengers on 4-CP degradation (pH = 7) and (b) corresponding inhibition rates. (c, d) EPR spectra of $\text{O}_2^{\cdot -}$ and $\cdot\text{OH}$, respectively. Figure S15. (a) Time-dependent H_2O_2 concentration profiles in the CA/Cu-Fe-CDP system with and without citric acid addition. (b) Concentrations of $\cdot\text{OH}$ and p-BHA during the reaction between sodium benzoate and Cu-Fe-CDP. Reaction conditions: [4-CP] = 10 mg/L, pH 7.0, [CA/Cu-Fe-CDP] = 2.0 g/L. Error bars represent standard deviation ($n = 3$). Figure S16. H_2O_2 concentration profiles in the CA/Cu-Fe-CDP system under ambient air and N_2 -purged conditions. Reaction conditions: [4-CP] = 10 mg/L, pH 7.0, [CA/Cu-Fe-CDP] = 2.0 g/L. Error bars represent standard deviation ($n = 3$). Figure S17. Degradation of 4-CP at (a) environmentally relevant concentrations (20, 100, 200, and 1000 $\mu\text{g/L}$) and (b) industrially relevant concentrations (50, 80, and 120 mg/L) by the CA/Cu-Fe-CDP system. Reaction conditions: pH 7.0, [CA/Cu-Fe-CDP] = 2 g/L. Error bars represent standard deviation ($n = 3$). Figure S18. Concentrations of leached Fe and Cu ions during the long-term column test over 192 h. Error bars represent standard deviation ($n = 3$). The dashed lines indicate the Chinese national standard limits for drinking water (GB 5749–2022: Fe < 0.3 mg/L, Cu < 1.0 mg/L). Table S1. Elemental contents of the Cu-Fe-CDP (Wt%, Wt% Sigma, and atomic percentage for C, O, Fe, Cu). Table S2. Surface elemental composition (at%) of Cu-Fe NPs and Cu-Fe-CDP determined by XPS. Table S3. Peak fitting parameters and relative contents of Fe species (Fe^0 , Fe(II), Fe(III)) in Cu-Fe NPs, Cu-Fe-CDP, and after reaction. Table S4. Kinetics of 4-CP removal by modified Cu-Fe materials derived from several biomacromolecular polymer materials (pseudo-first-order rate constants k^{obs} and R^2 values for Fe, Cu-Fe, Cu-Fe-GG, Cu-Fe-CC, Cu-Fe-SCC, and Cu-Fe-CDP). Table S5. Comparison of the CA/Cu-Fe-CDP system with previously reported catalytic systems for 4-chlorophenol degradation (including catalyst, conditions, removal efficiency, and references). Text S1. Contribution of adsorption and degradation—detailed methodology for distinguishing adsorption, catalytic degradation, and mineralization using methanol extraction, TOC analysis, and Cl^- monitoring. Text S2. Role of surface Fe(II) verified by BPY chelation—experimental procedure for BPY pre-incubation to interrupt Fe(II)/Fe(III) redox cycling. Text S3. Identification of Cu species contribution—methodology for comparing Fe-CDP without Cu, Fe-CDP with Cu^{2+}

ions, and complete Cu-Fe-CDP system. Text S4. Environmental application assays—detailed protocols for reusability test (S4.1), effect of competing ions and humic acid (S4.2), degradation of multiple pollutants (S4.3), performance in real water matrices (S4.4), long-term column test (S4.5), and metal leaching analysis (S4.6). Text S5. Identification of degradation intermediates and toxicity analysis—LC-MS/MS methodology, ECOSAR toxicity prediction, and wheat seed germination test protocol.

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