Mechanistic Study and Toxicity Evaluation of Quinoline Degradation by Electron Beam Irradiation and Electron Beam-Driven Advanced Oxidation Processes

Authors: Wang, Ms. Mengying, Wang, Ms. Xinxuan, Zhang, Dr. Zhonglei, Yang, Prof. Qi, Chen, Dr. Hai, Yang, Prof. Qi

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Abstract

In present work, the degradation of quinoline, the intermediates produced and their toxicity were evaluated using electron beam (EB) irradiation and its coupling with oxidants (H 2 O 2 and peroxymonosulfate) processes. Under the conditions of an initial quinoline concentration of 50 mg/L and pH=9, a complete removal 100% and 40% mineralization were achieved at an absorbed dose of 5 kGy. EB irradiation efficiently decomposed quinoline, with •OH identified as the dominant reactive species. However, high initial substrate concentration, low pH, and elevated salinity reduced mineralization efficiency by promoting radical scavenging. Coupling oxidants significantly enhanced system performance. EB/H 2 O 2 amplified •OH generation, achieving the highest TOC removal, while EB/PMS rapidly removed quinoline even in coking wastewater, demonstrating strong resistance to complex matrices. DFT Fukuiindex analysis revealed the most reactive electrophilic sites. EB alone generated multiple bi-aromatic intermediates, limiting mineralization. EB/H 2 O 2 redirected degradation toward the C9 pathway, producing fewer intermediates and facilitating deep oxidation. EB/PMS accelerated ring-cleavage, preferentially forming monoaromatic end-products. Toxicity evaluation showed that intermediates formed under EB alone were more toxic than quinoline. EB/PMS achieved the fastest detoxification and EB/H 2 O 2 achieved the highest mineralization. This work provides new mechanistic insights into EB-based advanced oxidation and supports its application in real industrial 3 wastewater treatment.

Full Text

Preamble

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Corresponding Author: Qi Yang: Tel/Fax: 86-13691491158, e-mail: yq@cugb.edu.cn

Abstract

In present work, the degradation of quinoline, the intermediates produced and their toxicity were evaluated using electron beam (EB) irradiation and its coupling with oxidants (H2O2 and peroxymonosulfate) processes. Under the conditions of an initial quinoline concentration of 50 mg/L and pH=9, a complete removal 100% and 40% mineralization were achieved at an absorbed dose of 5 kGy. EB irradiation efficiently decomposed quinoline, with ·OH identified as the dominant reactive species. However, high initial substrate concentration, low pH, and elevated salinity reduced mineralization efficiency by promoting radical scavenging. Coupling oxidants significantly enhanced system performance. EB/H2O2 amplified ·OH generation, achieving the highest TOC removal, while EB/PMS rapidly removed quinoline even in coking wastewater, demonstrating strong resistance to complex matrices. DFT Fukui-index analysis revealed the most reactive electrophilic sites. EB alone generated multiple bi-aromatic intermediates, limiting mineralization. EB/H2O2 redirected degradation toward the C9 pathway, producing fewer intermediates and facilitating deep oxidation. EB/PMS accelerated ring-cleavage, preferentially forming mono-aromatic end-products. Toxicity evaluation showed that intermediates formed under EB alone were more toxic than quinoline. EB/PMS achieved the fastest detoxification and EB/H2O2 achieved the highest mineralization. This work provides new mechanistic insights into EB-based advanced oxidation and supports its application in real industrial wastewater treatment.

Keywords: Electron beam, Quinoline, Environment variable, Coupling process, Degradation 1.Introduction Quinoline, a representative nitrogen-containing heterocyclic compound, major pollutant in industrial effluents, particularly those originating from coal chemical, coking, and petroleum-refining industries (Zhang et al., 2020). In heavily contaminated groundwater, quinoline concentrations can reach up to 10 mg L-1 and may be as high as 82 mg L-1 in certain coking wastewaters (Xiao et al., 2024).

Quinoline and its derivatives exhibit pronounced teratogenic, carcinogenic, and mutagenic effects. Moreover, their high solubility and bioavailability facilitate migration into receiving water bodies and groundwater systems, resulting in chronic toxicity to aquatic organisms and bioaccumulation along the food chain (Wang et al., 2019a). The persistence of quinoline in coking wastewater therefore poses serious ecological and human health risks (Wang et al., 2019b). As a refractory class of nitrogen-containing heterocyclic pollutants, quinoline constitutes a major obstacle to achieving stable and compliant discharge of coking wastewater, underscoring the urgent need for efficient degradation technologies with well-understood mechanisms (Ramos et al., 2005; Wan et al., 2023).

Advanced oxidation processes (AOPs) have emerged as effective strategies for removing recalcitrant organic pollutants. Typical AOPs, such as Fenton reactions, photocatalysis, and ozonation, can nonselectively oxidize persistent organic compounds (Du et al., 2022; Hu et al., 2023; Li et al., 2022b). Previous studies have demonstrated that acetic acid-modified Fe/Co-N-doped biochar markedly enhances peroxydisulfate activation and enables rapid and efficient quinoline degradation via singlet oxygen (1O2) and superoxide radicals (O2 • −) over a wide pH range (Xiong et al., 2024). In addition, Wang et al. achieved approximately 85-88% quinoline removal under both laboratory-scale and pilot-scale wastewater conditions by developing an oxygen-vacancy-rich, Ce-doped Bi-based photocatalyst coupled with ozone and LED irradiation to synergistically activate the advanced oxidation process (Wang et al., 2025).

Electron beam (EB) irradiation, as an emerging advanced oxidation process (AOP), can directly generate reactive oxygen species (ROS) through the radiolytic decomposition of water. Water radiolysis produces hydroxyl radicals (• OH), hydrated electrons ( ), and hydrogen radicals (H •), which can rapidly oxidize or reduce organic pollutants (Cheng and Wang, 2024a; Chu et al., 2018). Although the same types of free radicals possess inherent reactivity, different AOPs vary in radical generation rates, effective concentrations, and spatial distribution, leading to differences in pollutant degradation efficiency under practical conditions. Previous studies have shown that γ-irradiation combined with TiO_2 markedly enhances the degradation and mineralization of pyridine and quinoline, with quinoline exhibiting a higher removal efficiency and total organic carbon (TOC) reduction of up to 93% (Chu et al., 2018). Moreover, ionizing radiation has been reported to achieve 99.2% removal of indole at a low dose (2 kGy) while significantly reducing the toxicity of intermediate products, indicating its strong potential for the efficient and safe treatment of refractory aromatic nitrogen-containing heterocyclic pollutants (He et al., 2022).

Recent studies have proposed coupling EB with external oxidants, such as hydrogen peroxide (H_2O_2) or peroxymonosulfate (PMS), to enhance the generation of reactive species, including • OH and sulfate radicals ($SO_4 \cdot^-$), thereby significantly improving degradation kinetics and mineralization efficiency. It has been reported that treating aqueous carbamazepine with EB irradiation in combination with PMS markedly enhanced both degradation and mineralization, while reducing the required absorbed dose from 800 Gy to 300 Gy (Wang and Wang, 2019). Feng et al. further demonstrated that EB coupled with peroxydisulfate significantly improved the degradation of organic pollutants in coking wastewater by regulating reactive species pathways (Cheng and Wang, 2024b). However, studies systematically evaluating degradation intermediates and associated toxicity during quinoline removal by EB irradiation, either alone or coupled with H_2O_2 or PMS, remain scarce.

This study systematically investigates the degradation performance of quinoline under EB irradiation and the effects of key operational parameters. Degradation pathways and intermediates were comprehensively elucidated through a combination of density functional theory (DFT) calculations and liquid chromatography-mass spectrometry (LC-MS) analysis. In addition, a comparative evaluation of degradation intermediates and residual toxicity among EB, EB/H_2O_2, and EB/PMS systems was conducted, revealing distinct mechanistic differences among the treatment modalities.

Overall, this work provides valuable theoretical insights and practical guidance for ionizing radiation-induced advanced oxidation treatment of nitrogen-containing heterocyclic pollutants in wastewater.

2.1 Chemicals

Quinoline (\$ 99^{-1})*waspreparedwithdeionizedwaterandstoredat*4°*Cinthedarkpriortouse.Hydrogenperoxi*
30% v/v), sodium hydroxide (NaOH, \$ 96*{2}SO*{4}\$, \$ \$98%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Peroxymonosulfate (PMS, 42-46%) was supplied by Aladdin Reagent Co., Ltd. (Shanghai, China). All chemicals were of analytical grade and used as received without further purification. Deionized water was used throughout all experiments.

2.2. Experimental design

Irradiation experiments were conducted using a continuous-wave electron accelerator (10 MeV, 1 mA) at CGN Dasheng Accelerator Technology Co., Ltd. (Suzhou, China). The absorbed dose was calibrated before each run by alanine dosimetry, with a measurement uncertainty of approximately \$±3*{2}SO*{4}\$ or NaOH), and salinity (0, 0.5, 1.0, and 1.5%, adjusted by NaCl addition).

To enhance oxidation efficiency and investigate potential synergistic effects, EB irradiation was combined with H_2O_2 (EB/H_2O_2) and PMS (EB/PMS) systems. The H_2O_2 dosage ranged from 1.5 to 15.0 mM, while PMS concentrations were adjusted between 0.5 and 2.0 mM. These ranges were selected based on preliminary screening to ensure measurable removal efficiency while minimizing excessive scavenging of reactive species. The degradation mechanism was further examined through radical-scavenging experiments to distinguish the contributions of ·OH, , and H·. Specific quenchers were added in stoichiometric excess to selectively inhibit targeted species, including tert-butanol (TBA), ethanol (EtOH), O_2, and N_2. Residual quinoline concentrations after irradiation were measured to assess the role of each reactive species. All experiments were conducted in triplicate, and results are presented as mean values with corresponding standard deviations. Considering the complexity of industrial wastewater matrices, additional tests were performed using secondary biochemical effluent collected from Shougang Group Co., Ltd. to evaluate the practicality and robustness of the EB-assisted system under real environmental conditions.

2.3 Analytical methods

After irradiation, all samples were immediately filtered through 0.22 µm polyethersulfone membranes to remove suspended solids prior to chemical analysis.

Residual quinoline concentrations were quantified using a Thermo Fisher high-performance liquid chromatograph (HPLC, USA) equipped with a C18 reversed-phase column (250 mm$×$4.6 mm, 5 µm) and a UV detector set at 275 nm.

The mobile phase consisted of methanol and ultrapure water (65:35, v/v) at a flow rate of 1.0 mL/min, with an injection volume of 20 µL. Intermediate degradation products were identified and semi-quantified using liquid chromatography-mass spectrometry (Agilent LC/MSD iQ) operated in positive electrospray ionization (ESI^+) mode.

Chromatographic separation was performed under the same conditions as the HPLC analysis.

The total organic carbon (TOC) content of the irradiated samples was measured using a TOC analyzer (Multi N/C 2100, Jena, Germany) with a 500 µg/L detection limit and a 25 µL injection volume. The degradation kinetics of quinoline under EB irradiation were modeled using a pseudo-first-order kinetic equation (Eq. (1)): = 퐤 where the apparent rate constant k (kGy-1) was obtained from the slope of the linear regression between -ln(C/C0) and the absorbed dose D (kGy).

The radiochemical yield (G), defined as the number of quinoline molecules decomposed per 100 eV of absorbed energy, was calculated according to Eq. (2): × × 100 where R (mol L-1) is the concentration change of quinoline, Avogadro's number, and D is the absorbed dose expressed in eV L-1. The absorbed dose was initially measured in Gy and then converted to eV L-1 (1 Gy = 6.24 × 1018 eV kg-1, assuming the density of the solution to be 1.0 kg L-1).

To further elucidate the degradation mechanism at the molecular level, DFT calculations were conducted using Gaussian 16 software. Quinoline and pyridine structures were optimized at the B3LYP/6-311+G* level, and the Fukui function (f+ and f-) was applied to identify the electrophilic and radical attack sites as described by Guo et al. (Guo et al., 2022). The acute and chronic ecotoxicities of quinoline and its major intermediates were assessed using the Ecological Structure-Activity Relationship (ECOSAR, version 2.0, USEPA) model.

3.1 Efficacy and mechanism of quinoline degradation by EB irradiation

Fig. 1 [Figure 1: see original paper] shows that quinoline concentration decreased sharply with increasing absorbed dose. Higher doses generate more reactive species from water radiolysis, accelerating cleavage of parent molecules (Siwek and Edgecock, 2020). As shown in Fig. 1a, the initial quinoline concentration significantly affected the degradation rate.

At 1 kGy, the degradation rate at 50 mg L-1 was 1.125 times higher than at 100 mg L-1.

This can be explained by two factors. First, under a fixed absorbed dose, the number of generated radicals remains approximately constant; therefore, at higher concentrations, fewer radicals are available per quinoline molecule, reducing the degradation rate (Shao et al., 2018). Second, higher concentration increases radical scavenging and competitive reactions between parent molecules and intermediates, further inhibiting degradation. Similar trends have been reported, where increasing initial concentration lowers the pseudo-first-order degradation constant under EB irradiation (Song et al., 2025).

The G-value increased with initial quinoline concentration at low doses (Fig. 1b), indicating that higher substrate levels favor radical-quinoline collisions. However, at 10 kGy, all samples showed significantly lower G-values, with diminished differences among concentrations. This results from excessive radicals promoting radical-radical recombination and side reactions, which reduce radicals available for degradation (Alkhuraiji and Alkhuraiji, 2019). At 10 kGy, the 50 mg L-1 sample achieved 80% total organic carbon (TOC) removal, indicating incomplete mineralization and residual intermediates (Fig. 1c). Higher initial concentrations yielded even lower TOC removal, demonstrating inhibited mineralization at elevated loadings. This reflects the multi-step nature of quinoline radiolysis: while radicals rapidly degrade the parent compound, subsequent oxidation of intermediates to CO_2 proceeds more slowly, resulting in lower mineralization efficiencies compared to parent compound removal (Chen and Wang, 2020).

Degradation rate constants in the presence of different quenchers were normalized to the control (no quencher) and expressed as k/k0 (Fig. 1d). Addition of TBA, a selective ·OH scavenger, drastically reduced degradation to k/k0 0.18, indicating that suppression of ·OH formation nearly halted quinoline removal. This strong inhibition confirms ·OH as the predominant reactive species in EB-induced degradation. Ethanol (EtOH), which scavenges both ·OH and , caused a moderate decrease (k/k0 0.85), suggesting that although hydrated electrons participate, their contribution is secondary to ·OH.

Introducing O_2 (which promotes $\cdot$OH but scavenges likely due to O_2 reacting with) slightly reduced degradation (k/k0 0.78), to form superoxide radicals ($O_2\cdot^-$), decreasing electron availability and altering radical composition. Purging the solution with N_2 to remove dissolved oxygen and enhance production resulted in only a modest decline (k/k0 0.70), further confirming that $\cdot$OH primarily governs quinoline degradation, while and secondary radicals play lesser roles. Collectively, these results verify that $\cdot$OH generated via water radiolysis are the key oxidants (Svoboda et al., 2020; Zhu et al., 2018).

Fig. 2 [Figure 2: see original paper] shows that EB irradiation achieved near-complete quinoline removal at 5 kGy across all tested pH values (3.5-9.0). However, at the lower dose of 1 kGy, both parent compound removal (71.6-98.0%) and TOC mineralization (4.8-31.4%) exhibited clear pH dependence (Figs. 2a and 2e). This behavior can be explained by two coupled effects: (i) speciation —quinoline is protonated at low pH (3.5-5.5), and the ionic form is less reactive toward radiolytic transients than the neutral molecule, reducing effective attack rates (Eq. (3)) (Yang et al., 2024); (ii) radical availability and fate — pH influences the balance and reactivity of primary radiolysis species ($\cdot$OH, , $\cdot$H), their interconversion, and secondary losses. Under alkaline and neutral conditions, radical-molecule collisions and effective oxidative attack are favored, whereas under acidic conditions, $\cdot$OH availability and radical utilization are suppressed (Eqs. (4) and (5)) (Chen et al., 2023). These mechanistic factors explain the increase in G-values with pH at low dose (indicating higher effective decomposition yield per unit energy at higher pH) and the observed decline of G-values with increasing dose (due to enhanced radical–radical recombination and side reactions at high radical flux) (Fig. 2c) (Bujak et al., 2023). The data indicate that pH controls both quinoline speciation and the effective radical chemistry during EB treatment, consistent with recent studies on radiolytic and pH effects in EB-assisted degradation of aqueous organics (Tartaro Bujak et al., 2025; Zhang et al., 2024). $= 1.1 \times 10 = 5.0 \times 10$ In Figs. 2b and 2f, the impact of increasing salinity on EB irradiation removal of $= 3.0 \times 10$ 50 mg L-1 quinoline is evident. While parent compound removal at 5 kGy remained high as salinity increased, TOC removal at the same dose decreased markedly.

Additionally, G-values measured at 1 kGy declined with increasing salinity and further decreased with higher absorbed doses (Fig. 2d). These trends indicate that elevated ionic strength exerts a dual effect: although radical-driven degradation of the parent quinoline remains largely robust, energy-use efficiency (G-value) and mineralization are significantly impaired (Zhang et al., 2022). Higher salinity corresponds to increased concentrations of chloride (Cl^-) and sulfate (SO_4^{2-}) ions, which act as scavengers or modifiers of primary radiolytically generated radicals (Das et al., 2019). For example, Cl^- reacts with $\cdot$OH to form less oxidizing chlorine radicals ($\cdot$Cl, Cl_2^-), thereby reducing $\cdot$OH availability for quinoline degradation (Eqs. (6)-(9)) (Liang et al., 2024) ; similarly, SO_4^{2-} may alter radical speciation or lower the redox potential of sulfate-derived radicals under radical conditions (Eq. (10)) (Wu et al., 2015). Overall, these data show that while EB irradiation effectively degrades the parent quinoline molecule in saline water, elevated salinity hampers radical generation and utilization efficiency, as well as mineralization, due to ion-radical competition. Therefore, for practical application in high-salinity wastewater, careful consideration of ionic composition and radical scavenging effects is necessary (Wang and Wang, 2021; Yan et al., 2023). → = 4.3 × 10 → + 2 2 = 6.1 × 10 + → = 1.5 × 10 = 4.9 × 10

3.2 Enhancement of EB/H2O2 and EB/PMS

= 5.5 × 10 As shown in Fig. 3a [Figure 3: see original paper], coupling H_2O_2 with EB irradiation significantly enhanced quinoline removal compared to EB treatment alone. At low peroxide concentrations (1.5-3.0 mM H_2O_2) and absorbed doses of 1-5 kGy, the EB/H_2O_2 system exhibited optimal synergistic effects, with removal efficiency at 1.5 mM approximately 5% higher than EB alone, accompanied by the greatest TOC reduction during mineralization (Fig. 3b). EB-induced water radiolysis generates primary transient species (Liu et al., 2016), which react with added H_2O_2 to regenerate ·OH radicals (Eqs. (11)-(12)), amplifying the oxidative radical pool available for quinoline degradation and increasing effective radical flux (Khodadadi et al., 2022). However, when H_2O_2 exceeded the optimal concentration (>3.0 mM), excess peroxide acted as a significant ·OH scavenger (Eqs. (13)-(14)) and promoted radical self-quenching, thereby inhibiting mineralization (Cheng and Wang, 2024a). These findings indicate that the EB/H_2O_2 process enhances quinoline degradation through ·OH amplification at optimized peroxide levels, whereas overdosing suppresses this synergy via radical scavenging, consistent with recent studies radiolytic degradation nitrogen-containing aromatics (Guo et al., 2016). 2 2 + ·H → OH + = 1.1 × 10 2 2 + → OH = 9.0 × 10 2 2 + OH → = 2.7 × 10 OH + Similar to the H_2O_2-assisted system, the = 6.0 × 10 values markedly decreased with increasing absorbed dose, indicating effective quinoline degradation. However, unlike the H_2O_2 system, the addition of PMS further enhanced degradation efficiency (Fig. 3c). When PMS concentrations increased from 1.0 to 2.0 mM, complete quinoline removal was achieved at a dose of 3 kGy. This enhancement suggests that PMS activation under EB irradiation generated additional reactive species, such as sulfate radicals ($SO_4{\cdot}^-$), which possess strong oxidative capacity and accelerate the degradation process. Nevertheless, as shown in Fig. 3d, TOC removal PMS-assisted systems remained consistently lower than that achieved by EB irradiation alone, regardless of PMS concentration. Although PMS significantly promoted quinoline degradation, it did not facilitate complete mineralization. This implies that PMS preferentially attacks certain functional groups of quinoline, resulting in partial oxidation rather than full conversion to CO_2 and H_2O. The accumulation of intermediate products may also contribute to the lower TOC removal efficiency. Mechanistically, PMS can be activated by EB irradiation through homolytic cleavage of the O-O bond (~137 kJ/mol), producing both $SO_4{\cdot}^-$ and ·OH radicals (Eqs. (15)-(16)) (Saien et al., 2022). Compared with ·OH, $SO_4{\cdot}^-$ exhibits a higher redox potential, making it a more potent oxidant for attacking electron-rich aromatic compounds such as quinoline. However, excessive PMS may react with $SO_4\cdot^-$ to form less reactive $SO_5\cdot^-$ or undergo self-quenching with $\cdot$OH (Eqs. (17)-(18)), thereby scavenging active radicals and reducing the effective radical concentration available for mineralization (Yan et al., 2017). Similar observations were reported by Chu et al. (Chu et al., 2021), where PMS activation enhanced pollutant degradation but led to incomplete mineralization due to intermediate accumulation. $= 1.1 \times 10 = 1.1 \times 10 = 4.2 \times 10 + \cdot OH \rightarrow H$ 릥 $= 4.3 \times 10 \rightarrow$ 릥 2 8 The enhancement of quinoline degradation by EB/H_2O_2 and EB/PMS systems $= 9.3 \times 10$ was further evaluated in the treatment of coking wastewater. In deionized water, all three processes exhibited high degradation efficiencies, with EB/H_2O_2 and EB/PMS demonstrating pronounced synergistic effects at a low irradiation dose of 1 kGy, achieving removal rates of 91.4% and 88.4%, respectively.

In contrast, their performance declined markedly in coking wastewater; for instance, the degradation efficiency of EB alone decreased from 80.4% in deionized water to 52.4%. However, as the irradiation dose increased to 5 kGy, degradation efficiencies improved across all systems, with the EB/PMS process achieving complete (100%) quinoline removal in the coking wastewater matrix. This inhibitory effect is attributed to the complex composition of coking wastewater—such as organic matter, metal ions, and pH-buffering species—that competitively scavenge reactive species ($\cdot$OH and $SO_4\cdot^-$), lowering their effective concentrations and consequently reducing overall degradation efficiency (Gonçalves et al., 2023; Li et al., 2022a).

3.3 Degradation products and toxicity assessment

DFT Fukui-index analysis identified the C3 and C9 positions as the most reactive sites susceptible to electrophilic and radical attack on the quinoline molecule (Fig. 5A [Figure 5: see original paper]), indicating that the initial attack preferentially occurs at these two carbon atoms (Fig. 5F). Several detected intermediates can be attributed to hydroxylation or ring-opening initiated at C3 or C9, suggesting that quinoline mainly undergoes ring cleavage at these sites under irradiation before entering various downstream oxidation pathways (Fig. 5E). Based on DFT calculations and LC-MS data, the degradation induced by EB alone can be summarized into three major pathways: Pathway 1: $\cdot$OH preferentially hydroxylates the benzene or heterocyclic ring, followed by C-C or C-N bond cleavage, producing ring-opened intermediates containing two aromatic rings.

These intermediates are further oxidized into small carboxylic acids or aldehydes (E1, E2, E3). The accumulation of complex bi-aromatic intermediates in the EB-alone system limits mineralization (Chang et al., 2024). Pathway 2: Multiple hydroxylation and bond scission steps generate low-molecular-weight products dominated by mono-aromatic structures (E4), which serve as precursors subsequent mineralization (Nicolaescu et al., 2005). Pathway 3: Some intermediates undergo amination or reduction after ring opening, forming imine-containing products (E6), which then cleave into smaller molecules (Bu et al., 2024).

In the EB/H_2O_2 system, strong synergy between experimental observations and DFT calculations is evident. Under EB irradiation, H_2O_2 efficiently converts into $\cdot$OH, increasing the overall oxidative flux. DFT indicates that the C9 pathway is particularly sensitive to electron density and electrophilic attack (Fig. 5B), with the initial attack concentrated at C9. This results in fewer intermediates that are more readily oxidized, reducing the accumulation of complex bi-aromatic intermediates.

Consequently, higher mineralization efficiency is achieved, consistent with previous experimental results. H_2O_2 amplifies the $\cdot$OH flux and "directs" degradation rapidly along the C9 route, making the overall pathway more inclined toward continuous oxidation and fragmentation (Bhattacharya and Studer, 2025).

In the EB/PMS system, both sulfate radicals ($SO_4\cdot^-$) generated from PMS activation and $\cdot$OH coexist. Due to the selectivity and oxidation characteristics of $SO_4\cdot^-$, the initial degradation mode of EB/PMS resembles that of EB alone. However, EB/PMS disrupts the parent structure more rapidly, consistent with its faster removal efficiency, and LC-MS analysis reveals fewer complex bi-aromatic intermediates at early stages. The final product profile tends to consist of mono-aromatic end-products (P1, P2, P3), indicating that EB/PMS favors rapid fragmentation of the parent molecule into smaller mono-ring fragments rather than forming and accumulating bi-aromatic intermediates (Ling et al., 2017). Since these mono-ring terminal products may exhibit lower reactivity toward $SO_4\cdot^-/\cdot$OH or require higher energy for further oxidation, EB/PMS shows superior removal efficiency but contributes less to final mineralization than EB/H_2O_2.

Toxicity evaluation of the detected intermediates revealed clear differences between degradation systems (Fig. 6 [Figure 6: see original paper]). In the EB-alone process, most intermediates exhibited higher acute and chronic toxicity than quinoline, indicating accumulation of partially oxidized and multi-ring structures.

In contrast, the EB/H_2O_2 system produced a final product (H1) with lower toxicity, demonstrating that enhanced $\cdot$OH generation accelerates deep oxidation and suppresses toxic intermediate formation.

The EB/PMS system further improved detoxification performance: most final products showed lower toxicity than both quinoline and H1, consistent with PMS favoring rapid ring cleavage into mono-aromatic fragments. Overall, EB alone breaks the structure but tends to accumulate toxic intermediates, whereas EB/H_2O_2 and EB/PMS promote detoxification, with EB/PMS showing the fastest toxicity reduction and EB/H_2O_2 achieving better mineralization.

4. Conclusions

EB irradiation effectively degraded quinoline, with $\cdot$OH identified as the dominant reactive species. Degradation performance was influenced by operational parameters: high initial concentration, low pH, and elevated salinity suppressed radical utilization and reduced mineralization. Coupling with oxidants significantly enhanced system efficiency. EB/H_2O_2 amplified $\cdot$OH generation, increased radical availability, and achieved the highest TOC removal, while EB/PMS introduced $SO_4{\cdot}^-$ radicals, enabling rapid parent compound removal even in complex wastewater matrices. DFT Fukui-index analysis identified C3 and C9 as the most reactive sites, guiding three main degradation pathways. EB alone tended to accumulate multi-ring intermediates with elevated toxicity. In contrast, EB/H_2O_2 promoted deep oxidation producing lower-toxicity final products, and EB/PMS rapidly fragmented quinoline into mono-aromatic structures exhibiting the lowest overall toxicity. Thus, EB/H_2O_2 is preferable for mineralization, whereas EB/PMS excels in rapid detoxification, providing mechanistic insights for tailoring EB-based advanced oxidation processes for practical wastewater treatment.

Acknowledgments

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