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Removal of Typical Organic Pollutants in Biologically Treated Coking Wastewater by Ionizing Irradiation

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Abstract: Coking wastewater contains a variety of refractory organic pollutants, and among which phenolic compounds often persist in the effluent even after biological treatment, posing potential environmental risks. In this study, ionizing irradiation was used as an advanced treatment technology for the removal of phenolic pollutants from biologically treated coking wastewater. Based on GC-MS analysis of distilled ammonia wastewater and biologically treated effluent, 2,4-dimethylphenol (2,4-DP) was selected as a representative target compound to evaluate the degradation performance and mechanism. The results confirmed that phenolic compounds remained in the biologically treated effluent, while the abundance of alkanes increased compared to that in distilled ammonia wastewater. Ionizing irradiation effectively removed 2,4-DP, and its mineralization increased with increasing absorbed dose. Quenching experiments revealed that hydroxyl radicals ($\bullet\text{OH}$) played the dominant role in degradation, whereas hydrated electrons and hydrogen radicals contributed less. The addition of H_2O_2 enhanced mineralization by increasing the $\bullet\text{OH}$ concentration, and the highest removal efficiency was observed at pH 6. The effects of inorganic anions were concentration-dependent. Chloride ions promoted degradation at low concentrations but inhibited removal at high concentrations, while sulfate ions had little influence on pollutant removal but suppressed mineralization at 10 g/L. Application to actual biologically treated coking wastewater demonstrated efficient removal of phenolic pollutants (phenol and 2,4-DP). Under optimal conditions (5 kGy with 0.5 mM H_2O_2), the effluent COD decreased to 78 ± 4 mg/L, meeting the Chinese discharge standard for the coking chemical industry (GB16171-2012). These results demonstrate the potential of ionizing irradiation as an effective advanced treatment technology for coking wastewater.

Keywords: ionizing irradiation; coking wastewater; organic pollutants; advancing oxidation; radical mechanism

1. Introduction

Coal chemical industry refers to the industrial process in which coal is converted into gaseous, liquid, and solid fuels as well as chemical products through chemical methods. It is considered an important approach to addressing the shortage of oil and gas resources and ensuring secure energy supply [1]. Large volumes of wastewater are generated during coal chemical production processes [2,3]. It is estimated that approximately 300 million tons of coal chemical wastewater are produced annually in China [4]. According to the main production



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processes, coal chemical wastewater can be classified into coking wastewater, coal gasification wastewater, and coal liquefaction wastewater. Compared to coal liquefaction and coal gasification wastewater, coking wastewater contains a wider variety of organic pollutants, such as quinoline, polycyclic aromatic hydrocarbons, and heterocyclic compounds, making it more difficult to treat [5].

Currently, physicochemical processes (e.g., coagulation and steam stripping) combined with biological treatment are commonly employed for the treatment of coking wastewater [6,7]. However, due to the poor biodegradability of refractory organic pollutants in coking wastewater, residual organics remain in the effluent after biological treatment. The chemical oxygen demand (COD) of the biologically treated coking wastewater is typically in the range of 180-300 mg/L, which does not meet the discharge standard specified in the Emission Standard of Pollutants for Coking Chemical Industry (GB16171-2012) in China.

To further reduce the COD in the biologically treated coking wastewater, advanced treatment processes are generally applied. Currently, commonly used advanced treatment technologies include advanced oxidation processes (AOPs), membrane processes, and various combined technologies [8,9]. AOPs remove refractory organic pollutants in wastewater through highly oxidative radicals generated during the process [10,11]. Membrane processes (e.g., ultrafiltration and reverse osmosis) can effectively remove organic pollutants from biological effluent through physical retention and have advantages such as simple operation and high treatment efficiency [12]. With the continuous tightening of industrial wastewater discharge standards in China and the increasing demand for zero discharge of coal chemical wastewater, membrane technologies have received increasing attention in the treatment of coking wastewater.

Membrane fouling is one of the key factors limiting membrane service life and directly affects the operational cost of membrane processes. Reducing the concentration of organic pollutants in biologically treated effluent as much as possible prior to membrane treatment can effectively alleviate membrane fouling and prolong membrane lifespan. Therefore, combined processes integrating advanced oxidation and membrane technologies are commonly employed for the treatment of biologically treated coking wastewater [12,13]. Common AOPs include Fenton and ozonation processes. Fenton process is simple to operate and exhibits good treatment performance; however, it has a narrow applicable pH range and produces a large amount of iron sludge during operation [14]. Ozonation processes usually require catalysts to improve ozone utilization efficiency, resulting in relatively high operational costs [15].

Ionizing irradiation is an emerging wastewater treatment technology. Its primary mechanism in water treatment involves the water radiolysis under the action of high-energy radiation, producing a series of reactive species such as strongly oxidative hydroxyl radicals ($\bullet\text{OH}$) and strongly reductive hydrated electrons (e_{aq}^-). These reactive species interact with pollutants, thereby achieving the removal of contaminants from wastewater [14,16]. Compared to conventional AOPs, ionizing irradiation technology offers several advantages. Unlike conventional AOPs (e.g., Fenton and ozonation), which mainly rely on oxidative pathways, ionizing irradiation can simultaneously generate both $\bullet\text{OH}$ and e_{aq}^- as well as $\text{H}\bullet$, enabling a unique oxidative-reductive synergy for pollutant degradation. In addition, the process does not require continuous chemical addition, thereby avoiding secondary pollution such as iron sludge or residual oxidants. Previous studies have demonstrated that ionizing irradiation technology can effectively remove refractory organic pollutants in water [17]. The absorbed dose required for the removal of organic pollutants varies depending on the types of organic compounds present.

Currently, ionizing irradiation technology has been applied as an advanced treatment process for real textile dyeing wastewater and hospital wastewater [14,18]. The operating cost of ionizing irradiation process for dyeing wastewater treatment was demonstrated to be competitive compared to conventional advanced treatment processes [14]. The favourable treatment performance and competitive operation cost indicate that ionizing irradiation technology has broad application prospects in the field of industrial wastewater treatment. However, ionizing irradiation technology has not yet been systematically investigated for the advanced treatment of biologically treated coking wastewater, which is characterized by complex compositions and the presence of refractory organic pollutants. Moreover, the degradation behaviour and mechanisms of typical residual pollutants in such complex matrices remain unclear.

Therefore, this study aims to investigate the performance of ionizing irradiation in the advanced treatment of biologically treated coking wastewater. To better understand its removal efficiency toward organic pollutants, the composition of organic pollutants in ammonia-stripping wastewater and biological effluent was first analysed to identify the major organic pollutants present in the biological effluent. Targeted experiments were then conducted to investigate the degradation characteristics of typical organic pollutants by ionizing irradiation. Finally, ionizing irradiation was applied to treat actual biologically treated effluent to evaluate its treatment effectiveness. This study provides a novel approach for the advanced treatment of coking wastewater and offers technical support for the application of ionizing irradiation in coking wastewater treatment.

2. Materials and Methods

2.1. Chemicals

The reagents used in this study included methanol (Aladdin, purity > 99.9%), dichloromethane (Macklin, purity 99.8%), xylene (Aladdin, purity 99%), 2,4-dimethylphenol (Aladdin, >98.0%, 2,4-DP) and tert-butanol (Aladdin, purity > 99.0%, TB). Actual coking wastewater, including ammonia-stripping wastewater and biologically treated effluent, was collected from a coking plant in Hebei Province, China. The COD of the ammonia-stripping wastewater was 5600 ± 137 mg/L, whereas that of the biological treated effluent was 297 ± 17 mg/L.

2.2. Extraction of Organic Pollutants from Coking Wastewater

Ten milliliters of ammonia-stripping wastewater or biologically treated effluent was transferred into a 50 mL centrifuge tube. Subsequently, 10 mL of dichloromethane was added. After mixing, the tube was sealed and shaken in an oscillator for 30 min. The aqueous phase was then removed using a glass pipette. The centrifuge tube containing dichloromethane was placed in a fume hood and purged with nitrogen until complete evaporation. Afterward, 1 mL of methanol was added to redissolve the remaining residue. Once dissolution was completed, 0.5 mL of bis(trimethylsilyl)trifluoroacetamide was added to the centrifuge tube, followed by incubation in an oven at 50 °C for 60 min. The resulting samples were stored at 4 °C prior to GC-MS analysis.

2.3. Degradation of Typical Organic Pollutants in Biologically Treated Coking Wastewater by Ionizing Irradiation

Based on the analysis of organic pollutants in ammonia-stripping wastewater and biologically treated effluent, 2,4-DP was selected as the target organic pollutant.

A stock solution of 2,4-DP was first prepared using deionized water with an initial concentration of 100 mg/L. A predetermined volume of the solution was then transferred into a 25 mL quartz tube, resulting in an initial concentration of 20 mg/L. The tube was sealed with a cap and further wrapped with sealing film.

The ionizing irradiation experiments were conducted using a ^{60}Co radiation source at the Institute of Nuclear and New Energy Technology, Tsinghua University. The activity of Co-60 source was 3.6×10^{14} Bq and the dose rate used in this study was 165 Gy per min. The schematic diagram of the ionizing irradiation setup was shown in Figure 1.

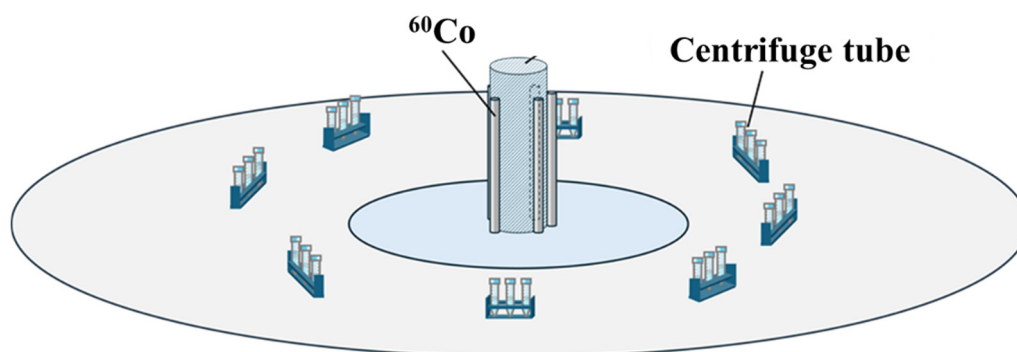


Figure 1. The schematic diagram of ionizing irradiation setup.

The sealed quartz tubes were subsequently subjected to ionizing irradiation. After irradiation, the concentration of 2,4-DP in the aqueous solution was determined to evaluate the removal efficiency of ionizing irradiation toward typical organic pollutants in biologically treated coking wastewater.

For experiments using actual wastewater, 20 mL of biologically treated coking wastewater was transferred into the quartz tube and irradiated under the same conditions. After irradiation, COD concentrations were measured to evaluate the treatment performance. In experiments involving ionizing irradiation coupled with hydrogen peroxide (H_2O_2), a predetermined amount of H_2O_2 was added to the wastewater prior to irradiation, while all other procedures remained identical. All experiments were conducted in duplicate, and the result was the average of two measurements.

2.4. Treatment of Typical Organic Pollutants in Biologically Treated Coking Wastewater by Ionizing Irradiation

Organic pollutants in ammonia-stripping wastewater and biologically treated coking wastewater were analyzed using GC-MS (Agilent 7890A-5975C, DB-624 column). The operating conditions were as follows: splitless injection mode; carrier gas: helium, flow rate 1 mL/min; injector temperature: 250 °C; initial oven temperature: 50 °C (held for 2 min); temperature ramp: 10 °C/min to 250 °C (held for 10 min); cooling rate: 20 °C/min to 50 °C. The concentration of 2,4-DP was determined using HPLC (Agilent 1200s) under the following conditions: detection wavelength: 285 nm, mobile phase: 80% acetonitrile and 20% water (0.1% formic acid), flow rate: 0.8 mL/min, column temperature: 25 °C.

Degradation products of 2,4-DP were analyzed using LC-MS (Q Exactive, Thermo Scientific, Waltham, MA, USA) with the following conditions: flow rate: 0.2 mL/min; initial mobile phase: 90% water (0.1% formic acid) and 10% acetonitrile; acetonitrile increased to 100% over 40 min and held for 3 min; returned to the initial composition within 2 min. The COD was measured using Hach COD digestion system. Changes in the composition of wastewater before and after irradiation were analyzed using three-dimensional excitation-emission matrix (3D-EEM) fluorescence spectroscopy. Total organic carbon (TOC) was measured using a TOC analyzer (Analytik Jena Multi N/C 2100, Jena, Germany).

3. Results and Discussion

3.1. Major Organic Pollutants in Ammonia-Stripping Wastewater and Biologically Treated Effluent

GC-MS analysis indicated that ammonia-stripping wastewater contained a large number of organic pollutants. The dominant compounds included benzene derivatives, phenolic compounds, nitrogen-containing heterocyclic compounds such as quinoline and pyridine, and polycyclic aromatic hydrocarbons (Table 1), which is consistent with previous reports [19].

After treatment through oil separation, dissolved air flotation, and biological processes, the COD of the wastewater decreased significantly but still did not meet the Chinese discharge standard for the coking chemical industry (GB16171-2012).

Table 1. Major organic pollutants in the distilled ammonia wastewater.

No.	Compounds	Molecular Formula	No.	Compounds	Molecular Formula
1	benzene	C ₆ H ₆	2	toluene	C ₇ H ₈
3	pyridineborane	C ₅ H ₈ BN	4	pyridine	C ₅ H ₅ N
5	xylene	C ₈ H ₁₀	6	2, 4-dimethylfuran	C ₆ H ₈ O
7	aniline	C ₆ H ₇ N	8	Benzonitrile	C ₇ H ₅ N
9	3-pyridine-methyl nitrile	C ₆ H ₄ N ₂	10	Phenol	C ₆ H ₆ O
11	phenylcarbinol	C ₇ H ₈ O	12	3-pyridine-acetonitrile	C ₇ H ₆ N ₂
13	ortho-toluidine	C ₇ H ₉ N	14	3-methyl-aniline	C ₇ H ₉ N
15	paratoluidine	C ₇ H ₉ N	16	p-cresol	C ₇ H ₈ O
17	3-methylphenol	C ₇ H ₈ O	18	benzonitrile	C ₈ H ₇ N
19	2,4-DP	C ₈ H ₁₀ O	20	naphthalene	C ₁₀ H ₈
21	3,5-DP	C ₈ H ₁₀ O	22	4-ethylphenol	C ₈ H ₁₀ O
23	3,4-DP	C ₈ H ₁₀ O	24	4-ethylphenol	C ₈ H ₆ N ₂
25	2,3-DP	C ₈ H ₁₀ O	26	1, 6-naphthidine	C ₈ H ₆ N ₂
27	Quinoline	C ₉ H ₇ N	28	2, 3-dihydrobenzofuran	C ₈ H ₈ O
29	isoquinoline	C ₉ H ₇ N			

GC-MS results showed that the organic pollutants in the biological effluent mainly consisted of phenolic compounds and alkanes (Table 2). Compared with ammonia-stripping wastewater, benzene derivatives and quinoline compounds were no longer detected, the abundance of phenolic compounds decreased significantly, while the types and abundance of alkanes increased.

Compared with alkanes, phenolic compounds exhibit stronger toxicity [20]. Moreover, phenolic compounds can undergo oxidative ring-opening reactions during chemical oxidation processes, leading to the formation of alkanes [21,22].

In our previous study, the characteristics and mechanisms of phenol degradation by ionizing irradiation were investigated [23]. Therefore, 2,4-DP, a representative phenolic compound, was selected as the target pollutant in this study to investigate the degradation characteristics of ionizing irradiation.

Table 2. Major organic pollutants in the effluents of biological treatment process.

No.	Compounds	Molecular Formula	No.	Compounds	Molecular Formula
1	2-chloro-2-methyl-butane	C ₅ H ₁₁ Cl	30	bromo-iso-octane	C ₈ H ₁₇ Br
2	amylene hydrate	C ₅ H ₁₂ O	31	decamethylcyclopentasiloxane	C ₁₀ H ₃₀ O ₅ Si ₅
3	3-methyl-2-butanone	C ₅ H ₁₀ O	32	2-cyclopentylacetonitrile	C ₇ H ₉ N
4	3-methyl-3-butene-2-ketone	C ₅ H ₈ O	33	2,3-dimethylsiloxane	C ₁₂ H ₂₆
5	3-pentene-2-alcohol	C ₅ H ₁₀ O	34	tridecane	C ₁₃ H ₂₈
6	4-pentenyl alcohol	C ₅ H ₈ O	35	N-benzylxycarbonyl-L-arginine	C ₁₄ H ₂₀ N ₄ O ₄
7	methyl isobutyl ketone	C ₆ H ₁₂ O	36	hexadecane	C ₁₆ H ₃₄
8	2,3,5-trimethyl-hexane	C ₉ H ₂₀	37	eicosane	C ₂₀ H ₄₁ I
9	3-ethylene-1-alcohol	C ₆ H ₁₂ O	38	2,4-dimethyl-undecane	C ₁₃ H ₂₈
10	4-methyl-2-amyl alcohol	C ₆ H ₁₄ O	39	2,6-dimethyl-undecane	C ₁₃ H ₂₈
11	2-methyl furan	C ₅ H ₆ O	40	Di-n-decyl sulfone	C ₂₀ H ₄₂ O ₂ S
12	dibromonitromethane	CHBr ₂ NO ₂	41	4,8-dimethyl-undecane	C ₁₃ H ₂₈
13	2-methyl-2, 3-pentanediol	C ₆ H ₁₄ O ₂	42	3-ethyl-3- methylnonadecane	C ₂₂ H ₄₆
14	2-methyl-nonane	C ₁₀ H ₂₂	43	2,4-DP	C ₈ H ₁₀ O
15	5-aminotetrazole	CH ₃ N ₅	44	2,6,11-trimethyl-dodecane	C ₁₅ H ₃₂
16	octamethylcyclotetrasiloxane	C ₈ H ₂₄ O ₄ Si ₄	45	7-methyl-pentadecane	C ₁₆ H ₃₄
17	decane	C ₁₀ H ₂₂	46	4-ethyl-undecane	C ₁₃ H ₂₈
18	2,4-dimethyl-octane	C ₁₂ H ₂₆	47	1,3-di-tert-butylbenzene	C ₁₄ H ₂₂
19	4-ethyl-heptane	C ₉ H ₂₀	48	5-ethyl-5-methylundecane	C ₂₂ H ₄₆
20	2,6-dimethyl-nonane	C ₁₁ H ₂₄	49	ethyl 4-toluidine-2-acetone	C ₁₂ H ₁₇ NO ₂
21	2,3,4-trimethyl-3-amyl alcohol	C ₈ H ₁₈ O	50	heptacosane	C ₂₇ H ₅₆
22	2-cyanoimidazole	C ₄ H ₃ N ₃	51	6,6-diethyloctadecane	C ₂₂ H ₄₆
23	4, 5-dimethyl-nonane	C ₁₁ H ₂₄	52	dodecamethylcyclohexasiloxane	C ₁₂ H ₃₆ O ₆ Si ₆
24	5-ethyl-2-methyl-octane	C ₁₁ H ₂₄	53	2,6,10,15-methylheptadecane	C ₂₁ H ₄₄
25	3-ethyl-2-methyl-pentane	C ₈ H ₁₈	54	3-butoxylaniline-1,1,5,5, 5-hexamethyl-3-phenyl-3-(trimethylsiloxy) trisiloxane	C ₁₃ H ₃₆ O ₄ Si ₄
26	phenol	C ₆ H ₆ O	55	1,4-cyclohexadiene	C ₁₅ H ₃₂ Si ₃
27	4,7-dimethyl-undecane	C ₁₃ H ₂₈	56	tetradecane	C ₁₄ H ₃₀
28	5-methyl-undecane	C ₁₂ H ₂₆	57	9-ethyl-9-heptyl-octadecane	C ₂₇ H ₅₆
29	2-methylphenyl ester dodecyl oxalic acid	C ₂₁ H ₃₂ O ₄	58	5-hydroxy-2,4-di-tert-butylbenzyl methyl valeric acid	C ₁₉ H ₃₀ O ₃

3.2. Degradation of 2,4-DP by Ionizing Irradiation

As shown in Figure 2A, the removal efficiency of 2,4-DP increased with increasing absorbed dose. When the absorbed dose was higher than 2 kGy, the removal efficiency reached 100%. Previous studies have shown that the addition of an appropriate amount of H₂O₂ can enhance the removal capacity of ionizing irradiation [24]. In this study, the addition of 0.5 mM H₂O₂ reduced the absorbed dose required for complete degradation of 2,4-DP. At 1.5 kGy, complete removal was achieved, which was lower than that obtained in the absence of H₂O₂. Figure 2B shows the variation in mineralization efficiency with absorbed dose. The mineralization efficiency increased with increasing absorbed dose and reached 19.2% at 3 kGy. Unlike the removal efficiency, the addition of H₂O₂ slightly inhibited mineralization when the absorbed dose was below 3 kGy. This phenomenon can be attributed to the existence of an optimal H₂O₂ dosage for a given absorbed dose. Excess H₂O₂ can scavenge •OH, thereby reducing mineralization efficiency [14].

Kinetic analysis showed that the degradation of 2,4-DP by ionizing irradiation, both in the presence and absence of H₂O₂, followed a pseudo-first-order kinetic model (Figure 2C). In the absence of H₂O₂, the pseudo-first-order rate constant was -1.8 kGy⁻¹. In contrast, the value nearly doubled to -3.5 kGy⁻¹ when H₂O₂ was present, indicating that the addition of H₂O₂ significantly enhanced the degradation of 2,4-DP.

The solution pH had a significant effect on the removal of 2,4-DP. The removal and mineralization efficiencies of 2,4-DP initially increased and then decreased with increasing pH (Figure 2D). The highest removal and mineralization efficiencies were observed at pH 6.0. This phenomenon can be attributed to variation of •OH yields caused by solution pH. Under strongly acidic conditions (pH = 3.0), the concentration of H• radicals in the solution is relatively high, which can scavenge •OH (Equation (1)) [25], thereby reducing the concentration of •OH available to react with 2,4-DP. Under alkaline conditions, hydroxide ions (OH⁻) in the system can also quench •OH (Equation (2)) [25], leading to a decrease in the concentration of •OH reacting with 2,4-DP and consequently resulting in lower removal and mineralization efficiencies.

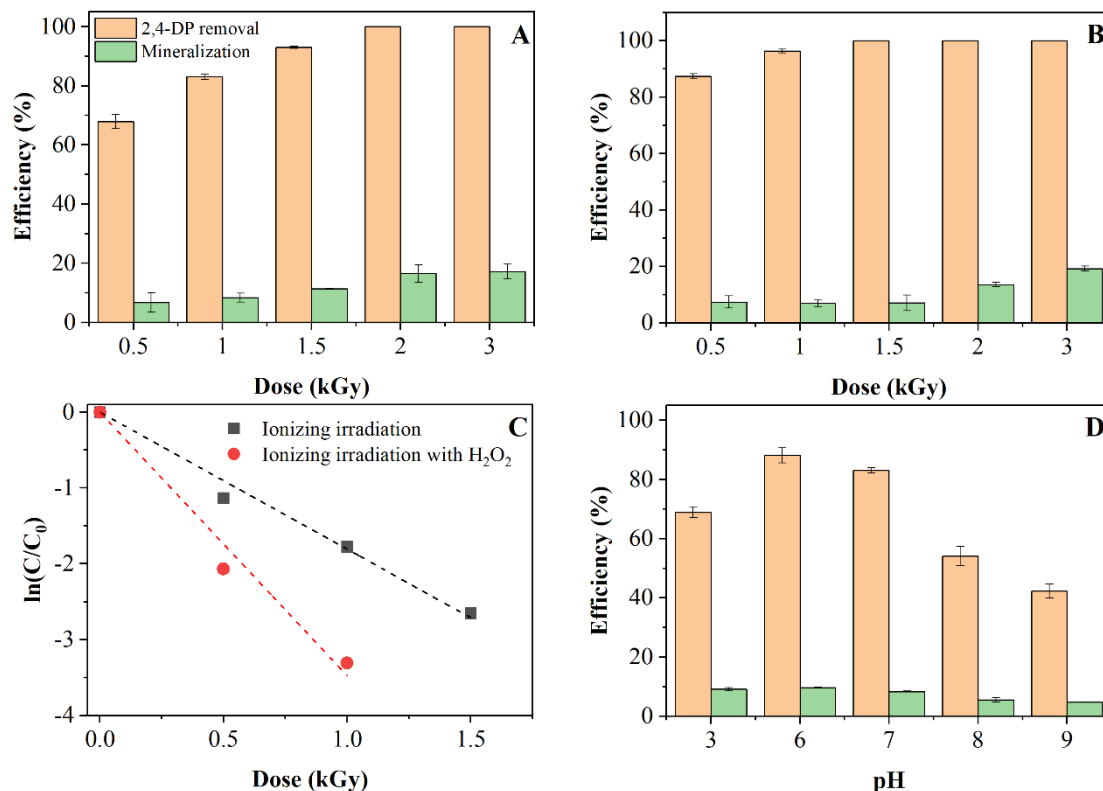


Figure 2. Removal of 2,4-DP from water by ionizing irradiation (A) ionizing irradiation; (B) ionizing irradiation coupled with H₂O₂; (C) pseudo-first-order kinetic of 2,4-DP degradation; (D) effect of solution pH. [2,4-DP] = 20 mg/L, [H₂O₂] = 0.5 mM.

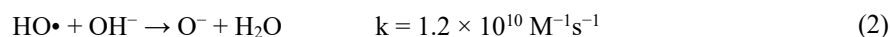
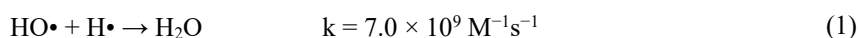


Figure 3A illustrates the possible degradation pathway of 2,4-DP during ionizing irradiation. A total of six major intermediates were identified during the degradation process, with mass-to-charge ratios (m/z) values of 93, 101, 113, 130, 145, and 159, respectively. The corresponding molecular structures of these intermediates were inferred based on their m/z . The detection of toluene ($m/z = 93$) among the degradation products indicates that demethylation of 2,4-DP occurred, which may be attributed to the action of e_{aq}^- [26]. Based on the structures of the identified intermediates, both 2,4-DP and toluene can undergo benzene ring-opening reactions induced by $\cdot\text{OH}$. These reactions ultimately lead to the mineralization of the organic compounds into carbon dioxide and water, thereby achieving the complete removal of 2,4-DP. In addition, the identified degradation intermediates also suggested that both oxidation and reduction reactions synergistically contributed to the degradation of 2,4-DP.

The potential toxicity of degradation products was predicted using ECOSAR software v2.2. The results were listed in Figure 3B. The toxicity of most degradation products was lower than that of 2,4-DP except for toluene (TP3) that exhibited slightly higher chronic toxicity than 2,4-DP, suggesting that ionizing irradiation could lower the toxicity of 2,4-DP solution.

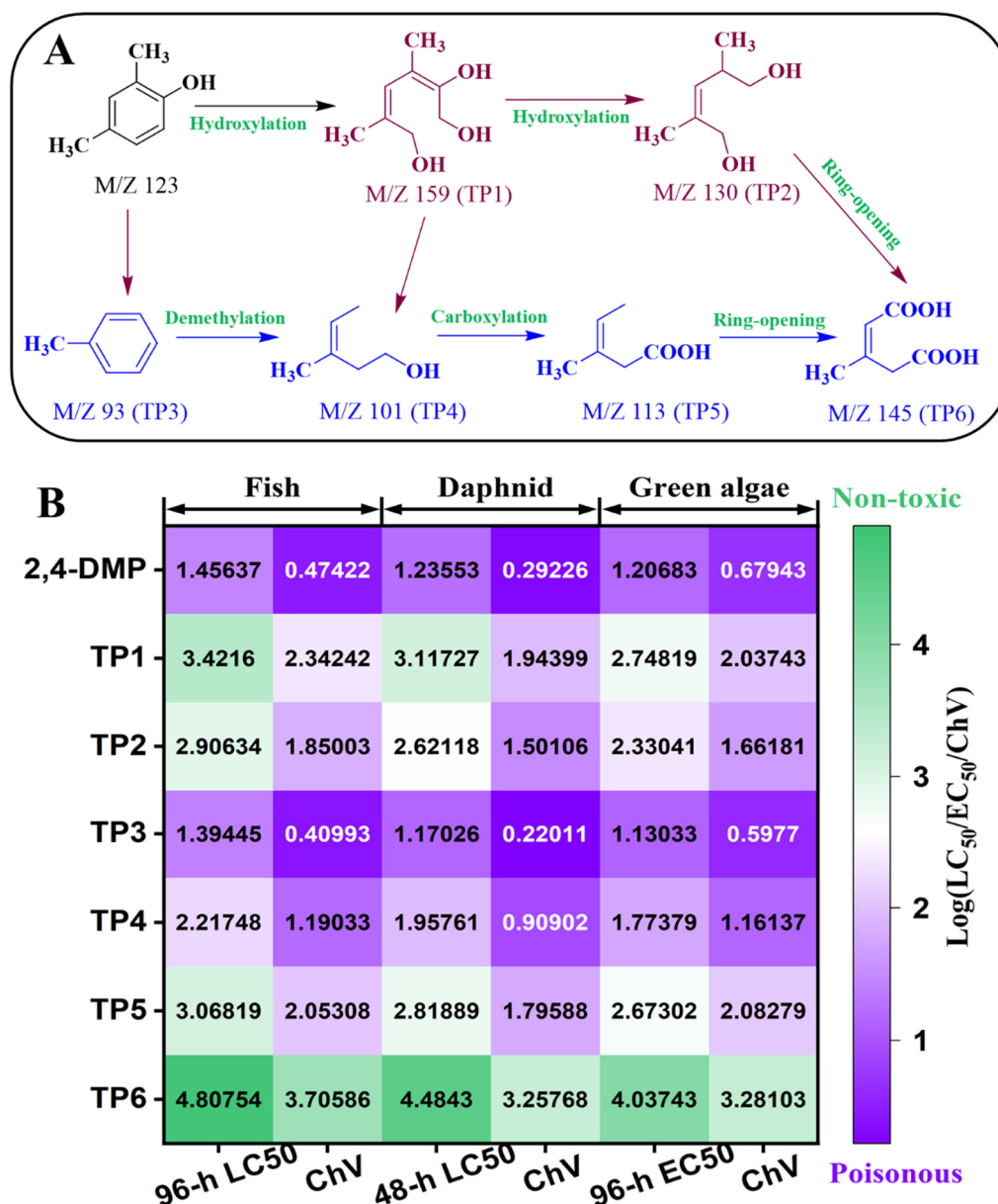


Figure 3. (A) Proposed degradation pathway of 2,4-DP during the process of ionizing irradiation; (B) toxicity prediction of degradation products.

3.3. Degradation Mechanism of 2,4-DP

The degradation mechanism was investigated using radical quenching experiments. TB was used as a scavenger for $\bullet\text{OH}$. Under oxygen-saturated conditions with excess TB, the role of $\bullet\text{OH}$ in the 2,4-DP degradation can be determined. When the solution pH is higher than 10, the yield of $\bullet\text{H}$ was very low; therefore, under a nitrogen atmosphere with excess TB, e_{aq}^- become the dominant reactive species. In addition, when the solution pH is lower than 2 in the presence of TB, $\bullet\text{H}$ are the predominant species.

As shown in Figure 4A, when $\bullet\text{OH}$ were quenched, the removal efficiency of 2,4-DP decreased to 19.6%. When e_{aq}^- and $\text{H}\bullet$ were the dominant reactive species, the removal efficiencies were 15.1% and 14.3%, respectively. These results indicate that $\bullet\text{OH}$ played the dominant role, while e_{aq}^- and $\text{H}\bullet$ contributed less to the degradation process. The dominant role of $\bullet\text{OH}$ can be attributed to its high oxidation potential and strong electrophilic reactivity toward aromatic compounds, which enables rapid attack on the benzene ring of 2,4-DP, leading to hydroxylation and subsequent ring-opening reactions. In contrast, e_{aq}^- and $\text{H}\bullet$ mainly contributed to limited transformation pathways (e.g., demethylation), as evidenced by the formation of intermediates such as toluene. Moreover, the observed enhancement in degradation efficiency with increasing $\bullet\text{OH}$ availability further supports the predominant role of $\bullet\text{OH}$ in the overall degradation process.

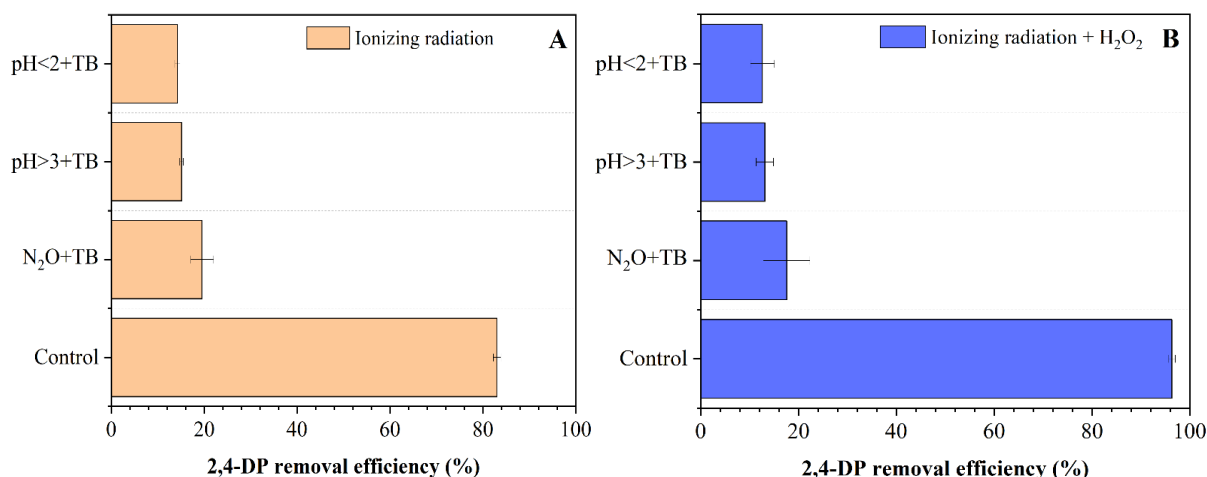
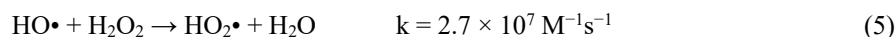
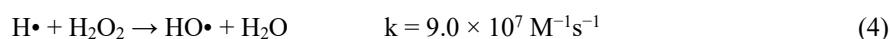
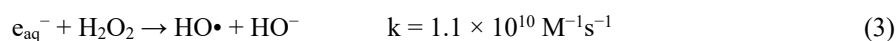


Figure 4. Removal mechanism of 2,4-DP by (A) ionizing irradiation (B) ionizing irradiation coupled to H₂O₂. Adsorbed dose of 1kGy, [2,4-DP] = 20 mg/L, [TB] = 270 mM, pH 7.0.

By comparison, it can be observed that the contribution of reactive species to the degradation of 2,4-DP followed the order $\text{HO}\cdot > e_{\text{aq}}^- > \text{H}\cdot$, which remained unchanged after the addition of H₂O₂. However, the contributions of e_{aq}^- and $\text{H}\cdot$ were slightly reduced compared with those in the absence of H₂O₂ (Figure 4B). This is because e_{aq}^- and $\text{H}\cdot$ can react with H₂O₂ to produce $\cdot\text{OH}$ (Equations (3) and (4)). Consequently, the addition of H₂O₂ increased the concentration of $\cdot\text{OH}$ in the solution, thereby enhancing the removal of 2,4-DP. However, when excessive H₂O₂ was added, it can react with $\cdot\text{OH}$ (Equation (5)), reducing the concentration of $\cdot\text{OH}$ available to react with 2,4-DP.



3.4. Effect of Inorganic Ions on the 2,4-DP Degradation

Actual coking wastewater contains not only organic pollutants but also various inorganic anions. Therefore, this study investigated the effects of common inorganic anions including chloride (Cl⁻) and sulfate (SO₄²⁻) anions on the degradation of 2,4-DP by ionizing irradiation.

As shown in Figure 5A, when the Cl⁻ concentration was lower than 5 g/L, no inhibition of the removal or mineralization of 2,4-DP was observed. At 2 g/L Cl⁻, both the removal and mineralization efficiencies were slightly enhanced. The enhancement may be attributed to the formation of chlorine radicals, which increased the concentration of reactive species in the system and consequently improved the removal and mineralization of 2,4-DP [27].

When the Cl⁻ concentration increased to 5 g/L, the removal and mineralization efficiencies of 2,4-DP slightly decreased but remained comparable to those observed in the absence of Cl⁻. However, when the Cl⁻ concentration reached 10 g/L, the removal efficiency decreased to 78.2% and the mineralization efficiency decreased to 1.7%, indicating that high concentrations of Cl⁻ significantly inhibit the ionizing irradiation degradation of 2,4-DP.

In contrast to Cl⁻, the addition of SO₄²⁻ did not significantly affect the removal efficiency of 2,4-DP. However, when the SO₄²⁻ concentration reached 10 g/L, the mineralization efficiency decreased to 3.3% (Figure 5B). This inhibition might be due to high ionic concentration [28].

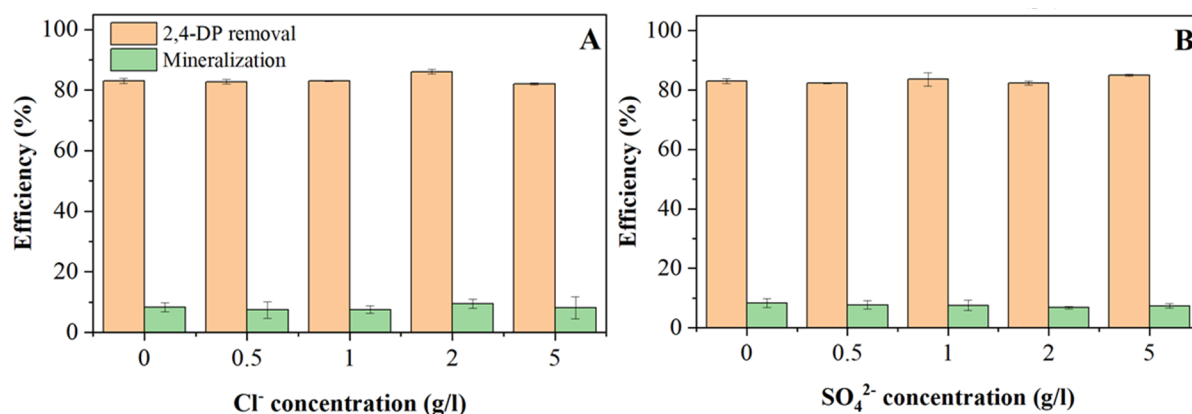


Figure 5. Effects of inorganic ions on the removal of 2,4-DP by ionizing irradiation (A) Cl⁻ (B) SO₄²⁻. Adsorbed dose of 1kGy, [2,4-DP] = 20 mg/L, pH 7.0.

3.5. Treatment of Real Biologically Treated Coking Wastewater by Ionizing Irradiation

To verify the effectiveness of ionizing irradiation in real wastewater, actual biologically treated effluent from a coking plant was used as the experimental matrix. When ionizing irradiation alone was applied, the COD of the effluent decreased to 115 ± 14 mg/L at 2 kGy. With the addition of 0.5 mM H₂O₂, the COD decreased to 94 ± 9 mg/L at 2 kGy. When the absorbed dose increased to 5 kGy, the COD further decreased to 78 ± 4 mg/L, meeting the direct discharge standard for newly constructed coking chemical industries in China (GB16171-2012).

3D-EEM reflect the composition of wastewater [29]. Figure 6 presents the 3D-EEM spectra of the biologically treated effluent before and after treatment with ionizing irradiation coupled to H₂O₂. By comparison, the fluorescence intensities of simple aromatic proteins (EX < 250 nm, EM < 350 nm), fulvic-acid-like organic substances (EX < 250 nm, EM > 350 nm), and soluble microbial by-product-like substances (250 nm < EX < 280 nm, EM < 380 nm) decreased significantly after ionizing irradiation treatment. These results indicate that ionizing irradiation can effectively transform organic pollutants in coking wastewater.

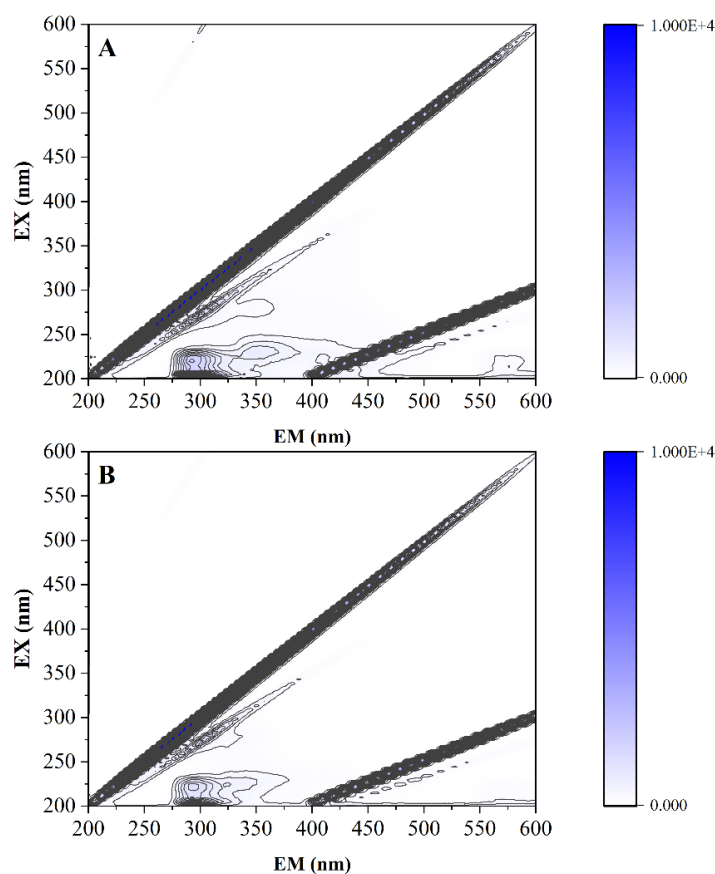


Figure 6. 3D-EEM of effluents of biological treatment process by ionizing irradiation (A) before treatment (B) after treatment.

Furthermore, HPLC analysis did not detect phenol and 2,4-DP in the treated effluent, confirming that ionizing irradiation technology can effectively remove phenolic compounds from biologically treated coking wastewater.

4. Conclusions

Biological treatment removed most organic pollutants from coking wastewater but phenolic compounds remained in the effluent. Ionizing irradiation effectively degraded 2,4-DP, with $\bullet\text{OH}$ identified as the dominant reactive species. The addition of H_2O_2 enhanced degradation by increasing $\bullet\text{OH}$ production, while the optimal removal and mineralization were achieved at pH 6. The presence of inorganic anions showed concentration-dependent effects. Cl^- slightly promoted degradation at low concentrations but significantly inhibited removal and mineralization at 10 g/L, whereas SO_4^{2-} had little effect on pollutant removal but suppressed mineralization at high concentrations. Ionizing irradiation efficiently removed typical phenolic pollutants (phenol and 2,4-dimethylphenol) from real biologically treated coking wastewater. Under optimal conditions (5 kGy with 0.5 mM H_2O_2), the effluent COD decreased to 78 mg/L, meeting the Chinese discharge standard for newly constructed coking chemical industries (GB16171-2012).

Author Contributions

S.W.: conceptualization, methodology, investigation, writing—original draft preparation; J.W.: supervision, writing—reviewing and editing; H.C.: data analysis. All authors have read and agreed to the published version of the manuscript.

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Data will be made available on request.

Conflicts of Interest

The authors declare no conflict of interest. Given their editorial roles, Shizong Wang (Editorial Board Member) and Jianlong Wang (Editor-in-Chief) had no involvement in the peer review of this paper and had no access to information regarding its peer-review process. Full responsibility for the editorial process of this paper was delegated to another editor of the journal.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

References

1. Shen, Z.; Li, J.; Liu, H. Outlook of energy storage via large-scale entrained-flow coal gasification. *Engineering* **2023**, *29*, 50–54.
2. Shi, J.; Xu, C.; Han, Y.; et al. Case study on wastewater treatment technology of coal chemical industry in China. *Crit. Rev. Environ. Sci. Technol.* **2021**, *51*, 1003–1044.
3. Ma, W.; Zhang, X.; Han, H.; et al. Overview of enhancing biological treatment of coal chemical wastewater: New strategies and future directions. *J. Environ. Sci.* **2024**, *135*, 506–520.
4. Na, C.; Zhang, Y.; Quan, X.; et al. Evaluation of the detoxification efficiencies of coking wastewater treated by combined anaerobic-anoxic-oxic (A^2O) and advanced oxidation process. *J. Hazard. Mater.* **2017**, *338*, 186–193.
5. Ren, Z.; Ma, J.; Ding, P.; et al. Autotrophic denitrification in coking wastewater treatment systems: Comprehensive comparative study of full-scale systems in China. *Bioresour. Technol.* **2025**, *427*, 132442.
6. Shi, J.; Huang, W.; Han, H.; et al. Review on treatment technology of salt wastewater in coal chemical industry of China. *Desalination* **2020**, *493*, 114640.
7. Nidheesh, P.V.; Couras, C.; Karim, A.V.; et al. A review of integrated advanced oxidation processes and biological

- processes for organic pollutant removal. *Chem. Eng. Commun.* **2022**, *209*, 390–432.
8. Shu, X.; Wang, S.; Wang, J.; et al. Treatment of high salinity wastewater by *Chryseobacterium* sp. coupled to ionizing irradiation technology. *Chin. Chem. Lett.* **2025**, 112321. <https://doi.org/10.1016/j.ccllet.2025.112321>.
 9. Shamshad, J.; Rehman, R.U. Innovative approaches to sustainable wastewater treatment: A comprehensive exploration of conventional and emerging technologies. *Environ. Sci. Adv.* **2025**, *4*, 189–222.
 10. Zhang, Q.; Zheng, D.; Bai, B.; et al. Insight into antibiotic removal by advanced oxidation processes (AOPs): Performance, mechanism, degradation pathways, and ecotoxicity assessment. *Chem. Eng. J.* **2024**, *500*, 157134.
 11. Wang, S.; Wang, J. Generation, Detection and Regulation Strategies of Reactive Species in Persulfate Activation Systems. *Environ. Microb. Technol.* **2026**, *1*, 8.
 12. Vatanpour, V.; Rezaia, H.; Al-Shaeli, M.; et al. Advances in self-cleaning membranes for effective water and wastewater treatment. *Sep. Purif. Technol.* **2025**, *373*, 133539.
 13. Zhang, F.; Sui, M. Progress of persulfate-based advanced oxidation process (PS-AOPs) coupled with ultrafiltration membrane to alleviate membrane fouling: A review. *Environ. Eng. Res.* **2025**, *30*, 240244.
 14. Wang, S.; Wang, J. Electron beam technology coupled to Fenton oxidation for advanced treatment of dyeing wastewater: From laboratory to full application. *ACS EST Water* **2022**, *2*, 852–862.
 15. Mahmood, Z.; Garg, S.; Yuan, Y.; et al. Performance evaluation and optimization of a suspension-type reactor for use in heterogeneous catalytic ozonation. *Water Res.* **2024**, *254*, 121410.
 16. Chu, L.; Wang, J. Degradation of antibiotics in activated sludge by ionizing radiation: Effect of adsorption affinity of antibiotics. *Chem. Eng. J.* **2023**, *468*, 143821.
 17. Chmielewski, A.G.; Sun, Y.; Wang, J.; et al. Emerging electron beam technology targeting hazardous micropollutants as quaternary treatment in wastewater treatment plants. *Sustainability* **2025**, *17*, 5963.
 18. Wang, J.; Wang, S.; Chen, C.; et al. Treatment of hospital wastewater by electron beam technology: Removal of COD, pathogenic bacteria and viruses. *Chemosphere* **2022**, *308*, 136265.
 19. Zhang, W.; Wei, C.; Yan, B.; et al. Identification and removal of polycyclic aromatic hydrocarbons in wastewater treatment processes from coke production plants. *Environ. Sci. Pollut. Res.* **2013**, *20*, 6418–6432.
 20. Ahmaruzzaman, M.; Mishra, S.R.; Gadore, V.; et al. Phenolic compounds in water: From toxicity and source to sustainable solutions—An integrated review of removal methods, advanced technologies, cost analysis, and future prospects. *J. Environ. Chem. Eng.* **2024**, *12*, 112964.
 21. Cheng, L.; Chen, X.; Gu, J.; et al. Ru-Loaded Nanosheet ZSM-5 for Bisphenol A Hydrodeoxygenation to Bicyclic Alkanes with Coke Resistance and Insights into the Ru-RuO₂ Hydrogenation Mechanism. *Adv. Funct. Mater.* **2025**, *36*, e17448.
 22. Shu, R.; Li, R.; Lin, B.; et al. A review on the catalytic hydrodeoxygenation of lignin-derived phenolic compounds and the conversion of raw lignin to hydrocarbon liquid fuels. *Biomass Bioenergy* **2020**, *132*, 105432.
 23. Wang, S.; Hu, J.; He, S.; et al. Removal of ammonia and phenol from saline chemical wastewater by ionizing radiation: Performance, mechanism and toxicity. *J. Hazard. Mater.* **2022**, *433*, 128727.
 24. Cheng, F.; Wang, J. Regulating hydroxyl radicals (\bullet OH) and hydrated electron (eaq) for enhanced radiolytic degradation of 4-nitrophenol by addition of H₂O₂. *ACS EST Water* **2024**, *4*, 5077–5088.
 25. Buxton, G.V.; Greenstock, C.L.; Phillips Helman, W.; et al. Critical review of rate constants for reactions of hydrated electrons. *J. Phys. Chem. Ref. Data* **1988**, *17*. <https://doi.org/10.1063/1.555805>.
 26. Robinson-Duggon, J.; Mariño-Ocampo, N.; Barrias, P.; et al. Mechanism of visible-light photooxidative demethylation of toluidine blue O. *J. Phys. Chem. A* **2019**, *123*, 4863–4872.
 27. Qin, W.; Guo, K.; Chen, C.; et al. Differences in the reaction mechanisms of chlorine atom and hydroxyl radical with organic compounds: From thermodynamics to kinetics. *Environ. Sci. Technol.* **2024**, *58*, 17886–17897.
 28. Wang, J.; Wang, S. Effect of inorganic anions on the performance of advanced oxidation processes for degradation of organic contaminants. *Chem. Eng. J.* **2021**, *411*, 128392.
 29. Li, L.; Wang, Y.; Zhang, W.; et al. New advances in fluorescence excitation-emission matrix spectroscopy for the characterization of dissolved organic matter in drinking water treatment: A review. *Chem. Eng. J.* **2020**, *381*, 122676.