

## Research Article

## Performance and Pathway of 4-Chloroaniline Degradation: A Comparative Study of Electro-Peroxone, Ozonation, and Electrolysis Processes

Supitchaya Jenjaiwit, Sumana Siripattanakul-Ratpukdi and Thunyalux Ratpukdi\*

Department of Environmental Engineering and Research Center for Environmental and Hazardous Substance Management, Faculty of Engineering, Khon Kaen University, Bangkok, Thailand

Atcharaporn Youngwilai

Department of Civil Engineering, Faculty of Engineering, Naresuan University, Phitsanulok, Thailand

\* Corresponding author. E-mail: thunyalux@kku.ac.th

DOI: 10.14416/j.asep.2025.05.009

Received: 29 January 2025; Revised: 19 March 2025; Accepted: 9 April 2025; Published online: 28 May 2025

© 2025 King Mongkut's University of Technology North Bangkok. All Rights Reserved.

### Abstract

4-chloroaniline (4CA) is a carcinogen in animals and a possible carcinogen in humans. It is widely used as a feedstock in various industrial processes, leading to environmental contamination and potential risks to drinking water sources. This study evaluates the Electro-peroxone process (E-peroxone) for 4CA removal under various applied currents. The reduction of dissolved organic carbon (DOC) and ultraviolet UV absorbance at 254 nm (UV254) was analyzed to assess mineralization among the E-peroxone, ozonation, and electrolysis processes. The E-peroxone process (all applied currents) achieved 4CA removal within 5 min and partially reduced DOC. The E-peroxone process (640 mA) exhibited the highest 4CA removal rate constant ( $1.256 \text{ min}^{-1}$ ). Among the three systems, both E-peroxone and ozonation showed comparable 4CA removal but E-peroxone achieved greater UV254 and DOC reduction indicating enhanced mineralization. 4-chloronitrobenzene was identified as a byproduct, suggesting that E-peroxone and ozone can convert 4CA to less toxic compounds. Overall, these findings demonstrate that E-peroxone is more effective than ozonation and electrolysis, offering a promising approach for 4CA removal and mineralization. Residual DOC after oxidation could be further treated using biological processes.

**Keywords:** Advanced oxidation processes, Electrolysis, Hydroxyl radicals, P-Chloroaniline, Water treatment

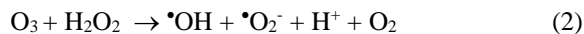
### 1 Introduction

4-chloroaniline (4CA) is a chlorinated aromatic amine widely used as a chemical feedstock for the manufacture of various products, including dyes, plastics, pesticides, rubber, pharmaceuticals, and drugs. Also, 4CA has been identified as an intermediate degradation product of phenylurea, acylanilide herbicide, nitroaniline fungicide, and triclocarban [1], [2]. Due to its extensive use and persistence, 4CA has been frequently detected in aquatic environments, posing contamination risks to drinking water sources [3], [4]. 4CA has been reported as recalcitrant in the environment, with an estimated half-life of 0.3–3.0 days in river water and 30–300

days in groundwater [5]. Furthermore, 4CA is classified as a carcinogen in animals and a possible carcinogen in humans [5]. Therefore, it is necessary to develop effective treatment technologies to ensure safe water quality.

Advanced oxidation processes (AOPs) are promising techniques for removing recalcitrant organic compounds from water by generating highly reactive hydroxyl radical ( $\bullet\text{OH}$ ). Previous works have demonstrated the successful removal of 4CA by various AOPs, such as persulfate activated with zero-valent iron, ozonation, and  $\text{TiO}_2$  photo-degradation [3], [4], [6]. However, the need for specific conditions (low pH of  $\sim 4.0$ ) and high catalyst doses, limits their practicality. Ozone-based processes, particularly

ozonation and the peroxone ( $\text{O}_3/\text{H}_2\text{O}_2$ ) system, offer an alternative due to their strong oxidation potential and cost-effectiveness [7], [8]. Contaminant degradation occurs through two reactions: direct oxidation by  $\text{O}_3$  molecules ( $E_0 = 2.07 \text{ V}$ ) and indirect oxidation by  $\bullet\text{OH}$  radicals ( $E_0 = 2.80 \text{ V}$ ) [8]. While peroxone enhances mineralization by increasing  $\bullet\text{OH}$  production, it faces operational challenges related to  $\text{H}_2\text{O}_2$  storage and handling [8], [9]. The E-peroxone process involves converting dissolved  $\text{O}_2$  to  $\text{H}_2\text{O}_2$  via cathodic  $\text{O}_2$  reduction, as shown in Equation (1). Concurrently,  $\text{O}_3$  molecules may react with  $\text{H}_2\text{O}_2$  and produce reactive oxygen species (ROS) including  $\bullet\text{OH}$  and superoxide radicals ( $\bullet\text{O}_2^-$ ), as shown in Equation (2). Through these reactions, the process is feasible for efficient degradation and mineralization of recalcitrant organic compounds in water than the ozonation or electrolysis processes individually [9]–[11]. Furthermore, compared to the general peroxone method, the E-peroxone process enables continuous  $\text{H}_2\text{O}_2$  generation, thus enhancing removal efficiency and mitigating the scavenging effect that can occur in the presence of excess  $\text{H}_2\text{O}_2$  [9].



The applied current greatly influences electron transfer during cathodic oxygen reduction, thus affecting the generation of  $\text{H}_2\text{O}_2$ , which subsequently produces  $\bullet\text{OH}$  [10], [12], [13]. Increasing the applied current beyond an optimal point results in lower degradation performance due to the  $\bullet\text{OH}$  scavenging effect caused by the accumulation of excess  $\text{H}_2\text{O}_2$  in the system [11]. The applied current varied specifically on the type of contaminants [11], [12], [14]. Although the E-peroxone process has the potential for 4CA degradation, no studies have specifically investigated the application of the E-peroxone process for 4CA degradation and mineralization in water. The influence of applied current on degradation performance, intermediate product formation, and energy efficiency remains unexplored.

This study aims to investigate the efficacy of the E-peroxone process for 4CA degradation and mineralization under different applied currents. Specifically, it examines 1) the degradation kinetics of 4CA, 2) the extent of mineralization of 4CA by monitoring dissolved organic carbon (DOC) and UV

absorbance at 254 nm (UV254), and 3) the formation of intermediate products to propose a potential degradation pathway. Additionally, a comparative assessment of 4CA removal using E-peroxone, electrolysis, and ozonation is conducted to evaluate their relative efficiency and energy consumption. By addressing these research gaps, this study provides valuable insights into optimizing water treatment technologies for the effective removal of 4CA and other recalcitrant contaminants.

## 2 Material and Methods

### 2.1 Chemicals

4CA, 4-chloronitrobenzene (4CNB), and hydroquinone (HQ) were obtained from international and local companies, including Sigma-Aldrich (Singapore) and Thermo Fisher Scientific (Thailand) for experimental and chemical analysis. High-performance liquid chromatography (HPLC)-grade acetonitrile ( $\text{CH}_3\text{CN}$ ; ACN) was obtained from RCI Labscan (Thailand).

### 2.2 Reactor setup

The reactor was assembled using a 1-L suction flask with carbon and platinum plates. To generate  $\text{O}_3$  and in situ  $\text{H}_2\text{O}_2$ , an  $\text{O}_3$  generator (OZ3070A, EBASE, Thailand) [14]. A magnetic stirrer was applied to mix the solution in the reactor. A detailed description of the reactor setup is provided in previous work [14].

### 2.3 Experimental procedures

Three reactor systems (E-peroxone, ozonation, and electrolysis) were operated in batch mode. The reactors containing E-peroxone, ozonation, and electrolysis were defined as EP, OZ, and EL, respectively. All the experiments were conducted in triplicate. In each reactor, a concentrated 4CA solution (500 mg/L) was added to deionized (DI) water to obtain an initial 4CA concentration of 10 mg/L. This high 4CA concentration was used to observe the mineralization and intermediate products of 4CA. The temperature was controlled ( $25 \pm 2 \text{ }^\circ\text{C}$ ) by a water-cooling bath. For the EP and OZ systems, the  $\text{O}_2$  gas was fed rate at a fixed rate of 0.5 L/min (equal to  $\text{O}_3$  mass rate of 53 mg  $\text{O}_3$ /min). Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) at a concentration of 10 mM was used as an electrolyte in all reactors.

In the first experiment (EP), various applied current intensities (40, 80, 160, 320, and 640 mA) were used to continually produce *in situ* H<sub>2</sub>O<sub>2</sub> throughout the experiment. In the second experiment (a comparison of the systems), a selected current intensity was applied to the E-peroxone and electrolysis systems. For the EL reaction, an oxygen feed of 0.5 L/min was supplied and the O<sub>3</sub> generator was turned off. The reaction was conducted for 60 min with samples collected at 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 15.0, 30.0, 45.0, and 60.0 min to analyze 4CA and its intermediate products (4CNB and HQ). The samples for DOC and UV254 measurement were collected every 15 min until the end of the reaction. The kinetic rate constant was calculated using the first-order kinetic model, as shown in Equation (3)

$$\ln\left(\frac{C_0}{C_t}\right) = kt \quad (3)$$

where C<sub>0</sub> and C<sub>t</sub> are the initial concentration and the concentration at time t (mg/L), respectively. The *k* and *t* values represent the reaction rate constant (min<sup>-1</sup>) and the reaction time (min), respectively. To investigate the synergistic effect of E-peroxone, the enchantment factor index (EI) was calculated using Equation (4) [15]:

$$EI = \left( \frac{k_{EP}}{k_{OZ} + k_{EL}} \right) \quad (4)$$

where *k*<sub>EP</sub>, *k*<sub>OZ</sub>, and *k*<sub>EL</sub> are the kinetic rate constants of the E-peroxone, ozonation, and electrolysis processes, respectively.

## 2.4 Energy consumption calculation

To evaluate the energy cost of the EP system in comparison to OZ, the electrical energy per order (EEO) was calculated using Equations (5)–(8). The EEO refers to the energy requirement (kWh unit) for removing the contaminant concentration by one order of magnitude (90% removal) of 1 m<sup>3</sup> of contaminated water [16].

$$EEO = \frac{P_{\text{system}} \times t \times 1000}{V \times 60 \times \log \frac{C_0}{C_t}} \quad (5)$$

$$P_{EP} = (C \times Q \times R) + (I \times U) \quad (6)$$

$$P_{OZ} = C \times Q \times R \quad (7)$$

$$P_{EL} = I \times U \quad (8)$$

The parameters for EEO calculation were as follows: *P*<sub>system</sub> (the power used by the system, kW), *C* (inlet ozone gas phase concentration, 106 mg O<sub>3</sub>/L), *Q* (ozone gas flow rate, 0.5 L/min), *R* (average energy requirement of ozonation, 15 kWh/kg), *t* (reaction time at 90% removal, min, obtained from equation 3), *I* (applied current, A), *U* (cell voltage, 10 V), *V* (reaction volume, 1.0 L), and C<sub>0</sub> and C<sub>t</sub>, which represent the initial and 10% of initial contaminant concentrations, respectively.

## 2.5 Analytical methods

4CA and its intermediate products were detected via HPLC (LC2050, Shimadzu, Japan) [14]. Prior to analysis, the samples were filtered using a syringe filter (0.2 μm) and stored in an amber vial at 4 °C. An injection volume of 20 μL was used for each sample. ACN and DI were used as the mobile phase with a ratio of 75:25 (v/v). The mobile phase flow rate was set at 1.0 L/min. The retention time was 7.5 min, with the peaks corresponding to 4CA, 4CNB, and HQ detected at 4.2, 5.8, and 3.1 min, respectively. The detection limits of 4CA, 4CNB, and HQ were 0.05, 0.01, and 0.01 mg/L, respectively.

The DOC concentration and UV254 were measured using a total organic carbon (TOC) analyzer (multi N/C, 2100S, Analytikjena, Germany) and a spectrophotometer (DR6000, HACH, USA) at a wavelength of 254 nm, respectively. All the samples were filtered using a 0.45-μm nylon syringe filter before analyses.

## 3 Results and Discussion

### 3.1 Effect of applied currents on 4CA, DOC, and UV254 reduction by EP

#### 3.1.1 Degradation of 4CA

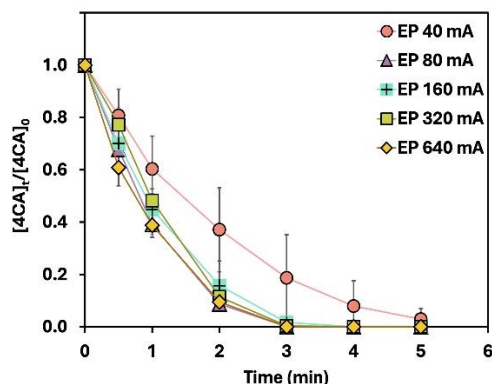
The performance of EP is influenced by electrical currents. Applied currents of 40, 80, 160, 320, and 640 mA were investigated. Figure 1 shows that the E-peroxone process achieves complete removal of 4CA for all applied currents within 5 min. Increasing the applied current enhances 4CA degradation by accelerating the reaction, thereby reducing the reaction time. The kinetic rate constants are shown in Table 1, with the highest reaction kinetic rate recorded at an applied current of 640 mA. Theoretically, increasing the applied current induces more electron

transfer on the cathodic surface and, therefore, increases  $\text{H}_2\text{O}_2$  production (Equation (1)), which in turn generates  $\bullet\text{OH}$  at sufficient  $\text{O}_3$  concentrations (Equation (2)) [17]. It is likely that  $\bullet\text{OH}$  plays a key role in the E-peroxone process as it is a highly reactive oxidant (2.8 V) and non-selective radical. In addition, high applied currents in the E-peroxone process could

accelerate  $\text{O}_3$  decomposition to produce greater  $\bullet\text{OH}$  yields [15]. On the other hand, applying a lower current (<40 mA) might lower the removal efficiency and kinetic rate of 4CA.

**Table 1:** First-order rate constants of 4CA degradation, UV254 reduction, and DOC reduction under E-peroxone, electrolysis, and ozonation processes.

Sample	4CA		UV254		DOC	
	k value ( $\text{min}^{-1}$ )	$R^2$	k value ( $\text{min}^{-1}$ )	$R^2$	k value ( $\text{min}^{-1}$ )	$R^2$
EP 40 mA	0.535	0.993	0.055	0.967	0.013	0.968
EP 80 mA	1.152	0.985	0.065	0.944	0.017	0.952
EP 160 mA	1.181	0.988	0.067	0.942	0.018	0.941
EP 320 mA	0.989	0.969	0.058	0.954	0.020	0.935
EP 640 mA	1.256	0.990	0.095	0.971	0.020	0.950
EL 640 mA	0.022	0.835	0.001	0.892	0.001	0.967
OZ	0.656	0.988	0.036	0.958	0.012	0.989



**Figure 1:** Effect of applied currents on 4CA degradation using E-peroxone. Reaction conditions:  $\text{O}_3 = 53 \text{ mg O}_3/\text{min}$ ,  $\text{Na}_2\text{SO}_4 = 10 \text{ mM}$ , and temperature =  $25 \pm 2 \text{ }^\circ\text{C}$ .

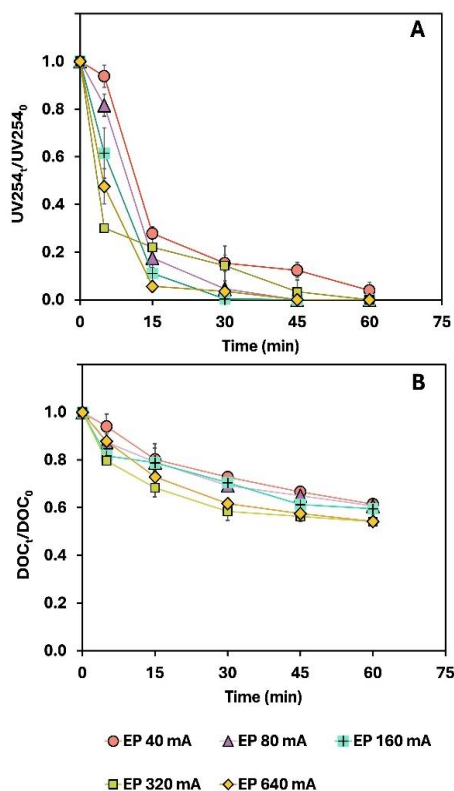
The rate constant doubled when the applied current increased from 40 mA to 80 mA. When the applied currents were higher than 80 mA, only a small difference in 4CA degradation was observed. The kinetic values did not significantly change ( $p > 0.05$ ). This observation may be explained by dissolved  $\text{O}_3$  being limited by  $\text{O}_3$  mass transfer from the gas phase to the liquid phase, resulting in insufficient  $\text{O}_3$  to react with  $\text{H}_2\text{O}_2$  to produce further  $\bullet\text{OH}$ . Similarly, excess  $\text{H}_2\text{O}_2$  may accumulate in the system and act as an  $\bullet\text{OH}$  scavenger [17]. Furthermore, increasing the applied current could produce more hydrogen bubbles on the cathode surface, thereby decreasing the active sites available for  $\text{H}_2\text{O}_2$  and  $\bullet\text{OH}$  production [11].

For these reasons, increasing the applied current beyond a certain may not provide additional benefits to the E-peroxone process. Similar trends in venlafaxine degradation were reported by Li *et al.*, [18], who suggested that increasing the applied current may limit  $\bullet\text{OH}$  generation. The work of Kashani *et al.*, [19] also reported that strong applied currents may form weak radicals by  $\text{H}_2\text{O}_2$  oxidation on the anode surface, resulting in lower oxidation potential by strong radicals. It was noted that the optimum applied current was lower than other compounds [9],[20]. Comparing with previous work, E-peroxone was more efficient than  $\text{Mn(VII)}-\text{H}_2\text{O}_2$  oxidation process which took 60 min for complete 4CA removal [21]. This result suggests the practical use of E-peroxone for removing 4CA in contaminated water.

### 3.1.2 Reduction of UV254 and DOC

Although 4CA was rapidly degraded within 5 min, it is necessary to evaluate the transformation of the contaminant to carbon dioxide. To investigate the aromatic structure reduction and mineralization of 4CA under different applied currents, the UV254 and DOC were measured. As shown in Figure 2(A), the UV254 was fully reduced under all applied currents, with a rapid decrease in UV254 recorded in the first 15 min and the highest rate at 640 mA (Table 1). This reduction of UV254 demonstrates that E-peroxone process can effectively degrade the aromaticity of compounds (i.e., 4CA and other aromatic byproducts). The DOC concentration decreased rapidly during the first 30 min and decreased slightly thereafter (Figure 2(B)).

At the end of the reaction (60 min), the DOC removal percentages were 38.59%, 39.26%, 40.50%, 45.84%, and 45.82%, for currents of 40, 80, 160, 320, and 640 mA, respectively. The DOC monitoring indicated that 4CA mineralization increased slightly as the applied current was increased from 40 mA to 320 mA; however, a further current increase to 640 mA did not improve DOC removal and kinetic rate (Table 1). A similar trend was observed by Wang *et al.*, [22] who reported substantial TOC mineralization of oxalic acid as the current increased from 100 mA to 400 mA, after which the mineralization degree reached a plateau as a result of  $O_3$  mass transfer limitation. Additionally, the oxidation of  $H_2O_2$  at the anode (the reverse of Equation (1)) under high current intensities can lead to a decrease in  $\cdot OH$  formation, resulting in decreased mineralization [22], [23].



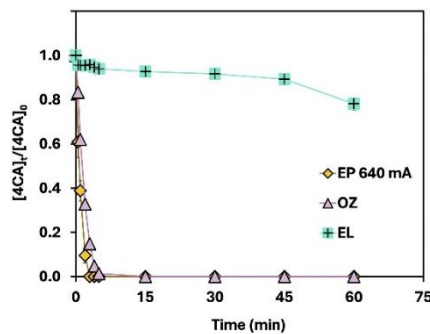
**Figure 2:** Effect of applied currents on UV254 (A) and DOC (B) reduction using EP. Reaction conditions: UV254<sub>0</sub> ~0.27 cm<sup>-1</sup>, DOC<sub>0</sub> ~6.70 mg/L,  $O_3$  = 53 mg  $O_3$ /min, Na<sub>2</sub>SO<sub>4</sub> = 10 mM, and temperature = 25±2 °C.

Furthermore, the pH of the reactions dropped from an initial value of 6 to around 3–4 in all the experiments in this study. Acid by-products (e.g.,

carboxylic acid) of aromatic organic compound degradation may have formed in the system [15]. Previous works have reported the oxidation of 4CA to benzoquinone via  $\cdot OH$ , with further transformation to acid by-products, thus decreasing the system's pH [6], [12]. The findings from the present study suggest that even though 4CA was completely degraded within the first 5 min by E-peroxone process. However, mineralization was not completed (based on DOC values). Typically, AOPs can oxidize the organic compounds to smaller molecules which become more readily biodegradable after a certain time [15], [17], [24]. Thus, prolonged reaction times and/or the use of biological treatment systems (such as a biofilter) might be considered to further remove DOC.

### 3.2 Comparison of EP, OZ, and EL systems in terms of 4CA, DOC, and UV254 reduction

The E-peroxone process combines both ozonation and electrolysis. To evaluate the synergistic effect of E-peroxone process for 4CA degradation, DOC removal, and UV254 reduction, the EP, OZ, and EL experiments were performed. An applied current of 640 mA was selected for electrolysis as this value provided the highest kinetic rate constants (Table 1). In EL, an oxygen gas feed was supplied with the same flow rate as that used in EP and OZ reactions. Figure 3 shows that 4CA was completely degraded by OZ and EP at a current of 640 mA within the first 5 min. In contrast, the EL process was able to only partially remove 4CA, with an efficiency of only 21.88% at the end of the experiment. The removal kinetic rate constants are shown in Table 1. These results confirm that OZ and EP performed at 640 mA have a high potential for 4CA degradation.



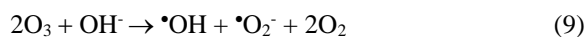
**Figure 3:** Degradation of 4CA by EP, OZ, and EL systems. Reaction conditions:  $O_3$  = 53 mg  $O_3$ /min (no  $O_3$  supplement in EL), Na<sub>2</sub>SO<sub>4</sub> = 10 mM, and temperature = 25±2 °C.

The EI value was calculated as 1.85, which is more than 1, thus indicating that EP achieved a synergistic effect by combining the ozonation and electrolysis processes. EP has significant potential to accelerate the reaction and achieve complete removal of 4CA because this process can generate more ROS than ozone or electrolysis alone by using *in situ* H<sub>2</sub>O<sub>2</sub> production.

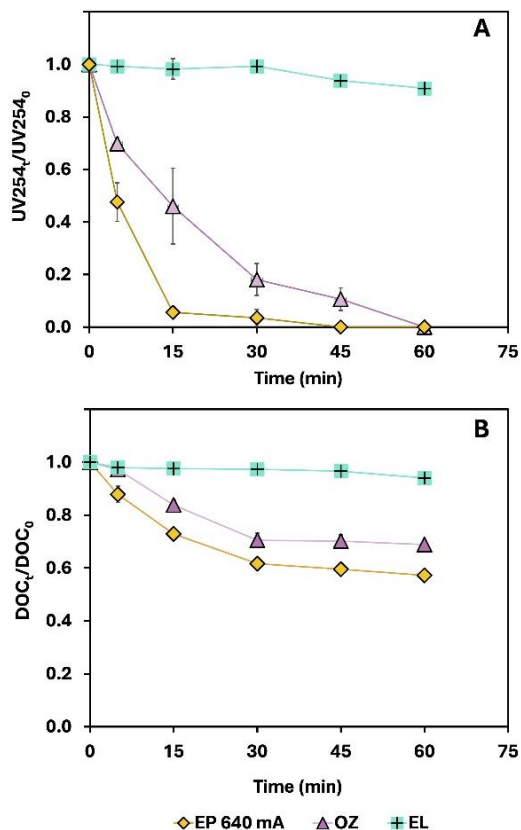
To investigate the potential of the EP 640 mA, OZ, and EL processes for 4CA mineralization, UV254 and DOC concentrations were monitored. As shown in Figure 4(A), the UV254 values decreased continuously, with complete removal achieved under EP 640 mA and OZ. Even though both EP 640 mA and OZ completely reduced UV254, a faster reduction was observed in the EP 640 mA process. In contrast, the UV254 value was only slightly decreased by EL, thus suggesting that the EL reaction is incapable of breaking aromatic rings. In terms of 4CA mineralization, EL and OZ only partially removed DOC, with removals of 6.33% and 31.14%, respectively. When the E-peroxone process was applied, the DOC removal increased to 45.82%.

Although 4CA is highly reactive with O<sub>3</sub> ( $k = 1.04 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ ) and can be readily degraded by ozone alone, the second order rate constant of 4CA with  $\bullet\text{OH}$  is  $1.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ , which is approximately 1340 times that of 4CA with O<sub>3</sub> [25]. This result suggests that  $\bullet\text{OH}$  formation is likely to enhance 4CA mineralization in the E-peroxone process.

In addition, Figure 4 shows that DOC reduction in the OZ process was slower than that in EP. During the initial stage of ozonation (15 min),  $\bullet\text{OH}$  was formed via the decomposition of O<sub>3</sub> by OH<sup>-</sup> (Equation (9)), rapidly achieving mineralization. As time passed, acid by-products were accumulated in the system due to oxidation of organic contaminants [11]. This decreased the pH, resulting in inhibited O<sub>3</sub> decomposition by OH<sup>-</sup>.



A similar finding was also reported in a previous study, where electrolysis and ozonation were insufficient for amoxicillin mineralization, achieving rates of only 3.1% and 47.3%, [9], whereas the E-peroxone process could mineralize up to 67.8% of TOC. To ensure higher mineralization performance, the pH should be monitored and adjusted during the E-peroxone process.



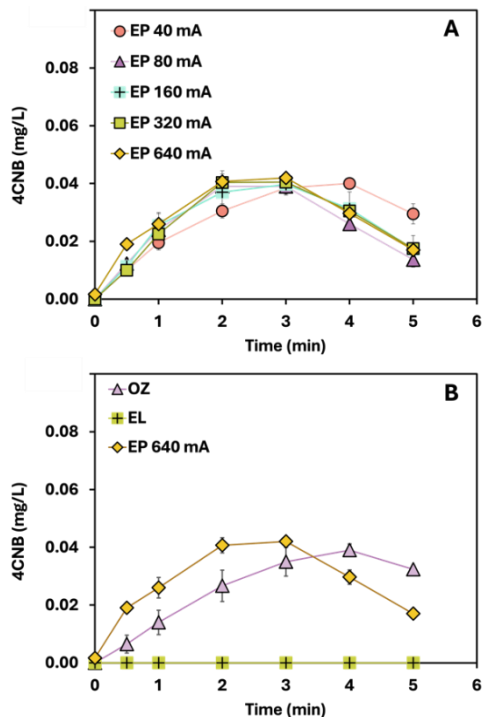
**Figure 4:** Reduction of UV254 (A) and DOC (B) by EP, OZ, and EL systems. Reaction conditions: O<sub>3</sub> = 53 mg O<sub>3</sub>/min (no O<sub>3</sub> supplement in EL), Na<sub>2</sub>SO<sub>4</sub> = 10 mM, and temperature = 25±2 °C.

### 3.3 Identification of degradation intermediate production and potential pathway

During 4CA degradation via the E-peroxone process with different applied currents and the EP, OZ, and EL reactions, the intermediate products were identified (Figure 5). 4CNB was detected at low concentrations in the EP systems with different applied currents. 4CNB was formed within the first 30 s and continuously increased to a reaction time of 2 to 3 min. Then, 4CNB gradually decreased and disappeared after a reaction time of 15 min. Notably, 4CNB formation was slower in the process with a current of 40 mA than in the other systems with higher applied currents (Figure 5(A)). Figure 5(B) shows that 4CNB was detected and generated with the same trends in the OZ and EP processes; however, 4CNB was formed and degraded at slower rates in OZ compared to EP. This observation relates to 4CA degradation kinetics,

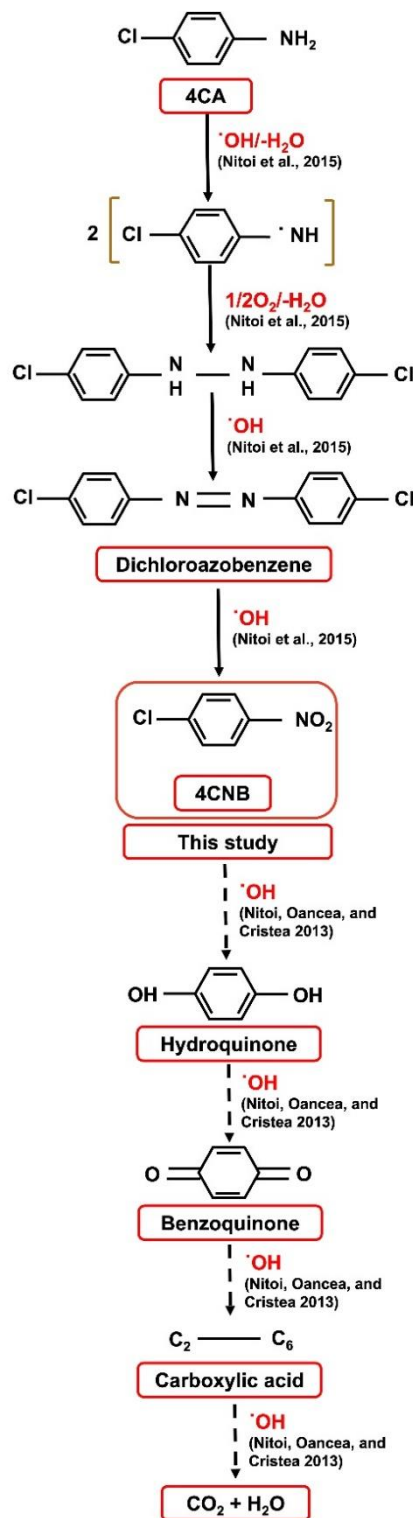


with slower degradation resulting in slower intermediate formation. As anticipated, 4CNB was not formed in EL, likely as a result of the lowest 4CA degradation in this process.



**Figure 5:** Monitoring of intermediate products in EP, OZ, and EL systems. Reaction conditions:  $O_3 = 53$  mg  $O_3$ /min (no  $O_3$  supplement in EL),  $Na_2SO_4 = 10$  mM, and temperature =  $25 \pm 2$  °C.

The 4CA degradation pathway (Figure 6) and the role of radicals in 4CA degradation were proposed. The detected intermediate product, 4CNB, is less reactive with ozone than it is with  $\cdot OH$  ( $k_{O_3} = 1.6$  L/mol-s,  $k_{\cdot OH} = 2.6 \times 10^9$  L/mol-s) [26]. The  $\cdot OH$  radical is known to be highly reactive with the benzene ring of the 4CA structure, thus resulting in the rapid transformation of 4CA to intermediate products [3], [6]. Additionally, 4CA may be attacked by  $\cdot OH$  via hydrogen abstraction (Figure 6). It is then dimerized with the same molecule and stabilized to become dichloroazobenzene. Then, dichloroazobenzene is further oxidized to 4CNB. In addition, 4CNB can be further oxidized to hydroquinone, benzoquinone, and organic acids and mineralized to  $CO_2$ .

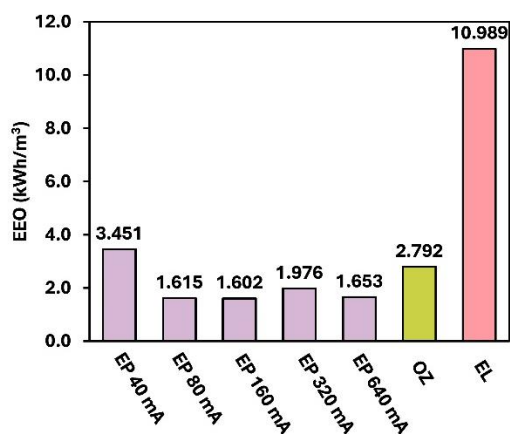


**Figure 6:** Potential 4CA degradation pathway from EP and OZ systems.

Based on the potential 4CA degradation pathway, the detected intermediate product, 4CNB, is less toxic than 4CA [27]. Furthermore, the E-peroxone and OZ processes can degrade 4CNB, thus indicating successful detoxification of 4CA-contaminated water. In future research, detoxification performance and the full 4CA degradation pathway as well as mechanism should be further studied.

### 3.4 Comparison of energy consumption by the E-peroxone, OZ, and EL systems

To investigate the energy consumption under different applied currents and processes, the EEO was calculated (Figure 7). For the E-peroxone process, a low applied current (40 mA) consumed more energy because this current corresponded to a low reaction kinetic rate constant in 4CA degradation (Table 1), thus requiring a longer time for water treatment. The E-peroxone process with applied currents ranging from 80 mA to 640 mA achieved lower EEO values than those of OZ and EL. The minimum EEO was achieved in the E-peroxone process operating under an applied current of 160 mA, which also consumed 42.62% and 85.42% less energy relative to the OZ and EL processes, respectively. The results of this study are consistent with previous works, which have reported lower energy usage in the E-peroxone process for several contaminants [12]. Also, the energy consumption by E-peroxone for 4CA was in the same range as other contaminants [12], [14]. This work confirmed that the E-peroxone process not only enhances the reaction kinetics and efficiencies but can also decrease the system energy usage.



**Figure 7:** Comparison of electrical energy per order (EEO) for E-peroxone, ozonation, and electrolysis reactions.

## 4 Conclusions

In this study, the E-peroxone process was successfully applied to treat 4CA in contaminated water. The results demonstrate that E-peroxone removed 4CA and reduced UV254 under various applied currents. The highest kinetic rate constant ( $1.256 \text{ min}^{-1}$ ) of 4CA mineralization (45.82%,) was achieved at an applied current of 640 mA. While both E-peroxone and ozonation completely degraded 4CA and reduced UV254, the E-peroxone process has lower energy consumption. 4CNB as an intermediate product was temporarily detected in the E-peroxone and ozonation systems suggesting the transformation of 4CA to less toxic or non-toxic compounds. A synergistic effect of E-peroxone over ozonation and electrolysis was observed; however, complete mineralization of DOC was not achieved. Future studies should explore prolonged reaction times and fundamental investigations (e.g., the mechanisms of radicals) are recommended to observe complete mineralization and more comprehensively understand the 4CA removal mechanism. Additionally, further research on the integration of biological treatment following the E-peroxone process is recommended.

## Acknowledgments

This research received financial supported from National Research Council of Thailand (NRCT) (The Royal Golden Jubilee Ph.D. Programme, Grant number N41A650076). Additional sources of funding were from the National Science, Research, and Innovation Fund (NSRF), Thailand (Fundamental Fund 2025–2026) and Khon Kaen University, Thailand (Research Administration Division). We also thank the Research Center for Environmental and Hazardous Substance Management (Khon Kaen University, Thailand), and Center of Excellence on Hazardous Substance Management, Thailand for the Research Team Promotion Grant (Grant number N42A640329 (NRCT)).

## Author Contributions

S.J.: methodology, investigation, data analysis, data curation, writing an original draft, writing—reviewing and editing; A.Y.: methodology, data curation; S.S.-R.: conceptualization, data analysis, writing—reviewing and editing, funding acquisition, project administration, supervision; T.R.: conceptualization, research design, data analysis, writing—reviewing



and editing, project administration, supervision. All authors have read and agreed to the published version of the manuscript.

### Conflicts of Interest

The authors declare no conflict of interest.

### References

- [1] A. S. Vangnai and W. Petchkroh, "Biodegradation of 4-chloroaniline by bacteria enriched from soil," *FEMS Microbiology Letters*, vol. 268, no. 2, pp. 209–216, 2007, doi: 10.1111/j.1574-6968.2006.00579.x.
- [2] S. Jenjaiwit, N. Supanchaiyamat, A. J. Hunt, Y. Ngernyen, T. Ratpukdi, and S. Siripattanakul-Ratpukdi, "Removal of triclocarban from treated wastewater using cell-immobilized biochar as a sustainable water treatment technology," *Journal of Cleaner Production*, vol. 320, 2021, Art. no. 128919, doi: 10.1016/j.jclepro.2021.128919.
- [3] I. Hussain, Y. Zhang, S. Huang, and X. Du, "Degradation of p-chloroaniline by persulfate activated with zero-valent iron," *Chemical Engineering Journal*, vol. 203, pp. 269–276, 2012, doi: 10.1016/j.cej.2012.06.120.
- [4] J. Sarasa, S. Cortés, P. Ormad, R. Gracia, and J. L. Ovelleiro, "Study of the aromatic by-products formed from ozonation of anilines in aqueous solution," *Water Research*, vol. 36, no. 12, pp. 3035–3044, 2002, doi: 10.1016/S0043-1354(02)00003-9.
- [5] International Agency for Research on Cancer, "Para-Chloroaniline," *IARC Monographs on the evaluation of Carcinogenic Risks to Humans*, vol. 57, pp. 305–321, 1993.
- [6] I. Nitoi, P. Oancea, I. Cristea, L. Constsntin, and G. Nechifor, "Kinetics and mechanism of chlorinated aniline degradation by TiO<sub>2</sub> photocatalysis," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 298, pp. 17–23, 2015, doi: 10.1016/j.jphotochem.2014.10.005.
- [7] J. Kong, Y. Lu, Y. Ren, Z. Chen, and M. Chen, "The virus removal in UV irradiation, ozonation and chlorination," *Water Cycle*, vol. 2, pp. 23–31, 2021, doi: 10.1016/j.watcyc.2021.05.001.
- [8] C. Wei, F. Zhang, Y. Hu, C. Feng, and H. Wu, "Ozonation in water treatment: The generation, basic properties of ozone and its practical application," *Reviews in Chemical Engineering*, vol. 33, no. 1, pp. 49–89, 2016, doi: 10.1515/revce-2016-0008.
- [9] W. Q. Guo, Q. L. Wu, X. J. Zhou, H. O. Cao, J. S. Du, R. L. Yin, and N. Q. Ren, "Enhanced amoxicillin treatment using electro-peroxone process: Key factors and degradation mechanism," *Royal Society of Chemistry*, vol. 5, pp. 52695–52702, 2015, doi: 10.1039/C5RA07951A.
- [10] S. Yu, Z. Xie, X. Wu, Y. Zheng, Y. Shi, Z. Xiong, P. Zhou, Y. Liu, C. He, Z. Pan, K. Wang, and B. Lai, "Review of advanced oxidation processes for treating hospital sewage to achieve decontamination and disinfection," *Chinese Chemical Letters*, vol. 35, 2024, Art. no. 108714, doi: 10.1016/j.cclet.2023.108714.
- [11] A. Shokri and B. Nasernejad, "Investigation of spent caustic effluent treatment by electro-peroxone process; Cost evaluation and kinetic studies," *Journal of Industrial and Engineering Chemistry*, vol. 129, pp. 170–179, 2024, doi: 10.1016/j.jiec.2023.08.030.
- [12] D. Amado-Piña, G. Roa-Morales, M. Molina-Mendieta, P. Balderas-Hernandez, R. Romero, C. E. Barrera Diaz, and R. Natividad, "Electro-peroxone Process of a Chlorinated Compound: Oxidant Species, Degradation Pathway and Phytotoxicity," *Journal of Environmental Chemical Engineering*, vol. 10, 2022, Art. no. 108148, doi: 10.1016/j.jece.2022.108148.
- [13] Y. Y. Lim, A. Miskon, and A. M. A. Zaidi, "CuZn complex used in electrical biosensors for drug delivery systems," *Materials*, vol. 15, no. 21, p. 7672, 2022, doi: 10.3390/ma15217672.
- [14] S. Jenjaiwit, S. Siripattanakul-Ratpukdi, E. Khan, J. Prasopsuk, and T. Ratpukdi, "Electro-peroxone process for triclocarban and triclosan removal and reclaimed water disinfection," *Journal of Water Process Engineering*, vol. 67, 2024, Art. no. 106200, doi: 10.1016/j.jwpe.2024.106200.
- [15] F. Ghanbari, F. Zirrahi, K. Y. A. Lin, B. Kakavandi, and A. Hassani, "Enhanced electro-peroxone using ultrasound irradiation for the degradation of organic compounds: A comparative study," *Journal of Environmental Chemical Engineering*, vol. 8, no. 5, 2020, Art. no. 104167, doi: 10.1016/j.jece.2020.104167.
- [16] P. Asaithambi, E. Alemayehu, B. Sajjadi, A. Raman, and A. Aziz, "Electrical energy per order determination for the removal pollutant from industrial wastewater using UV / Fe<sup>2+</sup> /H<sub>2</sub>O<sub>2</sub> process: Optimization by response surface

- methodology,” *Water Resources and Industrial*, vol. 18, pp. 17–32, 2017, doi: 10.1016/j.wri.2017.06.002.
- [17] A. Shokri and M. S. Fard, “Employing electro-peroxone process for industrial wastewater treatment: A critical review,” *Chemical Paper*, vol. 76, no. 9, pp. 5341–5367, 2022, doi: 10.1007/s11696-022-02269-y.
- [18] X. Li, Y. Wang, J. Zhao, H. Wang, B. Wang, J. Huang, S. Deng, “Electro-peroxone treatment of the antidepressant venlafaxine: Operational parameters and mechanism,” *Journal of Hazardous Material*, vol. 300, pp. 298–306, 2015, doi: 10.1016/j.jhazmat.2015.07.004.
- [19] M. R. K. Kashani, R. Kiani, A. Hassani, A. Kadier, S. Madihi-Bidgoli, K. Y. A. Lin, and F. Ghanbari, “Electro-peroxone application for ciprofloxacin degradation in aqueous solution using sacrificial iron anode: A new hybrid process,” *Separation and Purification Technology*, vol. 292, 2022, Art. no. 121026, doi: 10.1016/j.seppur.2022.121026.
- [20] Z. Dong, J. Yao, Y. Tang, Y. Jia, Y. Zhang, and H. Liu, “Process optimization of ozone-resistant compounds degradation in electro-peroxone process: From removal performance to mechanism investigation,” *Journal of Water Process Engineering*, vol. 59, 2024, Art. no. 104988, doi: 10.1016/j.jwpe.2024.104988.
- [21] K. Xu and U. V. Gunten, “The Mn(VII)–H<sub>2</sub>O<sub>2</sub> oxidation process: Abatement of electron-deficient N-containing organic compounds,” *Chemical Engineering Journal*, vol. 481, 2024, Art. no. 148630, doi: 10.1016/j.cej.2024.148630.
- [22] H. Wang, S. Yuan, J. Zhan, Y. Wang, G. Yu, S. Deng, J. Huang, and B. Wang “Mechanisms of enhanced total organic carbon elimination from oxalic acid solutions by electro-peroxone process,” *Water Research*, vol. 80, pp. 20–29, 2015, doi: 10.1016/j.watres.2015.05.024.
- [23] O. M. Cornejo and J. L. Nava, “Mineralization of the antibiotic levofloxacin by the electro-peroxone process using a filter-press flow cell with a 3D air-diffusion electrode,” *Separation and Purification Technology*, vol. 254, Art. no. 117661, 2021, doi: 10.1016/j.seppur.2020.117661.
- [24] P. Kiattisaksiri, N. Petmark, and T. Ratpukdi, “Combination of coagulation and VUV+H<sub>2</sub>O<sub>2</sub> for the treatment of color and organic matter in treated effluent wastewater from a sugar factory,” *Appl. Sci. Eng. Prog.* vol. 16, no. 4, p. 6192, 2023, doi: 10.14416/j.asep.2022.08.002.
- [25] L. Carena, D. Vione, M. Minella, S. Canonica, and U. Schönenberger, “Inhibition by phenolic antioxidants of the degradation of aromatic amines and sulfadiazine by the carbonate radical (CO<sub>3</sub>•<sup>-</sup>),” *Water Research*, vol. 209, 2022, doi: 10.1016/j.watres.2021.117867.
- [26] J. M. Shen, Z. L. Chen, Z. Z. Xu, X. Y. Li, B. B. Xu, and F. Qi, “Kinetics and mechanism of degradation of p-chloronitrobenzene in water by ozonation,” *Journal of Hazardous Material*, vol. 152, no. 3, pp. 1325–1331, 2008, doi: 10.1016/j.jhazmat.2007.08.009.
- [27] UNEP Publications. “SIDS initial assessment report for SIAM 15, 1-Chloro-4-Nitrobenzene.” [hvpchemicals.oecd.org](https://hvpchemicals.oecd.org/UI/handler.axd?id=ad5cafea-2e80-4360-9aba-9056532403f0). <https://hvpchemicals.oecd.org/UI/handler.axd?id=ad5cafea-2e80-4360-9aba-9056532403f0> (accessed Feb. 1, 2025).