



Kinetics and energy efficiency for the degradation of 1,4-dioxane by electro-peroxone process



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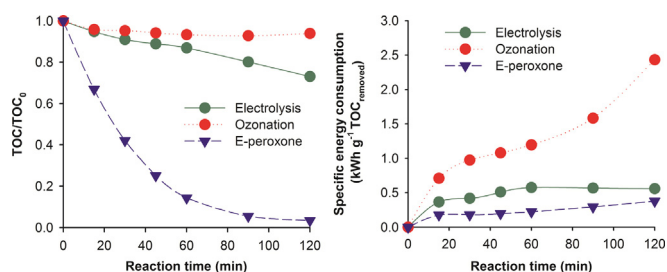
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HIGHLIGHTS

- E-peroxone couples electrolysis with ozonation to driven peroxone reaction for pollutant degradation.
- Significant amounts of $\cdot\text{OH}$ can be efficiently produced in the E-peroxone process.
- E-peroxone greatly enhances 1,4-dioxane degradation kinetics compared with ozonation and electrolysis.
- E-peroxone consumes less energy for 1,4-dioxane mineralization than ozonation and electrolysis.
- E-peroxone offers a cost-effective and energy-efficient alternative to degrade 1,4-dioxane.

GRAPHICAL ABSTRACT



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ABSTRACT

Degradation of 1,4-dioxane by ozonation, electrolysis, and their combined electro-peroxone (E-peroxone) process was investigated. The E-peroxone process used a carbon-polytetrafluoroethylene cathode to electrocatalytically convert O_2 in the sparged ozone generator effluent (O_2 and O_3 gas mixture) to H_2O_2 . The electro-generated H_2O_2 then react with sparged O_3 to yield aqueous $\cdot\text{OH}$, which can in turn oxidize pollutants rapidly in the bulk solution. Using *p*-chlorobenzoic acid as $\cdot\text{OH}$ probe, the pseudo-steady concentration of $\cdot\text{OH}$ was determined to be $\sim 0.744 \times 10^{-9}$ mM in the E-peroxone process, which is approximately 10 and 186 times of that in ozonation and electrolysis using a Pt anode. Thanks to its higher $\cdot\text{OH}$ concentration, the E-peroxone process eliminated 96.6% total organic carbon (TOC) from a 1,4-dioxane solution after 2 h treatment with a specific energy consumption (SEC) of $0.376 \text{ kWh g}^{-1} \text{ TOC}_{\text{removed}}$. In comparison, ozonation and electrolysis using a boron-doped diamond anode removed only $\sim 6.1\%$ and 26.9% TOC with SEC of 2.43 and $0.558 \text{ kWh g}^{-1} \text{ TOC}_{\text{removed}}$, respectively. The results indicate that the E-peroxone process can significantly improve the kinetics and energy efficiency for 1,4-dioxane mineralization as compared to the two individual processes. The E-peroxone process may thus offer a highly effective and energy-efficient alternative to treat 1,4-dioxane wastewater.

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1. Introduction

1,4-Dioxane is a polar cyclic diether and commonly used to manufacture a wide range of products such as dyes, resins, and

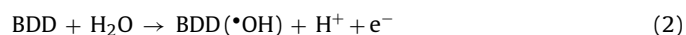
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plastics [1,2]. It is also present in many consumer products, e.g., shampoo, laundry detergents, and cosmetics [2]. Therefore, 1,4-dioxane has been frequently detected in industrial effluents and sewage wastewater [1,3,4]. Moreover, due to the improper disposal of industrial wastes, accidental solvent spills, and inefficiency of conventional wastewater treatment (e.g., biological treatment and adsorption) for 1,4-dioxane removal [1,2,5,6], 1,4-dioxane has now been increasingly identified in surface water, groundwater, and even drinking water [1,7]. The ubiquitous presence of 1,4-dioxane in the aquatic environment has raised increasing concern because it can pose significant threat to the ecosystem and human health. For example, previous research has indicated that 1,4-dioxane can cause kidney failure and liver damage, and is also a possible human carcinogen [1,2,7]. To protect water resources, 1,4-dioxane wastewater has to be sufficiently treated before it can be discharged into the environment.

Electrolysis has been considered a promising technology to treat 1,4-dioxane wastewater due to its environmental friendliness and easy operation [4,8]. Several researchers have shown that when boron-doped diamond (BDD) electrodes are used as the anode in electrolysis, complete mineralization of 1,4-dioxane can be obtained with relatively high energy efficiency [4,8,9]. For example, Barndök et al. [4] recently compared the energy consumption for 1,4-dioxane wastewater treatment by electrolysis (using BDD anodes), ozonation, and conventional peroxone (i.e., O₃/H₂O₂) processes. They concluded that among the three technologies, electrolysis using BDD anodes was the most energy efficient process for chemical oxygen demand (COD) removal from 1,4-dioxane wastewater. In comparison, ozonation cannot effectively degrade 1,4-dioxane because ozone (O₃) reacts very slowly with 1,4-dioxane ($k_{O_3} = 0.32 \text{ M}^{-1} \text{ s}^{-1}$ [10]). Addition of H₂O₂ during ozonation (i.e., peroxone process) to enhance O₃ transformation to hydroxyl radical (•OH) (Eq. (1)) considerably improved COD removal because •OH can rapidly oxidize 1,4-dioxane ($k_{\bullet OH} = 1.1 - 2.35 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [11,12]) and its degradation intermediates (e.g., aldehydes and carboxylic acids) [4]. This, however, increases wastewater treatment cost significantly because H₂O₂ is an expensive chemical [4]. Moreover, transportation, storage, and handling high concentration H₂O₂ solution are dangerous due to its high reactivity [13,14].

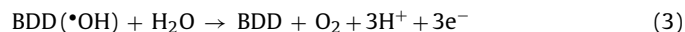


While some promising results have been shown for 1,4-dioxane degradation by electrolysis [4,8,9], the process performance has yet to be improved in terms of electrode cost, energy consumption, and pollutant degradation kinetics. It has been shown that 1,4-dioxane is not very electrochemically active and cannot be effectively degraded by electrolysis using conventional anodes such as Pt/Ti, Pt/steel, and RuO₂/Ti [8,15]. Consequently, expensive BDD anodes, which are effective at producing •OH from water discharge (Eq. (2)), are required to improve 1,4-dioxane degradation [4,8,9]. However, even when BDD anodes are used, electrolysis still requires long reaction time to completely destruct 1,4-dioxane (and its degradation by-products), and the current efficiency decreases significantly as electrolysis proceeds [8,9].



The slow degradation kinetics and low current efficiency in BDD electrolysis can be mainly attributed to the intrinsic limitation of anodic oxidation for pollutant degradation, i.e., pollutants have to be transported to the anode before they can be degraded, and this limitation becomes increasingly severe as the pollutant concentrations decrease during electrolysis [16,17]. Due to the mass transfer limitation, considerable fractions of the charge loading into electrolysis reactors are wasted in side reactions such as oxygen

evolution (Eq. (3)), decreasing the current efficiency for pollutant degradation [8,9].



To overcome the limitations of electrolysis, we proposed the electro-peroxone (E-peroxone) process [18] as a possible alternative to 1,4-dioxane wastewater treatment. The E-peroxone process is a novel electrocatalytic ozonation process developed by combining conventional electrolysis with ozonation processes [18]. It involves sparging an O₂ and O₃ gas mixture (i.e., ozone generator effluent) into an electrolysis reactor that contains wastewater to be treated. The reactor is equipped with a carbon-polytetrafluoroethylene (carbon-PTFE) cathode, which serves as the electrocatalyst to convert O₂ in the sparged O₂ and O₃ gas mixture to H₂O₂ (Eq. (4)). The in-situ generated H₂O₂ then diffuses into the bulk solution and reacts with sparged O₃ to yield aqueous •OH (Eq. (1), i.e., the so called “peroxone reaction”), which can in turn rapidly oxidize pollutants (e.g., •OH reacts with 1,4-dioxane at a rate of $1.1 - 2.35 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [11,12]). Thus, by electrochemically driving the peroxone reaction to produce •OH in the bulk solution, the E-peroxone process can circumvent the limitation of pollutant mass transfer on their degradation kinetics as in electrolysis [18]. In addition, because pollutants are mainly degraded by cathode-induced •OH in the bulk solution, the E-peroxone process does not need to use expensive BDD anodes to achieve fast pollutant degradation [14,18–20]. Therefore, we expected that the E-peroxone process may provide a cost-effective alternative to BDD electrolysis for 1,4-dioxane wastewater treatment.



It is noted that degradation of 1,4-dioxane by combined processes of electrolysis and ozonation has previously been investigated by Kishimoto et al.'s [15,21,22]. However, stainless steel or Pt was used as the cathode in the previous combined process (referred as electrolysis-O₃ hereafter) [15,21,22]. In contrast to carbon-based cathodes, which can electrochemically convert O₂ to H₂O₂ [23], stainless steel and Pt cathodes cannot produce H₂O₂ from O₂ [18,20,24,25] (actually, metallic cathodes may decompose H₂O₂ catalytically (Eq. (5) [25])). As a result, the electrolysis-O₃ process cannot exploit the peroxone chemistry to generate •OH, and is less effective at pollutant degradation as compared to the E-peroxone process [14,18,20].



To evaluate the effectiveness of E-peroxone process, this study compared the kinetics and energy consumption of 1,4-dioxane degradation by electrolysis, ozonation, and E-peroxone processes. The •OH concentrations in the three processes were measured using *p*-chlorobenzoic acid (*p*CBA) as •OH probe because it has a very low reactivity with O₃ ($k_{O_3} \leq 0.15 \text{ M}^{-1} \text{ s}^{-1}$), but reacts very rapidly with •OH ($k_{\bullet OH} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [26,27]. The effects of major operational parameters (e.g., current, ozone concentration, types of anodes and cathodes) on the E-peroxone process performance were evaluated systematically.

2. Experimental

2.1. Chemicals and reagents

1,4-Dioxane (AR grade) was purchased from Alfa Aesar. *p*CBA (99%) was from Sigma-Aldrich. Other chemicals (e.g., Na₂SO₄, NaOH, and H₂SO₄) were analytical grade and purchased from Beijing Chemical Works Co., China. All solutions were prepared using deionized water.

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