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Mechanisms of enhanced total organic carbon elimination from oxalic acid solutions by electro-peroxone process

Huijiao Wang [a], Shi Yuan [a], Juhong Zhan [a, b], Yujue Wang [a, *], Gang Yu [a], Shubo Deng [a], Jun Huang [a], Bin Wang [a]

[a] *School of Environment, Beijing Key Laboratory for Emerging Organic Contaminants Control, State Key Joint Laboratory of Environmental Simulation and Pollution Control, Tsinghua University, Beijing, 100084, China*

[b] *Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming, Yunnan, 650500, China*

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ABSTRACT

Electro-peroxone (E-peroxone) is a novel electrocatalytic ozonation process that combines ozonation and electrolysis process to enhance pollutant degradation during water and wastewater treatment. This enhancement has been mainly attributed to several mechanisms that increase O_3 transformation to •OH in the E-peroxone system, e.g., electro-generation of H_2O_2 from O_2 at a carbon-based cathode and its subsequent peroxone reaction with O_3 to •OH, electro-reduction of O_3 to •OH at the cathode, and O_3 decomposition to •OH at high local pH near the cathode. To get more insight how these mechanisms contribute respectively to the enhancement, this study investigated total organic carbon (TOC) elimination from oxalic acid (OA) solutions by the E-peroxone process. Results show that the E-peroxone process significantly increased TOC elimination rate by 10.2–12.5 times compared with the linear addition of the individual rates of corresponding ozonation and electrolysis process. Kinetic analyses reveal that the electrochemically-driven peroxone reaction is the most important mechanism for the enhanced TOC elimination rate, while the other mechanisms contribute minor to the enhancement by a factor of 1.6–2.5. The results indicate that proper selection of electrodes that can effectively produce H_2O_2 at the cathode is critical to maximize TOC elimination in the E-peroxone process.

1. Introduction

Ozone (O_3) has been widely used in water and wastewater treatment as an oxidant for decades. Due to its high oxidation potential, O_3 can rapidly degrade many pollutants, especially compounds with activated double bonds (e.g., activated aromatic systems, deprotonated amines, and reduced sulfur groups) (von Gunten, 2003; Hoigné and Bader, 1983). However, O_3 is also a highly selective oxidant, ozonation thus often results in the accumulation of many refractory oxidation by-products (e.g., aldehydes and carboxylic acids) that resist further O_3 oxidation in its effluents (Petre et al., 2013). Consequently, ozonation has often been shown to be ineffective at total organic carbon (TOC) abatement (von Gunten, 2003). This has restricted the application of ozonation when high TOC removal efficiency is desired to minimize the risks associated with degradation intermediates (e.g., in drinking water treatment and wastewater reclamation) (Petre et al., 2013; Vecitis et al., 2010).

To improve TOC removal, O_3 has often been used with other technologies such as UV, ultrasound, H_2O_2, and electrochemical processes (von Gunten, 2003; Weavers et al., 1998; Kishimoto et al., 2005; Yuan et al., 2013; Pines and Reckhow, 2002). These combinations can usually enhance O_3 transformation to hydroxyl radicals (•OH), which are a much stronger oxidant and can non-selectively oxidize most organics much faster than O_3. Consequently, pollutants can be degraded more rapidly in these combined processes than ozonation alone. Particularly, the combination of ozonation with electrolysis has gained increasing interest recently because electrolysis is a robust and environmentally-friendly technology and amenable to control and automation (Kishimoto et al., 2005; Yuan et al., 2013; García-Morales et al., 2013; Qiu et al., 2014).

In early combined ozonation and electrolysis processes (referred as O_3-electrolysis hereafter), metal electrodes were used as both the anode (e.g., Pt, RuO_2/Ti, and Pt/Ti) and cathode (e.g., stainless steel (SS), Ti, and Pt) (Kishimoto et al., 2005, 2007, 2008). During the

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* Corresponding author.
E-mail address: wangyujue@tsinghua.edu.cn (Y. Wang).

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O_3-electrolysis process, pollutants can be oxidized in the same way as in electrolysis alone, i.e., via direct electron transfer to the anode (i.e., direct electrolysis) and via chemical reactions with oxidants (e.g., HClO, $H_2S_2O_8$, and •OH) electrochemically generated at the anode (i.e., indirect electrolysis) (Panizza and Cerisola, 2009). In addition, pollutants can be oxidized in the O_3-electrolysis process by •OH generated from cathodically induced reactions, e.g., the electro-reduction of O_3 at the cathode (Eqs. (1)–(3)) (Kishimoto et al., 2005), as well as the decomposition of O_3 (Eqs. (4)–(6), (2), and (3) (von Sonntag and von Gunten, 2012; Merenyi et al., 2010a)) in the vicinity of the cathode, where the local pH is high due to OH^- formation from H_2 evolution. As a result of the enhanced •OH generation, the O_3-electrolysis process can considerably improve pollutant degradation (Kishimoto et al., 2005, 2007).

$$O_3 + e^- \rightarrow O_3^- \cdot \tag{1}$$

$$O_3^- \cdot \leftrightarrow O_2 + O^- \cdot \tag{2}$$

$$O^- \cdot + H_2O \leftrightarrow \cdot OH + OH^- \tag{3}$$

$$O_3 + OH^- \rightarrow HO_4^- \tag{4}$$

$$HO_4^- \leftrightarrow HO_2 \cdot + O_2^- \cdot \tag{5}$$

$$O_2^- \cdot + O_3 \rightarrow O_2 + O_3^- \cdot \tag{6}$$

More recently, boron-doped diamond (BDD) electrodes have been used to further enhance TOC removal in the O_3-electrolysis process (García-Morales et al., 2013; Qiu et al., 2014; Bakheet et al., 2014). Compared with metal electrodes, BDD electrode is more effective at producing •OH from water discharge (Eq. (7)) because it has an inert surface and high oxygen overpotential (Panizza and Cerisola, 2009). It is therefore mainly used as the anode to improve the oxidation of ozone-refractory compounds (e.g., carboxylic acid by-products formed) in the O_3-electrolysis process (Qiu et al., 2014; Bakheet et al., 2014).

$$BDD + H_2O \rightarrow BDD(\cdot OH) + H^+ + e^- \tag{7}$$

While the O_3-electrolysis process has considerably enhanced TOC elimination as compared to the two individual processes, we perceived that it still has vast potential for improvement. For example, ozone generators usually can convert only a small part of the feed O_2 gas to O_3. The gas mixture exiting ozone generators thus still contains significant amounts of O_2, e.g., usually >90% V/V of the O_2 and O_3 mixture when pure O_2 is used as the feed gas. However, O_2 has little use for pollutant removal after it is sparged with O_3 into the reactors. This wastes considerable amounts of O_2 feed gas and energy (e.g., for concentrating O_2 from air and sparging the gas into the reactor). We therefore proposed to utilize O_2 in the sparged gas to electro-generate H_2O_2 in the reactor (Eq. (8)), whose conjugated base (HO_2^-, Eq. (9)) can then react with the sparged O_3 to yield •OH (Eqs. (10), (11), (2) and (3)) (von Sonntag and von Gunten, 2012; Fischbacher et al., 2013; Merenyi et al., 2010b), and thus further enhance TOC elimination (Yuan et al., 2013). Because the reaction of O_3 with H_2O_2 has been commonly referred as the "peroxone" reaction, we have termed this electrochemically-driven process as "electro-peroxone" (E-peroxone) process (Yuan et al., 2013). Note that the overall peroxone reaction has previously been suggested as Eq. (12) (i.e., two •OH formed per H_2O_2 consumed). However, recent studies suggest that the efficiency of •OH formation is only one half of that given by the stoichiometry in Eq. (12) because HO_5^- (the adduct of O_3 with HO_2^-, Eq. (10)) undergoes decomposition to form O_2 and OH^- (Eq. (13)) at a comparable rate of Eq. (11) (Fischbacher et al., 2013).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{8}$$

$$H_2O_2 \leftrightarrow H^+ + HO_2^- \tag{9}$$

$$HO_2^- + O_3 \rightarrow HO_5^- \tag{10}$$

$$HO_5^- \rightarrow HO_2 \cdot + O_3^- \cdot \tag{11}$$

$$H_2O_2 + 2O_3 \rightarrow 2 \cdot OH + 3O_2 \tag{12}$$

$$HO_5^- \rightarrow 2\,^3O^2 + OH^- \tag{13}$$

The E-peroxone process can be easily achieved by replacing the metal cathodes used in previous O_3-electrolysis processes with a carbon-based cathode. In contrast to metal electrodes that may catalytically decompose H_2O_2 and thus cannot produce H_2O_2 from O_2 (Yuan et al., 2013; Sudoh et al., 1985; Bakheet et al., 2013), carbon-based electrodes (e.g., carbon-polytetrafluorethylene (carbon-PTFE), carbon felt, and activated carbon fiber) can convert O_2 efficiently to H_2O_2 due to their high overpotential for H_2 evolution and low catalytic activity for H_2O_2 decomposition (Brillas et al., 2009; Wang et al., 2012; Panizza and Cerisola, 2001).

In previous work, we have evaluated the E-peroxone treatment of several different wastewaters, e.g., landfill leachate and synthetic dyes (Bakheet et al., 2013; Li et al., 2013). It was found that under similar reaction conditions (e.g., applied current and O_3 dose), the E-peroxone process removed TOC from the wastewaters much faster than ozonation, electrolysis, and the O_3-electrolysis process (Bakheet et al., 2013; Li et al., 2013; Wang et al., 2015). This enhancement has been mainly attributed to the significant production of •OH from several mechanisms in the E-peroxone process, e.g., the aforementioned electro-reduction of O_3, O_3 decomposition at high local pH near the cathode, and O_3 reaction with electro-generated H_2O_2 (Bakheet et al., 2013; Li et al., 2013; Wang et al., 2015). These cathodically-induced •OH can oxidize ozone-refractory compounds (e.g., saturated carboxylic acids) to CO_2, thus enhancing TOC removal from water. However, how these mechanisms contribute respectively to the enhancement has not been well evaluated. This information is critical for further improving the design of the E-peroxone process toward more effective TOC elimination.

To this end, this study investigated TOC removal from oxalic acid (OA) solutions by ozonation, electrolysis, O_3-electrolysis, and E-peroxone treatment. OA is a common intermediate formed in ozonation of many organic pollutants, such as aromatics and natural organic matter (von Gunten, 2003; Vecitis et al., 2010; Panizza and Cerisola, 2009; Brillas et al., 2009; Li et al., 2014). It is essentially unreactive with molecular O_3 ($k_{O3} \leq 0.04\ M^{-1}\ s^{-1}$ (Hoigné and Bader, 1983)), but reacts much faster with •OH ($k_{\cdot OH} = 1.4 \times 10^6\ M^{-1}\ s^{-1}$ (Buxton et al., 1988)) directly to CO_2 and H_2O (Pines and Reckhow, 2002). In addition, OA has high solubility in water and does not volatilize during gas sparging. These characteristics of OA facilitate the evaluation of TOC elimination due to •OH oxidation during the E-peroxone process. The kinetics of TOC elimination in the ozonation, electrolysis, O_3-electrolysis, and E-peroxone processes were analyzed to evaluate the respective contribution of the different •OH generation mechanisms for TOC elimination in the E-peroxone process. The effects of electrodes, current, and ozone concentration on TOC elimination were evaluated systematically for the E-peroxone process.