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

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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 $\bullet OH$ 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 $\bullet OH$, electro-reduction of O_3 to $\bullet OH$ at the cathode, and O_3 decomposition to $\bullet OH$ 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.

Keywords: Advanced oxidation; Ozone; Hydrogen peroxide; Electrocatalytic ozonation; Electrolysis;

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 ($\bullet OH$), 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, Kishimoto et al. 2007,

Kishimoto et al. 2008). During the O₃-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, H₂S₂O₈, and •OH) electrochemically generated at the anode (i.e., indirect electrolysis) (Panizza and Cerisola 2009). In addition, pollutants can be oxidized in the O₃-electrolysis process by •OH generated from cathodically induced reactions, e.g., the electro-reduction of O₃ at the cathode (Eqs. (1–3)) (Kishimoto et al. 2005), as well as the decomposition of O₃ (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 H₂ evolution. As a result of the enhanced •OH generation, the O₃-electrolysis process can considerably improve pollutant degradation (Kishimoto et al. 2005, Kishimoto et al. 2007).

More recently, boron-doped diamond (BDD) electrodes have been used to further enhance TOC removal in the O₃-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 O₃-electrolysis process (Qiu et al. 2014, Bakheet et al. 2014).

90 While the O₃-electrolysis process has considerably enhanced TOC elimination as
 91 compared to the two individual processes, we perceived that it still has vast potential for
 92 improvement. For example, ozone generators usually can convert only a small part of the feed
 93 O₂ gas to O₃. The gas mixture exiting ozone generators thus still contains significant amounts
 94 of O₂, e.g., usually > 90% V/V of the O₂ and O₃ mixture when pure O₂ is used as the feed gas.
 95 However, O₂ has little use for pollutant removal after it is sparged with O₃ into the reactors.
 96 This wastes considerable amounts of O₂ feed gas and energy (e.g., for concentrating O₂ from
 97 air and sparging the gas into the reactor). We therefore proposed to utilize O₂ in the sparged
 98 gas to electro-generate H₂O₂ in the reactor (Eq. (8)), whose conjugated base (HO₂⁻, Eq. (9))
 99 can then react with the sparged O₃ to yield •OH (Eqs. (10), (11), (2) and (3)) (von Sonntag
 100 and von Gunten 2012, Fischbacher et al. 2013, Merenyi et al. 2010b), and thus further
 101 enhance TOC elimination (Yuan et al. 2013). Because the reaction of O₃ with H₂O₂ has been
 102 commonly referred as the “peroxone” reaction, we have termed this electrochemically-driven
 103 process as “electro-peroxone” (E-peroxone) process (Yuan et al. 2013). Note that the overall
 104 peroxone reaction has previously been suggested as Eq. (12) (i.e., two •OH formed per H₂O₂
 105 consumed). However, recent studies suggest that the efficiency of •OH formation is only one
 106 half of that given by the stoichiometry in Eq. (12) because HO₅⁻ (the adduct of O₃ with HO₂⁻,
 107 Eq. (10)) undergoes decomposition to form O₂ and OH⁻ (Eq. (13)) at a comparable rate of Eq.
 108 (11) (Fischbacher et al. 2013).

115 The E-peroxone process can be easily achieved by replacing the metal cathodes used in
 116 previous O₃-electrolysis processes with a carbon-based cathode. In contrast to metal
 117 electrodes that may catalytically decompose H₂O₂ and thus cannot produce H₂O₂ from O₂
 118 (Yuan et al. 2013, Sudoh et al. 1985, Bakheet et al. 2013), carbon-based electrodes (e.g.,
 119 carbon-polytetrafluoroethylene (carbon-PTFE), carbon felt, and activated carbon fiber) can
 120 convert O₂ efficiently to H₂O₂ due to their high overpotential for H₂ evolution and low
 121 catalytic activity for H₂O₂ decomposition (Brillas et al. 2009, Wang et al. 2012, Panizza and
 122 Cerisola 2001).

123 In previous work, we have evaluated the E-peroxone treatment of several different
 124 wastewaters, e.g., landfill leachate and synthetic dyes (Bakheet et al. 2013, Li et al. 2013). It
 125 was found that under similar reaction conditions (e.g., applied current and O₃ dose), the E-
 126 peroxone process removed TOC from the wastewaters much faster than ozonation,
 127 electrolysis, and the O₃-electrolysis process (Bakheet et al. 2013, Li et al. 2013, Wang et al.
 128 2015). This enhancement has been mainly attributed to the significant production of •OH
 129 from several mechanisms in the E-peroxone process, e.g., the aforementioned electro-
 130 reduction of O₃, O₃ decomposition at high local pH near the cathode, and O₃ reaction with
 131 electro-generated H₂O₂ (Bakheet et al. 2013, Li et al. 2013, Wang et al. 2015). These
 132 cathodically-induced •OH can oxidize ozone-refractory compounds (e.g., saturated carboxylic
 133 acids) to CO₂, thus enhancing TOC removal from water. However, how these mechanisms
 134 contribute respectively to the enhancement has not been well evaluated. This information is
 135 critical for further improving the design of the E-peroxone process toward more effective
 136 TOC elimination.

137 To this end, this study investigated TOC removal from oxalic acid (OA) solutions by

138 ozonation, electrolysis, O₃-electrolysis, and E-peroxone treatment. OA is a common
139 intermediate formed in ozonation of many organic pollutants, such as aromatics and natural
140 organic matter (von Gunten 2003, Vecitis et al. 2010, Panizza and Cerisola 2009, Brillas et al.
141 2009, Li et al. 2014). It is essentially unreactive with molecular O₃ ($k_{O_3} \leq 0.04 \text{ M}^{-1}\text{s}^{-1}$ (Hoigné
142 and Bader 1983)), but reacts much faster with •OH ($k_{\bullet OH} = 1.4 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ (Buxton et al.
143 1988)) directly to CO₂ and H₂O (Pines and Reckhow 2002). In addition, OA has high
144 solubility in water and does not volatilize during gas sparging. These characteristics of OA
145 facilitate the evaluation of TOC elimination due to •OH oxidation during the E-peroxone
146 process. The kinetics of TOC elimination in the ozonation, electrolysis, O₃-electrolysis, and
147 E-peroxone processes were analyzed to evaluate the respective contribution of the different
148 •OH generation mechanisms for TOC elimination in the E-peroxone process. The effects of
149 electrodes, current, and ozone concentration on TOC elimination were evaluated
150 systematically for the E-peroxone process.

152 2. Materials and methods

153 2.1. Chemicals and reagents

154 Anhydrous oxalic acid (99.99%), H₂O₂ (30 wt% solution), and potassium indigo trisulfonate
155 (80–85%) were purchased from Sigma-Aldrich. Potassium titanium (IV) oxalate and other
156 chemicals (e.g., Na₂SO₄, NaOH, and H₂SO₄) were analytical grade and purchased from
157 Beijing Chemical Works Co., China. All solutions were prepared with ultrapure water
158 (resistivity >18 MΩ).

160 2.2. Ozonation, electrolysis, O₃-electrolysis, and E-peroxone treatment of OA solution

161 Ozonation, electrolysis, O₃-electrolysis, and E-peroxone treatment of 400 mL OA solution
162 (initial concentration of 180 mg/L) were conducted in an undivided acrylic column reactor

(see Fig. 1). For ozonation treatment, an ozone generator (Tonglin Technology Co., China) was used to produce O_3 from high-purity O_2 gas (99.9%). The O_3 concentration in the ozone generator effluent (O_2 and O_3 gas mixture) can be adjusted by changing the ozone generator power. The ozone generator effluent was then sparged into the reactor at a constant flow rate of 0.4 L/min using a fine bubble diffuser. The electrolysis, O_3 -electrolysis, and E-peroxone treatment were conducted under galvanostatic conditions using a DC power supply. The anode was either a platinum (Pt) sheet or a BDD thin-film electrode purchased from Adamant Technologies (Swiss). The cathode was a stainless steel (SS) plate for the electrolysis and O_3 -electrolysis process and a carbon-PTFE electrode for the E-peroxone process. The carbon-PTFE electrode was prepared with Vulcan XC-72 carbon powder (Cabot Corp., USA), PTFE dispersion, and anhydrous alcohol (Wang et al. 2012). All the electrodes had an exposed area of 20 cm²; this was with the exception of BDD electrode, which had an area of 12.5 cm². Before the BDD electrode was used, it was preconditioned in the blank electrolyte solution (0.05 M Na₂SO₄) at a current density of 20 mA/cm² for 10 min to prevent the accumulation of adsorbed organic compounds on the electrode surface. The distance between the anode and cathode was 2 cm. The supporting electrolyte was a 0.05 M Na₂SO₄ solution. For electrolysis alone, the treatment was initiated by turning on the DC power supply while the ozone generator was off. For O_3 -electrolysis and E-peroxone treatment, the DC power supply and the ozone generator were turned on simultaneously. At applied currents of 100–500 mA, the average cell voltages were 3.9–9.0 V and 6.1–11.4 V for experiments conducted with the Pt and BDD anode, respectively. The ozone generator effluent was bubbled into the reactor at the same flow rate as in ozonation (0.4 L/min). In all experiments, the reactor was placed in a water bath (20 ± 1 °C), and the OA solution was thoroughly agitated with a magnetic stirring bar to achieve a homogeneous solution.

Fig. 1. Schematic of the reactor used for ozonation, electrolysis, O₃-electrolysis, and E-peroxone treatment of oxalic acid solutions.

2.3. Analytical methods

The O₃ concentration in the sparged gas was monitored using an ozone analyzer (UV-300, Sumsun EP Hi-Tech Co., Beijing). During OA treatment, an aliquot of solution sample was collected from the reactor at preset time intervals. The concentration of dissolved ozone in the solution was determined with the indigo method (Bader and Hoigne 1981). The H₂O₂ concentration was measured using potassium titanium (IV) oxalate method (Sellers 1980), whereby H₂SO₄ solution (3 M) was used to adjust the sample pH to ~0 to prevent the interference of O₃ with H₂O₂ measurement (Milan-Segovia et al. 2007, Tong et al. 2011). OA concentration was measured using an HPLC-UV (Waters, USA) with an Atlantis column T (3.5 μ m, 4.6 $\times$ 150 mm, Waters) at 210 nm (Wang et al. 2015). TOC was measured using a TOC-VCPH analyzer (Shimadzu Co. Japan).

3. Results and discussion

3.1. Electro-generation of H₂O₂ from O₂ at the carbon-PTFE cathode

The electro-generation of H₂O₂ from O₂ was evaluated by sparging pure O₂ into a 0.05 M Na₂SO₄ solution during electrolysis using the carbon-PTFE cathode. Fig. 2 shows that for a given applied current, H₂O₂ concentration increased almost linearly with reaction time. In addition, within the tested current range (100–500 mA), H₂O₂ concentration accumulated in the solution (1 h) also increased linearly with the current ($R^2 = 0.997$). This trend indicates that the rate of H₂O₂ generation is not limited by the mass transfer O₂ to the cathode, but by the applied current. The apparent current efficiency for H₂O₂ generation, which was calculated according to Eq. (14), was generally within 86.9–95.9% (see Fig. 2 inset). This

result indicates that H₂O₂ can be efficiently electro-generated from sparged O₂ with high current efficiencies at the carbon-PTFE cathode, and the generation rate can be easily controlled by the applied current.

$$CE(\%) = \frac{nFC_{H_2O_2}V}{\int_0^t Idt} \times 100 \quad (14)$$

where n is the number of electrons consumed for converting O₂ to H₂O₂ (2 electrons), F is the Faraday constant (96486 C/mol), C_{H₂O₂} is the concentration of H₂O₂ produced (mol/L), V is the solution volume (L), I is the current (A), and t is the electrolysis time (s).

Fig. 2. Electro-generation of H₂O₂ from sparged O₂ at the carbon-PTFE cathode (400 mL of 0.05 M Na₂SO₄ solution; O₂ gas flow rate of 0.4 L/min; 20 cm² carbon-PTFE cathode; 2 cm² Pt anode). The inset plot shows the concentration of H₂O₂ at 1 h and the current efficiency (CE) of H₂O₂ production as a function of the applied current.

3.2. Comparison of ozonation, electrolysis, O₃-electrolysis, and electro-peroxone process

TOC elimination from OA solutions by ozonation, electrolysis with the Pt anode and SS cathode (Pt/SS), O₃-electrolysis (Pt/SS), and E-peroxone (Pt/carbon-PTFE) process are compared in Fig. 3. The OA solution had an initial pH of 3, whereby OA is present predominantly as HC₂O₄⁻ (accounting for ~93% of the total OA (Vecitis et al. 2010)). Similar to oxalic acid, HC₂O₄⁻ reacts with O₃ very slowly (k_{O₃} = 5 × 10⁻⁴ M⁻¹s⁻¹) (Vecitis et al. 2010), but much faster with •OH (k_{•OH} = 3.2 × 10⁷ M⁻¹s⁻¹) (Buxton et al. 1988). As Fig. 4(a) shows, the solution pH was quite stable during the ozonation treatment. Oxidation of OA by •OH formed from O₃ decomposition with OH⁻, which occurs primarily at basic pH, is thus negligible in the ozonation treatment. Consequently, TOC was hardly removed by ozonation alone (Fig. 3). In comparison, electrolysis with the Pt anode and SS cathode removed 34.6%

TOC after 2 h. This result agrees with the previous finding that OA can be electrochemically mineralized at Pt anodes during electrolysis (Martinez-Huitle et al. 2004). However, the mineralization current efficiency (MCE, calculated according to Eq. (15) (Garcia-Segura and Brillas 2011)) was just 1.9% during the electrolysis process. This low MCE value indicates that OA mineralization is kinetically limited by its mass transfer to the Pt anode, and significant amounts of electricity are wasted in side reactions such as O₂ evolution during the electrolysis process.

$$\text{MCE}(\%) = \frac{nFV_s\Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7 \text{ mIt}} \times 100 \quad (15)$$

where n is the number of electrons consumed for mineralization of oxalic acid (2 electrons), F is the Faraday constant, V_s is the solution volume (L), Δ is the experimental TOC removal (mg/L), 4.32×10^7 is an homogenization factor ($3600 \text{ s/h} \times 12000 \text{ mg/mol}$), m is the number of carbon atoms of oxalic acid (2 C atoms), I is the current (A), and t is the electrolysis time (h).

Notably, TOC removal was significantly enhanced when ozonation and electrolysis were combined together (see Fig. 3). For the O₃-electrolysis process that used the Pt anode and SS cathode, TOC removal reached 70.2% at 2 h. Adapting the O₃-electrolysis process to E-peroxone process (i.e., changing the cathode from SS to carbon-PTFE) further significantly increased TOC elimination yield, which reached 95.3% after 1 h of the E-peroxone treatment (Fig. 3).

Fig. 3. TOC elimination by ozonation, electrolysis (Pt anode and SS cathode), O₃-electrolysis (Pt anode and SS cathode), and E-peroxone (Pt anode and carbon-PTFE cathode) processes (initial OA concentration = 2 mM; volume = 400 mL; sparging gas flow rate = 0.4 L/min; inlet O₃ gas phase concentration = 100 mg/L; current = 400 mA; average cell voltage = 7.8 V).

The above results agree with the previous finding that ozonation and electrolysis can have significant synergistic effects for TOC elimination when they are coupled together, especially, in the form of E-peroxone process (Yuan et al. 2013, Bakheet et al. 2013). To get more insight into the synergy, we monitored the evolution profiles of aqueous O_3 and H_2O_2 during the different processes (see Fig. 4). For ozonation alone, the aqueous O_3 concentration increased rapidly to a pseudo-steady level (~ 30 mg/L) in equilibrium with its gas phase concentration (~ 100 mg/L) in the sparged gas (Fig. 4(b)). In comparison, the aqueous O_3 concentration fluctuated slightly at lower levels ($\sim 23 \pm 3$ mg/L) during the O_3 -electrolysis process. This difference can be attributed to the consumption of dissolved O_3 in the O_3 -electrolysis process, e.g., electro-reduction of O_3 at the cathode and O_3 decomposition with OH^- near the cathode (Kishimoto et al. 2008). These reactions transform O_3 to $\bullet OH$, and can thus enhance OA oxidation in the O_3 -electrolysis process (see Fig. 3) (Qiu et al. 2014, Kishimoto et al. 2007, Kishimoto et al. 2008).

Adapting the O_3 -electrolysis to E-peroxone process (i.e., changing the cathode from SS to carbon-PTFE) further considerably decreased aqueous O_3 concentration (Fig. 4(b)). This result indicates that aqueous O_3 is more rapidly consumed in the E-peroxone process than in the O_3 -electrolysis process. As aforementioned, SS and other metal (e.g., Cu and Ti) electrodes cannot produce H_2O_2 from O_2 (Sudoh et al. 1985, Li et al. 2013), whereas carbon-based electrodes can effectively convert O_2 to H_2O_2 (see Fig. 2). The in-situ generated H_2O_2 then diffuses into the bulk solution and reacts with O_3 to yield $\bullet OH$. Thus, in addition to being transformed to $\bullet OH$ via reactions such as O_3 electro-reduction and O_3 decomposition with OH^- at the cathode in the O_3 -electrolysis process, extra O_3 can be transformed to $\bullet OH$ via the electrochemically driven peroxone reaction in the E-peroxone process. Consequently, both O_3 consumption and TOC elimination were considerably increased by adapting the O_3 -electrolysis process to the E-peroxone process.

Fig. 4. Profiles of (a) pH, (b) aqueous O_3 , and (c) H_2O_2 during ozonation, electrolysis (Pt anode and SS cathode), O_3 -electrolysis (Pt anode and SS cathode), and E-peroxone (Pt anode and carbon-PTFE cathode) processes (initial OA concentration = 2 mM; volume = 400 mL; sparging gas flow rate = 0.4 L/min; inlet O_3 gas phase concentration = 100 mg/L; current = 400 mA; average cell voltage = 7.8 V).

The evolution of H_2O_2 during the four different processes is compared in Fig. 4(c). Virtually no H_2O_2 was detected during the ozonation, electrolysis (Pt/SS), and O_3 -electrolysis (Pt/SS) processes. In contrast, high concentrations of H_2O_2 (up to 43.7 mg/L) were detected at the early stage (15–30 min) of the E-peroxone process. During the same period, TOC was also rapidly removed from the OA solution (see Fig. 3). These results confirm that when carbon-PTFE electrode is used as the cathode, considerable amounts of H_2O_2 can be generated in the E-peroxone process, and thus significantly enhance O_3 transformation to $\bullet OH$ for pollutant degradation.

Interestingly, the concentration of H_2O_2 increased rapidly in the first 15 min of the E-peroxone process, and then decreased considerably with further increase of the reaction time (Fig. 4(c)). This trend indicates that H_2O_2 was produced more rapidly than it was consumed at the early stage of E-peroxone treatment, whereas it was consumed more rapidly than it was produced after 15 min. This change can be possibly explained as follows.

In the E-peroxone process, H_2O_2 is produced stably from O_2 at the carbon-PTFE cathode (see Fig. 2), and then consumed mainly in the reaction with O_3 to yield $\bullet OH$ (H_2O_2 itself does not react actively with OA (Vecitis et al. 2010)). However, the reaction of $\bullet OH$ with OA can initiate a series of radical-chain reactions (Eqs. (16)–(19)) through which H_2O_2 is regenerated during OA oxidation to CO_2 (Vecitis et al. 2010, Martinez-Huitle et al. 2004, Garcia-Segura

and Brillas 2011). The regenerated H_2O_2 , together with the electro-generated H_2O_2 , can then further react with O_3 to yield $\bullet\text{OH}$, thus multiplying the chain-reaction loop shown in Fig. 5. As shown, the chain reactions are initiated by the reaction of OA with $\bullet\text{OH}$. The rate of H_2O_2 regeneration is thus expected to be proportional to the OA concentration in the solution. This may explain why H_2O_2 is produced more rapidly (from both electro-generation and chain-reaction regeneration) than it is consumed at the early stage of E-peroxone process when OA concentration is still high. However, as OA is rapidly removed from the solution, the rate of H_2O_2 regeneration decreases considerably. This led to the decrease of H_2O_2 concentration as the E-peroxone process proceeded. Finally, H_2O_2 regeneration via the chain-reaction loop stops after OA is completely eliminated from the solution. Only insignificant amount of H_2O_2 was detected at the late stage (60–120 min) of the E-peroxone process (Fig. 4(c)), suggesting that the electro-generated H_2O_2 is almost completely consumed in the reaction with O_3 .

Fig. 5. Schematic of radical-chain reactions that regenerate H_2O_2 during bioxalate oxidation in the E-peroxone process.

It should be pointed out that similar chain-reaction loop for H_2O_2 regeneration has also been suggested during OA oxidation by other AOPs (e.g., electro-Fenton and sonozone (combined process of ultrasonic and O_3)), and considered an important mechanism for enhanced TOC elimination in these processes (Vecitis et al. 2010, Garcia-Segura and Brillas

2011). However, this chain-reaction loop is unlikely to occur at typical pH values (~6–8) of water treatment, whereby $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ ($\text{pK}_a = 4.8$) exists mainly as $\text{O}_2^{\bullet-}$ (Bielski et al. 1985). At typical pH range of water treatment, the reaction of $\text{O}_2^{\bullet-}$ with H^+ to $\text{HO}_2^\bullet$ is therefore unfavorable, and $\text{O}_2^{\bullet-}$ would be more likely scavenged rapidly by O_3 (Eq. (6), $k = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (von Gunten 2003)).

3.3. Effect of anode type on TOC elimination

The above results indicate that the type of cathode (SS or carbon-PTFE) can play a critical role in TOC removal in combined processes of ozonation and electrolysis (O_3 -electrolysis or E-peroxone). To investigate the role of anode in TOC elimination, we replaced the Pt anode with a BDD anode and repeated the above tests. Because BDD has a greater O_2 -overpotential than Pt (Panizza and Cerisola 2009), the average cell voltage increased from ~7.8 V to ~10.2 V (current = 400 mA) when the Pt anode was replaced by the BDD anode. The result shows that TOC was removed at comparable rates when either Pt or BDD was used as the anode in the electrolysis and E-peroxone processes (see Fig. 3 and 6). However, for the O_3 -electrolysis process, TOC was removed much more rapidly when BDD was used as the anode (97.6% at 2 h) than when Pt was used (70.2% at 2 h). This result suggests that the type of anode can also have complicated influence on TOC elimination in combined processes of ozonation and electrolysis.

Fig. 6. TOC elimination by ozonation, electrolysis (BDD anode and SS cathode), O_3 -electrolysis (BDD anode and SS cathode), and E-peroxone (BDD anode and carbon-PTFE cathode) processes (initial OA concentration = 2 mM; volume = 400 mL; sparging gas flow rate = 0.4 L/min; inlet O_3 gas phase concentration = 100 mg/L; current = 400 mA; average cell voltage = 10.2 V).

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362 Unlike Pt anodes, which are inefficient at producing •OH from water discharge, BDD
363 anodes are well-known for their high activity for •OH generation when electrolysis is
364 operated at anodic potentials higher than for oxygen evolution (2.3 V vs. SHE for BDD)
365 (Panizza and Cerisola 2009, Bejan et al. 2012). Therefore, OA is oxidized via distinct
366 mechanisms in electrolysis that uses Pt or BDD anode (Martinez-Huitle et al. 2004, Garcia-
367 Segura and Brillas 2011, Scialdone et al. 2008). When Pt is used as the anode, OA is mainly
368 oxidized via direct electron transfer after it has been adsorbed onto the anode surface (Eqs.
369 (20) and (21)). In contrast, OA is mainly oxidized by •OH produced from water oxidation
370 when BDD is used as the anode (Eqs. (16–18)) (Martinez-Huitle et al. 2004, Garcia-Segura
371 and Brillas 2011, Scialdone et al. 2008). Despite the different reaction mechanisms, previous
372 studies have indicated that OA can be effectively oxidized by electrolysis using either Pt or
373 BDD anode (Martinez-Huitle et al. 2004). Consistently, the present study shows that OA was
374 oxidized at similar rates in the electrolysis process using the Pt or BDD anode (Fig. 3 and 6).

377 However, using BDD as the anode in the O₃-electrolysis process resulted in much higher
378 TOC elimination yield (97.6% at 2 h) than using Pt as the anode (70.2% at 2 h). This
379 difference can be probably attributed to the fact that BDD anode is effective at producing •OH
380 from water discharge, whereas Pt anode is not. Previous studies have indicated that some •OH
381 generated at the BDD anode would undergo recombination to form H₂O₂ (Panizza and
382 Cerisola 2009). Indeed, we found that small amounts of H₂O₂ (4.1 mg/L at 2 h) accumulated
383 in the solution when BDD was used as the anode in electrolysis alone. In contrast, no H₂O₂
384 accumulation was observed for the electrolysis process using the Pt anode (see Fig. 4(c)). In
385 electrolysis alone, the BDD anode-induced H₂O₂ would not contribute much to TOC removal

because H_2O_2 reacts with OA very slowly ($k < 0.2 \text{ M}^{-1}\text{s}^{-1}$ (Vecitis et al. 2010)). However, it can react with sparged O_3 to yield $\bullet\text{OH}$, thus enhancing OA oxidation in the O_3 -electrolysis process. This explains why using the BDD anode resulted in more rapid TOC elimination than using the Pt anode in the O_3 -electrolysis process (see Fig. 3 and 6).

Unlike in the O_3 -electrolysis process, the type of anode had little influence on TOC elimination rates in the E-peroxone process. As shown in Fig. 3 and 6, TOC was actually removed at almost the same rate when either Pt or BDD was used as the anode in the E-peroxone process. This result is possibly because as H_2O_2 is generated from O_2 much more rapidly at the carbon-PTFE cathode (Fig. 2), the contribution of BDD anode for H_2O_2 generation is negligible in the E-peroxone process.

3.4. Evaluation of the synergy for TOC elimination in the E-peroxone process

Kinetic analysis shows that TOC elimination follows pseudo-first-order kinetics in all processes, i.e., ozonation, electrolysis, O_3 -electrolysis, and E-peroxone process (see Table 1). Notably, the apparent rate constants of TOC elimination (k_{app}) in the O_3 -electrolysis and E-peroxone processes are significantly higher than the linear addition of the individual rates of corresponding ozonation and electrolysis processes. This result confirms that when ozonation and electrolysis are combined together (O_3 -electrolysis and E-peroxone), they have significant synergistic effects for TOC elimination.

Table 1. Pseudo-first-order rate constants and square regression coefficient for elimination of oxalic acid in different processes.

In previous studies, this synergy has been mainly attributed to the production of $\bullet\text{OH}$ from several mechanisms in the E-peroxone process, e.g., cathodic reduction of O_3 , O_3

decomposition near the cathode, and O₃ reaction with H₂O₂ electro-generated at the carbon-PTFE cathode (Yuan et al. 2013, Bakheet et al. 2013). In addition, the present study shows that when BDD is used as the anode, it can also produce small amounts of H₂O₂ from the self-termination reaction of BDD(•OH). The anode-induced H₂O₂ can also react with O₃ to yield •OH, and thus enhance TOC elimination (this effect is quite pronounced in the O₃-electrolysis process, but is negligible in the E-peroxone process, see discussion of Fig. 6).

To evaluate the respective contribution of the above mechanisms for TOC elimination, an approach similar to that proposed by Hoffmann's group (Vecitis et al. 2010, Weavers et al. 1998, Lesko et al. 2006) for sonozone process was taken to analyze the kinetics of TOC abatement in the O₃-electrolysis and E-peroxone processes. As shown in Eq. (22), the overall removal rate of OA in the combined processes of ozonation and electrolysis can be described by a linear combination of contributing terms.

$$-\frac{dC}{dt} = k_{O_3}[C] + k_E[C] + k_{O_3/E}[C] \quad (22)$$

where k_{O_3} , k_E , and $k_{O_3/E}$ are the pseudo-first-order rate constants of TOC elimination for ozonation, electrolysis, and the synergistic kinetic effect upon combining the two systems (O₃-electrolysis or E-peroxone), respectively.

When the terms are combined, Eq. (23) can be expressed as

$$-\frac{dC}{dt} = (k_{O_3} + k_E + k_{O_3/E})[C] = k_{\text{overall}}[C] \quad (23)$$

where k_{overall} is the overall pseudo-first reaction rate constant in the O₃-electrolysis and E-peroxone processes (i.e., those listed in Table 1).

The enhancement of OA elimination in O₃-electrolysis and E-peroxone processes is then calculated according to Eq. (24) (Weavers et al. 1998).

$$\text{Enhancement } (\%) = \frac{k_{O_3/E}}{k_{O_3} + k_E} \times 100 \quad (24)$$

The calculations show that O_3 -electrolysis using the Pt anode and SS cathode enhanced the rate of OA elimination by 155% (Table 1), which can be mainly attributed to the electro-reduction of O_3 to $\bullet OH$ at the SS cathode and O_3 decomposition to $\bullet OH$ near the cathode (Kishimoto et al. 2005). Using BDD as the anode in O_3 -electrolysis further increased the enhancement factor to 249%, probably due to the formation of small amounts of H_2O_2 at the BDD anode. Notably, by simply replacing the SS cathode with the carbon-PTFE cathode to electrochemically generate H_2O_2 from O_2 (i.e., adapting O_3 -electrolysis for E-peroxone), the enhancement factor increased dramatically to 1252 and 1016% for the E-peroxone with the Pt and BDD anode, respectively.

The kinetic analysis confirms that electro-generation of H_2O_2 at the carbon-PTFE cathode and its subsequent reaction with sparged O_3 to produce $\bullet OH$ are the most important mechanism for the enhanced pollutant degradation in the E-peroxone process. In comparison, O_3 reduction at the cathode, O_3 decomposition to $\bullet OH$ near the cathode, and H_2O_2 generation at the BDD anode contribute much less to the enhancement. Indeed, because O_3 has a low solubility in water, the rate of electro-reduction of O_3 to $\bullet OH$ is often kinetically limited by the mass transfer of O_3 to the cathode (Kishimoto et al. 2005, Bakheet et al. 2013)). Moreover, O_3 reacts only slowly with OH^- ($k = 70 \text{ M}^{-1} \text{ s}^{-1}$ (von Gunten 2003)). Consequently, cathodic reduction of O_3 to $\bullet OH$ and O_3 decomposition with OH^- to $\bullet OH$ enhanced TOC elimination just moderately (e.g., enhancement factor of 155–249% for the O_3 -electrolysis process using the SS cathode).

In comparison, Fig. 2 shows that H_2O_2 can be produced efficiently at the carbon-PTFE cathode (e.g., current efficiencies of 86.9–95.9%), and no mass transfer limitation of O_2 on H_2O_2 electro-generation was observed within the tested current range (100–500 mA). More importantly, H_2O_2 has much longer life time than $\bullet OH$. The electro-generated H_2O_2 can therefore diffuse out of the cathodic diffusion layer to react with O_3 in the bulk solution.

Consequently, considerable amounts of $\bullet\text{OH}$ can be generated to oxidize pollutants rapidly in the bulk solution. This circumvents the intrinsic limitation of electrolysis for pollutant degradation, i.e., the degradation kinetics of pollutants is limited by their mass transfer to the anode (Yuan et al. 2013, Li et al. 2014). Therefore, the E-peroxone process can eliminate TOC from water much more rapidly than ozonation, electrolysis, and O_3 -electrolysis processes.

3.5. Comparison with conventional peroxone process

Fig. 7 shows TOC removal from OA solutions by the E-peroxone and conventional peroxone process, in which H_2O_2 was externally added. Based on the result reported in Fig. 2, approximately 480 mg of H_2O_2 can be electro-generated during 2 h of the E-peroxone process operated at 400 mA. The same amount of H_2O_2 was therefore added in the conventional peroxone process. To minimize the side reaction of H_2O_2 with $\bullet\text{OH}$ (Eq. (25)), which may occur to some extent at high H_2O_2 concentrations (Vecitis et al. 2010, Li et al. 2013), one-eighth of the total H_2O_2 dose (480 mg) was stepwise added into the OA solution every 15 min during the 2 h of conventional peroxone process (e.g., add ~ 60 mg H_2O_2 at 0, 15, and 30 min, respectively).

As shown in Fig. 7, TOC was removed from OA solution more rapidly by conventional peroxone process than the E-peroxone process during the first 30 min. This difference can be mainly attributed to the different way of H_2O_2 supplying in the two processes. For the conventional peroxone process, approximately 60 mg H_2O_2 was added into OA solution at 0 min, whereas it took 15 min for the E-peroxone process to generate the same amount of H_2O_2 in the solution. Therefore, it is assumable that the “startup” of the peroxone reaction (and chain-reaction loop for H_2O_2 regeneration) would be more intense in the conventional peroxone process than in the E-peroxone process, leading to more rapid TOC removal at the

initial stage of conventional peroxone process. However, similar TOC removal efficiency was obtained for the two processes after 1 h treatment (Fig. 7) when considerable amount of H_2O_2 had been continuously electro-generated in the E-peroxone process.

Fig. 7. Comparison of TOC removal by conventional peroxone and electro-peroxone processes (initial OA concentration = 2 mM; volume = 400 mL; sparging gas flow rate = 0.4 L/min; inlet O_3 gas phase concentration = 100 mg/L; 20 cm² carbon-PTFE cathode; 20 cm² Pt anode; current = 400 mA for electro-peroxone; average cell voltage = 7.8 V; addition of 480 mg H_2O_2 for conventional peroxone process).

The above comparison suggests that the E-peroxone process may provide a comparably effective way to degrade pollutants as conventional peroxone process. Meanwhile, the electro-generation of H_2O_2 eliminates the potential risks associated with the transportation, storage, and use of high concentration H_2O_2 solutions in conventional peroxone process. Furthermore, when BDD is used as the anode, the E-peroxone process can anodically oxidize refractory Fe^{3+} -oxalate complexes that resist oxidation by aqueous $\bullet\text{OH}$, hence improving TOC removal from wastewater that contains Fe^{3+} ions (see SD for more detail). Compared with conventional peroxone process, the E-peroxone process may thus offer a safer and more convenient alternative for water and wastewater treatment.

3.6. Effects of applied current on TOC elimination in E-peroxone

Fig. 8 shows that as the applied current was increased from 100 to 400 mA (average cell voltage increased from 6.1 to 10.2 V), TOC was more rapidly eliminated from OA solutions. Nevertheless, further increasing the current to 500 mA (average cell voltage = 11.4 V) did not increase TOC elimination yet further. Similar trends have been observed in our previous E-

peroxone studies (Yuan et al. 2013, Bakheet et al. 2013). As Fig. 2 shows, the rate of H₂O₂ production is proportional to the applied current within the tested current range (100–500 mA). It was therefore anticipated that increasing the current would produce more H₂O₂ to react with O₃, hence yielding more •OH to enhance TOC elimination. However, our previous studies have found that under similar reaction conditions (e.g., reactor configuration, O₃ dosage, and electrodes), the •OH generation rate would become limited by the mass transfer of O₃ from the gas phase to liquid when the current is increased beyond 400 mA (Yuan et al. 2013, Bakheet et al. 2013). When there is insufficient aqueous O₃ to react with electro-generated H₂O₂, the excess H₂O₂ contributes less to TOC elimination since it reacts only slowly with OA ($k < 0.2 \text{ M}^{-1}\text{s}^{-1}$ (Vecitis et al. 2010)). Therefore, TOC elimination kinetics increased as the current was increased from 100 to 400 mA, but did not further increase by further increasing the applied current.

Fig. 8. Effects of applied current on TOC elimination in the E-peroxone process (initial OA concentration = 2 mM; volume = 400 mL; 20 cm² carbon-PTFE cathode; 12.5 cm² BDD anode; sparging gas flow rate = 0.4 L/min; inlet O₃ gas phase concentration = 100 mg/L).

3.7. Effects of O₃ concentration on TOC elimination in E-peroxone

As the O₃ concentration in the sparged gas was increased, TOC was removed from OA solutions more rapidly (Fig. 9). This can be easily rationalized because increasing the O₃ concentration in the sparged gas enhances the mass transfer of O₃ from the gas phase to the liquid. Consequently, more •OH can be generated from reactions such as O₃ reaction with H₂O₂ and O₃ cathodic reduction, resulting in enhanced TOC elimination in the E-peroxone process. Note that sparging pure O₂ (i.e., O₃ = 0 mg/L) during electrolysis using the carbon-PTFE cathode can produce significant amount of H₂O₂ in the solution (~600 mg/L at 400 mA,

see Fig. 2). Sparging pure O₂ thus enhanced TOC elimination slightly (44.9%) compared with electrolysis alone (39.2%) (see Fig. 6), although the reaction of H₂O₂ with OA is slow ($k < 0.2 \text{ M}^{-1}\text{s}^{-1}$ (Vecitis et al. 2010)).

Fig. 9. Effects of ozone concentration on TOC elimination in the E-peroxone process (initial OA concentration = 2 mM; volume = 400 mL; 20 cm² carbon-PTFE cathode; 12.5 cm² BDD anode; sparging gas flow rate = 0.4 L/min; current = 400 mA; average cell voltage = 10.2 V).

The results of this study show that the E-peroxone process can considerably enhance TOC removal from OA solutions as compared to ozonation, electrolysis, and O₃-electrolysis processes. This enhancement is mainly because significant amounts of •OH can be generated from electrochemically induced reactions such as O₃ with electro-generated H₂O₂ and O₃ electro-reduction at the cathode in the E-peroxone process. The electrochemically induced •OH can then oxidize ozone-refractory OA directly to CO₂ and H₂O. As a result, complete OA mineralization can be obtained by the E-peroxone process. However, it should be noted the present study was conducted under conditions that are different from typical conditions of water treatment. For example, all experiments were conducted in acidic OA solutions (pH ~3) prepared with ultrapure water; these conditions were employed to prevent •OH formation from O₃ reactions with OH⁻ (although this reaction is very slow and possibly tolerable at pH ~7) and other matrix components (e.g., natural organic matter (NOM)) in the bulk solution (von Gunten 2003, Pocostales et al. 2010), which would complicate the evaluation of the role of electrochemically induced •OH in the E-peroxone process. By contrast, typical water treatment involving ozone based processes is usually operated at pH of 6–9, and real water may contain some matrix components (e.g., NOM) that can react with O₃ to form •OH (von Sonntag and von Gunten 2012, Pocostales et al. 2010). It is therefore expected that a

distinctive oxidation of OA may occur under conditions of conventional ozonation. In addition, due to the small OA solution volume (400 mL) used in this study, much higher O₃ doses (e.g. ~100 mg/L gas phase) than typical conditions of water treatment were used to enhance O₃ mass transfer from the gas phase to liquid phase. Therefore, it is expected that complete mineralization of pollutants is unlikely to occur under typical conditions of water treatment, considering the presence of many side reactions with other water matrix components (e.g., NOM and carbonates) and the high energy demand to treat to such an extent. More research is needed to evaluate the performance and energy cost of the E-peroxone process for pollutant degradation under typical conditions of water treatment.

4. Conclusions

This study demonstrates that when conventional ozonation and electrolysis are combined in the E-peroxone process, they can achieve a significant synergy for TOC elimination from water. This synergy can be mainly attributed to several mechanisms that enhance O₃ transformation to •OH in the E-peroxone system, e.g., electro-generation of H₂O₂ from O₂ at the carbon-PTFE cathode and its subsequent peroxone reaction with O₃ to •OH, electro-reduction of O₃ to •OH at the cathode, and O₃ decomposition to •OH near the cathode. Among those, the electrochemically-driven peroxone reaction is the most important mechanism for the enhanced TOC elimination, while the other mechanisms contribute much less. Effective generation of H₂O₂ from O₂ at the cathode is thus the key to maximize TOC elimination in the E-peroxone process.

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Fig. 9. Effects of ozone concentration on TOC elimination in the E-peroxone process (initial OA concentration = 2 mM; volume = 400 mL; 20 cm² carbon-PTFE cathode; 12.5 cm² BDD anode; sparging gas flow rate = 0.4 L/min; current = 400 mA; average cell voltage = 10.2 V).

Table 1. Pseudo-first-order rate constants and square regression coefficient for mineralization of oxalic acid in different processes.

Process	Anode	Cathode	$K_{overall} \times 10^3 \text{ (min}^{-1}\text{)}$	r^2	Enhancement (%)
Ozonation	-	-	0.48	0.999	-
Electrolysis	Pt	SS	3.45	0.996	-
Electrolysis	BDD	SS	3.98	0.994	-
O ₃ -electrolysis	Pt	SS	10.02	0.998	155
O ₃ -electrolysis	BDD	SS	15.55	0.994	249
E-peroxone	Pt	Carbon-PTFE	53.10	0.970	1252
E-peroxone	BDD	Carbon-PTFE	49.76	0.984	1016

Figure 1

Fig. 1. Schematic of the reactor used for ozonation, electrolysis, O_3 -electrolysis, and E-peroxone treatment of oxalic acid solutions.

Figure 2

Fig. 2. Electro-generation of H_2O_2 from sparged O_2 at the carbon-PTFE cathode (400 mL of 0.05 M Na_2SO_4 solution; O_2 gas flow rate of 0.4 L/min; 20 cm^2 carbon-PTFE cathode; 2 cm^2 Pt anode). The inset plot shows the concentration of H_2O_2 at 1 h and the current efficiency (CE) of H_2O_2 production as a function of the applied current.

Figure 3

Fig. 3. TOC elimination by ozonation, electrolysis (Pt anode and SS cathode), O₃-electrolysis (Pt anode and SS cathode), and E-peroxone (Pt anode and carbon-PTFE cathode) processes (initial OA concentration = 2 mM; volume = 400 mL; sparging gas flow rate = 0.4 L/min; inlet O₃ gas phase concentration = 100 mg/L; current = 400 mA; average cell voltage = 7.8 V).

Figure 4

Fig. 4. Profiles of (a) pH, (b) aqueous O_3 , and (c) H_2O_2 during ozonation, electrolysis (Pt anode and SS cathode), O_3 -electrolysis (Pt anode and SS cathode), and E-peroxone (Pt anode and carbon-PTFE cathode) processes (initial OA concentration = 2 mM; volume = 400 mL; sparging gas flow rate = 0.4 L/min; inlet O_3 gas phase concentration = 100 mg/L; current = 400 mA; average cell voltage = 7.8 V).

Figure 5

Fig. 5. Schematic of radical-chain reactions that regenerate H_2O_2 during bioxalate oxidation in the E-peroxone process.

Figure 6

Fig. 6. TOC elimination by ozonation, electrolysis (BDD anode and SS cathode), O₃-electrolysis (BDD anode and SS cathode), and E-peroxone (BDD anode and carbon-PTFE cathode) processes (initial OA concentration = 2 mM; volume = 400 mL; sparging gas flow rate = 0.4 L/min; inlet O₃ gas phase concentration = 100 mg/L; current = 400 mA; average cell voltage = 10.2 V).

Figure 7

Fig. 7. Comparison of TOC removal by conventional peroxone and electro-peroxone processes (initial OA concentration = 2 mM; volume = 400 mL; sparging gas flow rate = 0.4 L/min; inlet O_3 gas phase concentration = 100 mg/L; 20 cm² carbon-PTFE cathode; 20 cm² Pt anode; current = 400 mA for electro-peroxone; addition of 480 mg H_2O_2 for conventional peroxone process).

Figure 8

Fig. 8. Effects of applied current on TOC elimination in the E-peroxone process (initial OA concentration = 2 mM; volume = 400 mL; 20 cm² carbon-PTFE cathode; 12.5 cm² BDD anode; sparging gas flow rate = 0.4 L/min; inlet O₃ gas phase concentration = 100 mg/L).

Figure 9

Fig. 9. Effects of ozone concentration on TOC elimination in the E-peroxone process (initial OA concentration = 2 mM; volume = 400 mL; 20 cm² carbon-PTFE cathode; 12.5 cm² BDD anode; sparging gas flow rate = 0.4 L/min; current = 400 mA; average cell voltage = 10.2 V).