Perchlorate formation during the electro-peroxone treatment of chloride-containing water: Effects of operational parameters and control strategies

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ABSTRACT

This study investigated the degradation of clofibric acid and formation of perchlorate during the electro-peroxone (E-peroxone) treatment of chloride-containing (26.1–100 mg L^{-1}) water (Na$_2$SO$_4$ electrolytes and secondary effluents). The E-peroxone process involves sparging O$_2$ and O$_3$ gas mixture into an electrolysis reactor where a carbon-based cathode is used to electrochemically convert the sparged O$_2$ to H$_2$O$_2$. The electro-generated H$_2$O$_2$ then reacts with sparged O$_3$ to produce ·OH, which can rapidly oxidize pollutants in the bulk solution. When boron-doped diamond (BDD) electrodes were used as the anode, perchlorate concentrations increased significantly from undetectable levels to ~15–174 mg L^{-1} in the different water samples as the applied current density was increased from 4 to 32 mA cm^{-2}. In contrast, no ClO$_4^-$ was detected when Pt/Ti anodes were used in the E-peroxone process operated under similar reaction conditions. In addition, when sufficient O$_3$ was sparged to maximize ·OH production from its peroxone reaction with electro-generated H$_2$O$_2$, the E-peroxone process with Pt/Ti anodes achieved comparable clofibric acid degradation and total organic carbon (TOC) removal yields as that with BDD anodes, but did not generate detectable ClO$_4^-$. These results indicate that by optimizing operational parameters and using Pt/Ti anodes, the E-peroxone process can achieve the goal of both fast pollutant degradation and ClO$_4^-$ prevention during the treatment of chloride-containing wastewater.

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1. Introduction

The electro-peroxone (E-peroxone) process is a promising electrochemically-driven advanced oxidation process (AOP) that has shown great potential for water and wastewater treatment (Li et al., 2015b, 2013; Wang et al., 2015a; Yuan et al., 2013). The E-peroxone process couples conventional ozonation with electrolysis process, and uses a carbon-based cathode to electrochemically convert O$_2$ in the sparged ozone generator effluents (O$_2$ and O$_3$ gas mixture) to H$_2$O$_2$ (Eq. (1)) (Yuan et al., 2013). The in-situ generated H$_2$O$_2$ then reacts with the sparged O$_3$ via the so-called peroxone reaction (Eq. (2)) to yield hydroxyl radical (·OH) (Bakheet et al., 2013; Li et al., 2013), which is a very powerful oxidant and can non-selectively oxidize most organic solutes at diffusion control limited rates. Previous work has indicated that by electrochemically

driving the peroxone reaction to produce ·OH in the bulk solution, the E-peroxone process can overcome several inherent limitations of conventional ozonation and electrolysis processes for organic pollutant degradation, e.g., the selective oxidation with O$_3$ and the limitation of pollutant mass transfer to the electrodes on their degradation kinetics (Bakheet et al., 2013). Consequently, the E-peroxone process can greatly improve the kinetics and energy efficiency for the degradation of pollutants, especially ozone-refractory pollutants such as 1,4-dioxane, ibuprofen, and oxalic acid (Li et al., 2014; Wang et al., 2015a, 2015b).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

$$H_2O_2 + 2O_3 \rightarrow 2\cdot OH + 3O_2 \qquad (2)$$
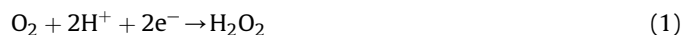
Besides enhancing pollutant degradation, the E-peroxone process can inhibit the formation of some undesired by-products (e.g., polymers and bromate) that would otherwise form during conventional electrolysis and ozonation processes (Bakheet et al., 2014;
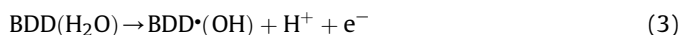

Li et al., 2015b). For example, we have found that the adaption of conventional ozonation to the E-peroxone process can inhibit the formation of carcinogenic bromate (BrO_3^-) during the treatment of bromide-containing water (Li et al., 2015b), which has been a major drawback associated with conventional ozonation process (von Gunten, 2003). This improvement is mainly because electro-generated H_2O_2 can rapidly reduce $HBrO/BrO^-$ (a key intermediate for BrO_3^- formation) back to Br^- (von Gunten and Hoigne, 1994), thus preventing their further oxidation to BrO_3^- (Li et al., 2015b). These promising results suggest that by electrochemically producing H_2O_2 in situ from O_2 that would otherwise be wasted in conventional ozonation process, the E-peroxone process may provide a simple and effective way to improve the performance of existing ozonation systems that are widely used in water and wastewater treatment.

Similar to Br^-, chloride (Cl^-) is another halide element that is ubiquitously present in natural water and wastewater, ranging from several mg L^{-1} for fresh water to thousands mg L^{-1} for high salinity water (Bagastyo et al., 2012; Bergmann et al., 2009; Jung et al., 2010; Wang et al., 2012; Zöllig et al., 2015). A vast number of studies have indicated that during electrochemical treatment, Cl^- may be oxidized to undesired oxychlorine species such as chlorate (ClO_3^-) and perchlorate (ClO_4^-) at the anode (Azizi et al., 2011; Bergmann et al., 2014, 2009; Hubler et al., 2014; Neodo et al., 2012; Sanchez-Carretero et al., 2011). Chlorate is currently not regulated because its adverse health effects have not been well established (von Gunten, 2003). By contrast, perchlorate is well-known to be associated with several severe health problems, and therefore under strict regulations in many countries, e.g., the USEPA has issued a health advisory level of 15 mg L^{-1} for drinking water sources (USEPA, 2008). As a combined process of ozonation and electrolysis, the E-peroxone process may also generate some un-desired oxychlorine species during the treatment of chloride-containing water, which requires further investigation.

During electrolysis, Cl^- is progressively oxidized at the anode to higher oxychlorine anions, i.e., hypochlorite (OCl^-), chlorite (ClO_2^-), chlorate (ClO_3^-) and perchlorate (ClO_4^-) (Hubler et al., 2014; Lacasa et al., 2012; Sanchez-Carretero et al., 2011). When Pt anodes and dimensionally stable anodes (DSA, e.g., IrO_2/Ti and RuO_2/Ti) are used, ClO_3^- is usually the highest oxychlorine species that can form in appreciable amounts, whereas ClO_4^- formation is insignificant (Bergmann et al., 2014; Jawando et al., 2015; Lacasa et al., 2012; Sanchez-Carretero et al., 2011). In contrast, ClO_4^- constitutes a major oxychlorine product when boron-doped diamond (BDD) electrodes are used as the anode, and complete conversion of Cl^- to ClO_4^- can be obtained with prolonged reaction time (Azizi et al., 2011; Bergmann et al., 2009; Hubler et al., 2014; Sanchez-Carretero et al., 2011).

The significant formation of ClO_4^- in electrolysis with BDD anodes can be mainly attributed to the high activity of BDD anodes for $^{\bullet}OH$ production from water discharge (Eq. (3)) (Azizi et al., 2011; Hubler et al., 2014; Lacasa et al., 2012; Sanchez-Carretero et al., 2011). In addition, BDD anodes are non-active electrodes whose surface does not interact with the generated $^{\bullet}OH$ to form the so-called higher oxide as what occurs on the surface of active electrodes (e.g., Pt, IrO_2/Ti, and RuO_2/Ti) (Jeong et al., 2009; Panizza and Cerisola, 2009). As a result, the $^{\bullet}OH$ can then react with $ClO_3^{\bullet}$ radicals that are also electrochemically generated at the BDD anode surface to form ClO_4^- (Eqs. (4) and (5)) (Azizi et al., 2011; Hubler et al., 2014). Due to their superb activity for $^{\bullet}OH$ generation, BDD electrodes have attracted increasing interest in water and waste-water treatment for the degradation of refractory organic pollutants (Panizza and Cerisola, 2009; Qiu et al., 2014). However, it seems that the same feature of BDD anodes promotes perchlorate formation, which represents a major challenge in the application of

BDD anodes, especially in drinking water related processes (Bergmann et al., 2014).

$$BDD(H_2O) \rightarrow BDD^{\bullet}(OH) + H^+ + e^- \tag{3}$$

$$ClO_3^- \rightarrow ClO_3^{\bullet} + e^- \tag{4}$$

$$^{\bullet}OH + ClO_3^{\bullet} \rightarrow HClO_4 \tag{5}$$

Notably, a recent study by Cotillas et al. (2015) suggested that by electrochemically generating H_2O_2 from sparged O_2 at a carbon felt cathode, ClO_4^- formation could be inhibited during electrochemical disinfection of chloride-containing water with BDD anodes. Similar mechanisms as those for BrO_3^- inhibition in the E-peroxone process were proposed for this phenomenon, that is, the electro-generated H_2O_2 can reduce ClO^- and ClO_3^- back to Cl^- and ClO_2, respectively (Eqs. (6) and (7)), thus impeding the formation pathway of ClO_4^- (Cotillas et al., 2015). It is therefore interesting to evaluate if similar reactions may occur in the E-peroxone process to minimize the formation of ClO_4^- during its treatment of chloride-containing water.

$$2ClO^- + 2H_2O_2 \rightarrow 2Cl^- + 3O_2 + 4H^+ \tag{6}$$

$$2H^+ + 2ClO_3^- + H_2O_2 \rightarrow 2ClO_2 + 2H_2O + O_2 \tag{7}$$
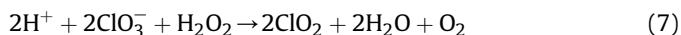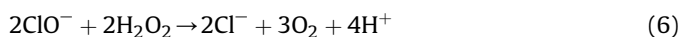
However, it should be noted that the introduction of O_3 would significantly change the reaction network involved in the formation and control of ClO_4^- in the E-peroxone process. For example, O_3 can compete with ClO^- and ClO_3^- for the electro-generated H_2O_2 (Eq. (2)). It can also participate in the oxidation of ClO^- and ClO_2^- to higher oxychlorine species (e.g., Eqs. (8)–(10) (Klaning et al., 1985; Nicoson et al., 2002; von Gunten, 2003)). It is therefore anticipated that the reaction mechanisms for ClO_4^- formation would be much more complicated in the E-peroxone process than in electrolysis with only pure O_2 sparging (see Table S1 in the Supplementary Data (SD) for a list of reactions that may be involved in ClO_4^- formation during the E-peroxone process).

$$ClO^- + O_3 \rightarrow O_2 + ClO_2^- \tag{8}$$

$$ClO_2^- + O_3 \rightarrow O_3^- + ClO_2 \tag{9}$$

$$ClO_2^- + O_3 \rightarrow O_2 + ClO_3^- \tag{10}$$

Therefore, the main objectives of this study were to (a) investigate the reaction mechanisms of ClO_4^- formation during the E-peroxone treatment of chloride-containing water, and (b) test possible control strategies to minimize ClO_4^- formation during effective pollutant degradation by the E-peroxone process. To this end, this study investigated the formation of ClO_4^- during the degradation of clofibric acid in chloride-containing water by the E-peroxone process. Clofibric acid was selected as the model compound of ozone-resisting contaminants because it reacts with O_3 very slowly ($k_{O3} < 20$ M^{-1} s^{-1}) and is commonly detected in various waters (e.g., surface water and municipal wastewater) (Huber et al., 2005). The evolution of chlorine species was monitored to investigate the fate of Cl^- during the E-peroxone process. The effects of main operational parameters (e.g., current, O_3 dose, and anode type) on clofibric acid degradation and oxychlorine formation were systematically evaluated.