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Removal of pharmaceuticals from secondary effluents by an electro-peroxone process

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ABSTRACT

This study compared the removal of pharmaceuticals from secondary effluents of wastewater treatment plants (WWTPs) by conventional ozonation and the electro-peroxone (E-peroxone) process, which involves electrochemically generating H_2O_2 in-situ from O_2 in sparged O_2 and O_3 gas mixture (i.e., ozone generator effluent) during ozonation. Several pharmaceuticals with k_{O3} ranging from <0.1 to 6.8×10^5 M^{-1} s^{-1} were spiked into four secondary effluents collected from different WWTPs, and then treated by ozonation and the E-peroxone process. Results show that both processes can rapidly remove ozone reactive pharmaceuticals (diclofenac and gemfibrozil), while the E-peroxone process can considerably accelerate the removal of ozone-refractory pharmaceuticals (e.g., ibuprofen and clofibric acid) via indirect oxidation with •OH generated from the reaction of sparged O_3 with electro-generated H_2O_2. Compared with ozonation, the E-peroxone process enhanced the removal kinetics of ozone-refractory pharmaceuticals in the four secondary effluents by ~40–170%, and the enhancement was more pronounced in secondary effluents that had relatively lower effluent organic matter (EfOM). Due to its higher efficiency for removing ozone-refractory pharmaceuticals, the E-peroxone process reduced the reaction time and electrical energy consumption required to remove ≥90% of all spiked pharmaceuticals from the secondary effluents as compared to ozonation. These results indicate that the E-peroxone process may provide a simple and effective way to improve existing ozonation system for pharmaceutical removal from secondary effluents.

1. Introduction

Wastewater treatment plants (WWTPs) have been identified as hotspots for the release of pharmaceuticals into the aquatic environment (Michael et al., 2013; Ribeiro et al., 2015; Rivera-Utrilla et al., 2013). Due to the inefficiency of conventional wastewater treatment (e.g., activated sludge process) for pharmaceutical removal, a great number of pharmaceuticals that enter WWTPs from different sources (e.g., industrial effluents, household wastewater, and storm water runoff) can still be detected in secondary effluents that are to be discharged into the aquatic environment (Huber et al., 2005; Rosal et al., 2008). Although most pharmaceuticals are present at low concentrations (e.g., ng–μg/L levels) in secondary effluents, their complex mixtures can pose a potential threat to the ecosystem (e.g., causing endocrine disruption to aquatic organisms) due to their possible synergistic adverse effects (Chelme-Ayala et al., 2011; Reungoat et al., 2010; Schwarzenbach et al., 2006). To protect water resources, reliable tertiary treatment technologies are needed to effectively remove most pharmaceuticals before secondary effluents can be discharged into the aquatic environment (Eggen et al., 2014; Michael et al., 2013; Ribeiro et al., 2015).

Ozonation has been extensively investigated as a promising tertiary treatment option for the removal of pharmaceuticals from secondary effluents of WWTPs (Esplugas et al., 2007; Hollender et al., 2009; Lee et al., 2013; Pisarenko et al., 2012; Prieto-Rodriguez et al., 2013; Rosal et al., 2010; Sgroi et al., 2014; Ternes et al., 2003; Wert et al., 2009; Zimmermann et al., 2011). During ozonation, pharmaceuticals can be oxidized by O_3 and indirectly by •OH generated mainly from the reaction of O_3 with effluent organic matter (EfOM) (Note that the reaction of OH^- with O_3 to •OH is negligible compared to EfOM at circumneutral pH of typical

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wastewater treatment) (Audenaert et al., 2013; Huber et al., 2003; Pisarenko et al., 2012; von Sonntag and von Gunten, 2012; Wert et al., 2009). Many studies have shown that ozonation is capable of removing most pharmaceuticals and other micropollutants (e.g. pesticides, personal care products, and industrial chemicals) present in secondary effluents (Hollender et al., 2009; Huber et al., 2003, 2005; Lee et al., 2013; Rosal et al., 2008, 2010). However, because O_3 is a highly selective oxidant, ozonation often cannot ensure the effective removal of O_3-refractory compounds (e.g., ibuprofen, clofibric acid, and atrazine) although a non-negligible removal degree can still be obtained for these compounds via indirect oxidation with •OH formed from O_3 decomposition (Hübner et al., 2015; Huber et al., 2003; Lee et al., 2013). Moreover, ozonation may generate potentially carcinogenic bromate from bromide present in secondary effluents (Gerrity et al., 2011; Hollender et al., 2009; Pisarenko et al., 2012; von Gunten, 2003). This may restrict the application of ozonation in certain cases such as water reclamation and reuse (Gerrity et al., 2011; Gerrity and Snyder, 2011; Lee et al., 2013; Schwarzenbach et al., 2006). Thus, although ozonation works very well and has been successfully applied in full-scale, there is still room for improvement.

The electro-peroxone (E-peroxone) process is a novel electrochemically driven advanced oxidation process (AOP) developed by combining conventional ozonation with an electrolysis process (Yuan et al., 2013). During the E-peroxone process, ozone generator effluent (O_2 and O_3 gas mixture) is sparged into a reactor that contains wastewater to be treated, which is the same as in conventional ozonation process. However, the reactor is equipped with a carbon-based cathode that can electrochemically convert the sparged O_2 to H_2O_2 (Eq. (1)). The in-situ generated H_2O_2 can then react with sparged O_3 via the so-called "peroxone reaction" to yield •OH (the overall reaction as Eq. (2) (Fischbacher et al., 2013; von Sonntag and von Gunten, 2012)), which can enhance the degradation of ozone-refractory pollutants (e.g., 1,4-dioxane and ibuprofen) (Li et al., 2014; Wang et al., 2015a). In addition, the E-peroxone process can effectively inhibit bromate formation during the treatment of bromide-containing water (Li et al., 2015), similar to what has often been reported in conventional peroxone process, whereby external H_2O_2 reagent is added during ozonation (Gerrity et al., 2011; Katsoyiannis et al., 2011; von Gunten and Hoigne, 1994). This improvement is mainly because the reaction of H_2O_2 with O_3 decreases the residual concentration of O_3, which is an indispensable reactant for the oxidation of bromide to bromate (von Gunten, 2003). In addition, the in-situ generated H_2O_2 can also rapidly reduce hypobromous acid (a key intermediate for bromate formation) back to bromide, thus impeding the formation pathways of bromate (von Gunten and Hoigne, 1994; von Sonntag and von Gunten, 2012). These promising results suggest that the E-peroxone process may provide a simple way to further improve the performance of conventional ozonation process for pharmaceutical removal from secondary effluents.

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

$$2HO_2^- + 2O_3 + H_2O \rightarrow 2OH^- + 3O_2 + HO_2^{\bullet} + {}^{\bullet}OH \quad (2)$$

However, it should be noted that previous E-peroxone studies focused on the degradation of high concentration model compounds (e.g., tens and hundreds mg/L of synthetic dyes, 1,4-dioxane, and oxalic acid) in electrolyte solutions (e.g., Na_2SO_4 solutions) that contain no other water matrix constituents (e.g., EfOM and carbonate), mainly to evaluate the mechanisms of E-peroxone process and investigate the degradation pathways of model compounds (Bakheet et al., 2013; Wang et al., 2015b; Yuan et al., 2013). In contrast, pharmaceuticals are present in much lower concentrations (e.g., ng–μg/L levels) than other constituents such as EfOM and carbonate (e.g., mg/L levels) in secondary effluents. Plenty of work has indicated that the water matrix of secondary effluents (especially, EfOM and carbonate) can have very complex effects on the removal of target pharmaceuticals by ozone-based processes (Carbajo et al., 2015; Lester et al., 2013; Rosal et al., 2010). For example, EfOM can react with O_3 to generate •OH, which can in turn oxidize ozone-refractory pharmaceuticals. However, EfOM can also compete with pharmaceuticals for oxidants such as O_3 and •OH, thus impeding the removal of pharmaceuticals (Katsoyiannis et al., 2011; Liu et al., 2015; Pisarenko et al., 2012; von Sonntag and von Gunten, 2012; Wert et al., 2009). How these water matrix constituents would affect the removal of low concentration pharmaceuticals has yet to be systematically evaluated for the E-peroxone process.

Therefore, the main objective of this study was to investigate the removal of pharmaceuticals from secondary effluents by the E-peroxone process. Several pharmaceuticals (e.g., diclofenac, bezafibrate, and ibuprofen) that have differing reactivity with O_3 (k_{O3} ranging from <0.1 to 6.8×10^5 M^{-1} s^{-1}) were selected as model compounds, and then spiked into an electrolyte solution (0.05 M Na_2SO_4) and four secondary effluents. These waters were then treated by conventional ozonation and the E-peroxone process. The removal of pharmaceuticals during the treatment was followed using LC/MS–MS techniques. The effects of pharmaceutical properties and water matrix on their removal were then evaluated by comparing their degradation kinetics in the treatment.

2. Materials and methods

2.1. Chemicals and reagents

Diclofenac, gemfibrozil, bezafibrate, ibuprofen, clofibric acid, and *p*-chlorobenzoic acid (*p*-CBA) with purity >98% were purchased from Sigma–Aldrich, and used as the model pharmaceuticals in this study. The properties of these compounds are listed in Table 1. *p*-CBA was used in this study mainly as •OH probe to measure •OH exposure during ozonation and the E-peroxone process because it reacts very slowly with O_3 ($k_{O3} < 0.1$ M^{-1} s^{-1}) and its transformation by direct electrolysis is also very slow (Elovitz and von Gunten, 1999; Wang et al., 2015a). All other chemicals (e.g. Na_2SO_4 and $NaHCO_3$) were analytical grade and purchased from Modern Eastern Fine Chemical (Beijing, China). All solutions (e.g., stock solutions of pharmaceuticals and electrolyte solutions) were prepared with Milli-Q ultrapure water (resistivity >18 MΩ).

2.2. Sample preparation

Four secondary effluent samples were collected from the outlet of secondary clarifiers in different WWTPs in Beijing, China. All these WWTPs employed conventional activated sludge process to treat municipal wastewater. After the collection, samples were immediately stored in a refrigerator (4 °C) inside polytetrafluorethylene (PTFE) bottles, and then tested within two weeks in ozonation and E-peroxone treatment. The background concentrations of model pharmaceuticals in these secondary effluents were very low (<1 μg/L). To better evaluate the degradation kinetics of model compounds in ozonation and E-peroxone treatment, small amounts of stock pharmaceutical solutions were spiked into the secondary effluents to achieve an initial concentration of ~400 μg/L for each pharmaceutical. This was with the exception of *p*-CBA, whose initial concentration was 100 μg/L. The four secondary effluents had a conductivity of between 818 and 1250 μS/cm (see Table 2), and were used directly in the E-peroxone process without addition of electrolytes.