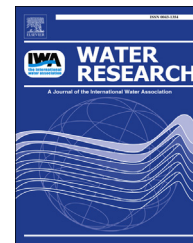




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Degradation of the anti-inflammatory drug ibuprofen by electro-peroxone process

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ABSTRACT

Electro-peroxone (E-peroxone) treatment of the anti-inflammatory drug ibuprofen aqueous solution was investigated in this study. The E-peroxone process combined conventional ozonation with electrolysis processes, and used a carbon-polytetrafluoroethylene cathode to electrochemically generate H₂O₂ from O₂ in the sparged ozone generator effluent (O₂ and O₃ mixture). The in-situ generated H₂O₂ then reacted with the sparged O₃ to produce aqueous •OH, which can in turn oxidize pollutants effectively in the bulk solution. The E-peroxone process overcomes several intrinsic limitations of conventional ozonation and electrolysis processes for pollutant degradation such as the selective oxidation with O₃ and mass transfer limitations of pollutants to the electrodes, and thus significantly enhanced both ibuprofen degradation and total organic carbon (TOC) mineralization. Results show that ibuprofen could be completely degraded much more rapidly in the E-peroxone process (e.g., 5–15 min under all tested reaction conditions) than in ozonation (≥30 min) and electrolysis (several hours) processes. In addition, thanks to the powerful and non-selective oxidation capacity of •OH, toxic intermediates formed during ibuprofen degradation could be completely mineralized in the E-peroxone process. The E-peroxone effluent (2 h) thus exhibited much lower toxicity (5% inhibition of bioluminescence of *Vibrio fischeri*) than the ozonation and electrolysis effluents (22% and 88% inhibition, respectively). The results of this study indicate that the E-peroxone process may provide a promising technology for pharmaceutical wastewater treatment.

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1. Introduction

Occurrences of pharmaceuticals and personal care products (PPCPs) in the aquatic environment have raised increasing concerns in recent years. Due to their bioactivity and pharmacological activity, PPCPs can pose considerable threat to

human health and the ecosystem when they are released into the environment. For example, they may cause chronic toxicity and endocrine disruption to aquatic life and human beings. Moreover, they may promote the development of antibiotics resistance in pathogenic bacteria (Rivera-Utrilla et al., 2013; Michael et al., 2013). PPCPs have been ubiquitously detected in natural waters worldwide because they are

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continuously introduced into the environment from many sources (e.g., production sites, hospitals, and households) (Brozinski et al., 2013). In particular, municipal wastewater treatment plants (WWTPs) have been identified as major hotspots for the release of PPCPs into the aquatic environment (Michael et al., 2013; Jelic et al., 2011). Due to the inefficiency of conventional biological treatment for PPCP removal, numerous PPCPs and their metabolites have been detected in secondary clarifier effluents of WWTPs (Jelic et al., 2011; Lee et al., 2013). The need exists for WWTPs to develop effective tertiary processes to remove PPCPs from secondary clarifier effluents before their final discharge.

Ozonation has been considered a promising technology for the removal of PPCPs from secondary clarifier effluents (Huber et al., 2003; Rosal et al., 2008; Quero-Pastor et al., 2014; Wert et al., 2009). However, because O_3 is a highly selective oxidant, ozonation can only degrade some types of PPCPs, but is ineffective at removing many others such as ibuprofen, diazepam, iopromide, and meprobamate (Lee et al., 2013; Huber et al., 2003; Wert et al., 2009). Moreover, due to the limited mineralization capacity of O_3 , ozonation effluents can still contain considerable amounts of oxidative intermediates of PPCPs (Quero-Pastor et al., 2014). Some of the intermediates may actually be more toxic than the original compounds (e.g., 1-(4-isobutylphenyl)ethanone and 4-ethylphenol produced from ibuprofen degradation) (Quero-Pastor et al., 2014; Marco-Urrea et al., 2009; Illes et al., 2013). To minimize the threat of degradation intermediates of PPCPs, it is desirable to improve the mineralization efficiency of conventional ozonation systems in WWTPs.

Addition of H_2O_2 during ozonation (i.e., the so-called “peroxone process”) has been shown to be able to significantly increase the degradation efficiency of PPCPs (Huber et al., 2003; Rosal et al., 2008; Wert et al., 2009; Zwiener and Frimmel, 2000). Huber et al. (2003) reported that ibuprofen degradation could be improved from 24 to 68% for ozonation to 78–90% for peroxone treatment of four natural waters. This improvement is mainly because O_3 can react with H_2O_2 to produce $\bullet OH$ (Eq. (1)) (Staelin and Hoigne, 1982), which are a much stronger oxidant and can oxidize most organic compounds much faster than O_3 . For example, the second-order rate constant is $7.4 \times 10^9 M^{-1} s^{-1}$ for the reaction of ibuprofen with $\bullet OH$, but is only $9.6 M^{-1} s^{-1}$ for the reaction with O_3 (Huber et al., 2003). More importantly, thanks to the non-selective oxidation capacity of $\bullet OH$, higher degrees of mineralization of PPCPs and their products can usually be achieved by peroxone processes than by ozonation alone (Rosal et al., 2008; Zwiener and Frimmel, 2000). Peroxone processes can thus decrease the potential environmental risks associated with incomplete mineralization of pollutants in conventional ozonation processes.



While the conventional peroxone process may offer a viable way to remove PPCPs from water, it requires the addition of external H_2O_2 , which is unsafe to transport, store, and handle due to its high reactivity. To eliminate the potential hazards of shipping and handling high concentration H_2O_2 solutions, we have recently developed an electro-peroxone (E-

peroxone) process that can drive the peroxone reaction using in situ electro-generated H_2O_2 (Yuan et al., 2013). The E-peroxone process combines conventional ozonation with electrolysis processes and uses a carbon-based cathode to electrochemically produce H_2O_2 from O_2 (Eq. (2)) in the sparged ozone generator effluent (O_2 and O_3 gas mixture). The electro-generated H_2O_2 then reacts with the sparged O_3 to produce $\bullet OH$ (Eq. (1)), which can in turn effectively oxidize organic pollutants. Thus, by electrochemically producing H_2O_2 in situ from the O_2 that is the predominant part (usually >90–95% V/V) of the sparged O_2 and O_3 gas, but would otherwise be wasted in conventional ozonation processes, the E-peroxone process can drive the peroxone reaction for pollutant degradation without using externally added H_2O_2 (Yuan et al., 2013).



Our previous studies have shown that significant amounts of aqueous $\bullet OH$ can be continuously produced in the bulk solution from the reaction of sparged O_3 and electro-generated H_2O_2 (Yuan et al., 2013; Li et al., 2013). As a result, E-peroxone processes can oxidize organic pollutants much more effectively than individual ozonation and electrolysis processes. For example, the E-peroxone process almost completely mineralized Orange II (a synthetic dye) and its intermediates in 45 min (total organic carbon (TOC) removal of 96%), whereas individual ozonation and electrolysis removed only 45% and 12% TOC in the same time duration, respectively (Bakheet et al., 2013). The high mineralization efficiency of E-peroxone suggests that it may serve as an effective tertiary process for WWTPs to remove PPCPs and their transformation products. However, PPCPs have very different properties than synthetic dyes and refractory organic matter (mainly humic acids and fulvic acids) in landfill leachates. The process performance of E-peroxone for PPCPs degradation has therefore yet to be systematically investigated. In addition, it is important to identify the transformation products of PPCPs in the E-peroxone process because of their potential risks to the environment.

The main objective of this study was therefore to investigate the degradation of PPCPs by the E-peroxone process. Ibuprofen, which is a widely used anti-inflammatory drug and frequently detected in WWTP effluents and natural waters, was used as a model compound of PPCPs. Degradation of ibuprofen in the E-peroxone treatment was investigated and compared with conventional ozonation and electrolysis processes. The effects of applied current, O_3 concentration, solution pH, and the presence of natural organic matter (NOM) on the E-peroxone process performance were evaluated systematically. Based on intermediates detected during E-peroxone treatment, a possible reaction pathway of ibuprofen degradation by the E-peroxone process was proposed.

2. Materials and methods

2.1. Chemicals and reagents

Ibuprofen ($\geq 98\%$) and humic acid were purchased from Sigma–Aldrich. Oxalic, glyoxylic, pyruvic and acetic acids were

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