Removing acesulfame with the peroxone process: Transformation products, pathways and toxicity

Chi-Hang Chow a, Kelvin Sze-Yin Leung a, b, c, *

a Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong
b HKBU Institute of Research and Continuing Education, Shenzhen Virtual University Park, Shenzhen, China
c School of Environment, Guangzhou Key Laboratory of Environmental Exposure and Health, Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou, 510632, China

HIGHLIGHTS

• The peroxone process effectively removes acesulfame.
• From the peroxone process, 15 transformation products, with 4 new, were identified.
• Transformation products derived from the peroxone process gave minimal ecotoxicity.

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ABSTRACT

Emerging contaminants (ECs) are receiving considerable attention because of their widespread occurrence, persistence and potential threat to the environment, wildlife and humans. Acesulfame (ACE), an extensively used artificial sweetener, is the most worrisome example of ECs. The photolysis/photo-catalysis, chlorination and/or permanganate oxidation of ACE produces transformation products (TPs) that are more persistent and toxic than precursors. Thus, an alternative treatment method to treat ACE is required; oxidation by the peroxone process could be that method and was systematically investigated, as reported here. During the peroxone process, ACE degradation followed pseudo-first-order kinetics, with a rate that was significantly higher than after conventional ozonation. The hydroxyl radical was the major reactive species. Amount of hydrogen peroxide (H2O2) used, pH and type of water matrix showed significant influence on ACE degradation. Fifteen TPs in ultrapure water extracts, including four newly reported compounds, were identified and characterized by high resolution mass spectrometry (HR-MS) based on accurate mass measurements and MS/MS fragmentation. The reduced toxicity compared to other reported treatments of ACE was likely due to different transformation pathways and TPs generated. The peroxone process therefore appears to be one viable choice for safe removal of ACE.

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1. Introduction

Emerging contaminants (ECs) are a group of natural and synthetic compounds that are ubiquitous in the aquatic environment and have known or potential adverse effects on the ecosystem and humans even at low concentrations (Noguera-Oviedo and Aga, 2016). Although ECs can be eliminated by different chemical treatment processes (i.e., in water treatment plants), some of the transformation products (TPs) produced show higher toxicity to the environment than parent compounds, raising concern that they pose threats to the environment (Escher and Fenner, 2011). Developing techniques that can safely eliminate ECs is crucial, and the criteria for “safety” must include evaluation of transformation products.

Acesulfame (ACE) is a widely used artificial sweetener. As it is being used in cosmetics, foods, and industrial products worldwide, it is also becoming one of the most common contaminants of the world’s water, reaching concentrations as high as 2.5 mg L−1 (Li et al., 2016; Loos et al., 2013). ACE was reported inducing oxidative stress in Cyprinus carpio at environmental relevant concentrations (0.05 and 149 μg L−1) within 96 h (Cruz-Rojas et al., 2019). It can damage to lipids and proteins in blood, liver, gill, brain and muscle and change the SOD and CAT antioxidant enzymes...
activities. Alarmingly, there are currently no treatments that can safely remove or degrade ACE in municipal water supplies (Li et al., 2017). ACE degradation by, and ecotoxicity after, various treatments have been investigated (Li et al., 2016, 2017; Ren et al., 2016; Sang et al., 2014; Yin et al., 2017) with results as summarized here: (a) Photocatalysis can successfully degrade ACE; however, their TPs were found to be more persistent, and >500 times more toxic than ACE in Vibrio fischeri and zebrafish embryos, as measured by tail detachment and heart/hatching/survival rates (Li et al., 2016; Sang et al., 2014). The photolytic by-products also increased oxidative stress in the liver of goldfish (Carassius auratus) (Ren et al., 2016). (b) Permanganate oxidation of ACE can lead to a complete degrada-

tion (i.e., 100% removal of parent compound), but its TPs were found to have enhanced toxicity towards V. fischeri. (Yin et al., 2017). (c) Chlorination is also not an optimal treatment for removing ACE as ACE is the precursor of several disinfection by-products (DBPs) - both regulated DBPs and also un-regulated nitrogenous-DBPs (N-DBPs) with carcinogenic properties (Li et al., 2017). Furthermore, chlorination of ACE in wastewater generates Br-

DBPs which have higher mutagenicity, cytotoxicity and geno-
toxicity related to Cl-DBPs (Yang et al., 2015). All these results indicate that alternative treatments for safe elimination of ACE from contaminated water are needed, and the need increases with every new use found for ACE.

\[ \text{O}_3/\text{H}_2\text{O}_2 \text{ (peroxone process)} \]

is an Advanced Oxidation Process (AOP) that generates stronger oxidant HO• compared with O3, through addition of \( \text{H}_2\text{O}_2 \) to accelerate \( \text{O}_3 \) decomposition. Previous study has indicated that the peroxone process yields ~50% HO•, which is a higher yield than \( \text{O}_3 \) decomposition with dissolved organic matter (DOM) (Flyunt et al., 2003). Therefore, the peroxone process can generate more HO• than ozonation for enhancing the rate of abatement of ozone-refractory compounds (Fischbacher et al., 2013; Wang et al., 2018). Pharmaceuticals, pesticides and beta-blockers have been shown to have higher removal rates (97–100%) during the peroxone process than during ozonation because of more HO• generated during the former (Ahmed et al., 2017). Moreover, the peroxone process has become more attractive as a water treatment than ozonation because it can rapidly reduce the formation of key intermediates of bromate (HOBr/OBr−) back to bromide (Li et al., 2015), thereby minimizing bromate for-

mation. Bromate is a potential human carcinogen, and its formation is the major limitation of using ozonation for bromate-containing water (Li et al., 2015). With regard to ACE, batch experiments treating wastewater effluent with the peroxone process have shown that ACE is removed; however, the TPs produced have not been studied, and their toxicity remains unknown (Phattarapatamawong et al., 2018).

The objective of the present work was to investigate the trans-

formation products of the peroxone process in degrading ACE in water. Operating parameters including \( \text{H}_2\text{O}_2 \) dose, pH and type of water matrix were studied. TPs produced were first identified, and then transformation pathways were proposed using UHPLC-QTOF-MS. The ecotoxicities of TP mixtures were evaluated by the inhibi-
tion test with the marine bacterium, V. fischeri. In addition, ACE transformation pathways were compared with those of various other treatment processes in order to present guidance for future research to improve water treatments for ACE and other ECs which would form toxic by-products in conventional degradation at municipal treatment plants.

2. Experimental materials and methods

2.1. Chemicals and reagents

A 10,000 mg L\(^{-1}\) acesulfame stock solution was prepared in Milli-Q water (Millipore, Billerica, MA, USA) and kept at 4 °C. \( \text{H}_2\text{O}_2 \) (35%, v/v). Both the stock acesulfame and tert-butanol (t-BuOH, ACS grade) were purchased from Acros Organics (Germany); anhydrous sodium thiosulfate (Na\(_2\)S\(_2\)O\(_3\), 99%) was from International Labora-

tory (USA).

For chromatographic analysis, methanol from Duksan Pure Chemicals (LC-MS grade, South Korea) and formic acid from In-

ternational Laboratory (98–100%, USA) were used to prepare the mobile phase. All reagents were filtered with 0.22 µm nylon membrane filter.

Microtox test reagents were purchased from Modern Water (Guildford, UK), including acute reagent, reconstitution solution, diluent and entailing osmotic adjusting solution. Phenol used as the positive control was obtained from Thermo Scientific (USA).

2.2. Experiments

ACE degradation experiments were performed by adding 5 mg L\(^{-1}\) of ACE solution (250 mL) into a three-neck round bottom flask. The solution pH was controlled at 7 by 1 mM phosphate buffer. Ozone was generated with high purity oxygen, which was supplied by Hong Kong Specialty Gas Co., Ltd (HP grade, Hong Kong) with a Quantum 5 Ozone system (Longevity Resources Inc. BCID, Canada). The output of ozone gas was bubbled into the flask with a constant output of 1.5 mg min\(^{-1}\) and temperature maintained at 21±2 °C. The reaction mixtures were mixed with a magnetic stirrer at a speed of 300 rpm; excess O\(_3\) was destroyed by an external ozone destruct unit (Longevity Resources Inc. BCID, Canada). A schematic diagram of the setup is given in Fig. S1. The dissolved ozone concentrations in the solution in both ozonation and the peroxone process are shown in Fig. S2. During the peroxone pro-

cess, only a trace level of dissolved ozone was detected in the presence of \( \text{H}_2\text{O}_2 \). 1-ml aliquot of ozonated sample solution was withdrawn at each time interval, quenched by excess Na\(_2\)S\(_2\)O\(_3\) to remove residual ozone, and filtered with a 0.22 µm nylon syringe filter before analysis by UHPLC-QqQ-MS. All experiments were performed in duplicate. Various doses of \( \text{H}_2\text{O}_2 \), different pHs, and different types of water (ultrapure water, tap water, and waste-

water from local sewage treatment plant) were investigated. In addition, 0.1 mg L\(^{-1}\) of ACE solutions were prepared with real water matrices to comprehensively evaluate the effectiveness of ozonation and the peroxone process to remove ACE in real environmental waters. Several water quality parameters (pH, chemical oxygen demand (COD), total alkalinity and UV\(_{254}\)) were determined according to APHA standards and are shown in Table S1 (APHA, 2005).

TP identification and ecotoxicity evaluations were performed with an initial concentration of 20 mg L\(^{-1}\) ACE for better detection of TPs. 60 mg L\(^{-1}\) of \( \text{H}_2\text{O}_2 \) was pre-spiked in the solution. The condition of ozone output was the same as above. At specified time intervals, 1-ml aliquot sample were withdrawn and quenched for TP identification.

For analytical methods and bioluminescence Microtox test, detailed conditions and procedures are shown in Supplementary S1 and S2.

3. Results and discussion

3.1. Degradation of acesulfame in the peroxone process

The degradation of ACE undergoing ozonation and the peroxone process occurs according to pseudo-first-order kinetics (Eq. (1)). The degradation was linear fit to ln (C/C\(_0\)) vs reaction time (Table S2).
\[ \frac{d[\text{ACE}]}{dt} = k_{\text{obs}}[\text{ACE}] \]  
\text{(1)}

where \( k_{\text{obs}} \) represents the pseudo-first-order rate constant (min\(^{-1}\)). 
[\text{ACE}] = \text{ACE concentration (mg L\(^{-1}\)}, and linear slope is equal to \( (\text{C}/\text{C}_0) \) vs reaction time.

The efficiency of the peroxone process for ACE degradation was then compared with that of ozonation (without \( \text{H}_2\text{O}_2 \)) and is contributing more significantly than \( \text{O}_3 \) to ACE degradation. (Wang et al., 2016; Ayala et al., 2011). Results indicate that the optimal \( \text{H}_2\text{O}_2 \) dose for ACE degradation is ACE concentration-dependent. Although 6 mg L\(^{-1}\) \( \text{H}_2\text{O}_2 \) is a relatively low concentration that can reduce cost while still being effective, approximately 5 mg L\(^{-1}\) of unreacted \( \text{H}_2\text{O}_2 \) is released in effluent that may still be a potential threat to living organisms (Souza et al., 2013). Chlorine is frequently applied to destroy residual \( \text{H}_2\text{O}_2 \) and provide long-term disinfection in the distribution system (Yang et al., 2016).

### 3.1.1. Effect of hydrogen peroxide

In order to optimize the efficiency of ACE degradation during the peroxone process, the effect of adding \( \text{H}_2\text{O}_2 \) to the reaction system was assessed as \( \text{H}_2\text{O}_2 \) can act as both the source and scavenger of \( \text{HO}^+ \) (Kosaka et al., 1998). The results show that, after adding 4–60 mg L\(^{-1}\) of \( \text{H}_2\text{O}_2 \) to the reaction system, the ACE degradation rate increased and reached a maximum rate of 60 mg L\(^{-1}\) of \( \text{H}_2\text{O}_2 \) (0.268 min\(^{-1}\)), which was significantly different from ozonation (0.091 min\(^{-1}\)) (Fig. S4a). Adding more \( \text{H}_2\text{O}_2 \) compromised degradation. That is, after adding 80 mg L\(^{-1}\) \( \text{H}_2\text{O}_2 \), the degradation rate of ACE decreased to 0.178 min\(^{-1}\). These results indicate that the peroxone process can enhance the rate of ACE degradation through increasing production of \( \text{HO}^+ \). However, excess \( \text{HO}_2 \) will rapidly consume \( \text{HO}^+ \) forming less reactive radicals such as \( \text{HO}_2^- \) and causing the inhibition effect. A similar phenomenon has been reported in previous studies with benzophenone-3 and ciprofloxacin (De Witte et al., 2009; Gago-Ferrero et al., 2013).

The residual \( \text{H}_2\text{O}_2 \) may require further quenching before the treated water is released into a distribution system because \( \text{H}_2\text{O}_2 \) can damage cell membranes of living organisms. (Wang et al., 2016; Yang et al., 2016). Therefore, \( \text{H}_2\text{O}_2 \) concentrations were monitored during the reaction period (Fig. S5). Although \( \text{H}_2\text{O}_2 \) degradation increased at lower doses of \( \text{H}_2\text{O}_2 \), the results show that only trace amounts of the added \( \text{H}_2\text{O}_2 \) were degraded during the reaction. Surprisingly, 60 mg L\(^{-1}\) of \( \text{H}_2\text{O}_2 \) was not the optimal dosage for degrading environmentally relevant concentrations of ACE (0.1 mg L\(^{-1}\)) (Fig. S4b). After addition of 0.6–6 mg L\(^{-1}\) \( \text{H}_2\text{O}_2 \), the degradation rate of ACE increased from 1.190 min\(^{-1}\) to the maximum rate of 2.914 min\(^{-1}\); in contrast, after adding 20 mg L\(^{-1}\) \( \text{H}_2\text{O}_2 \) to the reaction, the degradation rate was inhibited (0.613 min\(^{-1}\)). These results indicate that the optimal \( \text{H}_2\text{O}_2 \) dose for ACE degradation is ACE concentration-dependent. Although 6 mg L\(^{-1}\) \( \text{H}_2\text{O}_2 \) is a relatively low concentration that can reduce cost while still being effective, approximately 5 mg L\(^{-1}\) of unreacted \( \text{H}_2\text{O}_2 \) is released in effluent that may still be a potential threat to living organisms (Souza et al., 2013). Chlorine is frequently applied to destroy residual \( \text{H}_2\text{O}_2 \) and provide long-term disinfection in the distribution system (Yang et al., 2016).

### 3.1.2. Effect of pH

Degradation rates and mechanistic pathways of the peroxone process for organic micropollutants are affected by pH (Chelman-Ayala et al., 2011). Results indicate that ACE degradation rates for peroxone process increase at higher pH (Fig. S6).

The pH of a solution is one of the factors that can affect the peroxone process because it can alter the protonation/deprotonation of compounds of interest (e.g. benzophenone-3) (Gago-Ferrero et al., 2013). However, since ACE has a pKa of 2.0 (Lange et al., 2012), it was mainly dissociated at all pHs used in this study. Under acidic conditions, the peroxone process showed a lower reaction rate than under neutral and alkaline conditions, and \( \text{H}_2\text{O}_2 \) was not favored to dissociate to yield \( \text{HO}^+ \) which led to less formation of \( \text{HO}_2^- \) (Boczkaj and Fernandes, 2017). The reaction rate of ACE at neutral pH (0.268 min\(^{-1}\)) was increased compared to pH 6 (0.213 min\(^{-1}\)). The highest degradation rate of ACE in the peroxone process was found at pH 8 (0.271 min\(^{-1}\)). As \( \text{H}_2\text{O}_2 \) will generate \( \text{HO}_2^- \) at alkaline pH, it was more effective in promoting the decomposition of \( \text{O}_3 \) to \( \text{HO}_2^- \) than to \( \text{OH}^- \) (Boczkaj and Fernandes, 2017). Moreover, \( \text{O}_3 \) could also react with \( \text{OH}^- \) to yield \( \text{HO}_2^- \) (Boczkaj and Fernandes, 2017). Increase of reaction rate at alkaline pH was also reported for benzophenone-3 in the peroxone process (Gago-Ferrero et al., 2013).

### 3.1.3. Application to real water matrices

The applicability of both ozonation and the peroxone process for

\[ \text{Fig. 1. Degradation of acesulfame under ozonation and peroxone treatments. Conditions: O}_3 \text{ output: 1.5 mg min}^{-1}, [\text{ACE}]_0: 5 \text{ mg L}^{-1}, [\text{H}_2\text{O}_2]: 60 \text{ mg L}^{-1} \text{ for the peroxone process; Temp: 21 ± 2°C; pH: 7.} \]
degrading ACE in different water matrices was comprehensively studied by analyzing the influence of the chemical composition of the water on degradation. Phattarapattamawong et al. (2018) reported that ACE removal from wastewater during the peroxone process was 2–20% better than ozonation. However, the performance of the peroxone process in removing ACE in other water matrices is not clear. In our study (Fig. 2), both ozonation and the peroxone process performed similarly in degrading ACE. Within 30 min ozonation, removal rate for ultrapure water, tap water and wastewater with 0.1 mg L\(^{-1}\) ACE were 100%, 97.6% and 54.7%, respectively. The peroxone process significantly enhanced ACE degradation in different types of water matrices (Fig. 2b). Time required for complete removal of ACE by the peroxone process for ultrapure water and tap water were less than 2 min and 15 min, respectively. 74.8% of ACE were removed from wastewater in 30 min of peroxone process. In other words, ultrapure water had the highest degradation rate followed by tap water and then wastewater. The lower degradation rate in wastewater was probably because of its higher total alkalinity, with relatively large proportions of CO\(_3^{2-}\) and HCO\(_3^-\) (Table S1). Both CO\(_3^{2-}\) and HCO\(_3^-\) could react with HO\(^+\) to generate carbonate radicals (CO\(_3^{2+}\)) which were less reactive than HO\(^+\), and they could more selectively react with organic compounds, leading to further loss of reactivity (Boczkaj and Fernandes, 2017). In addition, the higher COD and UV\(_{254}\) value of wastewater indicated the presence of greater amounts of organic oxidizable compounds such as NOM and aromatic compounds which can be HO\(^+\) scavengers. In general, the peroxone process should be applied in water matrices with lower organic matter content and total alkalinity. In order to overcome the influence of higher COD and alkalinity, higher ozone dose should be used in wastewater treatment during peroxone process (Phattarapattamawong et al., 2018).

### 3.2. Identification of transformation products and proposed transformation pathways of ACE

ACE-TPs generated by the peroxone process have not been reported. It is vital to know the environmental risks of ACE-TPs generated by the peroxone process in order to properly evaluate this process for water treatment in municipal treatment plants. Table S3 summarizes retention times, molecular formulae, experimental and exact masses, mass errors and Double Bond Equivalents (DBE) for all TPs. A total of fifteen TPs were identified, and all proposed molecular formulae of TPs are in good agreement (<5 ppm error) with the accurate mass measurements.

Eleven TPs identified here have been previously reported in
various treatment processes (Castronovo et al., 2017; Gan et al., 2014; Li et al., 2016, 2017; Scheurer et al., 2012, 2014; Yin et al., 2017). Four new TPs, namely TP-182, TP-184, TP-210 and TP-226, are reported here for the first time. To elucidate the structure of these newly identified TPs, a level system was followed with the confirmation criteria based on accurate mass measurement, isotope patterns and MS/MS fragmentation and elucidation of probable structures of new TPs (Schymanski et al., 2014). Deprotonated molecular ions [M – H]− were chosen as the probable parent ions. MS/MS spectra of the new TPs are presented in Fig. 3. TP-182 was proposed to be a cyclic structure, because its DBE equals 2 and it has MS/MS fragments at m/z 121.9552 [CNO3S]+, 110.9757 [CH3O3S]+, 102.0201 [C2H4NO3]+ and 96.9605 [HSO4]+. TP-184 was proposed to have a straight chain structure, because its DBE equals 1 and it has MS/MS fragments at m/z 151.9658 [C2H4NO3]+, 123.9705 [CH3NO2]+, 95.9762 [HNO3S]+ and 72.0091 [C2H2NO2]+. In addition, we propose that TP-184 has a structure similar to TP-170 since TP-170 and TP-212 show similar time profiles of both TPs have the same fragment at m/z 152; in fact, this TP has been reported (Li et al., 2016; Scheurer et al., 2012). TP-182 and TP-184 could be formed by hydroxylation and hydration, respectively, of the intermediate ion (m/z = 166). We deduced that TP-210 has a cyclic structure, because its calculated DBE equals 2, and it has fragments at m/z 149.9864 [C2H3NO3]+, 105.9603 [CNO3S]+, 96.9604 [HSO4]+, 88.0401 [CH3NO3]+ and 59.0141 [C2H3O2]+. The structure of TP-210 appears to be similar to TP-168b since TP-168b also has a fragment at m/z 150; this was previously reported in Li et al. (2016). The structure of TP-226 is proposed according to the fragments at m/z 165.9818 [C3H4NO4S]+, 105.9609 [CNO3S]+, 96.9603 [HSO4]+ and 59.0139 [C2H3O2]−. Surprisingly, both TP-210 and TP-226 showed greater carbon numbers than ACE. This is rarely observed in ECs transformation; most TPs are smaller and more polar than parent compounds, except when polymerization occurs (Scheurer et al., 2014). One possible hypothesis is that the intermediates of ACE undergo esterification with acetic acid to yield both TP-210 and TP-226. This scenario is reasonable because acetic acid has been frequently identified in ozone-based treatments with different ECs (Feng et al., 2016; Li et al., 2014). Moreover, both TP-210 and TP-226 share a fragment at m/z 59, which is likely to be an acetate moiety. Our proposed transformation pathway of ACE in the peroxone process is shown in Fig. 4. Hydroxylation, hydrolysis, oxidation and (de)hydration are proposed to be the major reaction transformation mechanisms involved.

The time profile of ACE TP production was monitored to obtain a comprehensive understanding of TP evolution in the peroxone process (Fig. 5). The variations in relative yields of TPs according to reaction time are presented as (TP abundance)/[ACE abundance] against time. The ratio does not indicate the TP concentration in the solution and is only used for estimating variation in TP abundance (Li et al., 2017). TP-194 reached its maximum abundance during the first 20 min while TP-196 peaked at 50 min; both decreased gradually afterwards. These phenomena indicate that both TP-194 and TP-196 are formed as initial intermediates, and they then generate other TPs (Gan et al., 2014; Li et al., 2016; Yin et al., 2017). TP-152, TP-170 and TP-184 show similar time profiles, i.e., they rise steadily with time and reach a maximum at 60 min (ca. 28%, 70% and 12% respectively) and then slightly decrease. In contrast, TP-168a was found increased continuously even after 80 min. The trends for the formation of both TP-168a and TP-170 agreed with ozonation treatment trends (Scheurer et al., 2012). TP-96 increased to its maximum in 10 min and remained steady. The abundance of TP-168b, TP-210, TP-212 and TP-226 were quite low (<0.2%).

3.3. Ecotoxicity assessment by microtox assay

ACE TPs derived from photolysis/photocatalysis and permanganate treatment have been found to be toxic to a range of organisms of different trophic levels (Li et al., 2016; Ren et al., 2016; Sang et al., 2014; Yin et al., 2017), and by-products generated in chlorination are potentially carcinogenic (Li et al., 2017). Thus, in order to determine whether the peroxone process is in fact better for the environment and people than other treatments, ACE TPs from the peroxone process also need to be assessed for toxicity. A preliminary ecotoxicity assessment was conducted in this study using Microtox assay.

Inhibition as a function of time is illustrated in Fig. 6. At the beginning of the reaction without purging ozone, ACE exhibited 20% luminescence inhibition rate. When the peroxone process started, toxicity sharply increased and reached a maximum inhibition rate of 38% at 20 min; thereafter, it decreased gradually. The toxicity increase in the early stage of the peroxone process may indicate that initial intermediates are more toxic than ACE. TP-194 is one intermediate that possibly enhances toxicity because of its similar formation profiles to the change of toxicity (Fig. 5b). In the literature, ibuprofen, indigo dye and sulphamethoxazole showed similar changes of toxicity during ozone-based treatments due to the production of intermediates with higher toxicity (Gonçalves et al., 2012; Li et al., 2014; Qu et al., 2015). However, the final ACE TPs, upon completion of the entire peroxone treatment, showed similar toxicity with ACE instead of elevated toxicity as is true for photolysis/photocatalysis and permanganate oxidation do (Ren et al., 2016; Sang et al., 2014; Yin et al., 2017).

3.4. Comparison of transformation pathways under different treatments

A possible reason for the differences in observed toxicity responses to ACE degradation is that different transformation pathways and reaction mechanisms are initiated by different treatments, leading to the production of different TPs. All the reported ACE TPs from different treatments are summarized in Table S4. One of the main reaction pathways of the peroxone process is the addition of HO to the C=C bond of ACE to yield a dihydroxyl compound (TP-196). The hydroxyl group in TP-196 is then oxidized to a carbonyl group to open the ring of TP-194 by an intramolecular reaction (Gan et al., 2014). TP-194 can further undergo hydrolysis and hydration to generate relatively stable aldehyde hydrates of TP-170 and TP-212, which are stabilized by the adjacent α-carbonyl (Scheurer et al., 2012; Yin et al., 2017). Interestingly, TP-170 was found to be the dominant TP in both the ozone-based treatments and permanganate oxidation (Scheurer et al., 2012; Yin et al., 2017). That is likely because HO and Mn (VII) rapidly attack the C=C bond decomposing the entity into a carbonyl and carbonyl oxide moiety. Furthermore, TP-194 is also involved in the hydrolysis of the ester group and is further oxidized to carboxylic acid (TP-168a). The above TPs have also been identified during photocatalysis since both reaction mechanisms are attributed to HO (Boczkaj and Fernandes, 2017; Li et al., 2016). ACE can undergo hydroxylation to yield TP-178, and then further hydration and oxidation to produce TP-192 (Castronovo et al., 2017).

Some TPs reported in photolysis/photocatalysis, permanganate oxidation and chlorination were not found in the peroxone process. TP-180 appears to be the major ACE byproduct in both photolysis/photocatalysis and biodegradation (Castronovo et al., 2017; Sang et al., 2014; Scheurer et al., 2014). TP-180 can further undergo photo-rearrangement to generate TP-136 (Gan et al., 2014). Meanwhile, TP-137 can be produced by alternative UV-hydrolysis pathways by losing –NCO from ACE hydrolysate (Li et al., 2016). ACE can undergo intramolecular rearrangement to generate more polar TP-162 (Scheurer et al., 2014), TP-230a and TP-230b are unique TPs, identified in only photolysis/photocatalysis, which
indicates that these TPs require the input of light energy (Gan et al., 2014; Li et al., 2016; Scheurer et al., 2014). Enhancement in phototoxicity has been contributed to the presence of these unique TPs. In addition, permanganate may favorably react with the nitrogen-containing moieties of ACE which is electron-rich and yield unique major TP-164b. TP-164b can further undergo oxidation and hydrolysis to yield TPs without nitrogen (TP-149, TP-169 and TP-217) (Yin et al., 2017). The potential differences of major TPs formation can be due to different major reactive species between permanganate oxidation and peroxone process. Permanganate would react selectively to electron-rich moieties, for example, phenols, amines, alcohols and olefins while HO⁻ derived from

Fig. 3. Accurate MS/MS spectra and fragmentation routes for new acesulfame transformation products (a: TP-182; b: TP-184; c: TP-210; d: TP-226). Mass errors from theoretical m/z values are indicated in parentheses.
Fig. 4. Proposed transformation pathways of acesulfame degradation in the peroxone process. Mass numbers in black are published data, and represent previously known TPs; mass numbers in red are data from this study and represent TPs newly identified here. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5. Time profiles of acesulfame transformation products produced during the peroxone process. Conditions: O₃ output: 1.5 mg min⁻¹, [ACE]₀: 20 mg L⁻¹, [H₂O₂]: 60 mg L⁻¹; temp: 21 ± 2 °C, pH: 7. (a): TP-96, 152, 168a, 170 and 184; (b): TP-154, 168a, 178, 182, 192, 194, 196, 210, 212, 226).
peroxone process reacts non-selectively with ACE, thus leading to different transformation pathways (Feng et al., 2018).

4. Conclusions

This study systematically investigated the peroxone process for the degradation of ACE in water, with regard to degradation kinetics, TPs formed, and toxicity.

- In the peroxone process, the degradation of ACE follows pseudo-first-order kinetics in which HO₂ is the dominant reactive species. Degradation kinetics rates were affected by H₂O₂ dose, pH and type of water matrix.
- Altogether fifteen TPs were identified by UHPLC-QTOF-MS. Four TPs were reported for the first time and their structures were tentatively proposed. The possible transformation pathways were also proposed; hydroxylation, hydrolysis, oxidation and (de)hydration appear to be the main reaction mechanisms by which ACE is degraded during the peroxone process. Time-course profiles demonstrated that more persistent TPs than ACE were present during the reaction.
- Microtox assay revealed that, during initial stages, the peroxone treatment generated TPs with higher acute toxicity than ACE. As the reaction proceeded, the acute toxicity decreased to a level similar to ACE. This result shows that complete degradation of ACE during peroxone treatment generates TPs of less toxicity than other treatments, which typically generate TPs even more toxic than ACE.

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Appendix A. Supplementary data

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