



Redox mediators and irradiation improve fenton degradation of acesulfame

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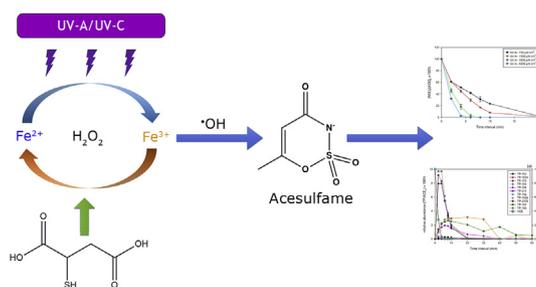
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HIGHLIGHTS

- Acesulfame was efficiently degraded by Fenton-based treatments.
- 14 TPs of acesulfame were observed to form under different Fenton-based treatments.
- UV-assisted photo-Fenton treatments did not lead to increase in toxicity.
- The degradation was accelerated at neutral pH by D,L-mercaptosuccinic acid.
- Substantial increase of ACE degradation by UV/Fe(II)/MSA/H₂O₂ system at neutral pH.

GRAPHICAL ABSTRACT



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ABSTRACT

Widely recognized as a promising approach to degrading recalcitrant pollutants, Advanced Oxidation Processes (AOPs) have drawn much attention for their effectiveness and efficiency. Among all the AOPs, the Fenton system has been widely applied for oxidation and mineralization of micropollutants due to its ease of implementation and high catalytic efficiency. However, the necessity of preceding acidification, together with rapid consumption and slow regeneration of Fe(II) resulting in deterioration of reactivity, has reduced its competitiveness as a practical option for water treatment. Acknowledging the above drawbacks, this study investigates the potential viable option to enhance the Fenton system. Acesulfame was chosen as the model compound due to its ubiquitous occurrence and persistence in the environment. UV-assisted photo-Fenton treatment was found to remove the parent compound effectively; the transformation profile of acesulfame was identified and elucidated with the ultra-high performance liquid chromatography-quadrupole time-of-flight mass spectrometry. Prolonged UV photo-Fenton treatment was effective for mineralization of the majority of the transformation products, without increasing the overall toxicity as indicated by *Vibrio fischeri* bioluminescence assay. The positive effects of the addition of redox mediators to Fenton systems at neutral pH were confirmed in this study. The results could be the basis for further development of homogeneous catalytic degradation techniques for the oxidation of environmental contaminants at circumneutral pHs to neutral pHs.

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1. Introduction

As the dangers of emerging contaminants (ECs) are increasingly recognized, chemical treatment technologies are being explored and developed to remove them. Advanced Oxidation Processes (AOPs) show particular promise in the field of degradation of ECs. Many different homogenous and heterogenous treatment technologies based on the use of highly oxidizing reactive species like hydroxyl radicals ($\cdot\text{OH}$) have been developed, aiming for contaminant destruction and water resources remediation (Ahmed et al., 2017; Barbosa et al., 2016). The Fenton process is one of the most widely applied AOPs for the oxidation and mineralization of micropollutants due to its ease of implementation and high catalytic efficiency (Bokare and Choi, 2014; Li et al., 2016b; Subramanian and Madras, 2017).

However, the Fenton system suffers from drawbacks that have, so far, hindered its implementation as a practical option for municipal water treatment. Traditional Fenton treatment requires an acidic environment to prevent the precipitation of Fe(III) produced during the Fenton reactions (Barbosa et al., 2016; Subramanian and Madras, 2017). The preceding acidification and subsequent neutralization of treated effluent increase the operation cost, and could strongly affect the salinity of the treated effluent. The optimum operational pH is ≤ 3 , and the degradation efficiency of the Fenton system deteriorates rapidly when the pH increases to circumneutral/neutral. In recent years, some low molecular weight compounds regarded as redox mediators (RMs) were applied to enhance the Fenton system by acceleration of the iron redox cycle. For example, cysteine ($\text{C}_3\text{H}_7\text{NO}_2\text{S}$, Cys) and mercaptoacetic acid (MAA) demonstrated that the presence of a thiol group can greatly accelerate the iron redox cycle, while chelation could stabilize the iron at circumneutral pH for multiple pollutant degradation (Li et al., 2016b; Subramanian and Madras, 2017). The application of RMs to enhance the Fenton degradation seems to be promising because the expenditures and downsides of preceding acidification and subsequent neutralization of Fenton-based systems can be reduced while, simultaneously, the Fe(III)/Fe(II) redox cycle can be accelerated.

Taking into account the above drawbacks and limitations, the main objective of this study was to investigate different options that could enhance the degradation efficiency of the Fenton system. Acesulfame (ACE) was chosen as the model compound. Due to the inability of conventional water treatment to remove ACE, it has been ubiquitously found in various water matrices worldwide (Van Stempvoort et al., 2011; Berset and Ochsenbein, 2012; Ordóñez et al., 2012; Gan et al., 2013; Loos et al., 2013; Nödler et al., 2013; Sang et al., 2014; Subedi and Kannan, 2014; Tran et al., 2014). Kattel et al. (2017) have reported on the use of photo-Fenton treatments (UV-A/Fe(II)/ H_2O_2 & UV-A/Fe(II)/ $\text{S}_2\text{O}_8^{2-}$) that could degrade ACE to different extents in ultrapure water (UW), groundwater (GW) and secondary effluent (WW) with preceding acidification; however, only limited degradation (<10% removal) in GW and WW could be achieved at the initial pH (7.75). The effects of [Fe(II)], [oxidant] and pH on ACE degradation were also addressed in that paper (Kattel et al., 2017). Nevertheless, the transformation profile of ACE by the Fenton system, including the identities of the transformation products (TPs), transformation mechanisms; and the potential toxicity effect of the suite of TPs produced, is still largely incomplete. Herein, we present the first report on the transformation and toxicity of ACE treated by Fenton systems. In addition, we evaluate the potential of D,L-mercaptosuccinic acid (MSA) as a redox mediator for the application of Fenton treatment in neutral pH conditions. The effect of selected RMs on the Fenton system in terms of degradation efficiency and operation pH were also studied.

This study suggests two ways to make the Fenton system more practical for municipal water treatment; in so doing the results pave the way for further development of homogenous degradation techniques.

2. Materials and methods

2.1. Materials & reagents

Sources and descriptions of chemicals are provided in the Supporting Information (SI) Text S1.

2.2. Experimental procedures

Photodegradation experiments were carried out in lab-made irradiation chambers. For UV-C and UV-A experiments, a lab-made irradiation chamber of dimensions 32 (W) \times 32 (D) \times 26 (H) cm^3 , equipped with a concentric series of either sixteen UV-C germicidal lamps (Sankyo G8T5, 8 W, Japan) or UV-A Blacklight Blue lamps (Sankyo F8T5BLB, 8 W, Japan) emitting at 253.7 nm (UV-C) and 352 and 368 nm (UV-A) was used, respectively. The total power was 128 W. For simulated sunlight experiments, another lab-made irradiation chamber was used, with dimensions of 80 (W) \times 60 (D) \times 70 (H) cm^3 , equipped with a 1 kW Xenon lamp and a filter, limiting the range of wavelength of light to be within 300–800 nm.

All experiments were carried out in a 150 mL Pyrex beaker under constant magnetic stirring at ambient temperature and pressure, with the initial pH of the solutions adjusted to 3.0 or neutral by addition of H_2SO_4 or NaOH. Adequate amount of ACE stock solution, Fe(II), Fe(III), Cys, hydroxylamine (HA), MAA and MSA were added as required for each experimental set-up before the reaction was switched on with the desired dosage of H_2O_2 . For photo-Fenton experiments, the UV lamps were switched on immediately after the addition of H_2O_2 . At desired time intervals, 0.5 ml of sample was withdrawn and mixed with equal volume of methanol for quenching. Samples were filtered through a 0.22 μm nylon syringe filter before analysis.

2.3. Analytical methods

Quantification of ACE was done using an ultra-high performance liquid chromatography – tandem mass spectrometer, while transformation products were analyzed using an ultra-high performance liquid chromatography-quadrupole time-of-flight mass spectrometer (UHPLC-QTOF-MS). Chemical oxygen demand (COD) was determined based on COD method 5220D (APHA, 2005) using a UV-Vis spectrophotometer (Agilent Cary 8454 UV-Vis Diode Array System, USA). Acute toxicity of samples was evaluated using the Microtox bioassay according to BS EN ISO 11348-3 (2008). Further details of instrumental analysis and Microtox bioassay are described in Supplementary Text S2 and S3.

3. Results and discussion

3.1. Effect of operation parameters

3.1.1. Influence of $[\text{Fe(II)}]_{\text{ini}}$

For a Fenton system to efficiently and effectively degrade pollutants, several operational parameters must be optimized. In the following part, the $[\text{Fe(II)}]_{\text{ini}}$, $[\text{H}_2\text{O}_2]_{\text{ini}}$ and the effect of light intensity were evaluated for the photo-Fenton system. Therefore, before study of the photo-Fenton system, the optimal $[\text{Fe(II)}]_{\text{ini}}$, $[\text{H}_2\text{O}_2]_{\text{ini}}$ and light intensity were determined.

As the catalyst in the Fenton system, the Fe(II) ions govern the

degradation efficiency since their concentration directly influences the $\cdot\text{OH}$ yield. Fig. 1a presents the degradation profile of ACE with varying initial concentrations of Fe(II). Minimal degradation of ACE was observed (<10%) without the addition of Fe(II). The low percentage of ACE removal without ferrous ion could be attributed to the low absorption of UV-A regions provided by the UV-A lamps of the hydrogen peroxide inside the reaction mixture (Gligorovski et al., 2015).

The addition of ferrous ion significantly accelerated the degradation process; that is, after the addition of 12.5 μM Fe(II), complete degradation of ACE was achieved after 20 min. Further increasing the initial concentration of Fe(II) to 25 μM and 250 μM led to even faster degradation, with complete removal achieved within 6 and 2 min, respectively. The same observations have been reported in other studies, regardless of whether Fe(II) or Fe(III) were used (Calza et al., 2013; Zhao et al., 2014; Romero et al., 2016; Funai et al., 2017). Higher Fe(II) concentration signifies increase in available catalyst to activate H_2O_2 , which in turn enhances $\cdot\text{OH}$ production for substantial increase of ACE degradation efficiency.

3.1.2. Influence of $[\text{H}_2\text{O}_2]_{\text{ini}}$

Even though in the reaction equation the amount of Fe(II) and H_2O_2 are in a stoichiometric relationship, the stoichiometric amount of H_2O_2 is usually not enough for the complete degradation of pollutants (Gligorovski et al., 2015). Fig. 1b displays the degradation profile with varying initial concentrations of H_2O_2 . Without

the addition of H_2O_2 , the combination of Fe(II) and UV-A light led to a slow degradation in the first 10 min, but achieved complete degradation after 20 min. This could be attributed to the indirect photochemical reaction mediated by iron species (Perkola et al., 2016). Introduction of H_2O_2 to the system promotes a significant increase in the degradation efficiency; using 25 μM H_2O_2 results in, complete degradation in 10 min. Further increase of H_2O_2 concentration led to a faster degradation (complete degradation within 6 min for 250 μM and 500 μM H_2O_2). However, the effect of increasing the $[\text{H}_2\text{O}_2]_{\text{ini}}$ was not as significant as the effect of increasing $[\text{Fe(II)}]_{\text{ini}}$. This may be because the whole reaction was more dependent on Fe(II) as the catalyst. If so then the more Fe(II), the more $\cdot\text{OH}$ produced, while the increase in $[\text{H}_2\text{O}_2]_{\text{ini}}$ only ensured the recycling of Fe(III) to Fe(II), and allowed the continued production of $\cdot\text{OH}$ until the consumption of all the H_2O_2 .

3.1.3. Influence of light intensity

In the photo-Fenton system, the energy source (i.e. light radiation) accelerates ferric ion reduction. It is likely that the light intensity of the radiation would affect the degradation efficiency of the system. Fig. 1c shows the result of varying the light intensity applied for the photo-Fenton degradation of ACE. Increasing light intensity increased degradation efficiency. In here, the light radiation provides another pathway for the reduction of Fe(III), in which simultaneously producing one equal molar of $\cdot\text{OH}$ during the photo-reduction process. Therefore, the higher the light intensity,

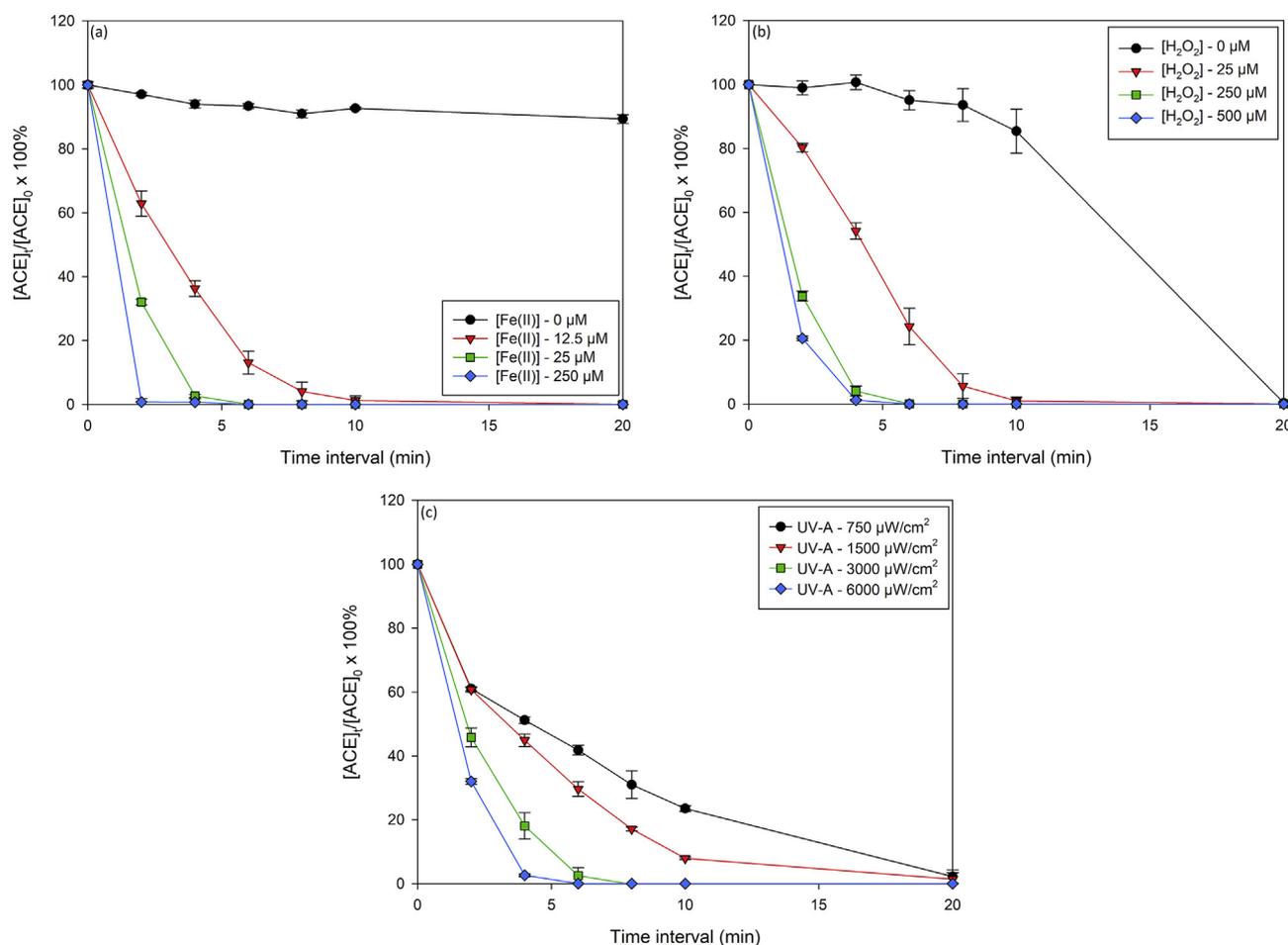


Fig. 1. Effect of operation parameters in the UV-A/Fe(II)/ H_2O_2 system. (a) Effect of Fe(II) dosage, (b) effect of H_2O_2 dosage and (c) effect of light intensity. (Conditions: $[\text{ACE}]_{\text{ini}} = 25 \mu\text{M}$, $[\text{Fe(II)}]_{\text{ini}} = 25 \mu\text{M}$, $[\text{H}_2\text{O}_2]_{\text{ini}} = 250 \mu\text{M}$, $\text{pH} = 3$ unless specified, $n = 2$).

the faster the complete degradation of ACE since $\cdot\text{OH}$ yield could be simultaneously increased due to faster reduction of Fe(III) back to Fe(II) and the $\cdot\text{OH}$ produced during the reduction process (Gligorovski et al., 2015).

3.1.4. Performance in wastewater matrix

As an indicator of treatment process performance, removal of contaminants from a real water matrix must be evaluated; great deviation exists in laboratory experiments using ultrapure water and actual/environmental water samples (Kattel et al., 2017; Li et al., 2017; Yin et al., 2017). Fig. S1 shows the effect on ACE degradation after applying the UV-A photo-Fenton system to wastewater samples collected from Sha Tin Sewage Treatment Works of Hong Kong. ACE was spiked at 25 μM and the Fenton system was applied with the molar ratio of Fe(II): H_2O_2 at 1:10.

It is not surprising to observe a decrease in degradation efficiency when the treatment was applied to wastewater samples (Fig. S1). Previous studies that applied the Fenton-based techniques for the degradation of ACE and Bisphenol-A (BPA) in real water matrices also shown a significant deterioration of degradation efficiency (Kattel et al., 2017; Molkenhain et al., 2013). As pointed out in Tokumura et al. (2016), substances that exist in real water matrices, like organic acids, natural organic matter (NOM) and inorganic ions, could scavenge the $\cdot\text{OH}$ produced by the Fenton reaction. Moreover, inorganic ions may also form complexes with the iron, thereby preventing the iron species from catalyzing the Fenton reaction. All the above factors could contribute to the observed decrease in degradation efficiency of the system. To compensate for the loss in degradation efficiency, we adopted a higher initial Fe(II) concentration (10x), which allowed a more effective decomposition of ACE with $\geq 95\%$ removal achieved in 20 min. However, the increase in [Fe(II)] could lead to the increase in the amount of undesirable Fe(III) sludge (Barbosa et al., 2016). Therefore, the amount of Fe(II) input requires serious consideration to strike a balance between degradation of pollutants and the formation of post-treatment waste.

3.2. Identification and toxicity evaluation of transformation products

The transformation products of ACE in various treatments including chlorination, ozonation, permanganate oxidation, photolysis and photocatalytic oxidation have been identified (Scheurer et al., 2012, 2014; Sang et al., 2014; Li et al., 2016a, 2017; Yin et al., 2017). Although the degradation of ACE by photo-Fenton treatments have been previously reported, the ACE-TPs in Fenton systems have not been identified (Kattel et al., 2017). Therefore, it is important to elucidate the transformation pathway of ACE when Fenton-based techniques are applied. In this study, a higher concentration of ACE (100 μM) was degraded to allow easier screening for potential TPs and structural elucidation with the use of UHPLC-QTOF-MS and MassHunter software.

The TPs identified in various systems [dark Fenton and photo-Fenton using different light sources (UV-A, UV-C and simulated sunlight (SS))] are presented in Table S1. In total, 12 out of 16 TPs known to be produced by different oxidation techniques have been identified when Fenton treatments were applied (Scheurer et al., 2012, 2014; Li et al., 2016a). Disparities in the transformation pathway for $\cdot\text{OH}$ -based treatments have also been observed in other studies using photo(oxidation) techniques for degradation of sucralose (SUC) and 5-fluorouracil (5-FU), in which different transformation pathways may proceed dominantly depending on the applied photo(oxidation) techniques because of deviation in $\cdot\text{OH}$ generation efficiency (Calza et al., 2013; Lutterbeck et al., 2015). Differences in TPs formation have also been observed between UV-

C photo-Fenton with UV-A and simulated sunlight photo-Fenton. UV-C photo-Fenton treatment produced two more TPs (TP-136 and TP-180), in which TP-180 was known to be one of the major TPs formed under UV-C photolysis or photocatalytic oxidation treatments (Scheurer et al., 2014; Li et al., 2016a). TP-180 has been proposed to have two plausible structures (acetacetamide-N-sulfonic acid & 5-hydroxy-6-methyl-4-oxo-1,2,3-oxathiazinan-3-ide 2,2-dioxide) in a study of biodegradation of ACE (Castronovo et al., 2017). TP-136 has been proposed to be formed by photo-rearrangement from a structural isomer of TP-180 in a study which elucidated the transformation of ACE in water under natural sunlight (Gan et al., 2014). This might indicate that TP-136 and TP-180 have a dependent relationship since TP-136 was only found when TP-180 was formed (UV-C photo-Fenton treatment). Direct photolysis, UV-induced homolytic cleavage of H_2O_2 and the photo-Fenton reaction could all occur simultaneously when UV-C radiation is applied, while only the photo-Fenton reaction would occur when UV-A or simulated sunlight radiation are utilized. Neither TP-136 nor TP-180 occurred when the photo-Fenton reaction took place in the presence of UV-A or simulated sunlight. This suggests that the wavelength of light contributes to the difference in TP profile during the photo-Fenton treatments since both TPs have been reported to be formed under light-initiated reactions (Gan et al., 2014; Scheurer et al., 2014; Li et al., 2016a), but here they were only observed to be formed with UV-C light.

The two new TPs (TP-182 & TP-184) observed to form have not yet been reported in the literature. Therefore, MS/MS fragmentation was conducted to elucidate the tentative structures of these new TPs. Structural elucidation was conducted according to a level system for identification of small molecules using high resolution mass spectrometry (Schymanski et al., 2014). The MS/MS spectra of TP-182 and TP-184 are presented as Fig. S2, respectively. Based on the double bond equivalent (DBE), calculated as being equivalent to 2, and fragments determined at m/z 121.9551 [CNO_4S] $^-$, 110.9759 [$\text{CH}_3\text{O}_4\text{S}$] $^-$, 102.0195 [$\text{C}_3\text{H}_4\text{NO}_3$] $^-$, 96.9599 [HO_4S] $^-$, 95.9759 [H_2NO_3] $^-$ and 72.0089 [$\text{C}_2\text{H}_2\text{NO}_2$] $^-$, we conclude that TP-182 has a ring structure. Our proposed formula for TP-182 is [$\text{C}_3\text{H}_4\text{NO}_6\text{S}$] $^-$, with a mass error less than 2 ppm. For TP-184, the proposed formula is [$\text{C}_3\text{H}_6\text{NO}_6\text{S}$] $^-$ with mass error 1.09 ppm. It is proposed that TP-184 has an acyclic structure based on calculated DBE = 1, and the fragments obtained at m/z 151.9660 [$\text{C}_2\text{H}_2\text{NO}_5\text{S}$] $^-$, 123.9708 [$\text{CH}_2\text{NO}_4\text{S}$] $^-$, 96.9599 [HO_4S] $^-$, 95.9761 [H_2NO_3] $^-$ and 72.0089 [$\text{C}_2\text{H}_2\text{NO}_2$] $^-$. The fragment of TP-184 at m/z 151.9660 [$\text{C}_2\text{H}_2\text{NO}_5\text{S}$] $^-$ matched another previously identified TP-152 (Gan et al., 2014), which was also proposed to be an open ring structure. This provides further evidence that TP-184 has an open ring structure. The formation of TP-182 and TP-184 were proposed to follow similar pathway as of TP-168b (exact m/z = 167.9972) with m/z = 165.9816 as the transitional precursor: hydroxylation yielded TP-182, while hydrolysis with ring-opening formed TP-184. The proposed ACE transformation pathway under photo-Fenton treatment applying different light sources is presented in Fig. 2. A majority of the reaction pathways are identical for UV-A, UV-C and simulated sunlight photo-Fenton treatment. However, only the use of UV-C light for photo-Fenton treatment induced the formation of TP-136 and TP-180.

To monitor the relative formation of the ACE transformation products, time profiles of the TPs were established according to the TPs' relative abundance $[(\text{TP abundance})_t/(\text{ACE abundance})_0]$ throughout the UV-A and UV-C photo-Fenton treatments. This approach does not necessarily indicate the concentration of TPs in the solution and is only for the discussion of change in TPs' abundance throughout the treatment period. The TPs' time profiles are shown in Figs. S3a–b. The degradation of ACE was completed within 10 min for both treatments, with 3 TPs (TP-152, TP-170, TP-

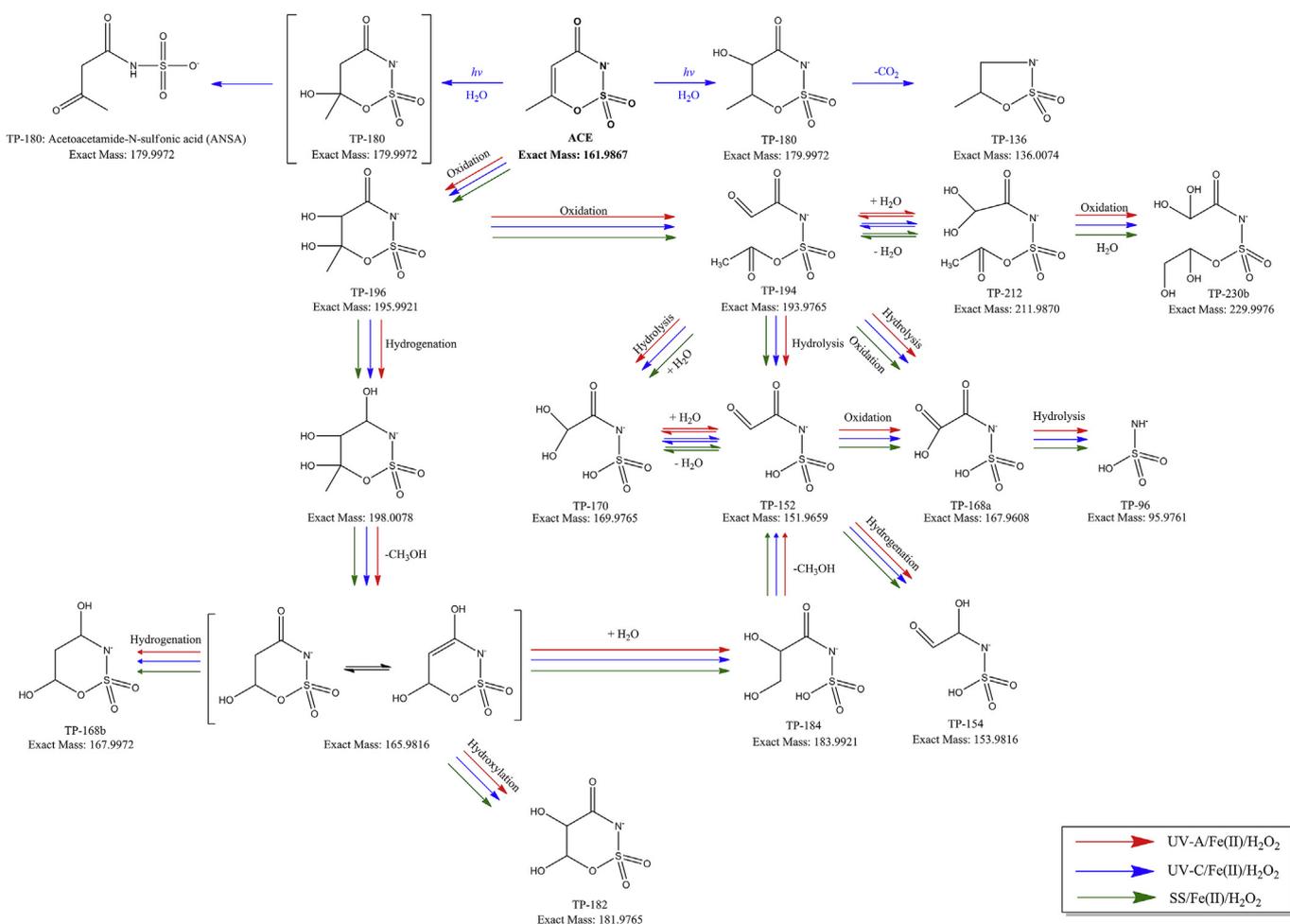


Fig. 2. Proposed transformation pathway of ACE by photo-Fenton treatments.

184) obtaining their maximum relative abundances at the same time interval in which ACE was completely removed. TP-152, TP-170 and TP-184 were also the TPs that had the highest relative abundance among all the detected TPs (except TP-96, confirmed to be sulfamic acid) (Castronovo et al., 2017). This fact suggests that they are among the dominant TPs formed during the UV photo-Fenton treatments. However, their abundances diminished quickly, and, after 20–30 min, they had disappeared. TP-194 and TP-212 were the other two relatively abundant ACE transformation products. Compared to TP-152, TP-170 and TP-184, they were formed more slowly, yet were more persistent as they existed for a longer time (40–50 min) during the treatment until they were no longer detected. It was quite surprising to observe that TP-182 was quite persistent in that its abundance remained relatively stable after it was formed. Among the 14 detected TPs, all except TP-96 (sulfamic acid) were observed to be further degraded with prolonged photo-Fenton treatment. For TP-96, its relative abundance remained high throughout the photo-Fenton treatment as indicated in Fig. S4. Under UV-A and UV-C photo-Fenton treatments, both COD results showed a decreasing trend of organics (Fig. S5). We then wanted to evaluate whether this treatment would induce increase in toxicity as other ACE treatment methods had (Sang et al., 2014; Li et al., 2016a, 2017; Ren et al., 2016; Yin et al., 2017). Assessment on the changes in toxicity after treatment is important, as many previous studies showed that incomplete mineralization could lead to a higher toxicity (Sang et al., 2014; Li et al., 2016a, Osin et al., 2018). The *V. fischeri* bioluminescence

inhibition assay was adopted for toxicity screening. This assay is widely used for evaluation of the change in ecotoxicity before/after treatment (Dudziak, 2015; Abbas et al., 2018). Toxicity units (TU) were calculated as $(100/EC_{50})$, and results are presented in Fig. 3a and b and Table S2. 120 min was determined to be the time point at which ACE and all other TPs except TP-96 were completely removed (data not shown). Compared with the initial (0 min), slight decreases in toxicity were observed with both UV-A and UV-C assisted photo-Fenton treatments. As TP-96 (sulfamic acid) was observed to be the most dominant and long-lasting TP in the time profile studies, the toxicity of its standard solution was also evaluated. The calculated experimental EC_{50} of sulfamic acid was 14429.2 mg/L (Table S2), which was much beyond the limit of >100 mg/L and could be classified as “non-harmful” according to the definition given by the European Union (European Commission, 1996). This finding further confirmed that the prolonged UV-assisted photo-Fenton-treated ACE mixture did not induce increased toxicity.

Different light intensities were used for photo-Fenton treatment of ACE, and the evolution profiles of the most abundant TPs were established to assess the effect of light intensity on their degradation and transformation. Figs. S6a–d presents the effect of light intensity on the removal of selected ACE-TPs. The increase in light intensity accelerated ACE-TPs degradation. For TP-152, TP-170 and TP-184, their relative abundance maxima were observed to occur before/at the point of complete removal of ACE regardless of light intensity, while for TP-182, TP-194 and TP-212, their relative

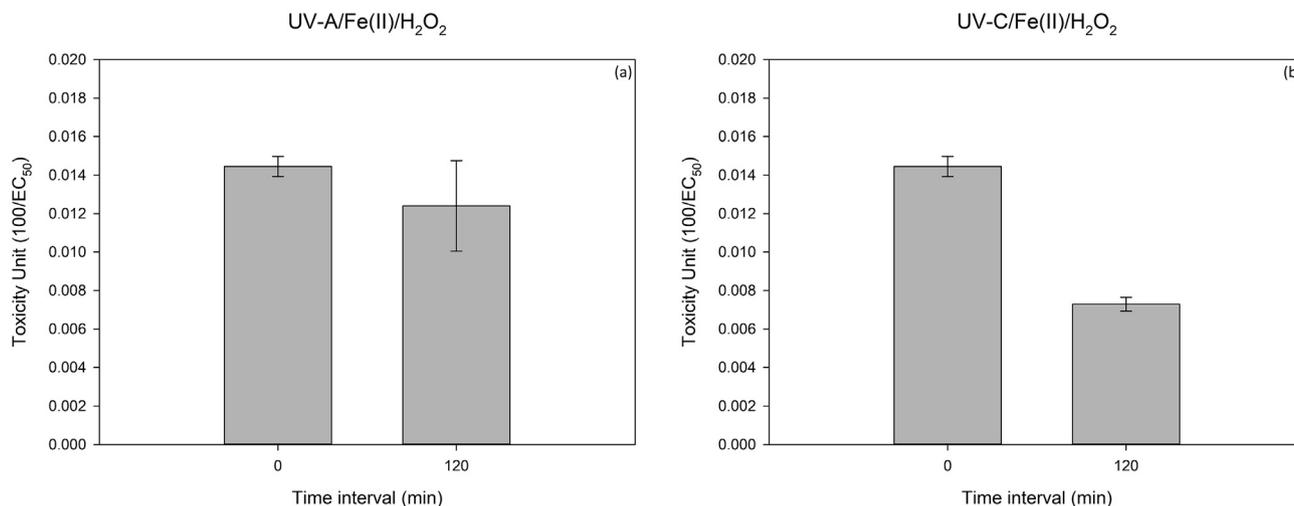


Fig. 3. Acute toxicity tests with *V. fischeri* of aceulfame before (0 min) and after (120 min) UV photo-Fenton treatment ($n = 2$) – (a) UV-A photo-Fenton, (b) UV-C photo-Fenton.

abundance maxima occurred after complete ACE removal, and took even longer when a lower light intensity was applied.

The above results suggest that photo-Fenton treatment is possibly an effective tool for the removal of both ACE and its TPs, thereby ultimately leading to detoxification. Detoxification was important because other ACE degradation studies have reported varying degrees of increased toxicity (Sang et al., 2014; Li et al., 2017; Yin et al., 2017). Complete degradation of the parent compound seems to be essential for TPs removal as shown from the above results. The use of UV radiation for ACE degradation (e.g. direct UV photolysis, UV-C/TiO₂ treatment) has been deemed to increase ecotoxicity (Sang et al., 2014; Li et al., 2016a; Ren et al., 2016); however, the UV-assisted photo-Fenton treatments applied here appeared to decrease toxicity. Therefore, in those previous studies, UV radiation may not have been what induced toxicity. On the contrary, the difference in toxicity may be caused by the variation in $\cdot\text{OH}$ generation efficiency of the different treatments. For example, Fenton systems have been reported to have a higher $\cdot\text{OH}$ yield compared to other AOPs system like peroxone (O₃/H₂O₂) and UV/H₂O₂ which yielded only 50%, or even 10% for UV/O₃ treatment (Reisz et al., 2003; Oppenländer, 2007; Fischbacher et al., 2013; Wiegand et al., 2017). As the photo-Fenton reaction also increased the production of $\cdot\text{OH}$, an even higher $\cdot\text{OH}$ yield could be expected in UV-assisted photo-Fenton system than the dark Fenton system. Therefore, the $\cdot\text{OH}$ generation efficiency may be causally related to the change in toxicity, and the high $\cdot\text{OH}$ generation efficiency would be key to the detoxification of contaminants and their TPs.

3.3. Addition of redox mediators for application at neutral pH

While UV-assisted photo-Fenton treatment can effectively remove ACE and ACE-TPs as shown above, the efficiency deteriorates at neutral pH because, in homogeneous Fenton systems, Fe(III) precipitation eventually occurs at $\text{pH} > 3$. Here, D,L-mercaptosuccinic acid was introduced as a redox mediator to accelerate the Fenton degradation at initially neutral pH conditions, with mercaptoacetic acid for comparison. Because MSA can act as a mono-, bi-, or tridentate ligand (Larkworthy and Sattari, 1980), and because it accelerates the iron redox cycle and chelation, it accelerates Fenton degradation at neutral pHs, thereby expanding the operational pH of the system. As shown in Fig. 4a and b, neither the dark Fenton/photo-Fenton process could proceed at neutral pHs, and negligible ACE degradation was observed. This is expected

since the Fe(II) spiked in originally would be transformed to Fe(III) and precipitate out in the form of oxyhydroxides at $\text{pH} > 3$ (Subramanian and Madras, 2017). The photodegradation of ACE was also observed to be suppressed with the increase of pH from 3 to 5.8 in a previous photo-Fenton study (Kattel et al., 2017). The addition of MSA allowed the Fenton degradation of ACE to proceed at a neutral pH, with 50% removal for 100 μM addition (molar ratio of Fe(II):RMs = 1:4), while only 20% removal could be achieved when MAA was added at the same molar ratio. Further increase of concentration of RMs did not necessarily lead to increase in degradation efficiency, as the degradation percentage remained almost the same (i.e. 50% removal) for increased MSA addition (200 μM , molar ratio of Fe(II):RMs = 1:8). Upon increase to 400 μM (molar ratio of Fe(II):RMs = 1:16), inhibition of ACE degradation was observed, with only 30% degradation. This could be related to the scavenging of produced $\cdot\text{OH}$ by the excess redox mediators. The decrease in degradation efficiency with continuous increase of redox mediators' concentration was also observed when cysteine was used to enhance the Fenton degradation for Rhodamine B (RhB) removal (Li et al., 2016b). The combination of UV-A photo-Fenton (light intensity: 1500 $\mu\text{W}/\text{cm}^2$) and the use of redox mediators allowed a further substantial increase of ACE degradation, with both additives (MAA and MSA) achieving up to 80% ACE removal. This increase in degradation efficiency is probably due to simultaneous occurrence of the photo-Fenton reaction and the acceleration of Fe(III)/Fe(II) cycle by the α -mercaptocarboxylic acids.

To further confirm the reducing ability of MSA, the Fe(II)/MSA/H₂O₂ system was compared with the Fe(III)/MSA/H₂O₂ system. As shown in Fig. S7, Fe(III)/MSA/H₂O₂ system could also lead to degradation of ACE, though with a lower efficiency compared to Fe(II)/MSA/H₂O₂ system. As Fe(III) needed to be reduced back to Fe(II) before the initiation of Fenton reaction, it was understandable to obtain a lower degradation efficiency using the Fe(III)/MSA/H₂O₂ system. While for Fe(II)/MSA/H₂O₂ system, the Fe(II) first reacted with H₂O₂, then turned into Fe(III) and thereby reduced by MSA. This proves that the oxidative activity of the Fe(III)/MSA/H₂O₂ system was promoted, and it is due to the reducing ability of MSA to accelerate the Fe(III)/Fe(II) redox cycle.

Comparing the effect of different concentrations of MAA and MSA on degradation efficiency, we found that MSA was more effective at lower stoichiometric ratios [Fe(II):RMs = 1:4]. There are several possible explanations. Firstly, the available vacancies for

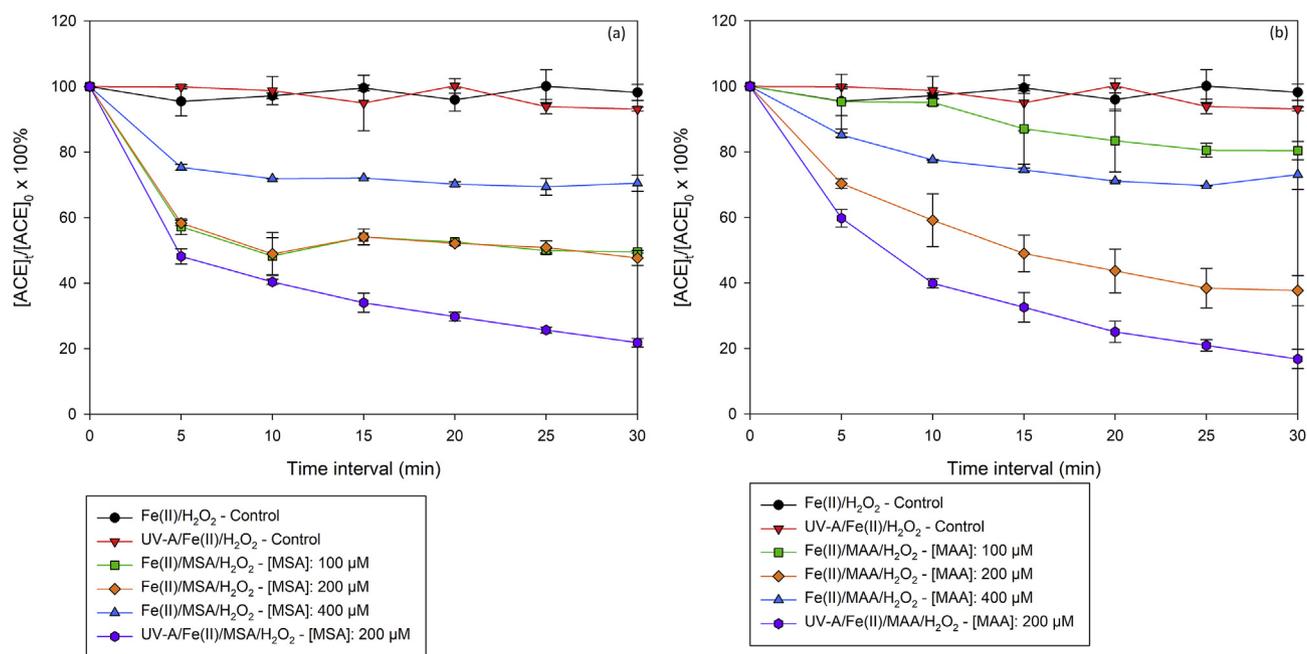


Fig. 4. Effect of redox mediators towards ACE degradation: (a) MSA, (b) MAA. (Conditions: $[ACE]_{ini} = 5 \mu\text{M}$, $[Fe(II)]_{ini} = 25 \mu\text{M}$, $[H_2O_2]_{ini} = 500 \mu\text{M}$, UV-A light intensity = $1500 \mu\text{W}/\text{cm}^2$, pH = 7 unless specified, $n = 2$).

H_2O_2 to bind with the complex of Fe(II) and Fe(III) could explain the differences of efficiency between MAA and MSA. As MAA could act as a mono- or bi-dentate ligand, while MSA could be a mono-, bi-, or tridentate ligand (Larkworthy and Sattari, 1980), the structures of the iron complexes formed with MAA and MSA could have different numbers of vacancies for the labile water ligand and H_2O_2 (McAuley, 1970; Ellis and McAuley, 1973; Ellis et al., 1975; Larkworthy and Sattari, 1980). This leads to the second potential explanation which correlates with the consumption of the two α -mercaptocarboxylic acids. Considering the difference in binding phenomena due to denticity of MAA and MSA, the RM consumption could be less with the use of MSA compared with MAA. In the case of MSA, the lower RM consumption in the MSA system may also help to prolong the Fenton reaction since more RMs would remain, allowing greater turnover of the Fe(III)/Fe(II) redox cycle. A third explanation is that the high amount of hydroxide ion present at neutral pH could weaken the reductive ability of redox mediators due to competition of complexation with Fe(III), as reported in a previous study (Subramanian and Madras, 2017). In any case, the complexation of Fe(III) with MSA seems to be more favourable than with MAA to outcompete the hydroxide ion at neutral pH because a lower dosage of MSA achieves a comparatively higher ACE degradation efficiency (Fig. 4a and b).

As a further assessment of the applicability of MSA as a redox mediator in the Fenton system, its performance was compared with other previously reported reducing agent/redox mediators. The degradation efficiency of the Fe(II)/MSA/ H_2O_2 system was further compared with Fe(II)/Cys/ H_2O_2 and Fe(II)/HA/ H_2O_2 systems. The results revealed that only the Fe(II)/MSA/ H_2O_2 system could allow significant degradation of ACE in neutral pH conditions (Fig. S8). For hydroxylamine, it could either act as the accelerating agent or the terminating agent depending on the pH. At pH higher than 4.0, HA would start to scavenge $\cdot\text{OH}$; at pH higher than 6.0, it could even terminate the reaction (Chen et al., 2011). For Cys-driven Fenton reaction, the oxidation reactivity would diminish when the pH is increased from 3.0 to 7.0, due to the precipitation of Fe(III) (Li et al., 2016b; Luo et al., 2016). The Fe(II)/MSA/ H_2O_2 system was also

evaluated with the use of water matrices other than ultrapure water. In tap water, the degradation efficiency was only 25%, which half of its efficiency in ultrapure water (Fig. S9). In wastewater, only insignificant degradation was observed (data not shown). This suggests that the constituents in natural water could hinder the performance of the MSA-mediated Fenton system; thus, further research on redox mediators-assisted Fenton system application in environmental relevant situations is warranted.

As additives to the Fenton system, the redox mediators employed would be degraded during treatment. Therefore, for actual usage or application in municipal settings, the by-products from the redox mediators must not be potentially harmful or toxic to the environment. For MSA, mass spectrometry analysis has revealed the major by-products to be sulfosuccinic acid ($m/z = 196.9759$, $[C_4H_5O_7S]^-$, $\Delta m = -1.02$) and succinic acid ($m/z = 117.0194$, $[C_4H_5O_4]^-$, $\Delta m = 0.85$). According to the ECOSAR software (Ecological Structure Activity Relationship) developed by the US Environmental Protection Agency (EPA), these by-products are considered to be non-harmful. Previous toxicological assays on the Fenton system accelerated by MAA have revealed that the treated water it produces is non-toxic, even at a ten times higher reagent dose, for the surrogate bacterium *Escherichia coli* and model plants *Vigna radiata* and *Macrotyloma uniflorum* (Subramanian and Madras, 2017). Nevertheless, a more comprehensive and systematic evaluation of the environmental activity of the redox mediators-assisted Fenton system would be optimal to confirm that the treatment would not generate additional danger to the environment.

4. Conclusions

- Photo-Fenton treatment degrades ACE into multiple transformation products; however, the degree of transformation depends on the wavelength of light used for irradiation. 14 TPs were formed independent with the choice of light wavelength, while 2 more TPs were formed using UV-C light.

- UV-assisted photo-Fenton treatment does not increase the toxicity of treated water. Efficiency of $\cdot\text{OH}$ generation appears to be the key to degradation of ACE into non-toxic TPs because a reduced toxicity to *V. fischeri* was observed.
- The use of redox mediators could expand the operational pH of homogenous Fenton systems. Through chelation with iron species, redox mediators accelerate Fe(II) regeneration thereby speeding up contaminant removal. Adding MSA, a redox mediator, eliminated the need for acidification such that Fenton degradation could proceed at circumneutral/neutral pH conditions, with removal of 50% (without UV light) or 80% (with UV light) of ACE.
- To summarize, UV-assisted photo-Fenton treatment effectively degrades both ACE and its TPs. The addition of redox mediators, such as MSA, enable the system to be used at neutral pH, thereby dramatically expanding its application to environmental and wastewaters. With further study, particularly exploration of other redox mediators and of the factors that govern their performance, Fenton systems and other AOPs can be improved.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2018.11.032>.

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