Oxidation of salicylic acid in water by the O₃ and UV/O₃ processes: removal and reaction byproducts


ABSTRACT

In this study, the removal of salicylic acid (SA) in water by ozone (O₃) and ultraviolet/ozone (UV/O₃) processes was investigated. Results showed that more than 50% of SA (10 mg/L) could be effectively removed after 1 min during these two processes. However, the UV/O₃ process was much more effective than the O₃ process for SA mineralization, and the total organic carbon reduction after 30 min was 69.5% and 28.1%, respectively. In the two processes, the optimum pH value for SA removal was 4.3, while that for SA mineralization was 10.0. Both bicarbonate and dissolved organic carbon significantly inhibited SA removal during the two processes. Eleven oxidation byproducts were detected in O₃ process, but only four byproducts were observed in UV/O₃ process. Three hydroxylation aromatic products were identified as the initial byproducts during SA degradation. Glyoxylic acid monohydrate, glycolic acid, and oxalic acid were accumulated in O₃ process but not observed in UV/O₃ process. Oxalic acid was the only detected small molecular byproduct in UV/O₃ process, and it could be further mineralized, thereby indicating that UV/O₃ had a greater potential for degrading both SA and its reaction byproducts.

Key words | byproduct, degradation pathway, ozone, removal efficiency, salicylic acid, ultraviolet/ozone

INTRODUCTION

Salicylic acid (SA), as an important organic synthetic raw material, is widely used in medicines, pesticides, dyes, rubber, foods and perfumes. In the last decade, owing to its vast usage, SA has become an emerging organic contaminant in the aquatic environment and has been frequently detected in surface water resources and groundwater (Petrie et al. 2015).

SA residual in the water environment can cause significant adverse effects on human health, such as central nervous system disorders and blood circulation failure (Chen et al. 2019). However, the removal efficiency of SA is limited during conventional water treatment processes. Data obtained from several wastewater treatment works in the UK show that SA removal by the secondary treatment processes is less than 50% (Petrie et al. 2015). The conventional drinking water treatment processes, including coagulation/flocculation, sedimentation, and sand filtration, can only degrade a part of SA in raw water (Yang et al. 2017). Therefore, advanced technologies are necessary to improve SA removal in water treatment processes, and the application of advanced oxidation processes (AOPs) is viable. AOPs are technologies based on the generation of hydroxyl radicals. The hydroxyl radical (HO·) has a very high oxidation potential of 2.8 V (Legrini et al. 1993). They can non-selectively react with various refractory organic pollutants, and usually achieve satisfactory removal and mineralization effects (Miklos et al. 2018).

Ozone (O₃) is an oxidant widely used for drinking water treatment because of its oxidation and disinfection potential (Gomes et al. 2017). Ozonation is also considered as an attractive option as a tertiary treatment step in wastewater treatment plants to reduce the discharge of micropollutants.
(Chon et al. 2013). O₃ can efficiently remove organic contaminants through selective molecular O₃ reactions and relatively non-selective HO• reactions (Gunten 2003). Because ozonation involves the HO• oxidation pathway, it can be considered an AOP or AOP-like process (Miklos et al. 2018). However, during the O₃ process, the mineralization of organic contaminants is generally low and may result in the production of harmful species (Gunten 2003). In order to further improve the performance of ozonation, O₃ can be used in combination with hydrogen peroxide (H₂O₂), catalysts, and ultraviolet (UV) light, thereby forming O₃/H₂O₂, O₃/catalyst, and UV/O₃ AOPs, respectively (Miklos et al. 2018). Compared with the O₃ process alone, these combined processes may reduce the O₃ dosage and the yields of harmful species and actively enhance the formation of HO• to promote mineralization (Gomes et al. 2017).

To date, SA ozonation has been investigated by several researchers, who have mainly focused on catalytic ozonation, such as O₃/Fe²⁺, O₃/Mn²+ and Fe-Cu@SiO₂/O₃ processes (Parisheva & Nusheva 2007; Gagnon et al. 2008; Korific et al. 2016; Chen et al. 2019). These authors found that catalytic ozonation is an effective method to remove SA from water. In contrast to individual ozonation, catalytic ozonation has greater potential for SA mineralization, and the mineralization rate possibly depends on the initial pH, O₃ concentration, and type of catalyst (Korific et al. 2016; Chen et al. 2019).

Besides catalytic ozonation, the UV/254 nm/O₃ process is also considered an attractive water treatment technology. UV and O₃ have been widely used for pretreatment, advanced treatment, and disinfection in water treatment plants. Many studies have demonstrated that the combination of UV and O₃ can significantly enhance the oxidation/mineralization of refractory organic contaminants and disinfection byproduct precursors compared with individual technologies (Legrini et al. 1995; Miklos et al. 2018; Munir et al. 2019). This is mainly because the UV/O₃ process involves complex chemical reactions; thus, organic contaminants and their reaction intermediates/byproducts can be degraded by multiple pathways. The main pathways include radical (HO•) oxidation, direct O₃ oxidation, and direct UV photolysis (Glaze et al. 1987; Peyton & Glaze 1988). Moreover, in the UV/O₃ system, HO• generation is complex and mainly results from the following reactions: first, UV254 nm photolysis of aqueous ozone produces H₂O₂ (Reaction (1)) and then UV photolysis of H₂O₂ generates HO• (Reaction (2)). In addition, the decomposition of O₃ initiated by peroxide and hydroxide ions can also produce HO• (Reactions (3)–(6)) (Staehelin & Hoigne 1982; Peyton & Glaze 1988; Oh et al. 2005).

\[
\begin{align*}
\text{O}_3 + \text{H}_2\text{O} + \text{hv} &\rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \text{hv} &\rightarrow 2\text{HO}• \\
\text{O}_3 + \text{H}_2\text{O}_2 &\rightarrow \text{HO}_2• + \text{HO}• + \text{O}_2 \\
\text{H}_2\text{O}_2 &\leftrightarrow \text{HO}_2• + \text{H}^+ \quad \text{pK}_a = 11.6 \\
\text{O}_3 + \text{OH}^- &\rightarrow \text{HO}_2^- + \text{O}_2 \quad k = 70 \text{ M}^{-1}\text{s}^{-1} \\
\text{O}_3 + \text{HO}_2^- &\rightarrow \text{O}_2•^+ + \text{HO}• + \text{O}_2 \\
&\quad k = 5.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1} 
\end{align*}
\]

However, studies on SA degradation by the UV/O₃ process are limited. Therefore, it is worth investigating the performance of UV/O₃ in SA degradation, which may provide useful data for the selection and optimization of water treatment methods to achieve complete removal of SA in real water. In this study, the degradation of SA by the UV/O₃ process was investigated, including the efficiency of removal and mineralization; influences of initial pH, bicarbonate (HCO₃⁻), and dissolved organic carbon (DOC); oxidation byproducts; and degradation pathways. Experiments on the O₃ process alone for SA degradation were conducted simultaneously, and the results were compared with those obtained by the UV/O₃ process. Based on these results, differences between the UV/O₃ and O₃ processes for SA degradation are discussed.

MATERIALS AND METHODS

Materials

SA (≥99.0%) was purchased from Sigma-Aldrich (USA). A stock solution of SA (500 mg/L) was prepared using ultrapure water (18.2 MΩ-cm, Millipore Corp., USA). All organic solvents were HPLC grade and purchased from Merck (Germany). Sulfuric acid (H₂SO₄), sodium hydroxide (NaOH), sodium thiosulfate (Na₂S₂O₃), and sodium bicarbonate (NaHCO₃) were analytical grade and purchased from Tianjin Ruimingwei Chemical Industry Co., Ltd (China). Humic acid was purchased from Beijing Huawei Ruike Chemical Co., Ltd (China) and its stock solution was prepared according to the report by Shawwa & Smith (2001). N-methyl-N-(trimethylsilyl)-2,2,2-trifluoroacetamide

with 1% trimethylchlorosilane was used for gas chromatography derivatization and purchased from Tianjin Hongfeng Weili Technology Development Co., Ltd (China). All solutions were prepared with ultrapure water.

**Experimental procedures**

Experiments were conducted in a cylindrical reactor with an inserted quartz glass tube. The volume of the reaction solution was 1 L. A UV lamp (253.7 nm; 9 W; Aqua zonic, China) was turned on to warm up for 30 min before being placed inside the quartz glass tube of the reactor. The UV light intensity in the water was measured by a UV-254 radiometer (LS125-P254-WP, China). It was specifically used for the light intensity measurement of the UVC lamp in water and the probe was waterproof within 1 m depth under water. The probe was inserted into water at different depths to detect the UV light intensity and the average intensity was 2,600 μW/cm². O₃ was produced by an O₃ generator (Com-AD-01, Anseros, China) using air as the source gas. O₃ gas was introduced into the reaction system through a bubble diffuser at a flow rate of 0.8 L/min. The equilibrium concentration of O₃ was 2.4 mg/L at 30 min in ultrapure water without UV radiation.

For the UV/O₃ experiment, after adding SA solution with a certain concentration to the reactor, the UV lamp and O₃ gas were simultaneously introduced to the reaction system. The procedures of the O₃-only and UV-only experiments were the same as those of the UV/O₃ experiment, but the UV lamp was turned off in the O₃ experiment and O₃ was not introduced in the UV experiment. The ambient temperature was 20 °C and the initial pH of the reaction solution was not adjusted (4.3 ± 0.1). H₂SO₄ and NaOH were used to adjust the pH of the solution during the pH-influenced experiments, and NaHCO₃ was added to the system to investigate the effects of HCO₃⁻. The appropriate volume of humic acid stock solution was added to the reaction solution to investigate the effect of initial DOC concentration. At given time intervals, a certain volume of sample was withdrawn from the reactor and used for analysis. The residual O₃ in the sample was quenched by the addition of an aliquot of 0.1 mol/L Na₂S₂O₃. Each experiment was repeated three times, and the error bar in the figures indicates the standard deviation of the mean.

**MSTFA derivatization**

Oxidation byproducts containing -OH/-COOH functional groups were derivatized with MSTFA. MSTFA could react with the -COOH and -OH groups, thereby forming trimethylsilyl derivatives (Yu et al. 1998). The detailed derivatization steps were as follows: 10 mL of reaction solution was freeze-dried and then 500 μL of dichloromethane and 10 μL of MSTFA were added. After shaking for 1 min, the sample was derivatized for 60 min in a water bath at 60 ± 1 °C. Finally, the sample was removed and prepared for gas chromatography/mass spectrometry (GC/MS) analysis.

**Analysis**

The SA concentration was detected at 300 nm by a high performance liquid chromatography (HPLC) instrument (Agilent 1100LC, USA) equipped with a UV detector and a ZORBAX SB-C18 column (4.6×150 mm, 5 μm). The mobile phase was water containing 0.1% formic acid (v/v) and acetonitrile with a ratio of 60:40. The detection limit of the method was 10 μg/L.

MSTFA-derivatized compounds were analyzed by gas chromatography with electron ionization mass spectrometry (GC/EI-MS) (GCMS-TQ8040, Shimadzu) with an RTx-5 MS column (Shimadzu). The GC temperature program was as follows: holding at an initial temperature of 60 °C for 1 min, increasing to 300 °C at rate of 10 °C/min, and holding for 2 min. The source temperature was maintained at 250 °C. The identification of MSTFA-derivatized compounds was conducted according to Yu et al. (1998).

Total organic carbon (TOC) was determined by a Shimadzu TOC-VCPH analyzer. The O₃ concentration was detected via the indigo method reported by Bader & Hoigné (1981) using disulfonate rather than trisulfonate.

**RESULTS AND DISCUSSION**

**Removal and mineralization of SA**

SA oxidation by the O₃ process in pure water is shown in Figure 1. It was observed that when the initial concentrations of SA were 5 mg/L and 10 mg/L, more than 50% of SA could be removed after 1 min and the SA concentration reduced below the detection limit after 3 min and 4 min, respectively. But for 20 mg/L of SA, the removal efficiency decreased under the same condition, and 86.2% of SA was removed at 10 min. Batch ozonation experiments conducted by Hu et al. (2016) also indicated that SA can be removed by ozonation within a short contact time. Thus, ozonation was an effective method to remove SA from water.
The trends of SA (5 mg/L, 10 mg/L and 20 mg/L) removal by the UV/O3 process were also studied, as illustrated in Figure 1. The results were similar between UV/O3 and O3 processes when the same initial SA concentration was used. For example, for 10 mg/L of SA, the maximum difference of SA removal efficiency was 5.4% in the two processes, at 2 min of the reaction time. UV photolysis of SA was also investigated because it is an important reaction process involved in the UV/O3 reaction. However, SA (10 mg/L) degradation was not observed in the UV process, as shown in Figure 1. Feng et al. (2018) also found that the degradation of SA (100 mg/L) was negligible under irradiation of two 8 W UVC lamps. UV-spectra of SA exhibited that SA had absorption peaks at 215 nm, 238 nm and 304 nm, respectively (Tian et al. 2019). This indicated that direct photolysis could not lead to significant degradation of SA when the UV lamp at 253.7 nm was used because of the weak absorbance of SA at this wavelength.

Even if SA was effectively removed by the O3 process and UV/O3 process, there were clear differences in SA mineralization between the two processes. As shown in Figure 2, during the O3 process, only 24% of mineralization was reached at 10 min, and then the TOC concentration changed insignificantly. Instead, the UV/O3 process was able to mineralize SA continuously, and 70% of TOC could be reduced at 30 min. The aqueous O3 concentrations in the reaction systems were also detected simultaneously. It was found that the O3 concentration differed clearly in the two processes (Figure 2). In the O3 process, the O3 concentration significantly increased from 0.13 mg/L at 1 min to 1.52 mg/L at 30 min, while in the UV/O3 process it increased from 0.18 mg/L at 1 min to 0.58 mg/L at 20 min, and then changed insignificantly.

In the UV/O3 process, UV irradiation provides an additional energy that promotes O3 decomposition to generate more HO• (Reactions (1) and (2)) (Miklos et al. 2018). This is helpful for the mineralization of reaction intermediates and byproducts because HO• has less discrimination regarding the type of functional group it will attack (Gunten 2003). Moreover, the reaction intermediates/byproducts of SA resulting from HO• and O3 oxidation can also be further degraded by UV photolysis, which does not exist in the O3 process. All the above reactions can enhance the mineralization of SA in the UV/O3 process.

Investigation of influencing parameters

The ozonation reaction and decomposition are affected by water quality, and main parameters are alkalinity, pH, and natural organic matter (NOM) (Lado Ribeiro et al. 2019). In this study, the effects of the initial solution HCO3−/C02−, pH, and NOM on the degradation of SA by O3 and UV/O3 processes were investigated.

Effect of HCO3−

Alkalinity in natural water is mainly caused by HCO3−, carbonate (CO32−), and hydroxide (OH−), and HCO3− is the main form in water. However, HCO3− is an inhibitor of O3 decomposition and a typical HO• scavenger, as shown in Reaction (7) (He et al. 2012). The effect of HCO3− on SA removal was studied, as shown in Figure 3. When HCO3− (20 mM) was added to the reaction solution, it exhibited
significant inhibition of SA removal in both the O₃ and UV/O₃ processes before 5 min, but the inhibition was insignificant after 7 min. This indicated that in both the O₃ and UV/O₃ systems, HO• played an important role in removing SA, and HCO₃⁻/CO₃²⁻ was an important factor that could influence the performances of these two processes. According to Reaction (7), HCO₃⁻ can scavenge HO• with the formation of CO₃²⁻, which is more selective than HO• as oxidant (Lado Ribeiro et al. 2019). Thus, the removal of SA was affected to a certain extent. But, in the two processes the inhibition of HCO₃⁻ gradually weakened as the reaction proceeded. This was probably because, in the presence of high HCO₃⁻ concentrations, the decomposition of ozone was inhibited due to the HCO₃⁻ scavenging of HO• (Lado Ribeiro et al. 2019), and the direct O₃ oxidation of SA could be enhanced. In addition, results in Figure 3 showed that the inhibition of SA removal by HCO₃⁻ in the O₃ process was greater than that in the UV/O₃ process, which proved that the O₃ process was susceptible to the effect of HCO₃⁻ in this study.

\[
\text{HO}^• + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{2-} \quad k = 8.5 \times 10^8 \text{M}^{-1}\text{s}^{-1} \quad (7)
\]

**Effect of initial solution pH**

The effect of initial solution pH (2.0, 4.3, and 10.0) on SA removal by the O₃ process and UV/O₃ process is shown in Figure 4(a). In these two processes, the removal efficiency was the highest at pH 4.3 while it was the lowest at pH 2.0. Moreover, there were no clear differences between the O₃ and UV/O₃ processes for removing SA under the conditions of pH 4.3 and 10.0. However, at pH 2.0, O₃ removed SA more effectively than UV/O₃ after 1 min of reaction.

Further study showed that the effect of initial solution pH on SA mineralization differed significantly from that on SA removal. As shown in Figure 4(b), in the O₃ process, with the increase in pH from 2.0 to 10.0, the mineralization of SA increased from 18% to 37% at 10 min. This indicated that a significant improvement in SA mineralization was obtained by increasing the pH value, which was consistent with the results observed by Parisheva & Nusheva (2007). Meanwhile, in the UV/O₃ process, SA mineralization was also significantly promoted by the increase in pH from 2.0 to 4.3.
to 4.3, but not further improved by the increase in pH to 10.0.

It was observed that alkaline conditions (pH 10.0) were more helpful for SA mineralization than acidic conditions (pH 2.0) in both the O₃ and UV/O₃ processes. This was mainly attributed to the influence of solution pH on the stability of dissolved O₃ molecules. According to Reactions (3)–(6), in both the O₃ and UV/O₃ processes, an increase in pH accelerated the decomposition of O₃ and the production of HO•, which promoted the mineralization of SA. However, in the UV/O₃ process, there were not obvious differences in SA mineralization when the pH value was 4.3 and 10.0, which differed from that observed in the O₃ process (Figure 4(b)). Compared with pH 4.3, pH 10.0 resulted in a significant increase of HO• concentration, which accelerated the decomposition of O₃ to HO•. However, it also significantly reduced the amount of available O₃ for UV photolysis to form H₂O₂, which was also a precursor for HO• formation (Reactions (1) and (2)) (Ratpukdi et al. 2010). In addition, as mineralization of SA increased, HCO₃⁻/CO₃²⁻ gradually formed in water because of the continuous production of carbon dioxide, and their scavenging effects on HO• became clearer (Reactions (7) and (8)). The effect of HO• scavenging by HCO₃⁻/CO₃²⁻ species was related to the value of pH (Ratpukdi et al. 2010). At higher pH, CO₃²⁻ concentration increased, and CO₂ (k = 3.9 × 10⁸ M⁻¹·s⁻¹) was more effective in scavenging HO• compared to HCO₃⁻ (k = 8.5 × 10⁶ M⁻¹·s⁻¹) (He et al. 2022). Therefore, at pH 10.0, the scavenging of HO• was more significant than that at pH 4.3. It was possible that for these reasons, in the UV/O₃ process, the mineralization of SA at pH 4.3 and 10.0 differed insignificantly.

\[ \text{HO•} + \text{CO}_3^{2-} \rightarrow \text{CO}_2^{•-} + \text{OH}^- \quad k = 3.9 \times 10^8 \text{M}^{-1} \cdot \text{s}^{-1} \quad (8) \]

**Effect of DOC**

In natural water, humic substances are important organic constituents of NOM, and humic acid is a principal component of humic substances (Lado Ribeiro et al. 2019). In this study, humic acid, as a representative of NOM, was added to the reaction system, and its concentration was indicated by DOC. The effects of the DOC concentration on SA removal by the O₃ and UV/O₃ processes were investigated, as shown in Figure 5. The results showed that humic acid could clearly inhibit SA removal and the O₃ process was inhibited more significantly than the UV/O₃ process. In the O₃ process with the addition of 1 mg/L and 5 mg/L of humic acid, at 2 min of reaction time, the SA removal efficiency decreased by 27.3% and 36.9%, respectively. Meanwhile, in the UV/O₃ process, the SA removal efficiency decreased by 18.6% and 27.3% respectively. This inhibition possibly resulted from the rich unsaturated structures in humic acid, which were preferentially attacked by HO• and O₃ (Gunten 2005). Therefore, humic acid could compete with SA for the oxidants HO• and O₃ in both the O₃ and UV/O₃ processes.

**Oxidation byproducts of SA during the O₃ and UV/O₃ processes**

The oxidation byproducts of SA containing -OH/-COOH groups, which were typical byproducts resulting from O₃/HO• oxidation (Gunten 2005), were analyzed by GC/MS. As shown in Table 1, during the O₃ process, 11 byproducts were identified. Three byproducts contained a benzene ring structure – 2,3-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, and pyrocatechol – as observed by Hu et al. (2016) and Chen et al. (2019). The other eight products (1,3-butanediol, butanedioic acid, maleic acid, fumaric acid, 2-hydroxypropanoic acid, glyoxylic acid mono-hydrate, glycolic acid, and oxalic acid) were chain compounds containing two to four carbons. Among them, maleic acid, fumaric acid, and oxalic acid were also reported by Hu et al. (2016) and Chen et al. (2019). By comparison, during the UV/O₃ process, only four byproducts...
(2,3-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, pyrocatechol, and oxalic acid) were detected.

Moreover, the yields of SA oxidation byproducts at different reaction times during the O₃ and UV/O₃ processes were also monitored, and were indicated by peak areas obtained in GC/MS chromatograms, as illustrated in Figures 6 and 7. In the O₃ process, all the SA oxidation byproducts obtained their highest yields before 5 min, except for oxalic acid (Figure 6). Among these byproducts, 2,3-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, pyrocatechol, whose structures contained a benzene ring, could be detected at 1 min and reached their maximum concentration at 3 min (Figure 6(a)). They were further degraded significantly and could not be detected at 10 min. Moreover, the amount of 2,5-dihydroxybenzoic acid was dominant, which was consistent with the report by Hu et al. (2016). In the SA molecular structure, −OH is a strong electron donating group, and −COOH is an

<table>
<thead>
<tr>
<th>Oxidation byproducts</th>
<th>Molecular formula</th>
<th>Structural formula</th>
<th>Derivative molecular weight</th>
<th>Useful GC/EI-MS ions (m/z)</th>
<th>O₃</th>
<th>UV/O₃</th>
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<tr>
<td>2,3-Dihydroxybenzoic acid</td>
<td>C₇H₆O₄</td>
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<td>370</td>
<td>73, 193, 265, 355, 370</td>
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<td>2,5-Dihydroxybenzoic acid</td>
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<td>73, 147, 223, 297, 355, 370</td>
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<td>Glyoxylic acid monohydrate</td>
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electron withdrawing group. Effects of both \(-\text{COOH}\) and \(-\text{OH}\) make position 5 more electron-rich than position 3 in the benzene ring (Hu et al. 2016). Meanwhile, \(-\text{COOH}\) has the steric hindrance effect at position 3. Therefore, the electrophilic addition of \(\text{O}_3/\text{HO}^\cdot\) is prone to occur at position 5 in the benzene ring, forming the prominent byproduct 2,5-dihydroxybenzoic acid. The results in Figure 6(b) show that four chain compounds (1,3-butanediol, butanedioic acid, maleic acid, and fumaric acid), whose structures contained four carbons, could be identified, and their maximum production was at 4 min. As the reaction continued, they were further oxidized and then could not be detected at 30 min. The yield of maleic acid was significantly higher than that of the other three byproducts. At the same time, the other four small molecular compounds containing two to three carbons were also detected before 5 min (Figure 6(c)): 2-hydroxypropanoic acid, glyoxylic acid monohydrate, glycolic acid, and oxalic acid. For 2-hydroxypropanoic acid, its production changed insignificantly during 3-5 min, but was degraded significantly after 5 min and could not be detected at 20 min. The yields of glycolic acid and glyoxylic acid monohydrate reached their maximum at 4 min, declined slightly at 5 min, and were then almost constant. By comparison, oxalic acid had much higher yields. It showed no clear changes during 4-20 min, but increased significantly after 20 min, thereby indicating that there was an accumulation of oxalic acid in the ozonation system, similar to that reported in the literature (Chen et al. 2019).

Comparing the results in Figures 6 and 7, it was found that the yields of SA byproducts during the UV/O\(_3\) process differed significantly from those during the O\(_3\) process. In the UV/O\(_3\) process, pyrocatechol, 2,3-dihydroxybenzoic acid, and 2,5-dihydroxybenzoic acid were also identified. Their maximum productions were observed at 2 min, 4 min, and 5 min, respectively. After 20 min, these three byproducts could not be detected. Oxalic acid was the only detected byproduct where the benzene ring was opened, but its production was not significant. Oxalic acid obtained its maximum yield at 20 min and was then further degraded rapidly; this significantly differed from the behavior observed in the O\(_3\) process. Thus, it could be observed that during the UV/O\(_3\) process, the yields of byproducts containing two to four carbons remarkably decreased compared with those during the O\(_3\) process.
Degradation pathways of SA by O₃ and UV/O₃ processes

Based on the above SA oxidation byproducts, possible degradation pathways during the two processes are shown in Figure 8. During the O₃ process, under the oxidation of O₃ and HO•, SA was first oxidized to 2,3-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, and pyrocatechol, as reported by Hu et al. (2016) and Chen et al. (2019). During the reaction, their benzene ring structures were opened and then 1,3-butanediol, butanediolic acid, maleic acid, and fumaric acid were formed; their structures contained four carbons. Through further oxidation, smaller molecular byproducts could be produced, namely 2-hydroxypropanoic acid, glyoxylic acid monohydrate, glycolic acid, and oxalic acid.

During the UV/O₃ process, 2,3-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, and pyrocatechol were also considered the initial byproducts of SA. However, these byproducts were destroyed more completely. Only one small molecular byproduct, namely oxalic acid, could be detected. It was believed that other small molecular byproducts might have been formed in the reaction, but their yields were too low to be detected. This clear difference between the two processes possibly resulted from the fact that the UV/O₃ process could produce more HO• than the O₃ process and that it additionally involved UV radiation, which could lead to greater mineralization of byproducts.

CONCLUSION

This study investigated the degradation, oxidation byproducts, and the possible degradation pathways of SA by O₃ and UV/O₃ processes. It was apparent that both the O₃ and UV/O₃ processes were effective in the removal of SA from water, but the UV/O₃ process had a significant advantage at mineralizing SA under the same conditions. The influence of the initial pH (2.0, 4.3, and 10.0) showed that the greatest removal of SA was achieved at pH 4.3 in the two processes, but the mineralization of SA could be significantly promoted by increasing the pH, especially in the O₃ process. Moreover, in the UV/O₃ process, the mineralization of SA at pH 4.3 and 10.0 differed insignificantly. The existence of HCO₃⁻ and DOC could influence the removal of SA in the two processes, and the O₃ process was influenced more significantly. The detection of SA oxidation byproducts showed that under the same conditions, 11 byproducts were identified in the O₃ process, but only 4 byproducts were identified in the UV/O₃ process. Three compounds containing benzene rings (2,3-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, and pyrocatechol) were identified as the initial byproducts during the two processes, and they could be further oxidized to small molecular chain compounds. The accumulation of byproducts was observed in the O₃ process, especially that of oxalic acid, which was not observed in the UV/O₃ process. This further proved
that the UV/O₃ process had the advantage of controlling the formation of SA byproducts.

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