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Oxidation of sulfadiazine and sulfamethoxazole through O_3, UV, and UV/O_3 processes

Xinshu Liu, Yahui Huang, Xiaoman Su, Sijie Tian, Yue Li, Rongfang Yuan*

Beijing Key Laboratory of Resource-oriented Treatment of Industrial Pollutants, Department of Environmental Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China, email: yuanrongfang@ustb.edu.cn

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ABSTRACT

As two kinds of sulfonamide antibiotics (SAs), sulfadiazine (SD), and sulfamethoxazole (SMX) have been found in wastewater. In this study, the removal of SD and SMX through O_3, UV, and UV/O_3 processes were investigated, and the effects of Cl^-, Ca^{2+}, and HCO_3^-/CO_3^{2-} on SAs removal were explored. SAs could be decomposed through hydroxylation and hydrolysis. Appropriate 80% and 55% of SD and SMX could be quickly decomposed in 12 mg/L O_3 solutions. SD is easier to be ozonized than SMX because the unsaturated degree of pyrimidine ring is higher than that of isoxazole ring. The SD removal rate by UV/O_3 process was lower than that by ozonation because SD was mainly decomposed by direct ozonation, and the O_3 molecules were decomposed under UV light. Nevertheless, the SMX removal was promoted since SMX was mainly degraded by $^{\bullet}OH$. The ions in water may affect the decomposition of SAs. As the $^{\bullet}OH$ capturer in water, Cl^- or HCO_3^-/CO_3^{2-} reacts with $^{\bullet}OH$ to produce radicals with weaker oxidizing ability, resulting in the reduction in the SAs removal rates. Meanwhile, they can accelerate the decomposition of O_3 to O_2, which limits the direct oxidation by O_3 molecules. The removal of SAs was promoted in the presence of Ca^{2+} because the complexation of Ca^{2+} with the pollutants can promote the indirect oxidation process. Furthermore, Ca^{2+} can reduce the activation energies of the degradation reaction because of its role as an electron transporter, thus facilitating the degradation of SD and SMX.

Keywords: Sulfadiazine; Sulfamethoxazole; Ultraviolet irradiation; Ozonation; Ions; Mechanisms

1. Introduction

The environmental pollution caused by emerging contaminants has received extensive attention in recent years [1]. Antibiotics have been considered as emerging micro-pollutants for many years due to their high consumption rate in chemical therapy, veterinary, and agriculture use [2]. As two kinds of sulfonamide antibiotics (SAs), sulfadiazine (SD), and sulfamethoxazole (SMX), which are usually prescribed in veterinary and human medical treatment for respiratory, urinal, and gastrointestinal diseases [3,4], have been found in both wastewater and surface water resources [5,6]. SAs cannot be completely decomposed by traditional water treatment processes. The average removal rates of SAs by the traditional activated sludge method is 51%–93% [7]. Compared with traditional water treatment technology, advanced oxidation technology can be more effective to remove SAs in water.

Ozone (O_3) is a strong oxidant with strong oxidation activity, and is widely used in the oxidation of organic matters [4,8]. During the oxidation process, O_3 has two mechanisms of action: direct reaction and indirect reaction. Direct reaction is that the O_3 molecules directly participate in the oxidation of organic matter in water. The indirect reaction means that the hydroxyl radical ($^{\bullet}OH$) with stronger oxidation and lower selectivity will be formed after O_3

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* Corresponding author.

molecule is decomposed. These oxidative active components can react with organic compounds to decompose or even mineralize them [9]. O_3 oxidation treatment has lots of advantages. It has high treatment efficiency, no secondary pollution, and can realize the rapid decomposition of SAs [10].

Photodegradation is the method in which UV or visible light are used to irradiate the antibiotic, leading to the decomposition of the antibiotics [11,12]. In addition, experiments have proved that UV/O_3 is a feasible and efficient advanced oxidation technology to degrade antibiotics. O_3 has a molar extinction coefficient of 3,300 L/(mol cm) and can strongly absorb UV light with a wavelength of 254 nm. Once O_3 absorbs UV light in water, it will produce H_2O_2, which is further decomposed into $^{\bullet}$OH [Eqs. (1) and (2)] [13]. The process is widely used in the degradation of various refractory organics and micro-pollutants. Bustos-Terrones et al. [14] compared the decomposition effects of O_3, UV, and UV/O_3 on organic matter, and found that when UV/O_3 process was employed, the removal efficiency of the pollutants was higher than the combined removal efficiencies by O_3 and UV treatment alone. Xu et al. [1] studied the removal of sucralose by UV/O_3 process, and found that the mineralization of sucralose is mainly due to the oxidation of $^{\bullet}$OH, and the UV/O_3 method can effectively detoxify the polluted solution. Fu et al. [15] compared the degradation of alkyl xanthate in aqueous solution by O_3 and UV/O_3 methods, and found that the removal rate of chemical oxidation demand in 40 min through UV/O_3 process was 66.2%–81.2%, much higher than that by O_3 alone (50.9%–61.2%):

$$O_3 + H_2O + h\gamma \rightarrow H_2O_2 + O_2 \tag{1}$$

$$H_2O_2 + h\gamma \rightarrow 2^{\bullet}OH \tag{2}$$

As the water matrix, inorganic anions may impact the removal of micro-pollutants [16]. There have been many researches focusing on the influences of anions [17,18]. Most anions performed a certain degree of a detrimental effect on the contaminant degradation [19]. As free radical scavengers, Cl^- and CO_3^{2-} can capture $^{\bullet}$OH and compete for active substances with organic matter in water, so as to maintain the molecular form of O_3 solution in water, weaken the oxidation ability, and inhibit the occurrence of ozonation reaction.

In this study, the removal rates of SD and SMX through O_3, UV, and UV/O_3 processes were investigated. The degradation mechanisms of the abovementioned SAs were revealed. In addition, the effects of common ions in water, including Cl^-, Ca^{2+}, and HCO_3^-/CO_3^{2-}, on removal rates of SD and SMX were also explored.

2. Materials and methods

2.1. Reagents

SD (≥99%) was purchased from Energy Chemical Reagent Co., Ltd., (Shanghai, China), and SMX (≥99%) was obtained from Jiuding Chemical Reagent Co., Ltd., (Shanghai, China). NaCl (≥99.8%), Na_2CO_3 (≥99.8%), and $CaCl_2$ (≥96%) were bought from Fuchen Chemical Reagent Co., Ltd., (Tianjin, China), while $Na_2S_2O_3{\cdot}5H_2O$ was obtained from Ouhe Technology Co., Ltd., (Beijing, China). Methanol (chromatography grade) was obtained from J.T. Baker (US), while chromatography grade acetonitrile and formic acid were gotten from Sigma (US). Deionized (DI) water used for sample preparation was obtained from Milli-Q water purification system (Millipore Synergy 185, US).

2.2. Oxidation experiments

For ozonation experiments, O_3 was produced by an O_3 generator (3S-Λ3, Beijing Tonglin Technology Co., Ltd., China) equipped with an oxygenator (FY5W, Beijing Beichen Yaao Technology Co., Ltd., China), and introduced into a 250 mL beaker containing 100 mL DI water (pH 6.0 ± 0.1) in an ice bath (Fig. 1). Samples were taken after a certain time to determine the O_3 concentration using the "Indigo Colorimetric Method" [20]. SD or SMX stock solution (20 mg/L) of 100 mL was poured into the O_3 solution, with the initial SA was 10 mg/L, while the O_3 was calculated by dividing the concentration measured before adding SAs by two. Samples were taken out at certain intervals after SA solution was added, and the reaction in the samples was terminated by adding 0.5 mL of 1.0 g/L $Na_2S_2O_8$ solution before the SA concentrations were determined. The experiments for the removal of SAs through UV and UV/O_3 processes were similar to that for ozonation, except that a xenon lamp with $UV_{254\ nm}$ intensity of 0.9 mW/cm² was turned on.

The effect of initial O_3 concentration on the removal rate of 10 mg/L SMX was investigated by controlling the

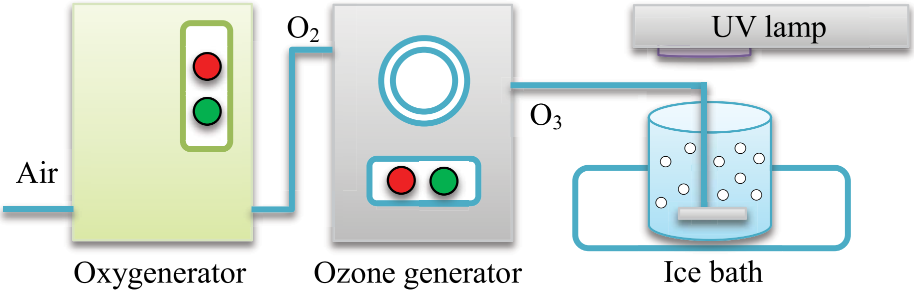

Fig. 1. Schematic diagram of the reaction system.

aeration time. Moreover, NaCl, $CaCl_2$, or Na_2CO_3 with a concentration of 3 mmol/L was added to DI water, then the pH value of the solution was adjusted to approximately 6.0, and the effects of Cl^-, Ca^{2+}, and HCO_3^-/CO_3^{2-} on removal rates of SD and SMX were explored. To investigate the degradation pathways of SD and SMX, the degradation products at 10 min were detected.

2.3. Analytical methods

The concentrations of SAs were quantified by high-performance liquid chromatography (HPLC, Shimadzu LC20AD, Kyoto, Japan) which was in conjunction with a SPD-20A UV detector at 265 nm, and a reversed-phase C8 column (5 µm, 4.6 mm × 150 mm) was employed [21]. The column temperature was 30°C, the injection volume was 20 µL, and the flow rate was 1 mL/min. The mobile phases were acetonitrile (*A*) and DI water with 0.1% formic acid (*B*). For SD analysis, the mobile phases were 60% *A* and 40% *B*, while the figures were 40% *A* and 60% *B* for SMX analysis. All samples were run in duplicates.

The degradation products of SD and SMX were detected by liquid chromatography-mass spectrometry (HPLC-MS) system (Agilent 1290-6460, US) equipped with an Agilent C18 column (3.5 µm, 2.1 mm × 150 mm). The analytical methods were the same as those for the quantitation of SAs concentrations. Positive ionization mode was used to acquire the products with a scan range of *m*/*z* 50–600.

3. Results and discussion

3.1. Removal rates of SD and SMX

The removal of SD and SMX by O_3, UV, and UV/O_3 were investigated, and the results are shown in Fig. 2.

3.1.1. Oxidation of SD and SMX by O_3 process

It can be seen from Fig. 2 that SD or SMX could be quickly decomposed, and the removal rates of SAs were almost unchanged 0.5 min after the reactions began. O_3 can react quickly with organics containing electron-rich functional groups such as aromatic C=C bonds [22]. It has been reported that the ozonation of micropollutants was a second-order reaction, with a constant of over 5.7 × 10^5 L/(mol s) [23]. Moreover, it could produce $^•OH$ which could oxidize most organics with rate constants of 10^8–10^9 L/(mol s) [24,25].

With the increase of the O_3 concentration, the removal rates of SD and SMX increased because more O_3 molecules and radicals were participated in the reactions with SAs. The removal rates of SD increased form 44.0% to 79.9% when the O_3 concentration increased from 6 to 12 mg/L, while those for SMX increased from 21.3% to 55.3%. Interestingly, the removal rates of SD were much higher than those of SMX, which might be related to the structures of the compounds. There is a pyrimidine ring in SD, which the function group is changed to be an isoxazole ring in SMX. The unsaturated degree of the pyrimidine ring is higher than that of isoxazole ring, resulting in a quicker reaction between O_3 and SD [26,27]. The removal rate of SMX in the presence of 100 mmol/L *tert*-butanol (BuOH, the $^•OH$ quencher) was much lower than that in the absence of *t*-BuOH, indicating that some of the SMX were indirectly oxidized by $^•OH$; however, the removal rate of SD was not reduced remarkable, showing that most of the SD were removed through direct ozonation (Fig. S1).

3.1.2. Oxidation of SD and SMX by UV process

The previous studies indicated that the degradation of SAs through UV irradiation was often reported to be a

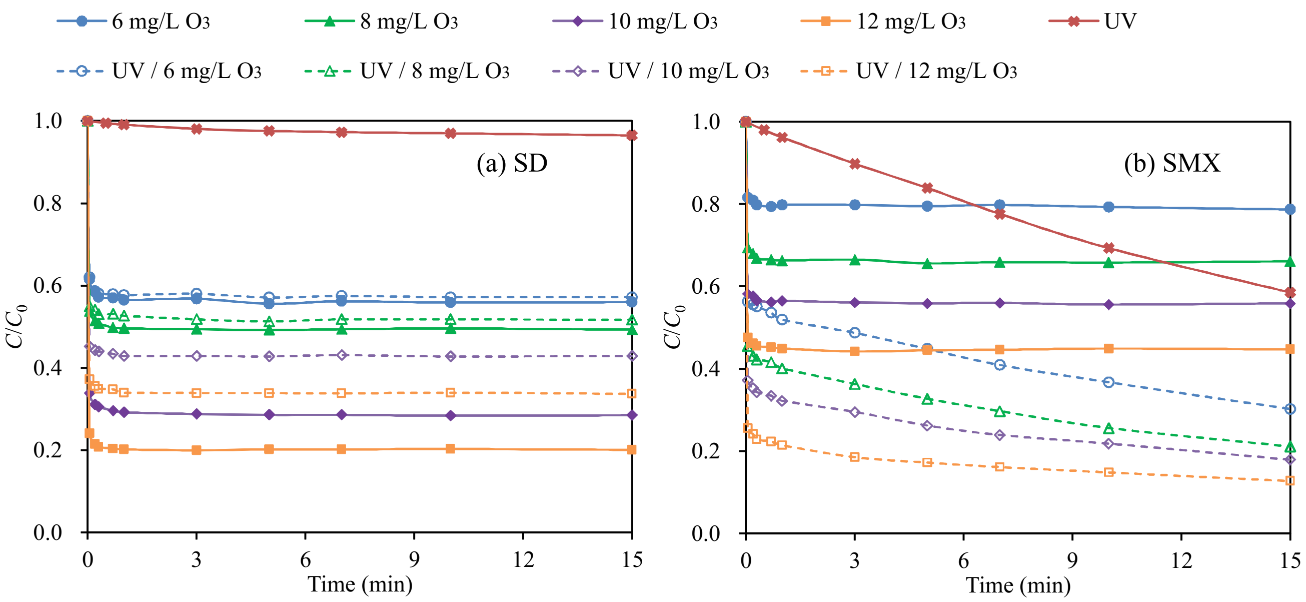

Fig. 2. Removal of (a) SD and (b) SMX in DI water through O_3, UV, and UV/O_3 processes ($UV_{254\ nm}$ intensity = 0.9 mW/cm², pH_0 = 6.0, temperature = 0°C, and $C_{SD/SMX,0}$ = 10 mg/L).

first-order reaction [28]. The concentrations of SD and SMX reduced with the extension of time. The removal rate of SD was quite low, with only 3.5% SD degraded in 15 min. However, the removal rate of SMX was much higher, indicating that SMX could be photolyzed effectively.

3.1.3. Oxidation of SD and SMX by UV/O_3 process

The effects of UV on the degradation of SD and SMX were quite different. For SD, the removal rate decreased when UV was employed, and the inhibitory effect was more obvious for the ozonation process with high O_3 concentration. As SD could hardly be decomposed by UV irradiation, the addition of UV could not promote the oxidation process. Moreover, the O_3 molecules could be decomposed under UV light [29,30], leading to the waste of O_3 and the reduction of SD removal rate. But for SMX, the removal rate raised in the presence of UV irradiation, which was concerned with the photolysis of SMX. It has been proved that the ozonation efficiencies of SMX were not high because the degree of unsaturation was not high. UV could promote the generation of $^{\bullet}$OH by O_3 decomposition [31,32], resulting in the non-selective oxidation of SMX.

3.2. Degradation pathways of SD and SMX

The SAs could not be mineralized completely by O_3, UV, and UV/O_3 process, especially in the static test, and the degradation products of SD and SMX at 10 min were detected (Fig. S2 and Fig. 3).

It can be seen that the degradation mechanisms of SD and SMX were similar. Hydroxylation and hydrolysis were found to be the main degradation pathways. As the product of SD ozonation, P267 was generated because of the attack of $^{\bullet}$OH or O_3 on the benzene ring or pyrimidine ring [33]. Similarly, P270 was found to be the hydroxylated product of SMX [34,35]. These products were also produced through UV/O_3 process, which has been reported in previous studies [36]. Moreover, the product P288, was then produced by the addition of H_2O to the isoxazole ring in P270B [37]. However, the hydroxylated products were not found during the UV irradiation process.

The hydrolyzed process at S–N bond led to the generation of P174 and P96 for SD [38], as well as P174 and P98 for SMX [37,39–41]. Aniline, marked as P94, might be generated by the loss of sulfonic group from P173 during hydrolysis. Interestingly, the hydrolyzed products could be found during the ozonation, UV irradiation, and UV enhanced ozonation of SMX [42,43], but not detected through the UV irradiation of SD. It has been found that SD was difficult to be photolyzed, resulting in the indetectable of the products.

3.3. Effect of ions on the removal of SD and SMX

3.3.1. Effect of Cl^-

Fig. 4a indicates that Cl^- has little effect on the photolysis of SD, which may be related to the low removal rate of SD itself. However, the ozonation rate of SD decreased from 71.5% to 62.4% after Cl^- was added. Cl^- has a

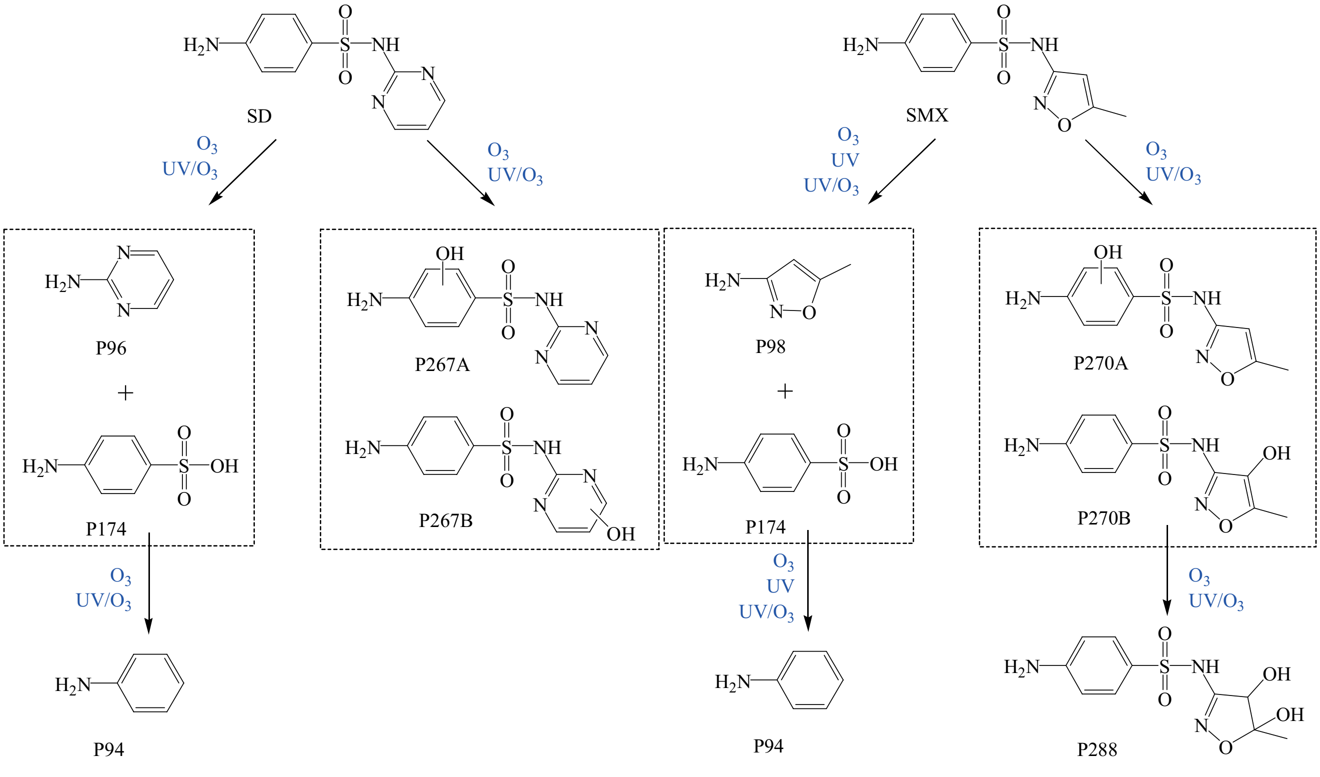

Fig. 3. Oxidation mechanisms of SD and SMX in DI water through O_3, UV, and UV/O_3 processes (UV$_{254\ nm}$ intensity = 0.9 mW/cm^2, pH$_0$ = 6.0, temperature = 0°C, $C_{SD/SMX,0}$ = 10 mg/L, and $C_{O_3,0}$ = 10 mg/L).

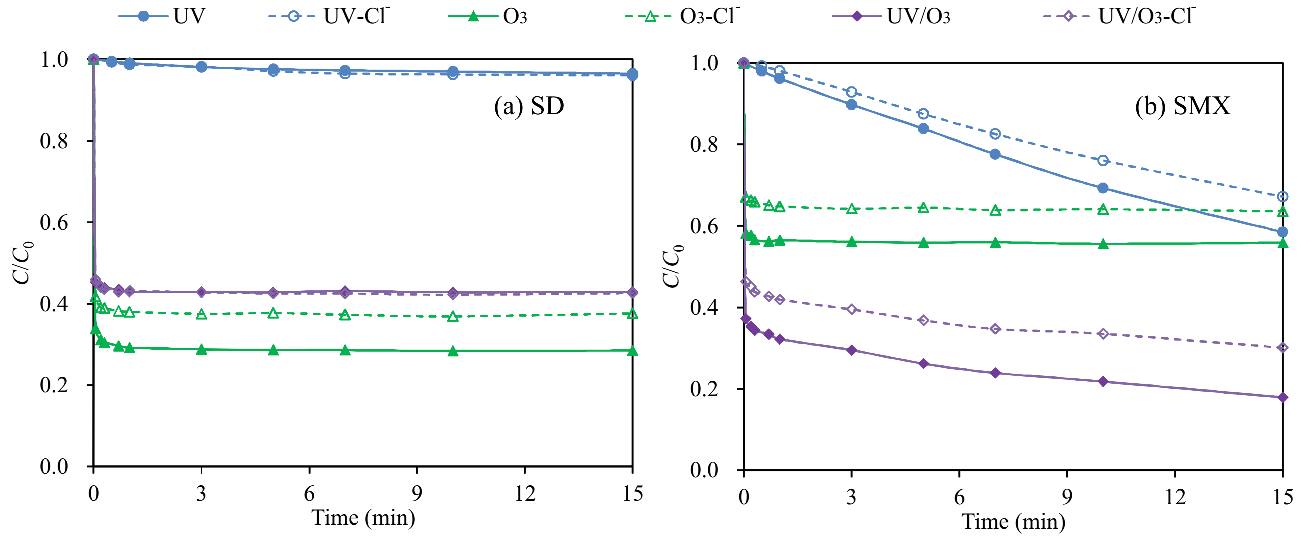

Fig. 4. Effect of Cl^- in water on oxidation of (a) SD and (b) SMX in ultrapure water through O_3, UV, and UV/O_3 processes (UV$_{254\,nm}$ intensity = 0.9 mW/cm^2, pH$_0$ = 6.0, temperature = 0°C, $C_{SD/SMX,0}$ = 10 mg/L, C_{Cl^-} = 3 mmol/L, and $C_{O_3,0}$ = 10 mg/L).

certain inhibitory effect on SD ozonation because the addition of Cl^- can accelerate the decomposition of O_3 in water to O_2 under pH < 7, which can limit the direct oxidation of O_3 in the reaction process (Eq. (3)), and therefore the ozonation rate of SD reduced somewhat [44]:

$$Cl^- + O_3 + H^+ \rightarrow Cl_2 + O_2 + H_2O \tag{3}$$

Cl^- has little effect on SD degradation through UV/O_3 process. The reaction solution system with the coexistence of Cl^- and $^{\bullet}OH$ under UV irradiation can form chlorine-free radicals ($Cl^{\bullet}$) (Eq. (4)) [45,46]. These free radicals may participate in the degradation of SD, thus reducing the influence of Cl^- on O_3 decomposition.

$$Cl^- + {}^{\bullet}OH \rightarrow Cl^{\bullet} + OH^- \tag{4}$$

Differently, the addition of Cl^- can inhibit the degradation of SMX through all three processes, with the SD removal rate through UV, O_3, and UV/O_3 reduced by 8.7%, 7.7%, and 12.2% in 15 min, respectively. The reason may be that the oxidation ability of $Cl^{\bullet}$ is lower than $^{\bullet}OH$, resulting in the inhibitory influence of Cl^- on the reactions which were based on the effect of radicals. The influence of Cl^- on SMX degradation through UV/O_3 process was greater than that on SD degradation, suggesting that the degradation of SMX is more dependent on $^{\bullet}OH$.

3.3.2. Effect of Ca^{2+}

As shown in Fig. 5, the removal rates of SD by UV, O_3, and UV/O_3 in 15 min were 5.0% (3.5%), 67.5% (71.5%), and 54.9% (57.1%) in the presence (absence) of $CaCl_2$, respectively, whereas those of SMX were 31.8% (41.5%), 58.8% (44.1%), and 82.8% (82.1%), respectively. Given that the addition of Cl^- may inhibit the degradation of the SAs, the Ca^{2+} in water can promote the degradation of micro-pollutants. The complexation of Ca^{2+} with SAs can promote the oxidative degradation of S–C bonds in SD and SMX by $^{\bullet}OH$ [47]. Furthermore, the additional Ca^{2+} can reduce the activation energies of the key step of SAs degradation reaction because of its role as an electron transporter, thus promoting the degradation of SAs [48].

3.3.3. Effect of HCO_3^-/CO_3^{2-}

As shown in Fig. 6, the addition of HCO_3^-/CO_3^{2-} inhibits the degradation of SD and SMX by all three processes. Among which, the greatest impact was obtained on the UV degradation of SMX, with the removal rate changed from 41.5% to 12.1% in 15 min. In most cases, as a ubiquitous $^{\bullet}OH$ capturer in water, HCO_3^-/CO_3^{2-} reacts with $^{\bullet}OH$ to produce $^{\bullet}CO_3^-$ which has a weaker oxidizing ability (Eqs. (5) and (6)) [36], therefore suppressing the removal of SD and SMX [49]. For SD ozonation which was mainly based on the direct oxidation by O_3 molecules, the generated $^{\bullet}HCO_3$ or $^{\bullet}CO_3^-$ can accelerate the decomposition of O_3 (Eqs. (7) and (8)), leading to the reduction of removal rate from 71.5% to 59.9%. Therefore, the HCO_3^-/CO_3^{2-} in water inhibited the removal of micro-pollutants by both capturing the $^{\bullet}OH$ and promoting the decomposition of O_3 molecules:

$$HCO_3^- + {}^{\bullet}OH \rightarrow OH^- + {}^{\bullet}HCO_3 \tag{5}$$

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow {}^{\bullet}CO_3^- + OH^- \tag{6}$$

$${}^{\bullet}HCO_3 + O_3 \rightarrow CO_2 + O_2 + H^+ + {}^{\bullet}O_2^- \tag{7}$$

$${}^{\bullet}CO_3^- + O_3 \rightarrow CO_2 + O_2 + {}^{\bullet}O_2^- \tag{8}$$

4. Conclusion

In this study, the removal of SD and SMX through O_3, UV, and UV/O_3 processes were investigated, and the effects

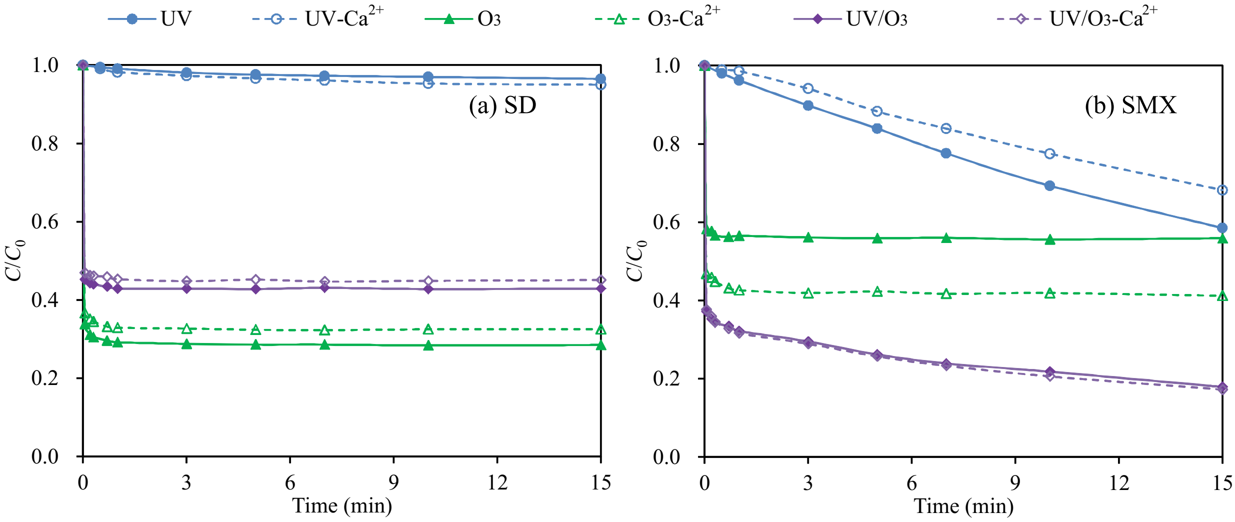

Fig. 5. Effect of Ca^{2+} in water on oxidation of (a) SD and (b) SMX in ultrapure water through O_3, UV, and UV/O_3 processes ($UV_{254\,nm}$ intensity = 0.9 mW/cm^2, pH_0 = 6.0, temperature = 0°C, $C_{SD/SMX,0}$ = 10 mg/L, $C_{Ca^{2+}}$ = 3 mmol/L, and $C_{O_3,0}$ = 10 mg/L).

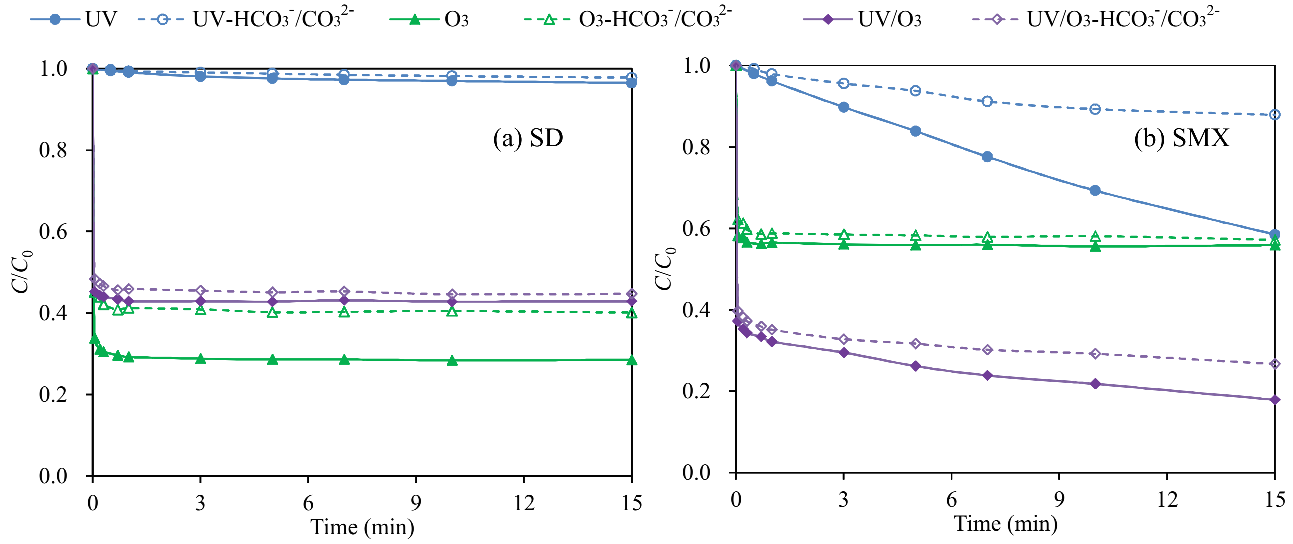

Fig. 6. Effect of HCO_3^-/CO_3^{2-} in water on oxidation of (a) SD and (b) SMX in ultrapure water through O_3, UV, and UV/O_3 processes ($UV_{254\,nm}$ intensity = 0.9 mW/cm^2, pH_0 = 6.0, temperature = 0°C, $C_{SD/SMX,0}$ = 10 mg/L, $C_{HCO_3^-/CO_3^{2-}}$ = 3 mmol/L, and $C_{O_3,0}$ = 10 mg/L).

of Cl^-, Ca^{2+}, and HCO_3^-/CO_3^{2-} on removal rates of SD and SMX were explored. SD and SMX were quickly decomposed during ozonation. With the increase of the O_3 concentration, their removal rates increased. SD is easier to be ozonized than SMX because the unsaturated degree of pyrimidine ring is higher than that of isoxazole ring. However, SMX can be photolyzed effectively, but SD cannot. The SD ozonation rate reduced when UV was employed because SD was mainly decomposed by direct ozonation, and the O_3 molecules were decomposed under UV light. Nevertheless, the SMX removal was promoted during the UV/O_3 process since SMX was mainly degraded by non-selective oxidation with the help of $^•OH$. The degradation mechanisms of SD and SMX during the UV/O_3 process were similar. Hydroxylation and hydrolysis were found to be the main degradation pathways. The Cl^- and HCO_3^-/CO_3^{2-} in water inhibited the degradation of SD and SMX by all three processes. As the $^•OH$ capturer in water, Cl^- or HCO_3^-/CO_3^{2-} reacts with $^•OH$ to produce $^•Cl$ or $^•HCO_3/^•CO_3^-$ which has the weaker oxidizing ability. Meanwhile, they can accelerate the decomposition of O_3 to O_2, which limits the direct oxidation of O_3 molecules in the reaction processes. The removal of SD and SMX was promoted in the presence of Ca^{2+} because the complexation of Ca^{2+} with the pollutants can promote the oxidative degradation of S–C bonds by $^•OH$. Furthermore, Ca^{2+} can reduce the activation energies of the key step of SAs degradation reaction because of its role as an electron transporter, thus facilitating the degradation of SD and SMX.

Acknowledgments

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Supporting information

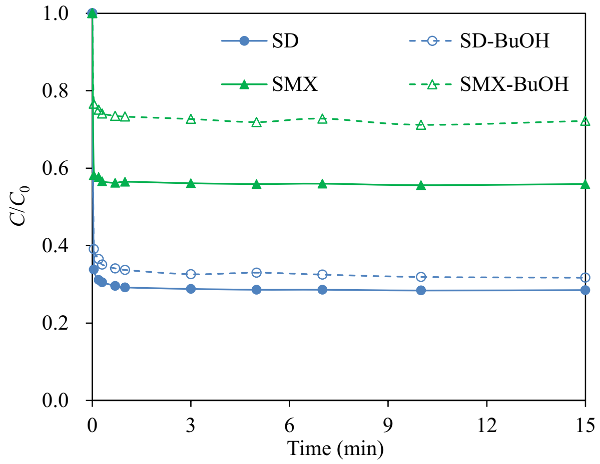

Fig. S1. Removal of SD and SMX in the presence and absence of 100 mmol/L *tert*-butanol (BuOH) through O_3 process (pH_0 = 6.0, temperature = 0°C, $C_{SD/SMX,0}$ = 10 mg/L, and $C_{O_3,0}$ = 10 mg/L).

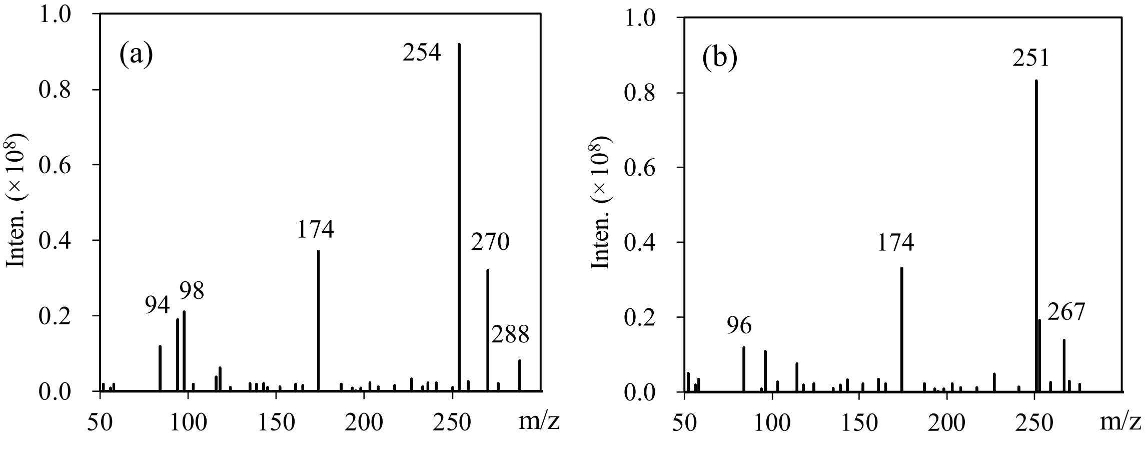

Fig. S2. HPLC-MS graphs of the degradation intermediates.