Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.960471

56 (2015) 2225–2233
November

Taylor & Francis
Taylor & Francis Group

Heat-activated persulfate oxidation of sulfamethoxazole in water

Yu-qiong Gao[a], Nai-yun Gao[a,*], Yang Deng[b], Da-qiang Yin[a], Yan-sen Zhang[a], Wen-lei Rong[c], Sheng-dong Zhou[c]

[a]*State Key Laboratory of Pollution Control and Resources Reuse, Ministry of Education, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, P.R. China, Tel. +86 21 65982691; Fax: +86 21 65986313; emails: gaoyuqiongtj@163.com (Y.-q. Gao), gaonaiyun2016@163.com (N.-y. Gao), yindaqiang2016@163.com (D.-q. Yin), zhangyansen2016@163.com (Y.-s. Zhang)*

[b]*Department of Earth and Environmental Studies, Montclair State University, Montclair, NJ 07043, USA, email: dengyang7@gmail.com (Y. Deng)*

[c]*Wuxi Water Supply General Company, Wuxi 214031, P.R. China, emails: wenlei_rong@sina.com (W.-l. Rong), zhoushengdong1@sina.com (S.-d. Zhou)*

Received 19 May 2014; Accepted 19 August 2014

ABSTRACT

Heat-activated persulfate to produce highly reactive sulfate radicals ($SO_4^{\bullet-}$) to oxidize sulfamethoxazole (SMX) in water was studied. The SMX degradation rate was significantly influenced by the reaction temperature, persulfate dose, initial pH, and co-existing anions. Higher temperature achieved higher degradation rate. The calculated activation energy for hot persulfate oxidation of SMX was approximately 130.93 kJ/mol. The degradation rate constant was proportional to the persulfate dose. An alkaline condition favored the SMX degradation. Effects of anions on the SMX degradation were species-dependent. Cl^-, SO_4^{2-}, and NO_3^- inhibited the SMX degradation, to different degrees. In contrast, HCO_3^- accelerated the treatment. The SMX decomposition was associated with hydroxylation, sulfonamide bond breakage, and oxidation of the amine groups. Toxicity tests revealed production of more toxic products. Therefore, appropriate post-treatments need to be considered to address the undesirable byproducts.

Keywords: Sulfamethoxazole; Heat-activated persulfate; Factors; Products; Mechanism; Toxicity

1. Introduction

Antibiotics in water, as a family of emerging contaminants, have been increasingly concerned because they are frequently identified in the aquatic environment and some of them exhibit adverse effects on ecosystems and human health [1–3]. Most of the antibiotics used are excreted in the forms of parent compounds or their metabolites, and may enter into the aquatic environment through different pathways [4–6]. The major concern of the introduction of large quantities of antibiotics into our environment is the occurrence of resistant bacteria and more pathogenic bacterial recombinants [7]. Sulfamethoxazole (SMX) is a commonly prescribed antibiotic used for treatment of urinary infection. SMX has been detected in many municipal sewage treatment plant effluents at a level of μg/L [8,9], as well as found at ng/L in surface water [10] and even in ground water [11]. Because SMX is biochemically persistent, and may lead to the increased

*Corresponding author.

bacterial resistance in water [12], there is an urgent demand to develop viable treatment technologies for control of the antibiotics in aquatic environments.

Over the past decade, sulfate radical ($SO_4^{\cdot-}$) based advanced oxidation processes (AOPs) as a new water treatment method have attracted great attention. $SO_4^{\cdot-}$ has a very high redox potential of 2.6 V close to that of ·OH in traditional AOPs (2.9 V), and exhibits an unselective pattern during rapid reactions with targeted micropollutants in water. $SO_4^{\cdot-}$ is produced by the activation of persulfate ($S_2O_8^{2-}$) through heat, UV, or transition metals [13–15]. Although ferrous-activated and microwave-activated persulfate methods have been tested for degradation of SMX in water [16,17], the information on the SMX degradation by heat-activated persulfate is limited. The objective of this study was to evaluate SMX degradation by heat-activated persulfate in water. Key factors including temperature, persulfate dose, pH, and co-existing anions on the SMX degradation were assessed. Identification of oxidation intermediate and final products provided mechanistic information behind the degradation. In addition, the toxic effect of SMX and its intermediate products released during the treatment has also been studied.

2. Materials and methods

2.1. Materials

All the chemicals used were of analytical grade, at least. SMX and high performance liquid chromatogram (HPLC)-grade acetonitrile were purchased from Sigma-Aldrich. Sodium persulfate ($Na_2S_2O_8 \geq 99.5\%$), sodium nitrate, sodium chloride, sodium sulfite, sodium bicarbonate, ethanol, and tert-butyl alcohol (TBA) were purchased from Sinopharm Chemical Reagent Co., China. The freeze-dried powder of bioluminescent bacterium (kept at −20℃) *V. qinghaiensis* sp. Nov-Q67 (Q67) was purchased from Beijing Hammatsu Photon Techniques Inc. All the solutions used in this study were prepared using Milli-Q water(18.2 MΩ cm).

2.2. Experimental procedure

All the tests were conducted in 45 mL glass bottles containing 40 mL SMX solution (40 μM). These reactors were installed in a shaker with water bath (Zhengzhou Great Wall Scientific Industrial and Trade Co., China). The oxidation was initiated once appropriate volumes of the $Na_2S_2O_8$ stock solution were added. The initial solution pH was adjusted to a desirable level with 1 N H_2SO_4 and NaOH solutions. At designated time intervals, 0.8 mL sample was collected from each reactor to a 1.5-mL sample bottle, and immediately chilled at 4℃ in an ice bath for 5 min to quench any further oxidation. All the tests were performed in triplicate, and the standard deviations of all measured data were < 5%.

2.3. Analysis

SMX was measured using a HPLC system (Waters e2695, USA) equipped with a UV–vis detector (Waters 2489) (λ = 270 nm) and a Symmetry C18 column (4.6 mm × 250 mm, 5 μm, Waters, USA). The mobile phase consisting of 40%/60% (v/v) acetonitrile and Milli-Q water had a flow rate of 0.8 mL min^{-1}. The sample injection volume was 10 μL and the column temperature was maintained at 35℃. The persulfate concentration was spectrophotometrically determined by a UV–vis spectrophotometer (HACH, DR5000, USA) using the method developed by Liang et al. [18]. Oxidation intermediates of SMX were identified by LC/MS/MS. The HPLC (Waters e2695, USA) was equipped with a Hypersil Gold C18 column (2.1 × 150 mm, 3 μm, Thermo, USA). A and B mobile phases were Milli-Q water with 0.1% formic acid and acetonitrile, respectively, at a flow rate of 0.25 mL min^{-1} with an injection volume of 10 μL. A gradient method was used to separate the intermediate products during the reaction. The elute was 1% B for the first 3 min, and the B solution was linearly increased to 5% in 5 min, and kept 5% B for 2 min. Subsequently, the elute was increased to 60% within 10 min and further increased to 90% in the following 10 min. Afterwards, the elution was maintained at 90% B for 2 min. Finally the elution was back to the initial condition. The HPLC system was connected with a triple stage quadrupole mass spectrometer (Thermo Scientific * TSQ Quantum Access MAX, USA) with ion sources under the following conditions: spray voltage = 3500 V, Sheath gas pressure = 20 au, aux gas pressure = 5 au, and capillary temperature =320℃. Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu TOC 5050A) equipped with an ASI5000 auto-sampler. The bioluminescent bacterium *V. qinghaiensis*sp. Nov-Q67 (Q67) was adopted to quantify the toxicity variation before and after the heat-activated persulfate treatment. Prior to the toxicity assessment, the bacteria was reactivated in 1 mL NaCl solution (0.8%) and then stored in an ice water bath. To 2.0 mL samples, 100 μL suspension of bacteria Q67 was added. The decrease in bioluminescence, as an indicator of the toxic effect, was measured by a water toxicity analyzer BHP 9511 (Beijing Hamamatsu Photon Tec. Inc., Beijing, China) after 15 min exposure at 15℃. Luminescence inhibition percentage was used to express the effect of

oxidation products of SMX on Q67, and the inhibition rate (I%) was calculated as follows.

$$I\% = \frac{I_0 - I_X}{I_0} \times 100\% \quad (1)$$

where I_X and I_0 are the luminosity of sample solution and blank solution, respectively.

3. Results and discussion

3.1. Effect of temperature

The effect of temperature (40–70°C) on the SMX degradation rate is shown in Fig. 1. At any particular temperature, the SMX degradation will fit a pseudo-first-order kinetics pattern. The degradation rate constant significantly increased from 9.13×10^{-4} to 7.11×10^{-2} min^{-1} as the temperature improved from 40 to 70°C. Accordingly, a complete SMX degradation was almost achieved after 45 min reaction at 70°C. In contrast, a 2-h treatment only degraded 10.2% SMX at 40°C. The findings suggest that the SMX degradation in the heat-activated persulfate system is highly temperature dependent. In general, higher temperatures provide more energy to rupture O–O bonds of persulfate, and more readily produce reactive species such as $SO_4^{\cdot-}$ and ·OH, thereby leading to more rapid degradation of target pollutants in water [19]. However, the TOC removal rates at 40, 50, 60, and 70°C were 1.5, 2.5, 7.9, and 34.8% after 2 h, respectively. Compared to molecular degradation, the TOC removal was not pronounced even at 70°C, suggesting that the degradation products of SMX were not amenable to the $SO_4^{\cdot-}$ or ·OH oxidation. Of note, the overall consumption of persulfate relied heavily upon the reaction temperature. The fractions of depleted persulfate were 2.23, 2.91, 4.07, and 13.2% after 2-h reactions under 40, 50, 60 and 70°C, respectively. A similar result was observed by Ghauch and Tuqan [20], when they applied heated persulfate/H_2O systems to oxidize bisoprolol.

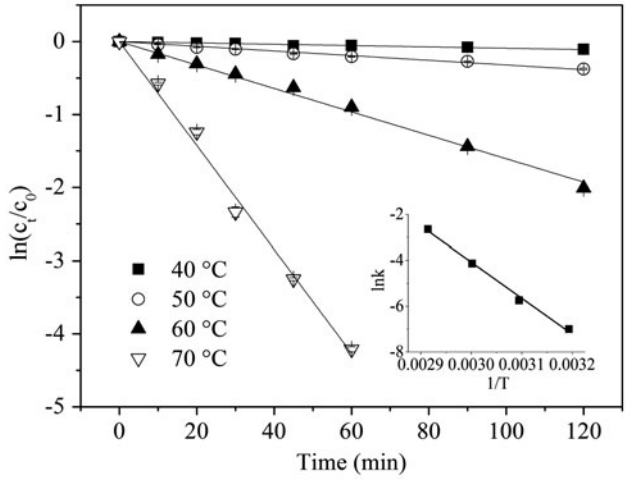


Fig. 1. Effect of temperature on the degradation of SMX by heat-activated persulfate. ($[SMX]_0$ = 40 μM, $[Na_2S_2O_8]_0$ = 2.4 mM, T = 40, 50, 60, and 70°C; insert: plot of ln k vs. $1/T$ for E_a estimation.)

Temperature dependency of the kinetics constant was further evaluated using the Arrhenius equation (Eq. (2)).

$$\ln k = \ln A - \frac{E_a}{RT} \quad (2)$$

where k is the pseudo-first-order rate constant, min^{-1}; A is the Arrhenius constant; E_a is the apparent activation energy, kJ/mol; R is the universal gas constant, 8.314×10^{-3} kJ/(mol·K); and T is absolute temperature, K.

As seen from the insert of Fig. 1, the lnk and $1/T \times 1{,}000$ had a linear relationship (R^2 = 0.99). The activation energy was 130.93 kJ/mol and the Arrhenius constant was 43.17 kJ/mol. The calculated E_a value was greater than that during the heated persulfate degradation of bisoprolol (E_a = 119.8 kJ/mol), indicating that SMX was more recalcitrant in a heated persulfate system [20].

3.2. Effect of persulfate dose

Persulfate dose is an essential operating factor, given that it is the source of sulfate radicals in a heat-activated persulfate process. The effect of persulfate dose is presented in Fig. 2. The SMX degradation well obeyed a pseudo-first-order kinetics pattern regardless of the persulfate dose. As the persulfate dose increased from 0.8 to 4.0 mM, the pseudo-first-order rate constants augmented from 1.83×10^{-2} to 3.99×10^{-2} min^{-1}.

We also noticed that the pseudo-first-order rate constant exhibited a linear relationship with the persulfate dose, as shown in insert of Fig. 2 ($k = 0.00694 \times [persulfate]_0 - 0.00175$, R^2 = 0.99), implying that the $SO_4^{\cdot-}$ yield was proportional to the persulfate dose at a constant temperature. This finding is consistent with the results of Deng et al. [21], who reported that the degradation rate of carbamazepine was proportional to the initial persulfate concentration.

3.3. Effect of initial pH

Effect of initial solution pH on the SMX degradation is shown in Fig. 3. The pseudo-first-order rate

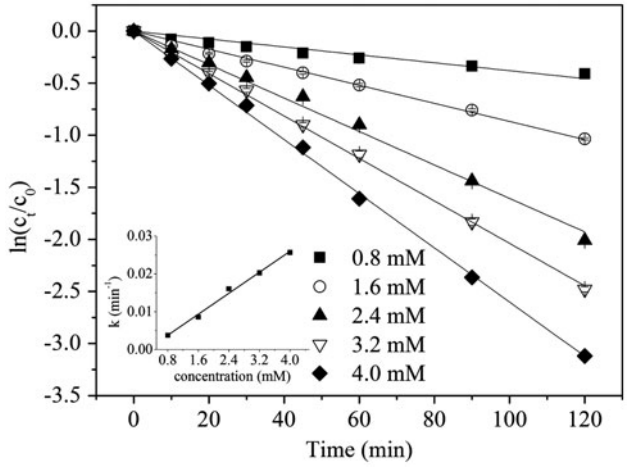


Fig. 2. Effect of persulfate dose on the degradation of SMX by heat-activated persulfate. ($[SMX]_0$ = 40 μM, $[Na_2S_2O_8]_0$ = 0.8, 1.6, 2.4, 3.2 and 4.0 mM, T = 60°C; insert: plot of k vs. $[persulfate]_0$.)

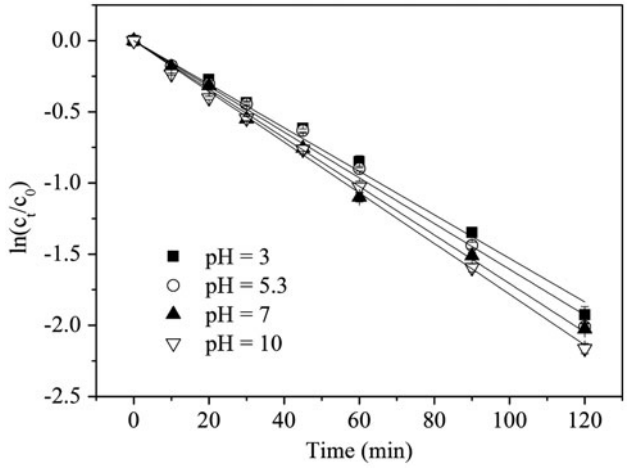


Fig. 3. Effect of initial pH on the degradation of SMX by heat-activated persulfate. ($[SMX]_0$ = 40 μM, $[Na_2S_2O_8]_0$ = 2.4 mM, T = 60°C.)

constant increased from 1.53×10^{-2} to 1.78×10^{-2} min^{-1} with the increasing initial pH from 3 to 10. At an acidic condition, the activation of persulfate into $SO_4^{\cdot-}$ could be inhibited by the generation of ineffectual anions or weaker oxidants, such as $HS_2O_8^-$, H_2SO_5, SO_4, HSO_4^-, and H_2O_2, through the following reactions (Eqs. (3)–(7)) [22], thereby lowing the SMX degradation rate.

$$SO_4^{\cdot-} + H_2SO_4 \rightarrow HSO_4^{\cdot} + HSO_4^- \quad (3)$$

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \quad (4)$$

$$HS_2O_8^- \rightarrow SO_4 + HSO_4^- \quad (5)$$

$$HS_2O_8^- + H_2O \rightarrow H_2SO_5 + HSO_4^- \quad (6)$$

$$H_2SO_5 + H_2O \rightarrow H_2O_2 + H_2SO_4 \quad (7)$$

$$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + {}^{\cdot}OH \quad (8)$$

When the solution pH was increased to an alkaline condition, $SO_4^{\cdot-}$ would transform to ·OH as shown in Eq. (8) [23]. ·OH processes a slightly higher redox potential (2.90 V) than $SO_4^{\cdot-}$ (2.60 V), and ensured a higher SMX degradation rate in an alkaline solution. Liang and Su [24] used nitrobenzene as a chemical probe to identify the active radical species, and found that $SO_4^{\cdot-}$ was the predominant radical species at pH < 7; both $SO_4^{\cdot-}$ and ·OH coexisted at pH 9, and ·OH prevailed at a higher pH. On the other hand, SMX is an ampholyte with both basic ($-NH_2$) and acidic ($-SO_2-NH-R$) groups, with $pK_{a,1}$ = 1.6 and $pK_{a,2}$ = 5.7 [25]. The fractions of protonated, neutral, and deprotonated forms of SMX are also pH dependent according to Eqs. (9)–(11).

$$a^+ = \frac{[H^+]^2}{[H^+]^2 + pK_{a,1}[H^+] + pK_{a,1}pK_{a,2}} \quad (9)$$

$$a^0 = \frac{pK_{a,1}[H^+]}{[H^+]^2 + pK_{a,1}[H^+] + pK_{a,1}pK_{a,2}} \quad (10)$$

$$a^- = \frac{pK_{a,1}pK_{a,2}}{[H^+]^2 + pK_{a,1}[H^+] + pK_{a,1}pK_{a,2}} \quad (11)$$

where a^+, a^0, and a^- are the mass fractions of the different SMX species in water.

The amino group of SMX was the likely sites subject to the $SO_4^{\cdot-}$ attack [26]. At a low pH, the non-protonated SMX accounted for the major fraction and appeared to be less susceptible to the $SO_4^{\cdot-}$ oxidation than that of the deprotonated form at higher pH. Our results indicated that an alkaline condition favored the SMX degradation in a heat-activated persulfate system. Similar findings were reported by Xie et al. [27], who found that degradation rates of aniline at different pH obeyed the following sequence in a heat-assisted persulfate system: pH 11 > pH 7 > pH 5 > pH 3.

3.4. Effect of co-existing anions

Effects of four common inorganic anions in water, including Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^-, on the performance of the heat-activated persulfate system in terms of SMX degradation are shown in Fig. 4. As seen, Cl^-, SO_4^{2-}, and NO_3^-, all showed an inhibition effect, whereas HCO_3^- favored the SMX degradation rate. Compared to the rate constant of 1.61×10^{-2} min^{-1} in the control group, the pseudo-first-order rate constants with the introduction of Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^- were 1.31×10^{-2} min^{-1}, 1.58×10^{-2} min^{-1}, 1.56×10^{-2} min^{-1}, and 2.80×10^{-2} min^{-1}, respectively.

The negative effects of SO_4^{2-} and NO_3^- were relatively minor, and the inhibition was due to the high ion strength that slowed down the persulfate decomposition [28]. Moreover, the presence of SO_4^{2-} would reduce the half-reaction reduction potential of $SO_4^{\cdot-}$ [29]. In contrast, a fraction of $SO_4^{\cdot-}$ in the presence of Cl^- might react with Cl^- according to Eqs. (12)–(15), to produce less reactive radicals such as $Cl_2/2Cl^-$ (1.36 V) and $Cl^{\cdot}/Cl^-$ (2.41 V) [30]. In this study, the three anions inhibited SMX degradation rate with the ascending order: $NO_3^- < SO_4^{2-} < Cl^-$.

$$SO_4^{\cdot-} + Cl^- \rightarrow SO_4^{2-} + C1^{\cdot}, \quad k = (3.2 \pm 0.2) \times 10^8 M^{-1}s^{-1} \tag{12}$$

$$Cl^{\cdot} + C1^- \rightarrow Cl_2^{\cdot-}, \quad k = (7.8 \pm 0.8) \times 10^9 M^{-1}s^{-1} \tag{13}$$

$$Cl_2^{\cdot-} + C1_2^{\cdot-} \rightarrow Cl_2 + 2Cl^-, \quad k = (98 \pm 1) \times 10^8 M^{-1}s^{-1} \tag{14}$$

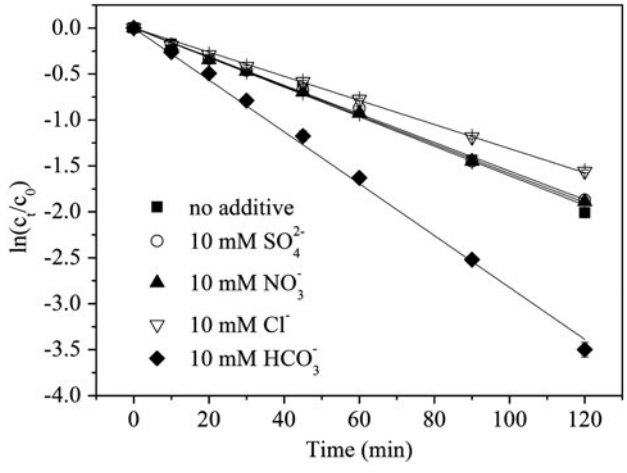


Fig. 4. Effect of anions on the degradation of SMX by the heat-activated persulfate process. ($[SMX]_0$ = 40 μM, $[Na_2S_2O_8]_0$ = 2.4 mM, T = 60°C, $[Cl^-]_0 = [NO_3^-]_0 = [SO_4^{2-}]_0 = [HCO_3^-]_0$ = 10 mM.)

$$C1^{\cdot} + Cl^{\cdot} \rightarrow Cl_2, \quad k = 1 \times 10^8 M^{-1}s^{-1} \tag{15}$$

It is of great interest that 10 mM HCO_3^- increased the pseudo-first-order rate constant by 74%. In general, once HCO_3^- is added to the solution, carbonate system would be formed (Eqs. (16) and (17)).

$$H_2CO_3(aq) \rightarrow H^+ + HCO_3^-, \quad pK_a = 6.37 \tag{16}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-}, \quad pK_a = 10.33 \tag{17}$$

$$SO_4^{\cdot-} + HCO_3^- \rightarrow SO_4^{2-} + HCO_3^{\cdot}, \quad k = 1.6 \times 10^6 M^{-1}s^{-1} \tag{18}$$

$$SO_4^{\cdot-} + CO_3^{2-} \rightarrow SO_4^{2-} + CO_3^{\cdot-}, \quad k = 6.1 \times 10^6 M^{-1}s^{-1} \tag{19}$$

$$HCO_3^{\cdot} \rightarrow H^+ + CO_3^{\cdot-}, \quad pK_a = 9.5 \pm 0.2 \tag{20}$$

$$SO_4^{\cdot-} + SO_4^{\cdot-} \rightarrow S_2O_8^{2-}, \quad k = 4.0 \times 10^8 M^{-1}s^{-1} \tag{21}$$

Both HCO_3^- and CO_3^{2-} could rapidly react with $SO_4^{\cdot-}$ to produce $CO_3^{\cdot-}$, as shown in Eqs. (18)–(20). In the $SO_4^{\cdot-}$-based advanced oxidation processes, the presence of too many $SO_4^{\cdot-}$ might lead to scavenge themselves according to Eq. (21) [31]. However, less reactive $CO_3^{\cdot-}$ (1.65 V) was produced in the presence of HCO_3^- to inhibit the degree of the Eq. (21) and achieve a higher SMX degradation. Moreover, the structure of SMX might play a role in the positive role of HCO_3^-. $CO_3^{\cdot-}$ could react with anilines in sulfonamides (SAs) with a bimolecular reaction rate [32] to accelerate the degradation of SMX. In addition, HCO_3^- could maintain the solution pH around 8.5 during the 2-h reaction that favored the SMX degradation as discussed earlier.

3.5. Oxidation products and degradation mechanisms

In order to better understand the degradation mechanisms and identify the major radicals ($SO_4^{\cdot-}$ and ·OH) responsible for the SMX degradation, we first investigate the SMX degradation by persulfate at 60°C with excess ethanol (EtOH) and TBA ([alcohol scavenger]:[persulfate] = 400:1) at natural pH. EtOH was a scavenger for both ·OH ($1.2–2.8 \times 10^9$ $M^{-1}s^{-1}$) and $SO_4^{\cdot-}$ ($1.6–7.7 \times 10^7$ $M^{-1}s^{-1}$), while the reaction rate of TBA with ·OH ($3.8–7.6 \times 10^8$ $M^{-1}s^{-1}$) was much higher than with $SO_4^{\cdot-}$ ($4–9.1 \times 10^5$ $M^{-1}s^{-1}$) [33]. As shown in

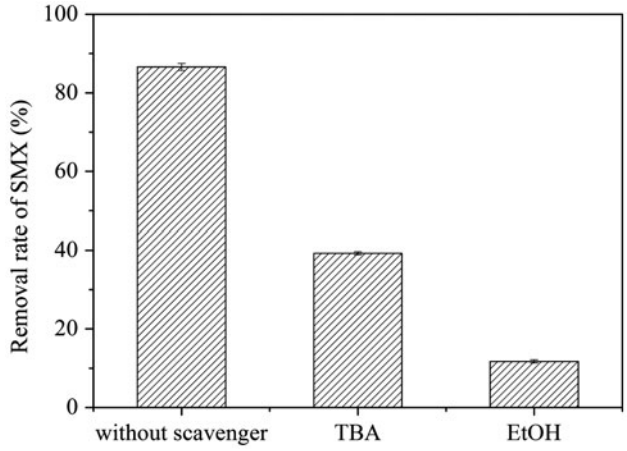
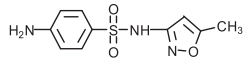
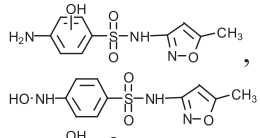
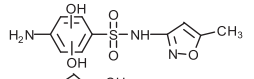
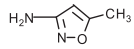
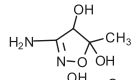
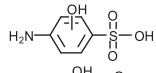
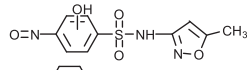


Fig. 5. SMX degradation without and with different scavengers. ($[SMX]_0$ = 40 μM, $[Na_2S_2O_8]_0$ = 2.4 mM, $[TBA]_0 = [EtOH]_0$ = 0.96 M, T = 60°C.)

Fig. 5, the addition of TBA decreased the degradation rate of SMX by 47.3%. In contrast, when EtOH was introduced, the degradation rate was reduced by 74.9%. This finding suggests that both $SO_4^{\cdot-}$ and ·OH were responsible for the degradation of SMX, and ·OH played a slightly more important role.

LC/MS/MS was used to identify the intermediate products (Table 1) during the treatment. Based on our results, in conjunction with literature data, we herein propose the plausible possible mechanisms of the SMX degradation in a heat-activated persulfate system. Hydroxylation could occur in the benzene or isoxazole rings, yielding the intermediate m/z 270 and m/z 286 that represent mono- and di-hydroxyl derivatives of SMX, respectively. ·OH more likely attacks organic molecules through hydrogen abstraction or addition reactions, while $SO_4^{\cdot-}$ preferentially participates in electron-transfer reaction. Both of them are responsible for the hydroxylated SMX formation [34]. Another major mechanism is the cleavage of the SA bond [35], resulting in the formation of 3-amino-5-methyl-isoxazole (m/z 99) and sulfanilic acid. Although we did not find the m/z of 174 for sulfanilic acid in this study, the m/z of 190 detected in this study is likely the hydroxylated form of sulfanilic acid at a retention time of 28.25 min, indicating that sulfanilic once existed in the system and quickly attacked by $SO_4^{\cdot-}$ or ·OH. The m/z of 174 might also originate from the N–S bond of hydroxylated SMX. We also observed the m/z of 133, the hydroxylation of 3-amino-5-methyl-isoxazole, which has also been reported by Lekkerkerker-Teunissen et al. [36]. The cleavage of C–N of m/z of 174 or m/z of 190 would further yield aniline with the m/z of 94. The m/z of 284 at a retention time of 27.37 min was consistent with the hydroxylation of nitroso derivative of SMX [37]. The proposed reaction pathways are presented in Fig. 6.

Table 1
Major intermediate oxidation compounds

Intermediates	Retention time (min)	m/z	Tentative structure
SMX	18.11	254	
1	18.87	270	
2	26.50	286	
3	2.09	99	
4	0.67	133	
5	28.25	190	
6	27.37	284	
7	1.82	94	

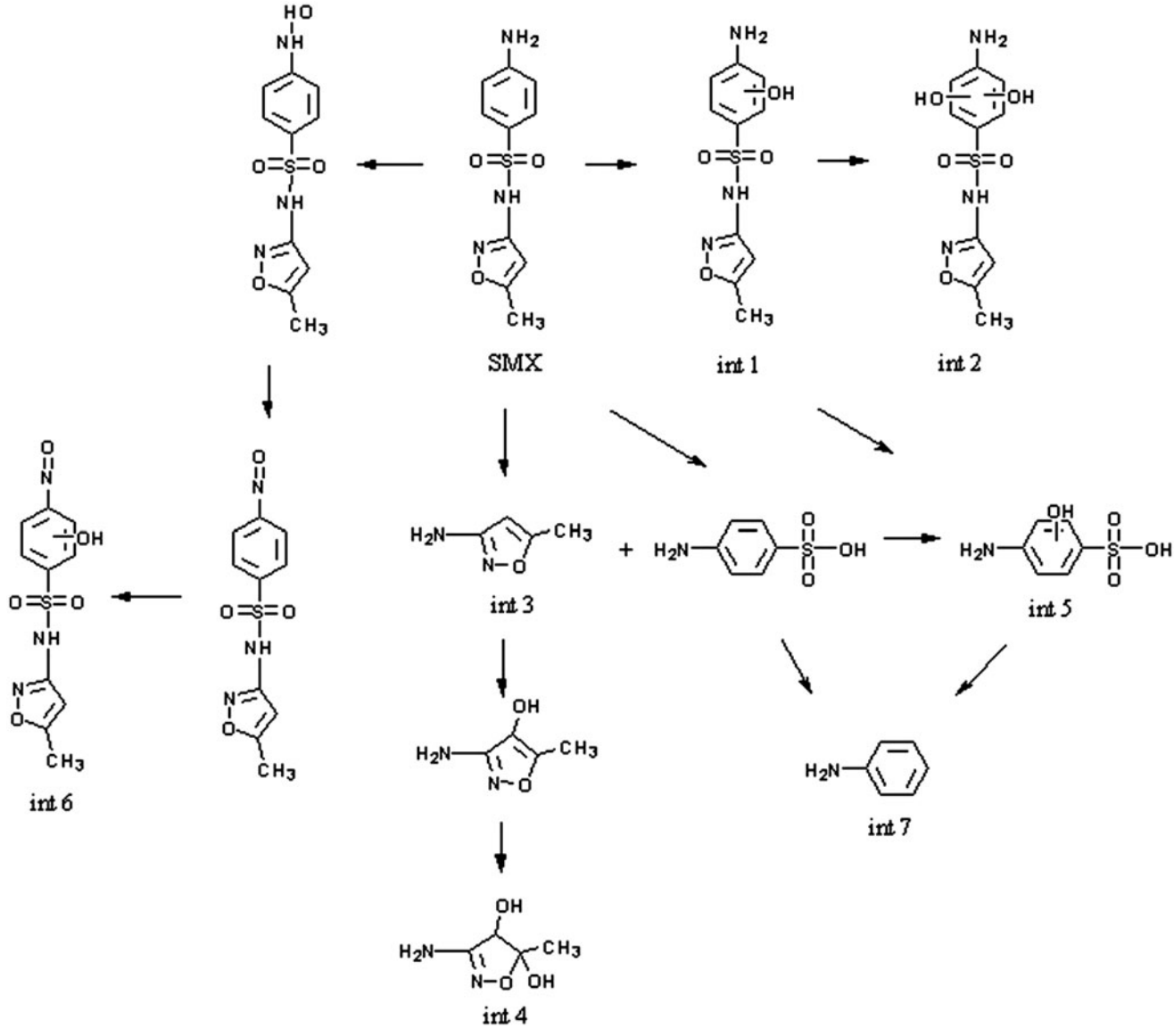


Fig. 6. Proposed reaction pathways for SMX degradation in the heat-activated persulfate system.

3.6. Toxicity and TOC

Toxicity of the oxidation byproducts and final products needs to be carefully assessed when chemical oxidation is applied in water treatment, because more toxic products may be produced. In this study, the toxicity of our treated SMX-containing water, expressed as a luminescence inhibition rate, was evaluated as shown in Fig. 7. The inhibition rate of the untreated solution containing SMX after a 10-fold dilution was approximately 7.90%. As the treatment proceeded, the inhibition rate gradually increased, and finally reached 71.46% after 120 min. According to Gomez-Ramos [38], hydroxylated derivatives or other minor degradation products might be involved in the increased toxicity. We also noticed that the heat-activated persulfate process could not significantly achieve a TOC removal. For example, after a 2-h treatment, the TOC removal was only 7.9%, though the corresponding SMX removal reached 86.6%. This finding suggests that few organic molecules were mineralized though the SMX degradation occurred. Therefore, appropriate polishing treatments need to be considered to address the undesirable degradation byproducts.

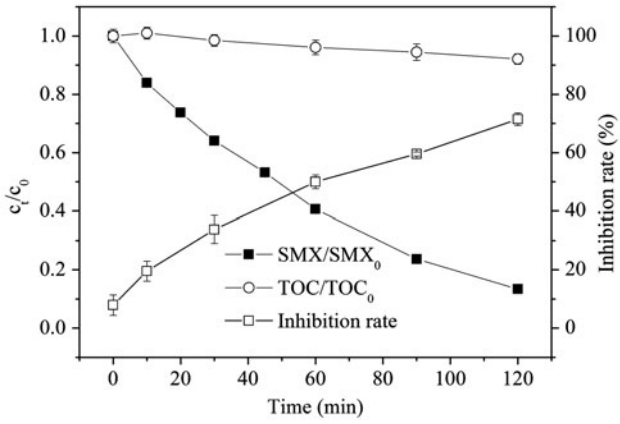


Fig. 7. Change of SMX/SMX$_0$, TOC/TOC$_0$, and toxicity during the oxidation process.

4. Conclusion

In this study, we evaluated the degradation of SMX in a heat-activated persulfate process. The SMX degradation rate was influenced by the reaction temperature, persulfate dose, initial pH, and con-existing anions. Scavenging tests revealed that both $SO_4^{\cdot-}$ and ·OH were responsible for SMX degradation, though the role of ·OH was slightly more weighted. The SMX decomposition in the heated persulfate system was associated with hydroxylation, SA bond breakage, and oxidation of the amine groups. Toxicity assessment indicated that more toxic products were generated. Therefore, post-treatments are needed for the elimination of the undesirable SMX oxidation products.

Acknowledgments

This work was financially supported by the China Postdoctoral Science Foundation (2014M551450), the National Major Project of Science & Technology Ministry of China (No. 2008ZX07421-002; No. 2012ZX07403-001), and the research and development project of Ministry of Housing and Urban-Rural Development (No. 2009-K7-4). We also thank anonymous reviewers and editors for their effects on this paper.

References

[1] J.W. Kim, H.S. Jang, J.G. Kim, H. Ishibashi, M. Hirano, K. Nasu, N. Ichikawa, Y. Takao, R. Shinohara, K. Arizono, Occurrence of pharmaceutical and personal care products (PPCPs) in surface water from Mankyung River, South Korea, J. Health Sci. 55 (2009) 249–258.

[2] L.J. Zhou, G.G. Ying, S. Liu, J.L. Zhao, B. Yang, Z.F. Chen, H.J. Lai, Occurrence and fate of eleven classes of antibiotics in two typical wastewater treatment plants in South China, Sci. Total Environ. 452–453 (2013) 365–376.

[3] C.G. Daughton, T.A. Ternes, Pharmaceuticals and personal care products in the environment: Agents of subtle change? Environ. Health Perspect. 107 (1999) 907–938.

[4] T. Heberer, Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data, Toxicol. Lett. 131 (2002) 5–17.

[5] D.G. Larsson, C. de Pedro, N. Paxeus, Effluent from drug manufactures contains extremely high levels of pharmaceuticals, J. Hazard. Mater. 148 (2007) 751–755.

[6] W.J. Andrews, J.R. Masoner, I.M. Cozzarelli, Emerging contaminants at a closed and an operating landfill in Oklahoma, Ground Water Monitor. Rem. 32 (2012) 120–130.

[7] F. Baquero, J.L. Martínez, R. Cantón, Antibiotics and antibiotic resistance in water environments, Curr. Opin. Biotechnol. 19 (2008) 260–265.

[8] R. Andreozzi, M. Raffaele, P. Nicklas, Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment, Chemosphere 50 (2003) 1319–1330.

[9] M.J. Martínez Bueno, A. Agüera, M.J. Gómez, M.D. Hernando, J.F. García-Reyes, A.R. Fernández-Alba, Application of liquid chromatography/quadrupole-linear ion trap mass spectrometry and time-of-flight mass spectrometry to the determination of pharmaceuticals and related contaminants in wastewater, Anal. Chem. 79 (2007) 9372–9384.

[10] W.H. Xu, G. Zhang, S.C. Zou, X.D. Li, Y.C. Liu, Determination of selected antibiotics in the Victoria Harbour and the Pearl River, South China using high-performance liquid chromatography-electrospray ionization tandem mass spectrometry, Environ. Pollut. 145 (2007) 672–679.

[11] F. Sacher, F.T. Lange, H.J. Brauch, I. Blankenhorn, Pharmaceuticals in groundwaters: Analytical methods and results of a monitoring program in Baden-Wurttemberg, Germany, J. Chromatogr. A 938 (2001) 199–210.

[12] T.X. Le, Y. Munekage, S. Kato, Antibiotic resistance in bacteria from shrimp farming in mangrove areas, Sci. Total Environ. 349 (2005) 95–105.

[13] X.X. Jiang, Y.L. Wu, P. Wang, H.J. Li, W.B. Dong, Degradation of bisphenol A in aqueous solution by persulfate activated with ferrous ion, Environ. Sci. Pollut. Res. 20 (2013) 4947–4953.

[14] D. Zhao, X. Liao, X. Yan, S.G. Huling, T. Chai, H. Tao, Effect and mechanism of persulfate activated by different methods for PAHs removal in soil, J. Hazard. Mater. 254–255 (2013) 228–235.

[15] Y.T. Lin, C. Liang, J.H. Chen, Feasibility study of ultraviolet activated persulfate oxidation of phenol, Chemosphere 82 (2011) 1168–1172.

[16] Y.F. Ji, C. Ferronato, A. Salvador, X. Yang, J.M. Chovelon, Degradation of ciprofloxacin and sulfamethoxazole by ferrous-activated persulfate: Implications for remediation of groundwater contaminated by antibiotics, Sci. Total Environ. 472 (2014) 800–808.

[17] C.D. Qi, X.T. Liu, C.Y. Lin, X.H. Zhang, J. Ma, H.B. Tan, W. Ye, Degradation of sulfamethoxazole by microwave-activated persulfate: Kinetics, mechanism and acute toxicity, Chem. Eng. J. 249 (2014) 6–14.

[18] C. Liang, C.F. Huang, N. Mohanty, R.M. Kurakalva, A rapid spectrophotometric determination of persulfate anion in ISCO, Chemosphere 73 (2008) 1540–1543.
[19] K.C. Huang, R.A. Couttenye, G.E. Hoag, Kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MTBE), Chemosphere 49 (2002) 413–420.
[20] A. Ghauch, A.M. Tuqan, Oxidation of bisoprolol in heated persulfate/H_2O systems: Kinetics and products, Chem. Eng. J. 183 (2012) 162–171.
[21] J. Deng, Y.S. Shao, N.Y. Gao, Y. Deng, S.Q. Zhou, X.H. Hu, Thermally activated persulfate (TAP) oxidation of antiepileptic drug carbamazepine in water, Chem. Eng. J. 228 (2013) 765–771.
[22] T.K. Lau, W. Chu, N.J. Graham, The aqueous degradation of butylated hydroxyanisole by UV/$S_2O_8^{2-}$: Study of reaction mechanisms via dimerization and mineralization, Environ. Sci. Technol. 41 (2007) 613–619.
[23] E. Hayon, A. Treinin, J. Wilf, Electronic spectra, photochemistry, and autoxidation mechanism of the sulfite-bisulfite-pyrosulfite systems. SO_2^-, SO_3^-, SO_4^- and SO_5^- radicals, J. Am. Chem. Soc. 94 (1972) 47–57.
[24] C.J. Liang, H.W. Su, Identification of sulfate and hydroxyl radicals in thermally activated persulfate, Ind. Eng. Chem. Res. 48 (2009) 5558–5562.
[25] A.L. Boreen, W.A. Arnold, K. McNeill, Photochemical fate of sulfa drugs in the aquatic environment: Sulfa drugs containing five-membered heterocyclic groups, Environ. Sci. Technol. 38 (2004) 3933–3940.
[26] P. Neta, V. Madhavan, H. Zemel, R.W. Fessenden, Rate constants and mechanism of reaction of sulfate radical anion with aromatic compounds, J. Am. Chem. Soc. 99 (1977) 163–164.
[27] X.F. Xie, Y.Q. Zhang, W.L. Huang, S.B. Huang, Degradation kinetics and mechanism of aniline by heat-assisted persulfate oxidation, J. Environ. Sci. 24 (2012) 821–826.
[28] I.M. Kolthoff, I.K. Miller, The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium, J. Am. Chem. Soc. 73 (1951) 3055–3059.
[29] Y.R. Wang, W. Chu, Degradation of a xanthene dye by Fe(II)-mediated activation of oxone process, J. Hazard. Mater. 186 (2011) 1455–1461.
[30] R.X. Yuan, S.N. Ramjaun, Z.H. Wang, J.S. Liu, Effects of chloride ion on degradation of Acid Orange 7 by sulfate radical-based advanced oxidation process: Implications for formation of chlorinated aromatic compounds, J. Hazard. Mater. 196 (2011) 173–179.
[31] C. Liang, Z.S. Wang, C.J. Bruell, Influence of pH on persulfate oxidation of TCE at ambient temperatures, Chemosphere 66 (2007) 106–113.
[32] S. Canonica, T. Kohn, M. Mac, F.J. Real, J. Wirz, U. von Gunten, Photosensitizer method to determine rate constants for the reaction of carbonate radical with organic compounds, Environ. Sci. Technol. 39 (2005) 9182–9188.
[33] G.P. Anipsitakis, D.D. Dionysiou, Radical generation by the interaction of transition metals with common oxidants, Environ. Sci. Technol. 38 (2004) 3705–3712.
[34] J.C. Yan, M. Lei, L.H. Zhu, M.N. Anjum, J. Zou, H.Q. Tang, Degradation of sulfamonomethoxine with Fe_3O_4 magnetic nanoparticles as heterogeneous activator of persulfate, J. Hazard. Mater. 186 (2011) 1398–1404.
[35] Z.B. Guo, F. Zhou, Y.F. Zhao, C.Z. Zhang, F.L. Liu, C.X. Bao, M.Y. Lin, Gamma irradiation-induced sulfadiazine degradation and its removal mechanisms, Chem. Eng. J 191 (2012) 256–262.
[36] K. Lekkerkerker-Teunissen, M.J. Benotti, S.A. Snyder, H.C. van Dijk, Transformation of atrazine, carbamazepine, diclofenac and sulfamethoxazole by low and medium pressure UV and UV/H_2O_2 treatment, Sep. Purif. Technol. 96 (2012) 33–43.
[37] M. Mahdi Ahmed, S. Barbati, P. Doumenq, S. Chiron, Sulfate radical anion oxidation of diclofenac and sulfamethoxazole for water decontamination, Chem. Eng. J. 197 (2012) 440–447.
[38] M.D.M. Gómez-Ramos, M. Mezcua, A. Agüeran, A.R. Fernández-Alba, S. Gonzalo, A. Rodríguez, R. Rosal, Chemical and toxicological evolution of the antibiotic sulfamethoxazole under ozone treatment in water solution, J. Hazard. Mater. 192 (2011) 18–25.