Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21336

86 (2017) 158–164
August

Comparison of sulfamethoxazole and ciprofloxacin degradation by UV/H_2O_2 process

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Received 9 May 2017; Accepted 14 August 2017

ABSTRACT

The rate constants of sulfamethoxazole (SMX) and ciprofloxacin (CIP) degradation as well as the removal of total organic carbon (TOC) by UV/H_2O_2 process was investigated under various parameters including different H_2O_2 dosage and initial pH values. The results indicated that both SMX and CIP were efficiently removed in UV/H_2O_2 process and they peaked at different pH values of 3 and 7 respectively, while CIP degradation was greater than that of SMX. TOC removal was decreased with the pH values increased in the degradation of SMX in UV/H_2O_2 process while no significant change for CIP with the pH values raised. Based on molecular structure analysis, the transformation of both sulfonamide bond and oxazole ring N–O band in SMX were more difficult than defluorination and change of piperazine ring in CIP.

Keywords: UV/H_2O_2; SMX; CIP; Degradation; Mineralization

1. Introduction

In recent years, pharmaceutical and personal care products (PPCPs) as emerging contaminants have been increasingly detected in river and soil with a level of micrograms per liter and milligrams per kilogram, respectively, in China [1–3]. Due to a large population and well-developed livestock husbandry, total production and consumption of PPCPs in China have been occurred at a rapid growing rate, which is possible to induce significant occurrence of PPCPs in aquatic environment and it will resultantly pose threats to human health. About two million tons of pharmaceuticals are produced in 2011 and the pharmaceutical production by China can account for more than 20% of the total production volume of the world [4]. In addition, the consumption rate is also remarkable, especially for the severe antibiotic abuse in current China [4]. However, the removal rate of PPCPs in conventional treatment of drinking water and domestic sewage is generally lower and limited, leading to discharge of untreated antibiotics into receiving waterbody [5–8].

Advanced oxidation processes (AOPs) have received growing attention with intensive studies on high degradation efficiency of refractory organic contaminants in water in recent years [9–11]. Hydroxyl radicals (·OH) generated in AOPs have strong oxidizing properties, they can mineralize the pollutants into carbon dioxide (CO_2), water (H_2O) and inorganics or, at least, transform them into harmless or biodegradable products [12]. The most advantage of AOPs is that they are totally “environment-friendly” as they neither transfer pollutants from one phase to the other nor produce massive amounts of hazardous sludge [13].

Sulfonamides are commonly used in some infectious diseases such as meningitis and plague and quinolones are widely used in genitourinary system diseases and

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gastrointestinal diseases caused by bacteria, both of which are highly resistant to degradation in water environment [14]. The best sulfonamides for the treatment of nocardiosis are sulfamethoxazole (SMX) ($C_{10}H_{11}N_3O_3S$), sulfadiazine, sulfisoxazole and trisulfapyridine. Ciprofloxacin (CIP) ($C_{17}H_{18}FN_3O_3$) is the strongest of widely used quinolones in vitro antibacterial activity against gram-negative bacteria as well as the most designated quinolone drug in Europe [15]. The highest concentration of SMX detected in Liaohe and Haihe river was 173 and 211 ng/L, respectively [1,2], and that of CIP was 651 μg/kg in soil of Shandong area [3], which cause potentially threatened on water environment. The structural formulas of SMX and CIP have been shown in Fig. 1. The advantages of strong oxidation, no introduction of new pollutants and easy operation have been presented in UV/H_2O_2 process. Direct photolysis and indirect oxidation of these substances by ·OH generated by H_2O_2 under irradiation of UV ($\lambda < 300$ nm) are the main degradation mechanism in UV/H_2O_2 process [16]. Moreover, it has already been applied to engineer project, such as the Netherlands Andjik sewage treatment plant which applied UV/H_2O_2 technology for disinfection and degradation of organic pollutants [17]. Several literatures have reported the effective removal of SMX and CIP by UV-based AOPs [18–20], while most of the current research focused on the level of mg/L which was far from the actual concentration of SMX in the water and there is a relative lack of research on microgram levels.

Since SMX and CIP appear to resist biodegradation, the degradation of the two pollutants via UV/H_2O_2 process was investigated in this study. The objectives were to: (i) determine the effects of H_2O_2 dosage and initial pH; (ii) evaluate mineralization efficiency of total organic carbon (TOC) with changing initial pH; and (iii) compare the degradation efficiency of SMX and CIP combining the structure of target compounds and identify the intermediates of SMX and CIP degradation by UV/H_2O_2.

2. Materials and methods

2.1. Experimental setup

The irradiation experiments were conducted in a cylindrical reactor with an effective volume of 1 L. A 10-W UV lamp (Beijing Education Au-light) emitting radiation at 254 nm was located on the central axis of the reactor to provide UV illumination and the average intensity of the UV lamp used in the experiment was 2.12 mW/cm^2. The quartz tube was covered with a jacket, and the reactor was provided with cooling water interlayer to keep temperature. Aqueous solutions were stirred in order to remain homogeneous by a magnetic stirrer placed on the bottom of the reactor throughout the experiment, and the outer wall of the reaction apparatus was covered with a shading cloth to avoid the influence of the surrounding environment while preventing other light from entrance. During the experiment, tap water was used as circulating cooling water.

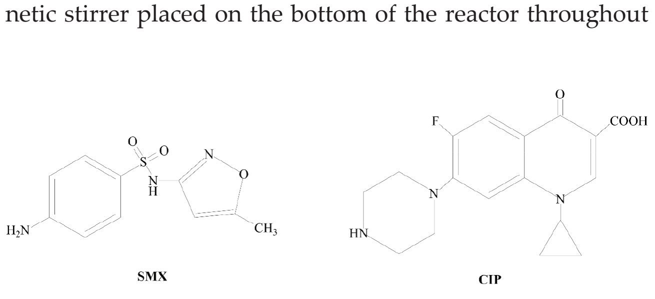

Fig. 1. Structure of sulfamethoxazole and ciprofloxacin.

2.2. Materials

SMX and CIP stock solutions used in degradation experiment were prepared by adding the pure compound to methanol (Tedia) to a concentration of 1 g/L, then dissolving with tap water (pH 6.8–7.3) filtered using an ultrafilter (Lisheng LH3-3Ad). H_2O_2 (30%), NaOH and H_2SO_4 were purchased from Beijing Chemical Factory, and tert-butanol was from Tianjin Jinke Fine Chemical Research Institute.

2.3. Experimental procedure

The experiment was carried out under the conditions of complete mixing and intermittent batch. The UV lamp was warmed up for 15 min before experiment to ensure the stability of UV energy output. Experiments were initiated by adding the SMX and CIP stock solutions to the UV reactor and then followed by a series of operations including starting the magnetic stirrer, putting in the preheated UV lamp and adding H_2O_2. Sample aliquots (5 mL) were collected at pre-specified time intervals, and then filtered by a 0.22 μm microporous membrane before analysis (Tengen, PES).

2.4. Analytical methods

The concentrations of SMX and CIP were determined by ultra performance liquid chromatography-mass spectrometry (UPLC-MS). The UPLC (Agilent 1290) system is equipped with an Agilent Zorbax SB-C18 column. The mobile phase consisted ratio of 65:35 of 0.2% formic acid in acetonitrile (v/v) with a flow rate of 0.3 mL/min. The peak time for SMX and CIP was 1.8 and 1.2 min, respectively. The injection volume of the sample was 5 μL. The triple quadrupole LC/MS (Agilent 6420) with an electrospray ionization source operating in positive ion mode was used as an analytical system. The TOC was determined by the non-purgeable organic carbon (NPOC) method using an Elementar vario TOC analyzer.

2.5. Reaction kinetics

The degradation rate of SMX and CIP by UV/H_2O_2 can be obtained from Eq. (1):

$$-dc_A/dt = k_0 c_A c_{\cdot \mathrm{OH}} \tag{1}$$

where c_A represents the concentration (μg/L) organic material after treatment over t time, c_{OH} represents the concentration (μg/L) of·OH, k_0 represents the pseudo-second-order rate constant (min^{-1}) and t represents the reaction time (min). During the experiment, c_{OH} can be almost regarded as constant due to excessive H_2O_2 added. Therefore, Eq. (1) could be rewritten as Eq. (2):

$$-\mathrm{d}c_A/\mathrm{d}t = kc_A,\ k = k_0 c_{\cdot \mathrm{OH}} \tag{2}$$

The k represents the pseudo-first-order rate constant (min^{-1}). The degradation of SMX and CIP by UV/H_2O_2 can be described with pseudo-first-order kinetic simulation. Furthermore, many studies have shown that the degradation of organic matter by UV/H_2O_2 process is in accordance with pseudo-first-order kinetics [21–23]. The curve of the linear regression analysis is confirmed by the following equation:

$$\ln(c_A / c_0) = -kt \tag{3}$$

The c_0 represents the initial concentration (μg/L) of organic matter. The degradation process of SMX and CIP by UV/H_2O_2 was also exhibited pseudo-first-order kinetics in previous studies. The average of the three experimental results was determined as the final value under different tested conditions and errors in rate constants were reported as the 95% confidence intervals from three independent irradiation experiments.

3. Results and discussion

3.1. Effect of H_2O_2 dosage

The initial concentration of SMX and CIP was 100 μg/L; both for the detection limit of analytical instruments and for the maximum concentration range detected in effluent from wastewater treatment plants [24]. Different H_2O_2 addition in the range of 3.4 – 3,400 mg/L was investigated at pH 7 and the degradation effects of SMX and CIP are shown in Fig. 2. Rate constant k and correlation coefficient (R^2) were obtained by fitting the reaction process to pseudo-first-order reaction model, as shown in Table 1.

Fig. 2 shows that both SMX and CIP were completely removed within 10 min at different H_2O_2 dosage. With the increase of H_2O_2 dosage, the degradation of the pollutants was promoted, but inhibited instead when the H_2O_2 dosage exceeded 340 mg/L. When the dosage of H_2O_2 was 3.4, 34, 340, 1,020, 2,380 and 3,400 mg/L, the removal rate at 2 min was 73.6%, 73.9%, 86.6%, 84.4%, 83.3%, 71.6% for SMX, and 63.4%, 80.6%, 99.4%, 99.3%, 97.9%, 94.4% for CIP, respectively. As shown in Table 1, the degradation rate constants of SMX and CIP increased first from 0.6 to 0.99 $min^{-1}$and from 0.51 to 2.52 min^{-1}, respectively, at low H_2O_2 dosage (<340 mg/L), and then gradually reduced back to 0.49 and 1.35 min^{-1}, respectively, with the degradation rate of CIP demonstrated better than that of SMX on the whole.

With increasing H_2O_2 dosage, more relatively unselective oxidant ·OH was induced as expressed in Eq. (2) [25], thus promoting the degradation of target pollutants. However, rate constants of SMX and CIP degradation got increased but decreased instead after increasing to some extent. High concentration of H_2O_2 additive system minimized the intensity of UV irradiation which SMX and CIP received because of the absorption of ultraviolet radiation by H_2O_2, resulting in evident decrease in degradation [26]. In addition, excessive H_2O_2 as ·OH inhibitors reacted with ·OH generating the much less effective $\cdot OH_2$ radical as expressed in Eq. (3) [25], which could further decline the efficiency of the pollutants.

$$H_2O_2 + h\nu \rightarrow 2\cdot OH \tag{4}$$

$$H_2O_2 + \cdot OH \rightarrow HO_2\cdot + H_2O \tag{5}$$

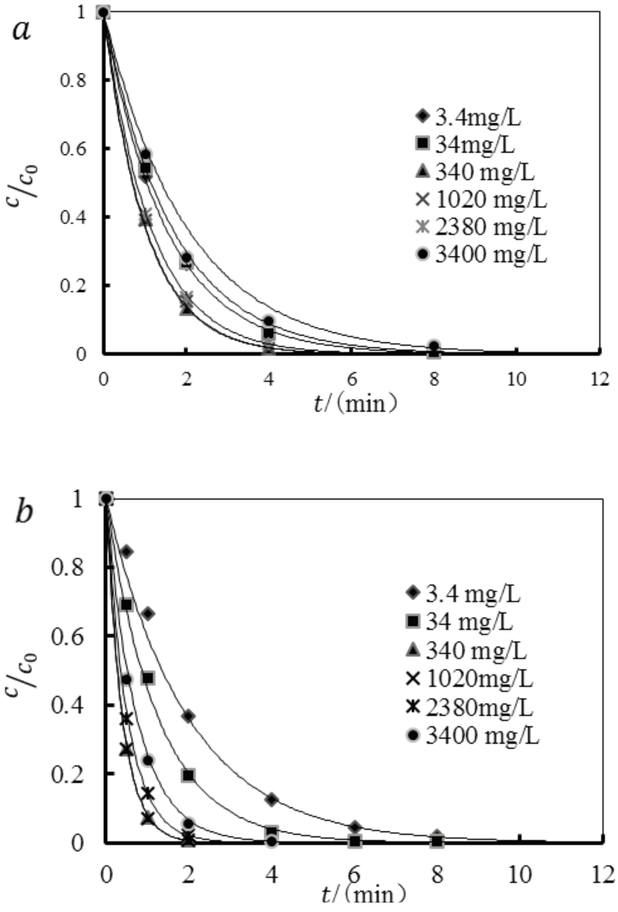

Fig. 2. Effects of H_2O_2 dosage on the degradation of SMX (a) and CIP (b) in UV/H_2O_2 process.

Table 1
Pseudo-first-order rate constants of SMX and CIP in UV/H_2O_2 process under the condition of different H_2O_2 dosage

H_2O_2 dosage (mg/L)	Pseudo-first-order rate model			
	SMX		CIP	
	k (min^{-1})	R^2	k (min^{-1})	R^2
3.4	0.60	0.9911	0.51	0.9985
34	0.66	0.9985	0.80	0.9872
340	0.99	0.9994	2.52	0.9993
1,020	0.97	0.9983	2.51	0.9984
2,380	0.87	0.9992	1.93	0.9996
3,400	0.49	0.9687	1.35	0.9971

All the relevant experimental results were average values from three independent irradiation experiments.

As shown in Table 1, the rate constants of SMX and CIP, respectively, reached the maximum values of 0.99 and 2.52 min^{-1} at H_2O_2 dosage of 340 mg/L. Therefore, the dosage was kept at 340 mg/L in the later experiments of this study.

3.2. Effect of initial pH value

With both initial concentration of SMX and CIP 100 μg/L, the dosage of H_2O_2 340 mg/L, pH value of the reaction solution was, respectively, adjusted to 3, 5, 7 and 10 to test the effect on the contaminants degradation. Fig. 3 shows the removal of SMX and CIP in aqueous solutions at different pH. The pseudo-first-order reaction model was fitted to determine the rate constant *k* and correlation coefficient (R^2), the corresponding results are shown in Table 2.

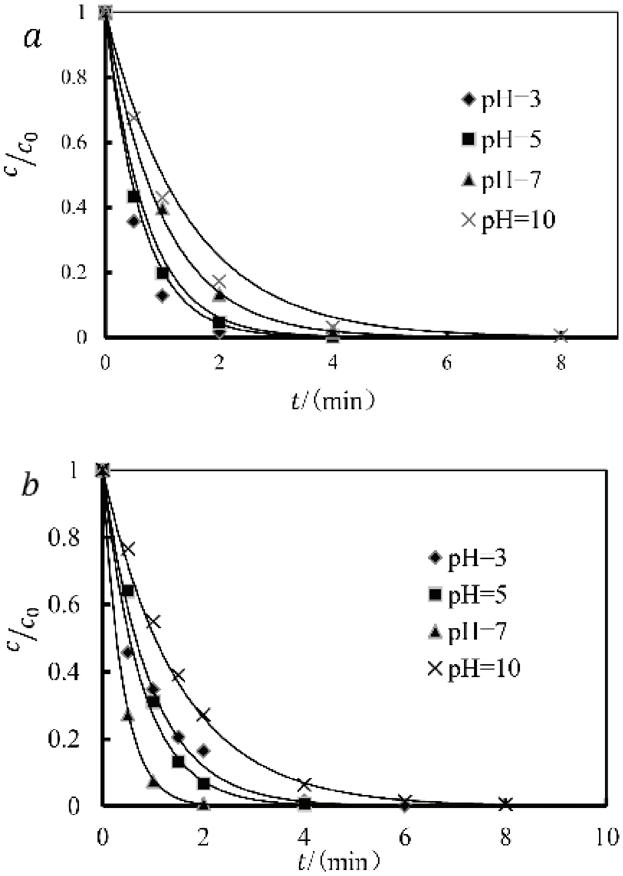

Fig. 3. Effect of different initial pH values on the degradation of SMX (a) and CIP (b) in UV/H_2O_2 process.

Table 2
Pseudo-first-order rate constants of SMX and CIP in UV/H_2O_2 process under the condition of different initial pH values

Initial pH value	SMX		CIP	
	k (min^{-1})	R^2	k (min^{-1})	R^2
3	1.57	0.9329	1.06	0.9944
5	1.39	0.9887	1.30	0.9958
7	0.99	0.9994	2.52	0.9993
10	0.78	0.9838	0.67	0.9955

All the relevant experimental results were average values from three independent irradiation experiments.

As shown in Fig. 3, the initial pH value of the reaction solution had a remarkable effect on the degradation of SMX and CIP. The best degradation efficiency of UV/H_2O_2 on SMX and CIP was, respectively, at pH 3 and 7, while the pollutants were both resistant to decompose at pH 10. When the initial pH value was 3, 5, 7 and 10, the removal rates were, respectively, 98.3%, 95.4%, 86.6%, 82.8% for SMX, and, respectively, 83.7%, 93.4%, 99.4%, 72.8% for CIP.

As shown in Table 2, the degradation of SMX and CIP by UV/H_2O_2 was clearly inhibited under the condition of higher pH values. Two reasons relevant to the reduction of ·OH may explain the pH-dependent trend. The first one is that alkaline liquid will promote the ionization of H_2O_2 to HO_2^- because H_2O_2 is a weak acid, and then HO_2^- reacts with H_2O_2 under higher energy of UV illumination leading to the formation of ·OH. In addition, HO_2^- can act as a scavenger for ·OH [25]. The other reason is that HCO_3^- and CO_3^{2-} as ·OH scavengers generally exist in alkaline conditions, especially HCO_3^- and ·OH reaction rate constant reached 3.9×10^8 M^{-1} s^{-1} [25]. Therefore, the poor degradation of pollutants by UV/H_2O_2 was conducted when the reaction solution was alkaline.

Nature of the compounds may also explain the pH-dependent trend. In general, the pH adjustment in the tested water led to structural modifications of the pollutants' molecule thus affected direct photolysis by UV light or indirect oxidation by highly reactive ·OH [27]. The dissociation constants of SMX were 1.6 and 5.7, which meant that SMX showed protonated, neutral and deprotonated states at pH < 1.6, 1.6 < pH <5.7 and pH > 5.7, respectively. Anne et al. [28] reported that different pH influenced the molar absorption coefficient of SMX at wavelengths less than 300 nm by changing the state of SMX. The molar absorption coefficient of SMX at different protonation states followed the order of neutral form > protonated form > deprotonated form [29]. Therefore, the SMX removal was better on condition of lower pH and greater molar absorptivity in UV/H_2O_2 process. Liu et al. [14] came to the similar conclusion regarding the behavior of pH while studying the degradation of SMX using UV treatment. CIP is an amphoteric compound, which the structure includes piperazine ring with a positive charge and carboxyl with a negative charge. Because the dissociation constants of CIP are 6.95 and 8.95 [30] and isoelectric point is 7.4, CIP could more easily absorb photons to reach the photo-excited state under neuter slightly alkaline conditions [31], which indicated that CIP was more likely to be photodegraded in this circumstances. In addition, under acidic conditions, it was mainly involved the attack of hydroxyl radical on the quinolone ring (decomposition of cyclopropane ring and defluorination) during the photodegradation of CIP [19]. Meanwhile, the transformation of piperazine ring connected to the aromatic ring on the side chain occurred except for the change of quinolone ring [32]. Excessive pH would make the piperazine ring more stable and lower pH would inhibit the hydrolysis of fluorine atoms, thereby increasing the difficulty of UV degradation; hence, only in the case of electrical neutrality can occur the largest degree of cracking [19,33]. Therefore, the removal of CIP by UV/H_2O_2 was optimal at pH 7 that is very close to the isoelectric point of CIP in the present study, which was in agreement with Vasconcelos et al. [33].

3.3. Removal efficiency of TOC

With both initial concentration of SMX and CIP 100 μg/L, the dosage of H_2O_2 340 mg/L, the initial pH of the reaction solution was 3, 7 and 10, respectively. The removal of TOC in the process of degradation of SMX and CIP by UV/H_2O_2 is shown in Fig. 4.

Fig. 4 shows that during the degradation of SMX and CIP in UV/H_2O_2 process, TOC was always gradually reduced and then basically remained unchanged with the reaction to a certain extent at different pH values. In the degradation of SMX by UV/H_2O_2, the removal rate of TOC reached 93% at pH 3 after 40 min and followed by 90% at pH 7 after 50 min and 82% at pH 10 after 70 min, afterwards it almost remained unchanged. Hence, obviously, the removal rate of TOC was the highest and fastest at initial pH 3 and consequently, the pH adjustment from 3 to 7 resulted in a significant resistance of TOC degradation from 93% to 82% although more time was carried out. For CIP, the removal rate of TOC was more than 96% under the tested pH values and reached the maximum rate at pH 7.

In the process of the degradation of SMX and CIP by UV/H_2O_2, pollutants were completely degraded within the first 10 min but much longer than 10 min for decay of TOC in Fig. 4, which was due to that SMX and CIP were first directly photodegraded by UV and indirectly oxidized by ·OH to different types of intermediates [20] (details of the intermediates as described in detail below), and further oxidized until complete mineralization to produce CO_2. TOC was highly degraded during the decay of SMX and CIP in UV/H_2O_2 process, especially, almost all complete mineralization was induced during the CIP degradation process. Some studies had shown that the biotoxicity of PPCPs degradation products was higher than that of PPCPs itself [34,35]; therefore, UV/H_2O_2 is considered as a potential method to remove these contaminants effectively.

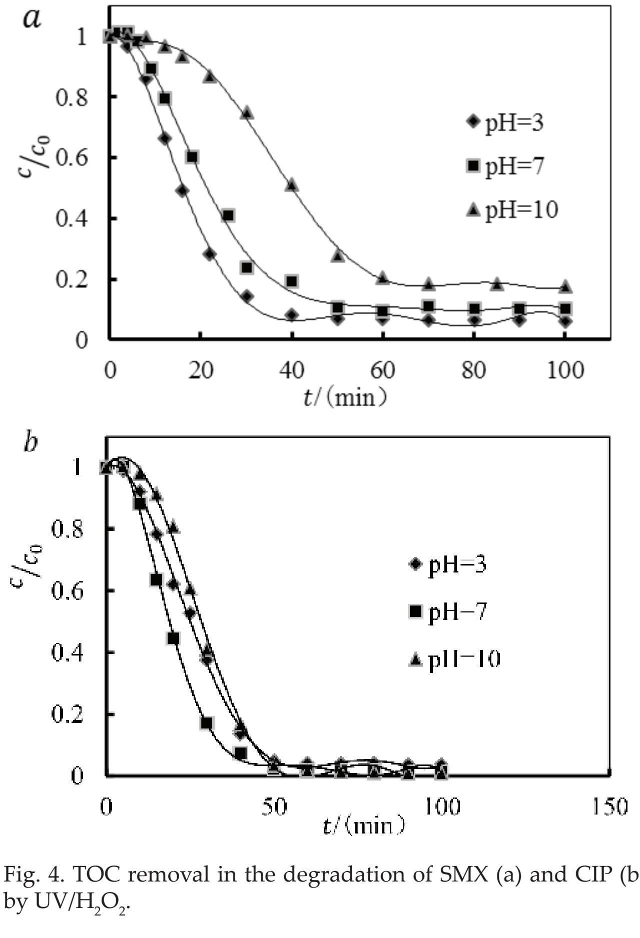

Fig. 4. TOC removal in the degradation of SMX (a) and CIP (b) by UV/H_2O_2.

Figs. 3(a) and 4(a) show that the degradation degree of SMX via UV/H_2O_2 decreased with the increase of the initial pH value of the reaction solution, as well as the TOC removal rate and efficiency, indicating that the initial pH affected not only the degradation of SMX itself but also the mineralization degree of SMX intermediates. Therefore, the removal rate of TOC was different with the changing initial pH value. Figs. 3(b) and 4(b) show that UV/H_2O_2 had the most effect on CIP degradation and the highest removal rate of TOC at pH 7, but there was no significant difference in TOC removal rate at pH 3 and 10, indicating that the initial pH value of the reaction solution affected the degradation of CIP rather than CIP intermediates. Therefore, no significant difference in the removal rate of TOC for CIP was induced under the tested initial pH value.

3.4. Intermediates/products of SMX and CIP degradation by UV/H_2O_2

It took much longer to remove TOC in UV/H_2O_2 process than SMX and CIP degradation, suggesting that many intermediates/products were formed and further oxidization until mineralization. In UV/H_2O_2 degradation process of SMX, the product S1 was assumed to correspond to the change of N–O bond of the isoxazole ring and would be converted to its imide form of isomers S2 [36]. The other oxidation products, identified as S3 (sulfamic acid) and S4 (3-amino-5-methylisoxazole) [35], were possible outcome of cleavage of sulfonamide bond, as detected by Borowska et al. [10] and Lekkerkerker-Teunissen et al. [37]. The main photo degradation pathways of CIP were defluorination and piperazine ring transformation [19]. Vasconcelos et al. [33], during the photodegradation of CIP, detected product C1 formed by defluorination and product C2 formed by conversion of piperazine ring. In addition, CIP degradation in the UV/H_2O_2 process found the two products [18]. Based on the intermediates and products, the pathways of SMX and CIP degradation by UV/H_2O_2 are proposed as Figs. 5 and 6, respectively.

The degradation rate of CIP by UV/H_2O_2 was higher than that of SMX. Therefore, the cleavage of N–O bond in the isoxazole ring and the sulfonamide bond during the degradation of SMX were more difficult than defluorination and conversion of piperazine ring of CIP.

4. Conclusions

In the present investigation, SMX and CIP in water could be effectively removed by UV/H_2O_2 process, and the degradation exhibited a pseudo-first-order kinetic behavior. When the initial concentration of SMX and CIP was 100 μg/L

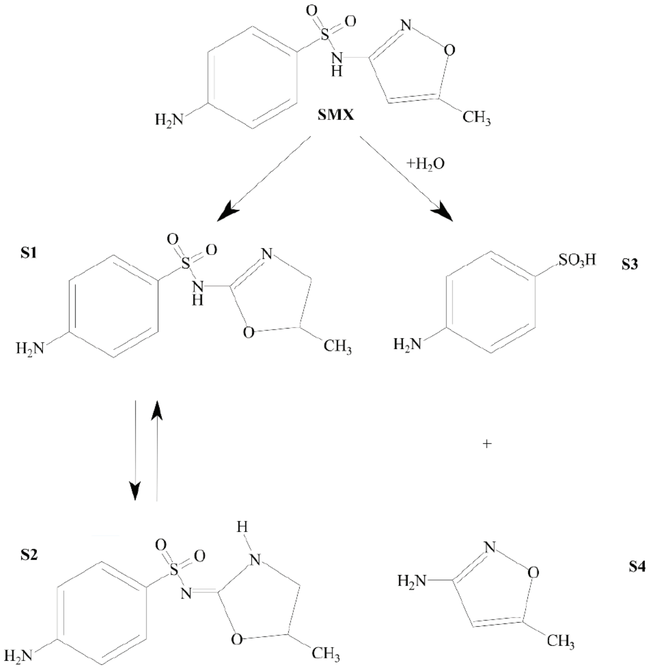

Fig. 5. Initial oxidation products of SMX in UV/H_2O_2 process.

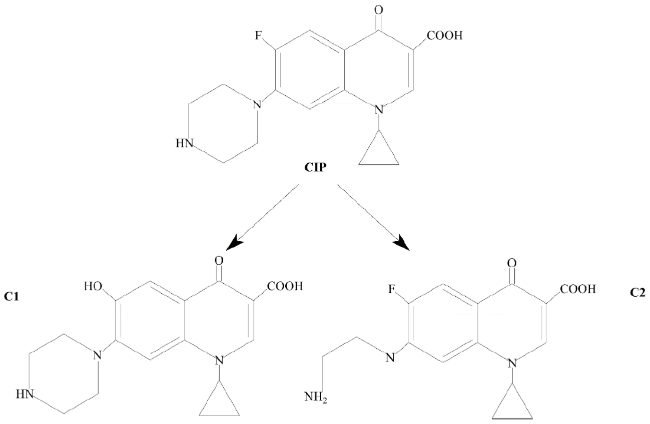

Fig. 6. Initial oxidation products of CIP in UV/H_2O_2 process.

and the dosage of H_2O_2 was 340mg/L, the rate constants of SMX and CIP reached the maximum values for 0.99 and 2.52 min^{-1}, respectively. Initial pH value had a remarkable effect on the degradation of SMX and CIP and the two contaminants showed the best degradation at pH 3 and 7, respectively. The removal rate of TOC during the SMX degradation decreased with the increase of the initial pH value, while for CIP pH had no significant effect on TOC decay with removal rate being basically more than 96%. Through analyzing the molecular structure of SMX and CIP, it was found that the cleavage of both N–O bond in the isoxazole ring and the sulfonamide bond during the degradation of SMX were more difficult than defluorination and conversion of piperazine ring of CIP.

Acknowledgments

We gratefully appreciate the financial support from the Importation and Development of High-Caliber Talents Project of Beijing Municipal Institutions (1147515207) and the Open Research Fund Program of Key Laboratory of Urban Stormwater System and Water Environment (Beijing University of Civil Engineering and Architecture), Ministry of Education.

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