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Degradation of ofloxacin in aqueous solution with UV/H_2O_2

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ABSTRACT

Trace levels of antibiotics in water bodies could present a public health risk. However, advanced oxidation can potentially transform trace antibiotics; therefore, this study investigates the degradation of typical pharmaceuticals such as ofloxacin (OFL) in aqueous solution by the UV/H_2O_2 advanced oxidation process. The results show that OFL could be rapidly degraded by UV/H_2O_2, and that the degradation process is dependent on the H_2O_2 concentration and on the initial concentrations of OFL. The pseudo-first-order rate constant (k) of OFL is significantly improved by ·OH generated by H_2O_2; however, with an increased OFL concentration, the k declines. In actual water bodies, the rate constant of OFL is lower than that in ultrapure water. Further analysis has indicated that the acidic and basic environments or the existence of natural organic matter and chloride ion inhibit the degradation of OFL. The experimental results indicate that the laboratory results could not be extended directly to actual water treatment without further consideration. Six degradation products of OFL were determined by ultra-performance liquid chromatography-high resolution mass spectrometry. The degradation pathways mainly encompass ring openings at both the piperazinyl substituent and the quinolone moiety.

Keywords: Degradation; Kinetics; Mechanism; Ofloxacin; UV/H_2O_2

1. Introduction

In recent years, the use of pharmaceuticals has increased worldwide [1], mainly in medical processes [2]. As most antibiotics cannot be absorbed completely by human beings or animals, researchers have detected various types of antibiotics in their original form or as metabolites in surface water, groundwater, and even drinking water [3]. The presence of such antibiotics in the environment could affect the water quality, potentially damage the aquatic ecosystem, and threaten public health [4]. Consequently, the interest of scientists in the occurrence, fate, and behavior of antibiotics has been increasing [5].

As a typical fluoroquinolone pharmaceutical, ofloxacin (OFL) is widely used to cure respiratory diseases and bacterial infections. OFL has been detected in many aquatic ecosystems, with concentrations reaching the ng/L-μg/L level [6]. OFL is difficult to hydrolyze or biodegrade because of the stability of the quinolone ring in the OFL molecule and OFL can therefore remain in the environment for quite a long time.

Various treatment technologies have been used to remove antibiotics, such as adsorption [7], biodegradation [8], Fenton oxidation [9], O_3 oxidation [10], photocatalysis [11], and the like. However, traditional sewage treatment plants are problematic, as they are not designed to remove such chemical compounds effectively [3]. For decades, significant progress has been made with advanced oxidation processes (AOPs) that employ the high and non-selective

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oxidation ability of the hydroxyl radical (·OH). One of the most advanced and widely used AOPs to degrade antibiotics in water is UV/H_2O_2, which can mineralize the target pollutant effectively in a considerably short reaction time [12]. Recently, significant advances have been made in understanding the aquatic UV/H_2O_2 degradation of some pharmaceuticals; however, tailored data on the phototransformation of OFL in the aquatic environment are still mainly lacking.

In this work, we focused on the degradation of OFL by UV/H_2O_2 and established the degradation kinetics in ultrapure water. In addition, considering the sophisticated composition of actual water bodies, we determined the optimum H_2O_2 concentration, and we examined the effect of the pH value and the existence of natural organic matter (NOM) and inorganic ion on the degradation of OFL. Furthermore, we determined the photo products of OFL and proposed transformation mechanisms. The results we obtained can provide a fundamental basis for the treatment of water that contains antibiotics.

2. Methods

2.1. Reagents

Ofloxacin ($C_{17}H_{20}FN_3O_4$, 98%) was purchased from Hefei Bomei Biotechnology Co. Ltd., China and H_2O_2 (30%), acetic acid, and sodium chloride, all of analytic grade, were supplied by the Beijing Chemical Plant, China. Humid acid (HA) and fulvic acid ($C_{14}H_{12}O_8$, FA) were separately obtained from Aldrich, US and the Shanghai Future Industrial Co. Ltd, China. Acetonitrile and methanolof a suitable grade for high performance liquid chromatography (HPLC) were obtained from Tedia Chemicals, US. All the reagents were used as received, without further treatment, and all the aqueous solutions were prepared with ultrapure water.

2.2. Analytical methods

The OFL was determined by HPLC (Agilent 1200 series, US), equipped with a variable wavelength detector (VWD) and a Symmetry-C_{18} column (4.6 × 150 mm, 5 µm). The mobile phase was 10% acetonitrile and 90% acetic acid solution (0.8%, v/v), the flow rate was 1 mL/min, the detection wavelength was 286 nm, the column temperature was 30°C, and the injection volume was 20 µL. An ultraviolet-visible (UV-vis) spectrophotometer (Analytikjena Specord Plus 200, Germany) was used to measure the absorbance spectra of the OFL solution. The total organic carbon (TOC) was analyzed by a TOC-Vcph analyzer (Shimadzu, Japan) and the pH value was determined by a PHSJ-5 pH-meter (Shanghai Precision & Scientific Instrument Co. Ltd., China).

The degradation products of OFL by UV/H_2O_2 were analyzed by ultra- high-performance liquid chromatography-high resolution mass spectrometry (UPLC-HRMS). UPLC analysis was performed by using a Waters ACQUITY UPLC system (Waters Corporation, Milford, USA) with a Waters ACQUITY UPLC BEH C_{18} Column (1.7 µm, 2.1 × 50 mm) (Milford, MA, USA). The column temperature was maintained at 30°C. Elution was performed at a flow rate of 0.3 mL/min by using the mobile phases of solvent A (0.1% formic acid in water) and solvent B (acetonitrile). The solvent gradient was 0–3 min, 5%–20% B; 3–4 min, 20%–40% B; 4–6 min, 40–100% B, 6–7 min, 100% B, 7–7.1 min, 100%–5% B, 7.1–11 min, 5% B.

Mass spectrometry (MS) detection was carried out on a Waters SYNAPT G2 HDMS system (Waters MS Technologies, Manchester, UK), equipped with a dual electrospray ionization probe. Before analysis, sodium formate was used for calibrating. The optimal conditions for analysis were set as follows: the resolution mode was selected for both positive and negative ionization modes, source temperature was set at 120°C, desolvation gas temperature was 350°C, cone gas flow was 50 L/h, desolvation gas flow was 700 L/h, capillary voltage was 3.0 kV for the positive mode and 2.0 kV for the negative mode, sample cone voltage was 30 V, and the extraction cone voltage was 5.0 V. A lock mass calibrant leucine-enkephalin (2 ng/mL) in 0.1% formic acid water/acetonitrile (50:50, v/v) was continuously introduced into the mass spectrometer via the second Lock-Spray ESI probe at a flow rate of 5 µL/min, generating reference ions for the positive ion mode ($[M+H]^+$ = 556.2771) and the negative ion mode ($[M–H]^-$ = 554.2615), to ensure accuracy during the MS analysis. Data were acquired between m/z 100 and 1000 Da, with a scan time of 0.2 s, and were further processed with the MassLynx 4.1 software (Waters).

2.3. UV/H_2O_2 degradation reaction

The degradation reactor comprised a 500 mL self-made cylinder, an 11 W low-pressure Hg vapor lamp (Institution of Light Source, Beijing), emitting UV light at 254 nm, and a quartz sleeves set between the cylinder and the lamp. Magnetic stirring was conducted during the reaction to ensure homogeneous UV exposure. As reported in our previous work [4], the UV fluence was calculated by multiplying the average photon fluence rate with the exposure time. A photon fluence rate of 4.5×10^{-5} E/m^2/s was obtained using atrazine as the actinometer by referring to the published procedures [1], which is equal to the power output of 2.12 mW cm^{-2}. The effective path length of our photochemical reactor was 1.9 cm determined by hydrogen peroxide actinometry [13].

Solutions (500 mL) of mixed OFL and H_2O_2 were transformed in the reactor, and, after magnetic stirring for 2 min, the lamp was switched on at given time intervals. Finally, two samples were withdrawn and were analyzed immediately by HPLC. When required, HA, FA, and Cl^- would be added to the OFL solution before the reaction took place.

2.4. Actual water sampling and treatment method

In this study, we conducted the degradation reaction of OFL in three types of actual water, i.e., raw water from the Xinlicheng reservoir, sand filter effluent from the secondary water purification plant, and sedimentation tank effluent from the secondary sewage plant. The sample locations were all in Changchun, Jilin province, China. These three types of water were defined as surface water (SW), drinking water (DW), and waste water (WW), respectively. The water samples were filtered by using 0.45 µm filter membranes and were stored at 4°C. Table 1 shows the water quality parameters.

Table 1
Actual water quality

	SW	DW	WW
pH value	8.05	7.91	8.04
Dissolved organic carbon (DOC, mg/L)	2.65	0.85	2.20
A_{254} (cm^{-1})	0.0785	0.0601	0.1125
Alkalinity (HCO_3^-, mM)	2.28	1.75	4.35

3. Results and discussion

3.1. Effect of H_2O_2 dose

In practical application, the H_2O_2 dose is an important parameter, as the removal efficiency for organic matter would be low when the concentration of H_2O_2 was low; however, a high H_2O_2 concentration could result in excess H_2O_2 and increasing treatment costs. Therefore, it was necessary to determine the optimal concentration of H_2O_2. Fig. 1 shows that adding H_2O_2 efficiently accelerated the removal of OFL; the higher the dose of H_2O_2 the faster would be the OFL degradation. This is because H_2O_2 could generate the strongly oxidizing substance ·OH under UV irradiation, and, in turn, ·OH could oxidize OFL.

Conversely, as shown in Fig. 2, with a further increase of the H_2O_2 concentration, until the molecular ratio of H_2O_2/OFL was more than 1000, that is, the concentration of H_2O_2 was 5 mM, reaction rate constant of OFL decreased. This is because H_2O_2 is also an ·OH quencher, which could react with ·OH and result in the formation of less-active HO_2· [Eq. (1)]. This dual role of H_2O_2 has been reported by previous studies; for example, Ghaly et al.[14] found that when the H_2O_2 concentration was greater than 20 mM, the chlorophenol degradation decreased because of the ·OH capture effect.

$$H_2O_2 + \cdot OH \rightarrow HO_2\cdot + H_2O \quad (1)$$

Consequently, we chose 240 μM H_2O_2 as the optimal condition for the following experiments.

3.2. Effect of initial concentration of OFL

The contaminant concentration has a significant effect on the selection of the removal technique and the specific treatment parameters. The effects of the initial OFL concentrations on the degradation of UV/H_2O_2 are shown in Fig. 3, which indicates that with an increase in the OFL concentration, the removal efficiency of OFL decreased. However, with the increase of the initial concentration, the absolute degradation amount increased at the same UV fluence, especially in the latter part of the reaction. This can be ascribed to a stronger reaction impetus from a greater initial concentration. For the following procedure, we chose 5 μM OFL.

The experimental results indicate that in the early stage of the reaction, the target pollutant was degraded quickly; however, as the reaction time continued, the amount of degradation per UV fluence input slowed rapidly. This is ascribed to the high concentration of H_2O_2 generating a

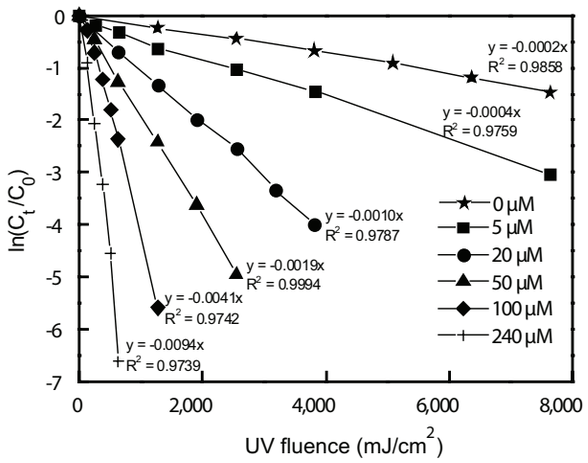

Fig. 1. Degradation of ofloxacin in the UV/H_2O_2 process with different concentration of H_2O_2, $[OFL]_0$ = 5 μM.

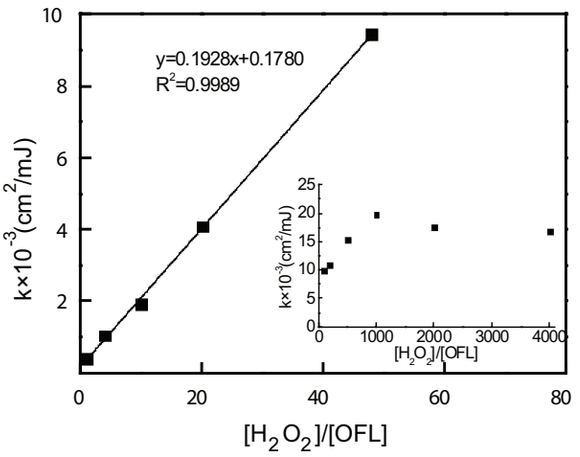

Fig. 2. Effect of initial concentration of H_2O_2 on the degradation of ofloxacin in the UV/H_2O_2 process, $[OFL]_0$ = 5 μM.

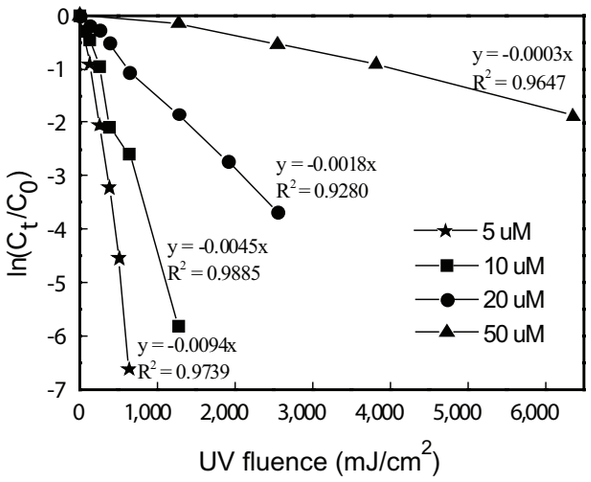

Fig. 3. Effects of initial concentration of ofloxacin on its degradation in UV/H_2O_2 process, $[H_2O_2]_0$ = 240 μM.

high concentration of ·OH, efficiently degrading the OFL; however, with the consumption of H_2O_2, the OH concentration was also low, which led to the degradation of OFL being reduced.

When the concentrations of OFL and H_2O_2 were 5 μM and 240 mM, the degradation of OFL in the UV/H_2O_2 system obeyed the pseudo-first-order kinetics equation, as shown in Figs. 1 and 3. The reaction rate constant was 9.44 × 10^{-3} cm^2/mJ.

3.3. Effect of initial solution pH

The pH value is an important factor in the degradation of organic pollutants. The pH value changes the existing form of the organic matter, and different forms of organic matter have different UV absorption capacities, which further change the reactivity. What is more, the photolysis rate of H_2O_2 is different at different pH values; generally, alkaline conditions are beneficial to the photolysis of H_2O_2. Therefore, we inspected the effect of the pH value on the degradation of OFL in ultrapure water (Fig. 4). The original pH value for a mixed solution of OFL and H_2O_2 was 7.29, and sulfuric acid and sodium hydroxide were used to adjust the pH value. Fig. 4 indicates that both acidic and alkaline conditions prohibit the degradation of OFL, and, with the increase of pH, the prohibition effect increases.

OFL is considered an amphoteric compound, and with changes in the pH of aqueous solutions, it is ionized into three forms, namely, cationic (OFL^+), zwitterionic (OFL^0), and anionic (OFL^-) [see Eqs. (2) and (3)]. The literature refers to the molecular structure and form distribution of OFL [15].

$$OFL^+ \leftrightarrow OFL^0 + H^+ \quad pK_{a1} = 6.08 \tag{2}$$

$$OFL^0 \leftrightarrow OFL^- + H^+ \quad pK_{a2} = 8.25 \tag{3}$$

The UV absorption of the different speciations of OFL differed. As shown in Fig. 5, the OFL^+ absorption for UV_{254} was stronger, and OFL^0 and OFL^- were relatively weaker. In strong alkaline (pH = 10.85) and neutral conditions, the OFL mainly exist in the form OFL^- and OFL^0, separately, with the absorption of these two speciations being similar (Fig. 5). However, the degradation of OFL in an alkaline condition (pH = 10.85) is strongly inhibited (Fig. 4), which indicates that the speciation of OFL may not be the predominant factor influencing the degradation. Further more, we consider that H_2O_2 is a weak acid (pk_a = 11.7), it stably exists in acidic and neutral conditions, whereas, in alkaline conditions, H_2O_2 could ionize to generate HO_2^-. As the HO_2^- could scavenge ·OH, it leads to a decline in the degradation rate of OFL in alkaline conditions.

3.4. Effect of water quality

The laboratory experimental results of OFL degradation in ultrapure water were considered to give reference to practical applications. However, as the composition of actual water is quite complicated, we needed to know how the degradation of OFL would take place in actual water; therefore, in this study, we investigated the degradation of OFL in three different actual water samples. The results are shown in Fig. 6. It is obvious that the degradation of OFL in the actual water by UV/H_2O_2 was strongly prohibited compared with that of the ultrapure water. The degradation rate constant of OFL decreased in the order $k_{UW} > k_{DW} > k_{SW} > k_{WW}$. However, for UV direct photolysis of OFL without H_2O_2 in the actual water samples, the degradation of OFL was enhanced compared with that in the ultrapure water (Fig. 7). The degradation rate constant of OFL was found to follow $k_{DW} > k_{SW} > k_{WW} > k_{UW}$.

By comparison, it was obvious that the role of actual water in OFL degradation was different in UV and UV/H_2O_2 system. This was because actual waters were alkaline (the pH value of DW, SW, and UW was 8.05, 7.91, and 8.04 separately), and alkaline condition inhibited the degradation of OFL in UV/H_2O_2 system (Fig. 4), but improved the direct photolysis of OFL (Fig. 8). Therefore, we inferred that pH value of actual water played important role in the degradation of OFL.

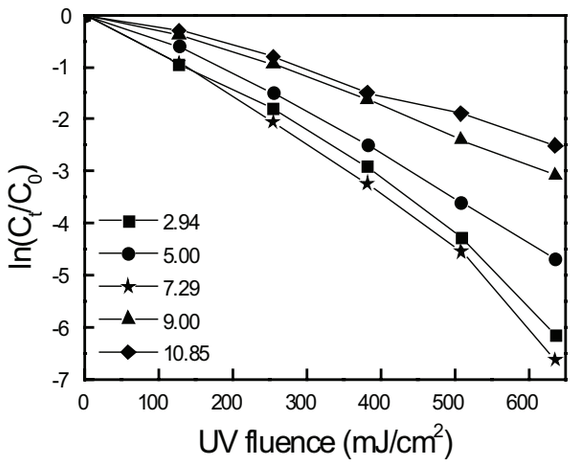

Fig. 4. Effects of initial pH values on the degradation of ofloxacin in the UV/H_2O_2 process, $[OFL]_0$ = 5 μM $[H_2O_2]_0$ = 240 μM.

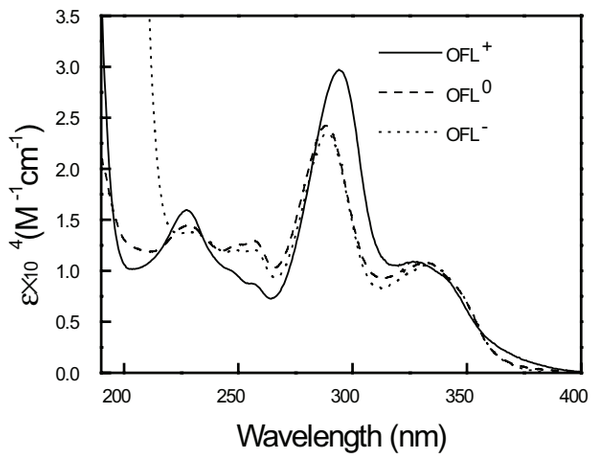

Fig. 5. The absorption spectra of ofloxacin with different species.

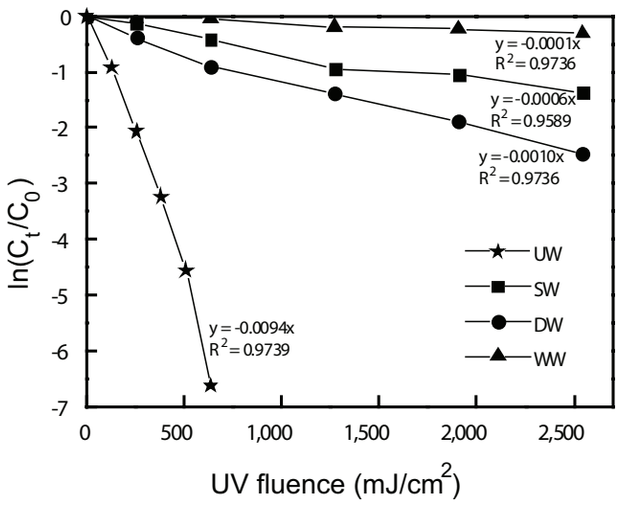

Fig. 6. Effects of natural water on the degradation of ofloxacin in UV/H_2O_2 process, $[OFL]_0$ = 5 μM $[H_2O_2]_0$ = 240 μM.

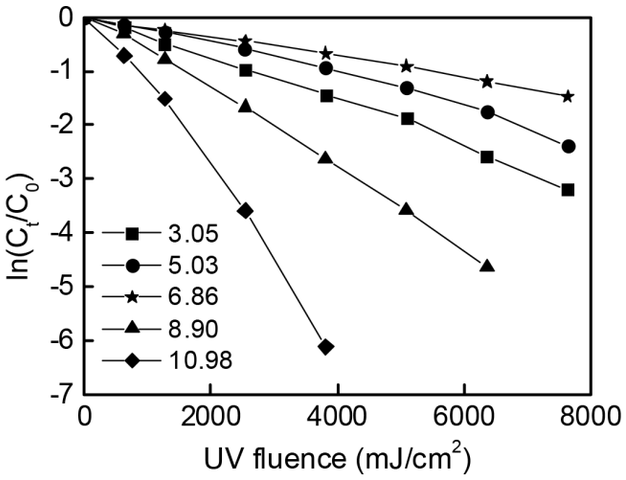

Fig. 8. Effects of initial pH values on the degradation of ofloxacin in direct UV photolysis $[OFL]_0$ = 5μM.

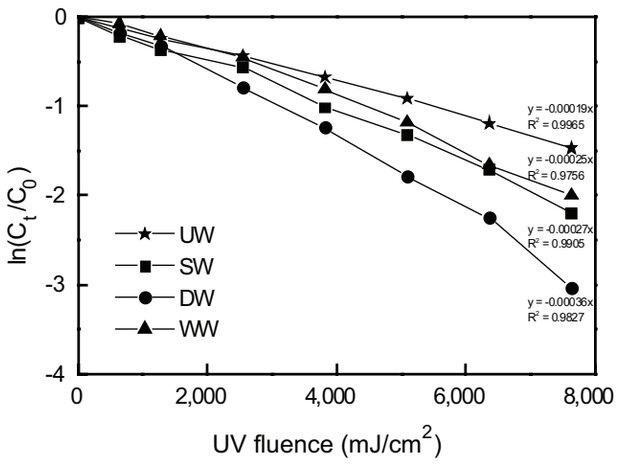

Fig. 7. Direct UV photolysis of ofloxacin in natural waters $[OFL]_0$ = 5 μM.

3.5. Effect of NOM

Because of the non-selective oxidation of ·OH during the UV/H_2O_2 treatment, NOM reacts with ·OH, such as HA and FA. Therefore, we considered the effect of HA and FA on the degradation of OFL, with the results being shown in Fig. 9. The figure indicates that both HA and FA reduce the degradation rate of OFL and, with an increasing concentration of HA and FA, this reduction effect increases and the OFL degradation rate declines. This phenomenon could be explained as follows: HA and FA absorb the incident light, thereby decreasing the UV transmittance, further lowering the production of ·OH, and inhibiting the degradation of OFL because of radical oxidation [16]. In addition, both HA and FA could scavenge ·OH, and OFL could compete with HA and FA for ·OH, leading to the OFL degradation rate slowing down [17].

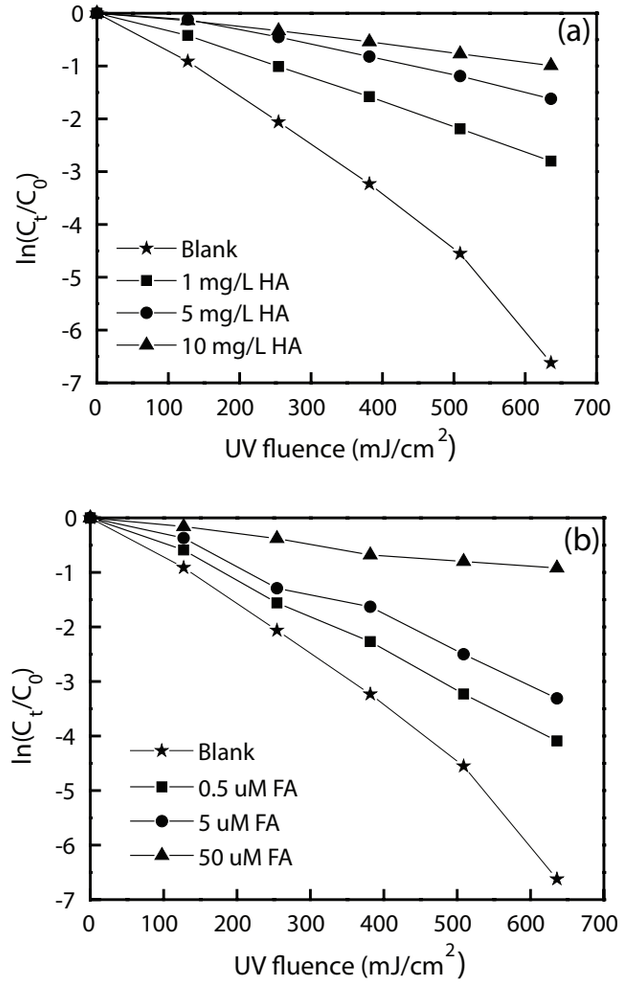

Fig. 9. Effects of NOM on the degradation of ofloxacin in the UV/H_2O_2 process, $[OFL]_0$ = 5 μM $[H_2O_2]_0$ = 240 μM a HA, b FA.

3.6. Effect of chloride ion

Similar to NOM, the inorganic ions Cl^- could react with ·OH; therefore, we also studied the effect of Cl^- on the degradation of OFL. Our results are shown in Fig. 10. It is obvious that Cl^- reduced the degradation of OFL; when the concentration of Cl^- increased, the inhibitory effect on OFL also increased (Fig. 10). This is because the Cl^- would react with ·OH to produce less-active oxidants ($ClOH\cdot^-$, $HClOH\cdot$, $Cl\cdot$, and $Cl_2\cdot^-$) [Eqs. (4)–(7)][17], with the dominant species being $Cl_2\cdot^-$ [18]. The redox potential of $Cl_2\cdot^-$ (1.36 V) was much less than that of $OH\cdot$ (2.9 V). As a result, in the presence of a high level of Cl^-, less OFL would be degraded.

$$Cl^- + \cdot OH \leftrightarrow ClOH\cdot^- \quad (4)$$

$$ClOH\cdot^- + H^+ \leftrightarrow HClOH\cdot \quad (5)$$

$$HClOH\cdot \leftrightarrow Cl\cdot + H_2O \quad (6)$$

$$Cl\cdot + Cl^- \leftrightarrow Cl_2\cdot^- \quad (7)$$

3.7. Identification of intermediates and degradation pathways of OFL

During the degradation process of OFL by UV/H_2O_2 ($[OFL]_0$ = 5 μM, $[H_2O_2]_0$ = 240 μM) the pH value of the mixed solution changed from 7.29 to 6.75 after irradiation for 5 min, and after irradiation for 30 min, the TOC of the mixed solution decreased from 1.43 mg/L to 1.36 mg/L. The degradation efficiency of OFL reached 100% after irradiation for 5 min, suggesting that despite OFL being decomposed, it had not completely mineralized. To obtain more intermediates information, high concentration of OFL(50 μM)and H_2O_2 (1 mM), and prolonged UV irradiation time (10 min) were applied. Finally, six degradation products of OFL were determined by UPLC-HRMS, on which detail information is shown in Table 2.

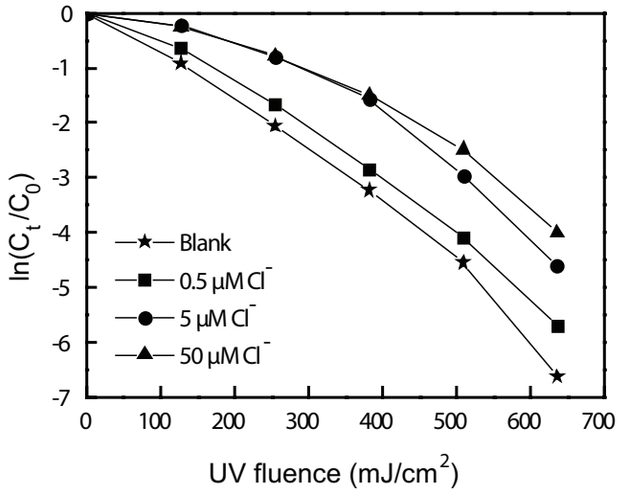

Fig. 10. Effects of chloride ion on the degradation of ofloxacin in UV/H_2O_2 process, $[OFL]_0$ = 5 μM $[H_2O_2]_0$ = 240 μM.

Given the structure of OFL and the characteristics of the UV/H_2O_2 system, a degradation mechanism of OFL is proposed, as shown in Fig. 11. The main substitutes in OFL were piperazinyl, quinolone, and oxazine substituent. Previous studies have reported that OFL was prone to degradation in piperazinyl and quinolone moiety, and resistant to degradation in oxazine moiety, and that it was difficult to defluorinate [19]. The experimental results we obtained are in agreement with these previous deductions.

In quinolone substituent, the oxidization of the oxygen-centered radical to undergo decarboxylation formed m/z = 318, and the ·OH attack at the quinolone moiety resulted in the formation of the carbon ring-centered radical, leading to the formation of m/z = 334. After the breakage of the carbon double-bonded side chain on the ring structure with a keto group, m/z = 338 was formed with the aid of ·OH.

In piperazinyl substituent, the m/z = 378 formation is attributed to hydroxylation at the piperazinyl ring, and m/z = 336 was formed after multiple reactions, leading to the opening of the N-piperazine ring. Furthermore, m/z = 279 was generated by the oxidation of the piperazine side chain and an amino group was reduced, which had also been reported within the sonophotocatalytic treatment of OFL [20].

4. Conclusions

The UV/H_2O_2 advanced oxidation process was able to rapidly degrade OFL, with the degradation process following the first-order reaction kinetics. The ·OH generated by H_2O_2 significantly improved the reaction rate of OFL; the rate constant increased linearly with the concentration of H_2O_2. However, with a continuous increase of the H_2O_2 dosage, the rate constant of OFL slowed down, and when the concentration of H_2O_2 was greater than 5 mM, the rate constant of the OFL decreased. However, the absolute amount of degradation of OFL increased with an increase in the initial concentration of H_2O_2. In all three types of actual water, the degradation of OFL was prohibited compared with that

Table 2
Degradation products of ofloxacin by the UV/H_2O_2 process, identified by UPLC-HRMS $[OFL]_0$ = 50 μM, $[H_2O_2]_0$ = 1 mM, irradiation for 10 min

m/z	Retention time (min)	Molecular formula	Error (ppm)	Difference with OFL	Degradation site moiety
279	1.40	$C_{13}H_{11}FN_2O_4$	3.6	–5C 9H N	piperazinyl
318	1.43	$C_{17}H_{20}FN_3O_2$	0.3	–C 2O	quinolinic
334	1.06	$C_{17}H_{20}FN_3O_3$	–5.7	–C O	quinolinic
336	1.32	$C_{16}H_{18}FN_3O_4$	–2.7	–2C 2H	piperazinyl
338	0.99	$C_{16}H_{20}FN_3O_4$	0.0	–2C	quinolinic
378	1.61	$C_{18}H_{20}FN_3O_5$	0.5	+O	piperazinyl

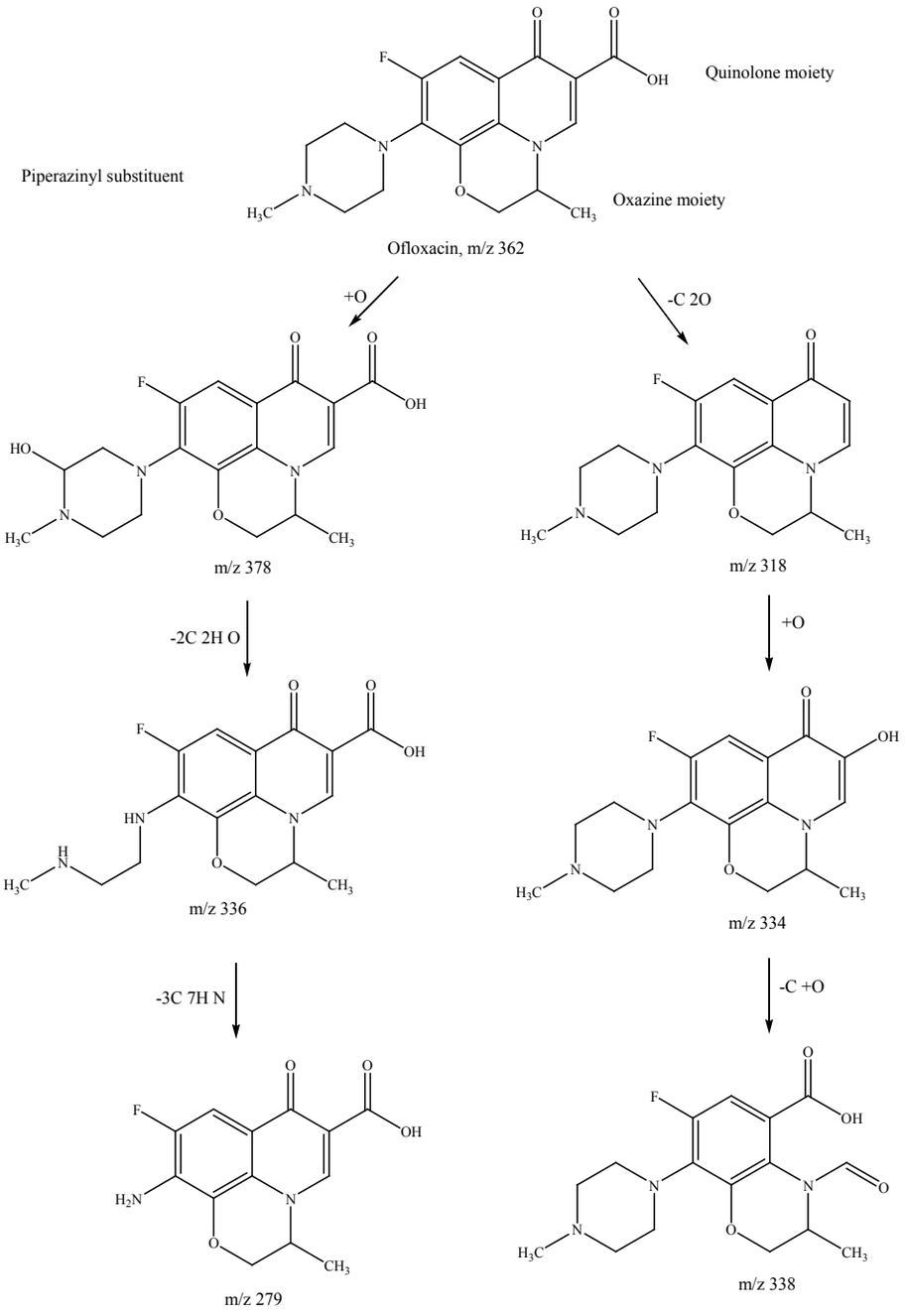

Fig. 11. OFL degradation pathways induced by the UV/H_2O_2 process.

of the ultrapure water. The degradation rate constant of OFL decreased in the order $K_{UW} > K_{DW} > K_{SW} > K_{WW}$, which could be related to the actual water environment. Further analysis indicated that the acidic and basic environments or the existence of NOM and chloride ion inhibited the degradation of OFL, validating our deduction. The findings of the study indicate that laboratory results could not be directly extended to actual water treatment without further consideration. Six degradation products of OFL were determined by UPLC-HRMS, with the degradation pathways mainly encompassing ring openings at both the piperazinyl substituent and the quinolone moiety.

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