#### Accepted Manuscript

Title: Ciprofloxacin degradation in UV/chlorine advanced oxidation process: Influencing factors, mechanisms and degradation pathways

Authors: Jia Deng, Guangxue Wu, Shoujun Yuan, Xinmin Zhan, Wei Wang, Zhen-Hu Hu



PII:	S1010-6030(18)31131-6
DOI:	https://doi.org/10.1016/j.jphotochem.2018.10.043
Reference:	JPC 11559
To appear in:	Journal of Photochemistry and Photobiology A: Chemistry
Received date:	11 August 2018
Revised date:	22 October 2018
Accepted date:	23 October 2018

Please cite this article as: Jia D, Guangxue W, Shoujun Y, Xinmin Z, Wei W, Zhen-Hu H, Ciprofloxacin degradation in UV/chlorine advanced oxidation process: Influencing factors, mechanisms and degradation pathways, *Journal of Photochemistry and amp; Photobiology, A: Chemistry* (2018), https://doi.org/10.1016/j.jphotochem.2018.10.043

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# Ciprofloxacin degradation in UV/chlorine advanced oxidation process: Influencing factors, mechanisms and degradation pathways

Jia Deng<sup>a</sup>, Guangxue Wu<sup>b</sup>, Shoujun Yuan<sup>a</sup>, Xinmin Zhan<sup>c</sup>, Wei Wang<sup>a,\*</sup>, Zhen-Hu Hu<sup>a,\*</sup>

<sup>a</sup> School of Civil Engineering, Hefei University of Technology, Hefei 230009, China
 <sup>b</sup> Key Laboratory of Microorganism Application and Risk Control (MARC) of
 Shenzhen, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China
 <sup>c</sup> College of Engineering and Informatics, National University of Ireland, Galway,
 Ireland

#### \*Corresponding author

Prof. Zhen-Hu Hu, Dr. Wei Wang School of Civil Engineering, Hefei University of Technology, Hefei, 230009 China Tel:86-551-62904144 Fax: 86-551-62902066

E-mail: zhhu@hfut.edu.cn; dwhit@126.com

## **Graphical Abstract**



#### **Highlights**

Ciprofloxacin (CIP) is quickly degraded in UV/chlorine process CIP degradation in UV/chlorine process is affected by many anions and humic acid Hydrated electron, Cl<sup>-</sup>, HO<sup>-</sup>, and UV photolysis play key role in CIP degradation Degradation pathway of CIP in UV/chlorine process is proposed

#### Abstract

Ciprofloxacin (CIP) is a widely used third generation fluoroquinolone antibiotics, and has been often detected in wastewater treatment plants. Finding an effective way to remove them from wastewater is of great concern. Ultraviolet (UV)/chlorine advanced oxidation process (AOP) has many advantages in micropollutant removal. In this study, CIP degradation in UV/chlorine process was investigated. Only 41.2% of CIP was degraded by UV photolysis and 30.5% by dark chlorination in 30 min, while 98.5% of CIP was degraded by UV/chlorine process in 9 min. HCO<sub>3</sub><sup>-</sup> had markedly inhibition, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> had slight inhibition, and Cl<sup>-</sup> had a marginal inhibition on the CIP

degradation in UV/chlorine system. The degradation of CIP in UV/chlorine process was mainly attributed to the attack of reactive species. The relative contributions of hydrated electrons ( $e_{aq}$ ), hydroxyl radicals (HO·), chlorine atoms (Cl·), and UV photolysis were investigated. Under neutral condition in aqueous solution, CIP degradation had highest pseudo first-order reaction rate constants, in which  $e_{aq}$  had the highest contribution, followed by Cl·, HO·, and UV photolysis. The intermediates and byproducts were identified and the degradation pathway was proposed. The total organic chlorine (TOCl) and biotoxicity were further assessed. CIP and natural organic matters (NOMs) were removed efficiently in real water. UV/chlorine showed the potential for the wastewater treatment containing CIP.

**Keywords**: Ciprofloxacin; UV/chlorine process; advance oxidation process; reactive species; UV photolysis; wastewater

#### **1. Introduction**

Fluoroquinolones are typical antibiotics that are widely used around the world as human and veterinary medicines. They have been frequently detected in surface water and wastewater over the last few decades [1]. But, due to the persistence and biotoxicity of fluoroquinolones, these antibiotics could not be well degraded in conventional water treatment processes [2]. Ciprofloxacin (CIP) is a widely used third generation fluoroquinolone, which has been often detected in wastewater treatment plants effluents (WWTPE) water, surface water, groundwater and soils [3,4]. The presence of low concentration of CIP may induce selective pressure for microbial populations leading to fluoroquinolones resistant pathogens [5,6]. Thus, finding an effective way to remove them from wastewater is of great concern.

Advanced oxidation processes (AOPs) are efficient for the degradation of recalcitrant pharmaceuticals and personal care products (PPCPs) [7]. Many AOPs technologies have been conducted for the destruction of fluoroquinolones, such as UV photolysis, UV/H<sub>2</sub>O<sub>2</sub> and ozonation [8-10]. Aqueous chlorine oxidation and electrochemical oxidation were also investigated [11,12].

UV and chlorine are widely used for the disinfection in water treatment plants [13]. UV/chlorine AOP has been reported to produce hydrated electrons ( $e_{aq}$ ), hydroxyl radicals (HO<sup>·</sup>), chlorine atoms (Cl<sup>·</sup>) and other oxidation radicals at wavelengths less than 400 nm [14,15]. HO<sup>·</sup>, O<sup>-</sup> and Cl<sup>·</sup> are generated due to the UV photolysis of HOCl and OCl<sup>-</sup>, as listed in Eq. (1).

$$HClO/ClO^{-} + hv \rightarrow HO\bullet/O\bullet^{-} + Cl\bullet$$
(1)

HO is a nonselective oxidant with oxidation potential approximately 2.70 V [16]. Cl is a selective oxidant and can react with electron-rich moieties through one-electron

oxidation, H-abstraction and unsaturated carbon-carbon bonds with oxidation potential 2.47 V [17]. The reactive species have synergism effect and enhance the degradation of persistent contaminants such as chloramphenicol, ibuprofen, benzotriazole, tolytriazole, iopamidole, ronidazole and atrazine [18-22]. However, the degradation of CIP in UV/chlorine process and the relative contributions of reactive species have not been reported before.

The aims of this study were to (1) compare the degradation of CIP by UV, dark chlorine and UV/chlorine; (2) analyze the factors affecting CIP degradation in UV/chlorine process; (3) investigate the relative contributions of the reactive species on CIP degradation; and (4) propose CIP degradation pathways in UV/chlorine process.

#### 2. Materials and Methods

#### 2.1. Materials

Ciprofloxacin (purity > 98.0%) was purchased from TCI (Shanghai) Development Co. Ltd., China. Sodium hypochlorite (NaClO, 6.0-14.0% - free chlorine w/w) and tert-butanol (t-BuOH) were purchased from Aladdin Industrial Co. Ltd., China. Sodium thiosulfate, sodium bicarbonate, potassium phosphate monobasic and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Methanol, acetonitrile, and formic acid were purchased from Sigma-Aldrich (Shanghai) Co. LLC., China. All chemicals were of analytical grade and used without further purification. Aqueous solutions were prepared using ultrapure water and all reagents were stored in the dark at 4.0 °C. The NaClO stock solution was prepared weekly and standardized [23].

The surface water was collected from Hubing pond in the campus of our university (Hefei, China). The waste water treatment plant effluent (WWTPE) water was collected from Zhuzhuanjing municipal wastewater treatment plant, Hefei, China. The characteristics of the surface water and WWTPE water were listed in Table 1.

#### 2.2. Experimental design

The CIP degradation by UV, dark chlorination and the UV/chlorine were performed in a light-proof tank. The schematic diagram of the apparatus was shown in Fig. S1. A low pressure UV lamp (16-20 W, ZW40S24Y, Sanyi Co., China) with monochromatic emissions at 254 nm was installed at the top of tank. Two 300 mL glass beakers were used as the reactor with working volume of 250 mL. Magnetic stirrer was used for the mixing. The average UV fluence rate was determined with 0.4 mW.cm<sup>-2</sup> [24]. The UV lamp was warmed up for 30 min before experiments. Control test of CIP degradation by UV photolysis or dark chlorination was also conducted in a similar way but only by UV light or chlorine.

In the investigation of the impacts of environmental conditions (e.g., anions, humic acid, and pH) and application in surface water and WWTPE water, the CIP concentration was set at 10.0  $\mu$ M, and 20.0 mM phosphate buffer was used to adjust the solution pH. Samples (1.0 mL) were collected at different time intervals, and immediately quenched with 10.0 mM Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. To identify the intermediate products and analyze total organic carbon (TOC) and total organic chlorine (TOCl), 100.0  $\mu$ M of CIP and 1.0 mM of chlorine were used and the reaction time was extended to 240 min. To assess the toxicity of intermediates and byproducts, biotoxicity analysis experiments were conducted in 240 min and samples in different reaction time were collected and

quenched by ascorbic acid. All experiments were carried out in triplicate and the average values with error bar were presented.

#### 2.3. Analytical Methods

The concentration of CIP in the solution was measured using high-performance liquid chromatography (HPLC, 1260 Infinity, Agilent, USA) equipped with a C18 column (4.6 mm × 250 mm, 5  $\mu$ m, Shimadzu Ltd., Japan) and detected by a diode array detector at 254 nm. The mobile phase was composed of acetonitrile, methanol, water and formic acid (20: 15: 64.5: 0.5, v/v/v/v) at a flow rate of 0.8 mL.min<sup>-1</sup>. The ions in the degradation solution were analyzed using an ion chromatograph equipped with a conductivity detector (ICS-90, Dionex, USA). An anion-exchange column (AS9-HC) was used to separate the ions with an eluent of 9.0 mM Na<sub>2</sub>CO<sub>3</sub> at a flow rate of 1.0 mL.min<sup>-1</sup>. TOC of the solution was measured by total organic carbon analyzer (TOC-V<sub>CPN</sub>, Shimadzu Ltd., Japan). The TOCl was determined using a precombustion method (USEPA, 1988) with an ion chromatograph (IC) system.

The decomposition intermediates of CIP in UV/chlorine process were analyzed using liquid chromatography/electrospray ionization quadrupole time-of-flight mass spectrometry (LC/Q-TOFMS, Acquity UP, Waters, USA). A C18 column (4.6 mm × 150 mm, 5  $\mu$ m, GL Sciences Inc., Japan) was used to separate the relevant components at a flow rate of 0.4 mL/min. The mobile phase was composed of acetonitrile (solvent A), methanol (solvent B) and water (solvent C) (20: 20: 60, v/v/v). The scanning mode was set to m/z 100–1000. The temperature of the desolvation and the ion source block was set to 350 °C and 110 °C, respectively. Nitrogen was used as the nebulizer (40.0 L.h<sup>-1</sup>) and as the desolvation gas (400.0 L.h<sup>-1</sup>). Byproducts were identified using gas

chromatography mass spectrometry (GC-MS, Elite-1, Perkin Elmer, USA) and equipped with a HP-5MS fused silica capillary column (30 m  $\times$  0.25 mm, 0.25  $\mu$ m, Perkin Elmer, USA). The details of pretreatment procedure and parameters for byproducts analysis were shown in Text S1.

The biotoxicity was evaluated using Salmonella typhimurium (Sal94) and luminescent bacteria photobacterium phosphoreum (Synergy HT, BioTek Ltd., USA). The details of operation procedure for biotoxicity analysis were shown in Text S2. NOMs in solution were detected using a three-dimensional excitation-emission matrix spectrofluorometer (Varian, Palo Alto Co., USA), which used a Xe excitation source. The parameters of excitation-emission matrix for NOMs analysis were shown in Text S3.

#### 3. Results and Discussion

3.1. CIP degradation in UV, Dark Chlorine and UV/chlorine processes

Fig. 1 showed the CIP degradation by UV photolysis, dark chlorination and UV/chlorine at the same oxidant molar dosage and pH 7.0. Only 41.2% of CIP was degraded by UV photolysis and 30.5% by dark chlorination in 30 min. It was interesting that 98.5% of CIP was degraded by UV/chlorine in 9 min, indicating the strong oxidative capacity of UV/chlorine process.

3.2. CIP degradation in UV/chlorine process

3.2.1. Effects of anions

Generally,  $HCO_3^-$ ,  $Cl^-$ ,  $NO_3^-$ , and  $SO_4^{2-}$  widely exist in wastewater and may affect the oxidation process. Thus, the effects of these ions on CIP degradation in UV/chlorine process were investigated. Principal reactions (2-16) in UV/chlorine system were listed in Table 2. Fig. 2a showed that the degradation was obviously inhibited when  $HCO_3^{-1}$ concentration was more than 5.0 mM. It has been reported that HCO<sub>3</sub><sup>-</sup> could scavenge HO based on reactions 2 and 3, as listed in Table 2. HCO<sub>3</sub><sup>-</sup> could react with HO and Cl<sup>-</sup> to generate  $CO_3^{-}$ , which had a low oxidation potential [35]. Cl<sup>-</sup> could react with HO and Cl<sup>-</sup> to form the weak oxidizing capability radicals. Meanwhile, these weak oxidizing capability radicals could be decomposed into HO<sup>-</sup> and Cl<sup>-</sup> again with a high rate constant, as listed in reactions 4-7 in Table 2. So, the presence of Cl<sup>-</sup> had a marginal effect on CIP degradation, as shown in Fig. 2b. Fig. 2c showed the degradation of CIP was also inhibited by NO<sub>3</sub><sup>-</sup>. A possible explanation was that NO<sub>3</sub><sup>-</sup> was reduced to NO<sub>2</sub><sup>-</sup> which consumed HO to form low oxidizing capability radicals, as listed in reactions 8-10 in Table 2, which resulted in the inhibition effect. Few studies reported SO<sub>4</sub><sup>2-</sup> could impact the HO and Cl. But, Fig. 2d showed CIP degradation was slightly inhibited in the presence of SO<sub>4</sub><sup>2-</sup> which was similar to NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup>. So, high concentration of  $SO_4^{2-}$  might influence the radicals, too.

#### 3.2.2. Effects of humic acid

Natural organic matters (NOMs) widely exist in natural water bodies, and humic acid is a typical NOM. Fig. 3 showed the influence of humic acid on CIP degradation. 0.4 mg.L<sup>-1</sup> of humic acid showed significant inhibition on the degradation, and the degradation efficiency decreased from 98.5% to 62.2%. With the continuous increase of

humic acid to 4.0 mg.L<sup>-1</sup>, the degradation efficiency further decreased to 43.2%. The inhibition might be due to the following reasons. Firstly, NOMs absorbed UV light at 254 nm and underwent photolysis which reduced the UV absorption of chlorine and CIP. So, NOMs acted as an inner filter to impede CIP photodegradation and decrease the rate at which chlorine photolysis produced radicals. Secondly, in the same system, NOMs might compete radicals with CIP which decreased the degradation efficiency of CIP [9]. Therefore, NOMs had a negative effect on the organic degradation in UV/chlorine process.

3.3. Kinetics analysis and relative contribution of reactive species

Kinetics analysis could describe the reaction process of CIP degradation. In this study, a pseudo-first-order reaction kinetics model was used to describe the CIP degradation by UV/chlorine in different pH conditions as Eq. (17):

$$k = \frac{-\ln(C/C_0)}{t} \tag{17}$$

where C<sub>0</sub> and C are the CIP concentration at initial time and time *t*, and *k* is the pseudo-first-order rate constants. The values of *k* in different pH conditions were showed in the inset of Fig. 4a. These values were  $3.3 \times 10^{-3} \text{ s}^{-1}$ ,  $3.8 \times 10^{-3} \text{ s}^{-1}$ ,  $7.4 \times 10^{-3} \text{ s}^{-1}$ ,  $7.1 \times 10^{-3} \text{ s}^{-1}$  and  $6.7 \times 10^{-3} \text{ s}^{-1}$  at pH 5.0, 6.0, 7.0, 8.0 and 9.0, respectively. In this work, CIP degradation showed higher degradation efficiency in neutral and alkaline conditions than acidic conditions. It might be attributed to the relative contributions of reactive species in different pH conditions.

Actually, CIP degradation in UV/chlorine process was effected by many factors, including UV photolysis and the attack of reactive species. The reactive species

included Cl<sup>•</sup>, HO<sup>•</sup>,  $e_{aq}^{-}$ , Cl<sub>2</sub><sup>-•</sup>, O<sup>-•</sup>, ClO<sup>•</sup> and ClOH<sup>-•</sup>. Due to the low oxidation-reduction potential, the reactive species of Cl<sub>2</sub><sup>-•</sup>, O<sup>-•</sup>, ClO<sup>•</sup> and ClOH<sup>-•</sup> were negligible [17]. Taking the contribution of main reactive species into consideration, the CIP degradation kinetics could be described using Eq. (18):

$$-\ln(C/C_0) = k_{\rm UV}t + k_{\rm CIP-HO} C_{\rm HO} t + k_{\rm CIP-e_{aq}} C_{\rm e_{aq}} t + k_{\rm CIP-CI} C_{\rm CI} t$$
(18)

where  $k_{UV}$  represents the first-order reaction rate constant of CIP degradation by UV photolysis.  $k_{CIP-HO.}$ ,  $k_{CIP-eaq.}$  and  $k_{CIP-Cl.}$  are the second-order reaction rate constants of CIP degradation by the attack of HO,  $e_{aq}$  and Cl, respectively.  $C_{HO.}$ ,  $C_{eaq.}$  and  $C_{Cl.}$  are the steady state concentration of HO,  $e_{aq}$  and Cl, respectively.

 $k_{UV}$  was obtained experimentally from CIP degradation by UV photolysis, and was calculated using Eq. (19):

$$k_{\rm UV} = \frac{-\ln(\dot{\mathbf{C}} / \dot{\mathbf{C}}_0)}{t} \tag{19}$$

where C'<sub>0</sub> and C' are the CIP concentration at initial time and time *t* in UV photolysis experiment. Fig. S2 showed the value of  $k_{UV}$  in different pH conditions in UV photolysis.  $k_{UV}$  obtained in this study was similar to the values which had been reported before [9].

The relative contribution of HO<sup>•</sup> was investigated using 10.0  $\mu$ M nitrobenzene (NB) as the probe compound in UV/chlorine system which only reacted with HO<sup>•</sup>. The reaction rate constant of NB with HO<sup>•</sup> ( $k_{NB-HO}$ ) had been reported ( $k_{NB-HO} = 3.9 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>) [36]. According to the steady-state assumption, C<sub>HO</sub>. was calculated using Eq. (20):

$$C_{\text{HO.}} = \frac{-\ln(C_{\text{NB}}/C_{\text{NB0}})}{k_{\text{NB-HO.}}t}$$
(20)

$$k_1 = k_{\text{CIP-HO.}} \mathbf{C}_{\text{HO.}}$$
(21)

where  $C_{NB0}$  and  $C_{NB}$  are the concentration of NB at initial time and time t. The result of

NB degradation was shown in Fig. S3a. The reaction rate constant of CIP with HO· ( $k_{CIP-HO}$ ) has been reported ( $k_{CIP-HO} = 6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) [9].  $k_1$ ' was defined as the pseudo-first order rate constant of CIP with HO· and the value was obtained in Eq. (21) as  $4.1 \times 10^{-4} \text{ s}^{-1}$ ,  $5.4 \times 10^{-4} \text{ s}^{-1}$  and  $5.3 \times 10^{-4} \text{ s}^{-1}$  at pH 5.0, 7.0 and 9.0, respectively.

To investigate the relative contribution of  $e_{aq}$ , excessive tertiary butyl alcohol (t-BuOH) was added in UV/chlorine system as radicals quencher because of its high reaction rate constants with HO and Cl  $(k_{t-BuOH-HO} = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$ , and  $k_{t-BuOH-Cl} = 3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$  [37]. In this system, 100.0 mM t-BuOH was added to scavenge HO and Cl Thus,  $e_{aq}$  could be remained to react with CIP, and the kinetics was listed in Eq. (22):

$$k'_{2} = k_{\text{CIP-}e_{\text{aq}}} \cdot C_{e_{\text{aq}}} = \frac{-\ln(C'/C')}{t}$$
 (22)

where C"<sub>0</sub> and C" are the concentration of CIP at initial time and time *t* in t-BuOH scavenging experiment. The CIP degradation kinetics was shown in Fig. S3b.  $k_2$ ' was defined as the pseudo-first-order rate constant of CIP with  $e_{aq}$ . These values were  $1.0 \times 10^{-3} \text{ s}^{-1}$ ,  $2.0 \times 10^{-3} \text{ s}^{-1}$  and  $2.9 \times 10^{-3} \text{ s}^{-1}$  at pH 5.0, 7.0 and 9.0, respectively. Therefore, the only unknown value was the relative contribution of Cl·, which could be described in Eq. (23):

$$k'_{3} = k_{\text{CIP-CI}} \cdot C_{\text{CI}} = k - (k_{\text{UV}} + k_{\text{CIP-HO}} \cdot C_{\text{HO}} + k_{\text{CIP-e}_{aq}} \cdot C_{e_{aq}})$$
 (23)

where  $k_3$ ' was defined as the pseudo-first order rate constant of CIP with Cl<sup>.</sup> Eq.7 can be simplified into Eq. (24):

$$\dot{k}_{3} = k - (k_{\rm UV} + k_{1} + k_{2})$$
 (24)

 $k_3$ ' was calculated as  $1.7 \times 10^{-4} \text{ s}^{-1}$ ,  $1.8 \times 10^{-3} \text{ s}^{-1}$  and  $2.3 \times 10^{-5} \text{ s}^{-1}$  at pH 5.0, 7.0 and 9.0, respectively.

Fig. 4b showed the relative contributions of UV, HO, Cl and  $e_{aq}$  in UV/chlorine

process at different pH conditions. It could be found that the contribution of HO<sup>•</sup> remained relatively stable. With the increase of pH value, contributions of UV and  $e_{aq}$ <sup>•</sup> increased. The contribution of Cl<sup>•</sup> was extremely low in non-neutral conditions. Under acid condition, H<sup>+</sup> combined Cl<sup>•</sup> and  $e_{aq}$ <sup>•</sup> to form low reduction ·H and Cl<sup>-</sup> according to the reaction 15. The reaction of OH<sup>-</sup> with Cl<sup>•</sup> to form the low oxidation ClOH<sup>-</sup> based on reaction 16, as listed in Table 2. So, comparing with acidic condition, CIP degradation was more quickly in neutral and alkaline conditions.

3.4. CIP degradation pathway in UV/chlorine process

The degradation of CIP could be evaluated by the generation of anions during AOPs. As shown in Table S1, CIP contains carbon-fluorine bond. Thus, the concentration of  $F^-$  was measured during the degradation to evaluate the broken of CIP structure. Because the energy of carbon-fluorine bond is much higher than carbon-carbon bond and carbon-nitrogen bond, the carbon-fluorine bond of CIP is very difficult to be broken. Some reactive species with high oxidation reduction potential such as sulfate radicals ( $E_0 = 2.5 \text{ V} \sim 3.1 \text{ V}$ ), HO· ( $E_0 = 2.7 \text{ V}$ ) and  $e_{aq}$ . ( $E_0 = -2.9 \text{ V}$ ) could attack carbon-fluorine bonds [38]. Fig. 5a showed the defluorination in three systems. Obviously, dark chlorine was invalid for the defluorination, indicating that free chlorine could not break carbon-fluorine bond down. UV photolysis had a defluorination efficiency of 40.2% and 68.8% for UV/chlorine defluorination. UV/chlorine showed a higher defluorination efficiency when compared to UV photolysis, indicating the advantages of UV/chlorine process.

The mineralization of CIP in UV/chlorine process was assessed using TOC. As shown in Fig. 5.b, 22.3% of TOC was removed after 4 hours reaction in UV/chlorine

process, while there was no obvious decline in dark chlorine and UV photolysis. The degradation intermediates and byproducts formed during AOPs might bring potential hazard to the environment. Thus, it was essential to identify the molecular structures of these intermediates and byproducts. The intermediates were detected via LC/Q-TOF-MS analysis. Parts of intermediate products structure could be identified, such as P1 (m/z=332), P2 (m/z=306), P3 (m/z=263) and P4 (m/z=223). In addition, some detected compounds could be proposed such as a (m/z=320) and b (m/z=320). The MS spectrum was shown in Fig. S5. P1 (m/z=332) was detected at initial time. Its secondary amines on the piperazyl ring were attacked firstly. Subsequently, Carbon-nitrogen bonds were broken down. Then, there were two possible pathways. The carbon-fluorine bond was broken down and substituted by hydroxyl. In another pathway, the piperazinyl ring was dropped out and the whole cyclopropyl was dropped from benzene ring. Some byproducts such as dichloroacetonitrile (DCAN) and trichloroacetaldehyde (chloral) were detected in CIP degradation process. The MS spectrum of byproducts was shown in Fig. S6. These intermediates and byproducts could be further degraded into CO<sub>2</sub>, H<sub>2</sub>O, F<sup>-</sup> and other low molecular compounds. The proposed degradation pathway was shown in Fig. 6.

#### 3.5. TOCl and biotoxicity analysis

For assessing the potential risk of intermediates, the generation of TOCl during CIP degradation in dark chlorine and UV/chlorine process was investigated, as shown in Fig. 7. In dark chlorine process, 130  $\mu$ M of TOCl was formed at initial 10 minutes, then decreased to around 70  $\mu$ M until the end of the process. In UV/chlorine process, the TOCl concentration continuously increased from initial 0 to about 90  $\mu$ M at 120 min,

and then decreased to 30  $\mu$ M after 240 min. Initially, dark chlorine and UV/chlorine all had chlorine substitution process which resulted in TOCl increasing quickly. Comparing with dark chlorine, UV/chlorine process had a low rate of chlorine substitution before 10 min. For dark chlorine, substitution was attributed to chlorine direct oxidation. However, for UV/chlorine, substitution was attributed to the effect of radicals which lead to the constant reaction of chlorine substitution. After 120 min, chlorine substitution rate was lower than decomposing rate which resulted in the decrease of TOCI.

The biotoxicity of the CIP degradation solution was evaluated. Fig. S7 showed the change of biototoxicity during CIP degradation in UV/chlorine process. At the initial time, the inhibition of CIP leaded to the very low bioluminescent. The value of bioluminescence reached highest at 60 min and decreased subsequently. It represented the biotoxicity was the lowest on 60 min. After 60 min, with the reaction continued, byproducts were generated such as DCAN and chloral. So, controlling the reaction time in UV/chlorine process is very important.

#### 3.6. CIP degradation in surface water and WWTPE

Fig. 8 showed UV/chlorine process degraded CIP in surface water and WWTPE. After 9 min, CIP degradation efficiency reached 80.3% and 72.7% in surface water and WWTPE water, respectively. The values were lower than that in ultrapure water. According to the investigation results of anions concentration in Table 1, mixing water containing 0.5 mg.L<sup>-1</sup> NH<sub>4</sub><sup>+</sup>, 7.0 mg.L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>, 30.0 mg.L<sup>-1</sup> Cl<sup>-</sup> and 68.0 mg.L<sup>-1</sup> SO<sub>4</sub><sup>2-</sup> was used to assess the effect of ions on UV/chlorine process. Interestingly, Fig. 8b showed a negligible effect of ions on CIP degradation in mixing water. The result might

be attributed to the NOMs in real water which consumed the reactive species in solution. From three-dimensional fluorescence spectra, humic acid-like organics as typical NOMs were detected in surface water and WWTPE [39]. Fig. 8 c-f showed NOMs could be efficiently removed in UV/chlorine process. Although, the degradation of CIP in real water was lower than it in ultrapure water, but the rate constants still maintained a high value due to the synergism of multiple reactive species [40]. These results showed the potential of UV/chlorine process for the wastewater treatment containing CIP.

#### 4. Conclusions

In this study, the degradation of CIP in aqueous solution by UV/chlorine AOP was investigated. Only 41.2% of CIP was degraded by UV photolysis and 30.5% by dark chlorination in 30 min, and 98.5% of CIP was degraded by UV/chlorine AOP in 9 min. The effect of HCO<sub>3</sub><sup>-</sup> on CIP degradation in UV/chlorine process depended on HCO<sub>3</sub><sup>-</sup> concentration, while of NO<sub>3</sub><sup>-</sup> and SO4<sup>2-</sup> was slight inhibitory, but of CI<sup>-</sup> wasn't obvious. The degradation of CIP in UV/chlorine process was mainly contributed to the attack of reactive oxygen species and UV photolysis. Under neutral condition in aqueous solution, CIP degradation had highest first-order reaction rate constants, in which  $e_{aq}$  had the highest contribution, followed by CI<sup>-</sup>, HO<sup>-</sup>, and UV photolysis. Based on the intermediates and byproducts identified, the degradation pathway of CIP in UV/chlorine process was lowest at about 60 min. CIP could be degraded efficiently by UV/chlorine in real water. The results showed the potential of UV/chlorine process for the wastewater treatment containing CIP.

#### Acknowledgements

This research was partially supported by the National Natural Science Foundation of China (51578205, 51538012, and 51728801), and the Project of Science and Technology in Anhui Province (1501041130).

#### References

- [1] A. Jia, Y. Wan, Y. Xiao, J. Hu, Occurrence and fate of quinolone and fluoroquinolone antibiotics in a municipal sewage treatment plant. Water Res. 46 (2012) 387-394.
- [2] Z.L. Ye, Y. Deng, Y. Lou, X. Ye, S. Chen, Occurrence of veterinary antibiotics in struvite recovery from swine wastewater by using a fluidized bed. Front. Environ. Sci. Eng. 12 (2018) 7.
- [3] E. Zuccato, S. Castiglioni, R. Bagnati, M. Melis, R. Fanelli, Source, occurrence and fate of antibiotics in the Italian aquatic environment. J. Hazard. Mater. 179 (2010) 1042-1048.
- [4] K. He, A.D. Soares, H. Adejumo, M. Mcdiarmid, K. Squibb, L. Blaney, Detection of a wide variety of human and veterinary fluoroquinolone antibiotics in municipal wastewater and wastewater-impacted surface water. Journal of Pharmaceutical & Biomedical Analysis 106 (2015) 136-143.
- [5] H.J. Adam, K.N. Schurek, K.A. Nichol, C.J. Hoban, T.J. Baudry, N.M. Laing, D.J. Hoban, G.G. Zhanel, Molecular characterization of increasing fluoroquinolone resistance in Streptococcus pneumoniae isolates in Canada, 1997 to 2005. Antimicrob Agents Chemother 51 (2007) 198-207.
- [6] K. Kümmerer, A. Henninger, Promoting resistance by the emission of antibiotics from hospitals and households into effluent. Clinical Microbiology & Infection 9 (2003) 1203-1214.
- [7] S. Cheng, X. Zhang, X. Yang, C. Shang, W. Song, J. Fang, Y. Pan, The multiple role of bromide ion in PPCPs degradation under UV/chlorine treatment. Environ. Sci. Technol. 52 (2018) 1806-1816.
- [8] H.S. Ou, J.S. Ye, S. Ma, C.H. Wei, N.Y. Gao, J.Z. He, Degradation of ciprofloxacin by UV and UV/H<sub>2</sub>O<sub>2</sub> via multiple-wavelength ultraviolet light-emitting diodes: Effectiveness, intermediates and antibacterial activity. Chem. Eng. J. 289 (2016) 391-401.
- [9] V.J. Pereira, H.S. Weinberg, K.G. Linden, P.C. Singer, UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm. Environ. Sci. Technol. 41 (2007) 1682-1688.
- [10] W.B. De, J. Dewulf, K. Demeestere, L.H. Van, Ozonation and advanced oxidation

by the peroxone process of ciprofloxacin in water. J. Hazard. Mater. 161 (2009) 701-708.

- [11] Y. Wang, C. Shen, M. Zhang, B.T. Zhang, Y.G. Yu, The electrochemical degradation of ciprofloxacin using a SnO<sub>2</sub>-Sb/Ti anode: Influencing factors, reaction pathways and energy demand. Chem. Eng. J. 296 (2016) 79-89.
- [12] M.C. Dodd, A.D. Shah, G.U. Von, C.H. Huang, Interactions of fluoroquinolone antibacterial agents with aqueous chlorine: reaction kinetics, mechanisms, and transformation pathways. Environ. Sci. Technol. 39 (2005) 7065-7076.
- [13] D. Wang, J.R. Bolton, S.A. Andrews, R. Hofmann, UV/chlorine control of drinking water taste and odour at pilot and full-scale. Chemosphere 136 (2015) 239-244.
- [14] M.J. Watts, K.G. Linden, Chlorine photolysis and subsequent OH radical production during UV treatment of chlorinated water. Water Res. 41 (2007) 2871-2878.
- [15] J. Fang, Y. Fu, C. Shang, The roles of reactive species in micropollutant degradation in the UV/free chlorine system. Environ. Sci. Technol. 48 (2014) 1859-1868.
- [16] L. Yunho, U.V. Gunten, T. Ternes, Oxidative transformation of micropollutants during municipal wastewater treatment: comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate VI, and ozone) and non-selective oxidants (hydroxyl radical). Water Res. 44 (2010) 555-566.
- [17] J.E. Grebel, J.J. Pignatello, W.A. Mitch, Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters. Environ. Sci. Technol. 44 (2010) 6822-6828.
- [18] Y. Xiang, J. Fang, C. Shang, Kinetics and pathways of ibuprofen degradation by the UV/chlorine advanced oxidation process. Water Res. 90 (2016) 301-308.
- [19] C. Sichel, C. Garcia, K. Andre, Feasibility studies: UV/chlorine advanced oxidation treatment for the removal of emerging contaminants. Water Res. 45 (2011) 6371-6380.
- [20] L. Qin, Y.L. Lin, B. Xu, C.Y. Hu, F.X. Tian, T.Y. Zhang, W.Q. Zhu, H. Huang, N.Y. Gao, Kinetic models and pathways of ronidazole degradation by chlorination, UV irradiation and UV/chlorine processes. Water Res. 65 (2014) 271-281.
- [21] X. Kong, J. Jiang, J. Ma, Y. Yang, W. Liu, Y. Liu, Degradation of atrazine by UV/chlorine: Efficiency, influencing factors, and products. Water Res. 90 (2016) 15-23.
- [22] H. Dong, Z. Qiang, J. Hu, J. Qu, Degradation of chloramphenicol by UV/chlorine treatment: Kinetics, mechanism and enhanced formation of halonitromethanes. Water Res. 121 (2017) 178-185.
- [23] M.H. Mccrady, Standard methods for the examination of water and wastewater (12th ed.). American Journal of Public Health & the Nations Health 4 (2011) 137.
- [24] J.R. Bolton, K.G. Linden, Standardization of methods for fluence (UV dose) determination in bench-scale UV experiments. Journal of Environmental Engineering 129 (2003) 209-215.
- [25] Z. Wang, Y. Shao, N. Gao, N. An, Degradation kinetic of dibutyl phthalate (DBP) by sulfate radical- and hydroxyl radical-based advanced oxidation process in

18

UV/persulfate system. Separation & Purification Technology 195 (2017) 92-100.

- [26] P. Sun, W.N. Lee, R. Zhang, C.H. Huang, Degradation of DEET and Caffeine under UV/Chlorine and Simulated Sunlight/Chlorine Conditions. Environ. Sci. Technol. 50 (2016) 13265-13273.
- [27] Z. Wu, J. Fang, Y. Xiang, C. Shang, X. Li, F. Meng, X. Yang, Roles of reactive chlorine species in trimethoprim degradation in the UV/chlorine process: Kinetics and transformation pathways. Water Res. 104 (2016) 272-282.
- [28] T.Y. Zhang, Y.L. Lin, B. Xu, S.J. Xia, F.X. Tian, N.Y. Gao, Effect of UV irradiation on the proportion of organic chloramines in total chlorine in subsequent chlorination. Chemosphere 144 (2016) 940-947.
- [29] Y. Yan, Q.N. Liao, F. Ji, W. Wang, S. Yuan, Z.H. Hu, Decomposition of 3,5-dinitrobenzamide in aqueous solution during UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub> oxidation processes. Environ. Sci. Pollut. Res. 24 (2017) 5360-5369.
- [30] F. Wang, W. Wang, S. Yuan, W. Wang, Z.H. Hu, Comparison of UV/H<sub>2</sub>O<sub>2</sub> and UV/PS processes for the degradation of thiamphenicol in aqueous solution. J. Photochem. Photobiol. A 348 (2017) 79-88.
- [31] C. Anastasio, B.M. Matthew, A chemical probe technique for the determination of reactive halogen species in aqueous solution: Part 1–Bromide solutions. Atmospheric Chemistry & Physics Discussions 6 (2006) 2439-2451.
- [32] R.E. Connick, The interaction of hydrogen peroxide and hypochlorous acid in acidic solutions containing chloride ion. Journal Of The American Chemical Society 69 (1947) 1509-1514.
- [33] D. Zehavi, J. Rabani, The oxidation of aqueous bromide ions by hydroxyl radicals. A pulse radiolytic investigation. J. Phys. Chem. 76 (1972) 312-319.
- [34] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O−) in aqueous solution. J. Phys. Chem. Ref. Data 17 (2009) 513-886.
- [35] C. Tan, N. Gao, S. Zhou, Y. Xiao, Z. Zhuang, Kinetic study of acetaminophen degradation by UV-based advanced oxidation processes. Chem. Eng. J. 253 (2014) 229-236.
- [36] Y. Ji, Y. Shi, L. Wang, J. Lu, Denitration and renitration processes in sulfate radical-mediated degradation of nitrobenzene. Chem. Eng. J. 315 (2017) 591-597.
- [37] P. Neta, R.E. Huie, A.B. Ross, Rate Constants for Reactions of Inorganic Radicals in Aqueous Solution. J. Phys. Chem. Ref. Data 17 (1988) 1027-1284.
- [38] T. An, H. Yang, G. Li, W. Song, W.J. Cooper, X. Nie, Kinetics and mechanism of advanced oxidation processes (AOPs) in degradation of ciprofloxacin in water. Applied Catalysis B Environmental 94 (2010) 288-294.
- [39] S. Xue, W. Jin, Z. Zhang, H. Liu, Reductions of dissolved organic matter and disinfection by-product precursors in full-scale wastewater treatment plants in winter. Chemosphere 179 (2017) 395-404.
- [40] L. Tang, G.X. Lyu, W. Mao, Y.C. Xue, L. Li, C.T. Jia, M.H. Wu, Synergistic effects between hydroxyl radicals and hydrated electrons on strengthening decomposition of an s-triazine compound: A combined experimental and theoretical study. Chemosphere 195 (2018) 365-371.

#### **Figure captions**

**Fig. 1.** CIP degradation in ultrapure water by UV, dark chlorination and UV/chlorine. Experimental conditions: pH = 7.0,  $[CIP]_0 = 10 \ \mu M$ ,  $[NaOCl]_0 = 100 \ \mu M$ , and UV fluence rate = 0.4 mW.cm<sup>-2</sup>.

**Fig. 2.** Effect of anions on CIP degradation in UV/chlorine process. Influence of (a)  $HCO_3^-$  ([NaHCO\_3] = 0-10.0 mM), (b) Cl<sup>-</sup> ([NaCl] = 0-10.0 mM), (c) NO\_3^- ([NaNO\_3] = 0-10.0 mM), and (d) SO\_4^{2-} ([Na\_2SO\_4] = 0-10.0 mM). Experimental conditions: pH = 7.0, [CIP]\_0 = 10.0  $\mu$ M, [NaOCl]\_0 = 100.0  $\mu$ M, and UV fluence rate = 0.4 mW.cm<sup>-2</sup>.

**Fig. 3.** Effect of humic acid on CIP degradation in UV/chlorine process. Experimental conditions: [humic acid]<sub>0</sub> = 0-4.0 mg/L, [CIP]<sub>0</sub> = 10.0  $\mu$ M, [NaOCl]<sub>0</sub> = 100.0  $\mu$ M, and UV fluence rate = 0.4 mW.cm<sup>-2</sup>.

**Fig. 4.** Kinetic analysis and relative contribution of reactive species in CIP degradation in UV/chlorine process. (a) Effect of pH and reaction rate constants analysis, and (b) the relative contribution of HO, Cl, hydrated electrons and UV in the UV/chlorine process. Experimental conditions: pH = 5.0 - 9.0,  $[CIP]_0 = 10.0 \ \mu\text{M}$ ,  $[chlorine]_0 = 100.0 \ \mu\text{M}$ , and UV fluence rate = 0.4 mW.cm<sup>-2</sup>.

**Fig. 5.** The generation of F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and TOC in time-dependent CIP degradation by different ways. (a) The generation of F<sup>-</sup>, (b) NO<sub>3</sub><sup>-</sup>, and (c) TOC. Experimental conditions:  $[CIP]_0 = 100.0 \ \mu\text{M}$ ,  $[NaOCl]_0 = 1.0 \ \text{mM}$ , pH = 7.0, and UV fluence rate = 0.4 mW.cm<sup>-2</sup>.

Fig. 6. Proposed pathways of CIP decomposition in UV/chlorine process.

**Fig. 7.** The generation of total organic chlorine during CIP degradation by dark chlorine and UV/chlorine. Experimental conditions:  $[CIP]_0 = 100.0 \ \mu\text{M}$ ,  $[NaOCl]_0 = 1.0 \ \text{mM}$ , and UV fluence rate = 0.4 mW.cm<sup>-2</sup>.

**Fig. 8.** (a) CIP degradation by UV/chlorine process in surface water and WWTPE. (b) CIP degradation by UV/chlorine process in ultrapure water and mixing water. (c-f) Fluorescence spectra for NOMs in surface water and WWTPE water. Experimental conditions:  $[CIP]_0 = 10.0 \ \mu\text{M}$ ,  $[NaOCI]_0 = 100.0 \ \mu\text{M}$ , UV fluence rate = 0.4 mW.cm<sup>-2</sup>.



Fig. 1



Fig. 2



Fig. 3



Fig. 4



Fig. 5



Fig. 6



Fig. 7



Fig. 8

						-		
Parameters	pН	COD	NH4 <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	NO <sub>2</sub> <sup>-</sup> -N	TP	Cl-	$SO_4^{2-}$
Surface water	7.2	42.5	0.3	0.3	ND	ND	12.9	23.7
WWTP effluent	6.9	89.3	0.5	7.1	ND	0.2	30.3	68.2

Table 1. Characteristics of surface water and WWTPE water (mg/L)

Note: (1) the unit is mg/L excluding pH, (2) COD chemical oxygen demand, TP total phosphorus, ND not detected.

No.	Reaction	Rate constants	ref
2	$HO_{\bullet}+HCO_{3}^{\bullet} \rightarrow CO_{3}^{\bullet}+H_{2}O$	$k = 8.5 \times 10^6 M^{-1} s^{-1}$	[25]
3	$Cl + HCO_{3}^{-} \rightarrow COe_{3}^{-} + H^{+} + Cl^{-}$	$k = 2.2 \times 10^8 M^{-1} s^{-1}$	[15]
4	$HO_{\bullet}+Cl^{-} \rightarrow ClOH_{\bullet}^{-}$	$k = 4.3 \times 10^9 M^{-1} s^{-1}$	[17]
5	$ClOH^{\bullet} \rightarrow HO^{\bullet} + Cl^{\bullet}$	$k = 6.1 \times 10^9 M^{-1} s^{-1}$	[17]
6	$Cl \bullet + Cl \bullet \rightarrow Cl \bullet_2$	$k = 6.5 \times 10^9 M^{-1} s^{-1}$	[26]
7	$Cl \bullet_2^{-} \rightarrow Cl \bullet + Cl^{-}$	$k = 1.1 \times 10^5 M^{-1} s^{-1}$	[27]
8	$NO_3^- \rightarrow NO_2^- + 1/2O_2$		[28]
9	$O\bullet^- + H_2O \leftrightarrow HO\bullet + OH^-$		[29]
10	$HO_{\bullet}+NO_{2}^{-} \rightarrow NO_{2}^{\bullet}+OH^{-}$		[30]
11	$HO \bullet + HClO \rightarrow ClO \bullet + H_2O$	$k = 2.0 \times 10^9 M^{-1} s^{-1}$	[31]
12	$HO_{\bullet}+CIO^{-} \rightarrow CIO_{\bullet}+OH^{-}$	$k = 8.8 \times 10^9 M^{-1} s^{-1}$	[32]
13	$Cl \bullet + HClO \rightarrow ClO \bullet + H^+ + Cl^-$	$k = 3.0 \times 10^9 M^{-1} s^{-1}$	[33]
14	$Cl \bullet + ClO^{-} \rightarrow ClO \bullet + Cl^{-}$	$k = 8.2 \times 10^9 M^{-1} s^{-1}$	[27]
15	$\mathrm{Cl}\bullet+e_{aq}\bullet+\mathrm{H}^+\to\bullet\mathrm{H}+\mathrm{Cl}^-$		[34]
16	$Cl \bullet + OH^{-} \rightarrow ClOH \bullet^{-}$	$k = 1.8 \times 10^{10} M^{-1} s^{-1}$	[26]

 Table 2. Principal reactions in UV/chlorine system