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Degradation kinetics and mechanism of diclofenac by UV/peracetic acid

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In this work, the degradation kinetics and mechanism of diclofenac (DCF) by UV/peracetic acid (PAA) was investigated. The effects of pH, PAA dose and common water components such as inorganic ions and dissolved organic matter (DOM) on DCF degradation by UV/PAA were also evaluated. It was observed that the addition of PAA promoted the photodegradation of DCF due to the generation of reactive radicals in the photolysis of PAA, which was also confirmed by the radical scavenging experiment. The best degradation efficiency of DCF was obtained at pH 8.5. The removal of DCF was enhanced gradually with increasing PAA dose. Since NO_3^- is a photosensitive substance which can generate $HO^{\bullet}$ under UV irradiation, its existence promoted the degradation of DCF. The presence of CO_3^{2-} could slightly improve DCF degradation, which might be due to the role of generated carbonate radicals. Cl^-, SO_4^{2-} and Fe^{3+} had little effect on DCF removal, while Cu^{2+} could enhance DCF degradation because of its catalytic ability for PAA decomposition. An inhibition effect on DCF removal was observed in the presence of DOM, and it was more obvious in higher concentration of DOM. The elimination of total organic carbon (TOC) was low. According to the twelve reaction products detected in the UV/PAA system, the probable transformation mechanism of DCF was proposed exhibiting eight reaction pathways, *i.e.*, hydroxylation, decarboxylation, formylation, dehydrogenation, dechlorination–hydrogenation, dechlorination–cyclization, dechlorination–hydroxylation and amidation. This study indicates that UV/PAA is a promising method for DCF removal from contaminated water.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) as emerging contaminants have received more and more attention in recent years. Due to their widespread use and low human metabolic capability, they have been detected frequently in wastewater treatment plants (WWTPs) and natural water environment with concentrations of ng L^{-1} to μg L^{-1}.[1-4] Studies have shown that WWTPs are important sources of PPCPs in natural water, because most of them cannot be completely removed by traditional wastewater treatment processes.[5-7] Diclofenac (DCF), a non-steroidal anti-inflammatory drug (NSAID), is extensively utilized to treat rheumatism or arthritis, relieve fever and ease pain.[8,9] Since DCF cannot be effectively removed in WWTPs due to its stable chemical structure, it is detected widely in surface water, groundwater and even drinking water.[10-12] Although DCF has a low acute toxicity, its occurrence can not only induce the production of drug-resistant bacteria but also have adverse effects on aquatic organisms, thus threatening human health and the ecosystem.[13,14] Therefore, developing a few new effective technologies to degrade DCF from the contaminated water is very essential.

Advanced oxidation processes (AOPs) are considered to be promising methods to remove refractory organic pollutants, which are mainly attributed to the role of highly active radicals like hydroxyl radical ($HO^{\bullet}$). Until now, AOPs have been widely used in the treatment of refractory organic wastewater with high concentration and emerging contaminants, which can improve the biodegradability of pollutants or even completely mineralize them. A number of AOPs such as UV/H_2O_2,[15] photocatalysis,[16,17] photo-Fenton reaction,[18] Fenton-like reaction,[19] electrochemical oxidation,[20] transition metal catalyzed persulfate or peroxymonosulfate,[21,22] *etc.* have been successfully applied to degrade DCF or other pharmaceuticals in wastewater.

The oxidation potential of PAA is 1.96 V, higher than H_2O_2 (1.78 V) and aqueous chlorine (1.48 V) but slightly lower than that of persulfate (2.01 V).[23-25] More importantly, PAA exhibits an excellent disinfection activity without mutagenic and carcinogenic disinfection byproducts during its use, and thus it is widely used for medical, food and wastewater disinfection.[26,27] Additionally, PAA can be activated to generate many kinds of radicals in a wide range of pH.[28] Therefore, PAA may be a promising oxidant in AOPs. However, PAA has not been extensively studied for the removal of PPCPs in wastewater so far. Similar to H_2O_2, PAA can be decomposed to produce $HO^{\bullet}$ through different activation methods like UV irradiation, transition metal catalysis and so on.[29,30] Among them, UV activated

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PAA (UV/PAA) is considered to be a promising technology for the removal of organic pollutants based on two facts that: (1) UV is now widely used for wastewater disinfection in WWTPs, and (2) it will not bring secondary pollution. Currently, the information on the destruction of organic contaminants by UV/PAA is very limited. Daswat et al.[31] found that the addition of PAA could improve the degradation of chlorophenol compared with UV alone. Cai et al.[32] reported that six PPCPs could hardly be oxidized by PAA but be removed quickly by UV/PAA. Chen et al.[33] studied the influence of water components on naproxen degradation in UV/PAA system. Rizzo et al.[34] found that UV/PAA was more efficient than sunlight/PAA for the degradation of emerging contaminants in the tertiary treatment of urban wastewater. To date, very limited literature is available on DCF removal by UV/PAA.

In this work, the degradation of DCF by UV/PAA was systematically studied. Firstly, the contribution of UV photolysis and reactive radicals to DCF removal in UV/PAA system was investigated. Then, the effects of various factors including initial pH, PAA dose and common water components like inorganic ions and dissolved organic matter (DOM) on DCF degradation were explored. Finally, the degradation products of DCF were detected and identified, and probable transformation mechanism was subsequently proposed.

2. Materials and methods

2.1. Materials

Peracetic acid (15%, w/w) was purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Diclofenac sodium (>99%) and fulvic acid (FA) were obtained from Aladdin (China). Methanol and acetic acid were HPLC grade. Sodium chloride ($NaCl$), sodium sulfate (Na_2SO_4), potassium nitrate (KNO_3), sodium carbonate (Na_2CO_3), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), monosodium phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$), disodium hydrogen phosphate heptahydrate ($Na_2HPO_4 \cdot 7H_2O$), sodium hydroxide ($NaOH$), sulphuric acid (H_2SO_4), potassium iodide (KI), manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$), ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), soluble starch, potassium permanganate ($KMnO_4$) and sodium hyposulfite pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) were all analytical reagent grade and purchased from Chengdu Kelong Chemical Reagent Co. Ltd. (China). All the chemicals were used as received without further purification. Ultrapure water (18 MΩ cm) was used to prepare aqueous solutions.

2.2. Analysis

The quantification of DCF was measured by a high performance liquid chromatograph (HPLC, Waters 2695, USA), and its degradation products were determined by an ultra performance liquid chromatograph coupled with a quadrupole time-of-flight mass spectrometer (UPLC-QTOF/MS, Waters Xevo G2-XS QT, USA). The detailed analytical processes can be obtained in our previous researches.[35,36] The UV light intensity was measured by an ultraviolet radiometer (UVC-254, Lutron, Taiwan). The total organic carbon (TOC) value was measured by a TOC analyzer (VCSH-ASI, Shimadzu, Japan). The absorption spectrum of DCF was measured by a UV-Vis spectrometer (8452A, Hewlett Packard). The concentration of PAA was determined using a titration method and the detailed procedures referred to the national standard of peracetic acid water solution (GB/T 19104-2008, China). The pH of solution was measured by a pH meter (PHS-3C, Leici, China). The degradation of DCF by UV/PAA followed pseudo first-order kinetic model based on data fitting degree and the observed rate constants (k_{obs}) for DCF were calculated by the eqn (1):

$$\ln\left(\frac{C_0}{C_t}\right) = k_{obs}t \tag{1}$$

where C_0 and C_t were the concentration of DCF at initial time and time t, respectively.

2.3. Photochemical experiments

Experiments were performed in a self-made collimated beam device equipped with two low pressure UV lamps (15 W) which emitted nearly monochromatic light at 254 nm. The average UV intensity was measured to be 2.1 mW cm^{-2}. A glass Petri dish was used as the reactor that was placed at a magnetic stirrer for better mixing. The pH of solution was adjusted by 5 mM phosphate buffer to the desired value. For DCF degradation experiments, the initial concentration of DCF and PAA were 1 and 50 μM, respectively. At each given time, 0.5 mL sample was taken out and quenched immediately with 0.5 mL 5 mM $Na_2S_2O_3$. For DCF transformation mechanism investigation, the initial concentration of DCF was increased to 10 μM. All experiments were repeated three times to minimize error.

3. Results and discussion

3.1. Degradation of DCF by UV/PAA

DCF could hardly be oxidized by PAA alone within 15 min, while it could be degraded by direct UV photolysis and its degradation rate increased when PAA was added into the reaction solution, as depicted in Fig. 1a. The promotion might be attributed to the production of HO[·] which came from the photolysis of PAA, as shown in eqn (2).[37,38] In order to prove the effect of HO[·], methanol (MeOH) and tert-butyl alcohol (TBA), two widely used scavengers for HO[·] ($k_{MeOH/HO·} = 9.7 \times 10^8$ M^{-1} s^{-1}, $k_{TBA/HO·} = 6 \times 10^8$ M^{-1} s^{-1}),[39,40] were added into the UV/PAA system, respectively. The radical oxidation of DCF in UV/PAA system was almost inhibited by adding MeOH, while it was partly inhibited by adding TBA. This result showed that in addition to HO[·], other radicals such as $CH_3COO·$ probably enhanced the removal of DCF and MeOH might be also a scavenger for $CH_3COO·$. The degradation of DCF in UV, UV/PAA and UV/PAA/TBA systems all followed the pseudo first-order kinetic model, and their observed rate constants (k_{obs}) were 0.0655, 0.1161, and 0.0789 min^{-1}, respectively. The degradation of DCF by UV/PAA was probably attributed to direct photolysis, HO[·] oxidation and other radicals oxidation. The contribution of each process was estimated based on the k_{obs} obtained from DCF degradation by
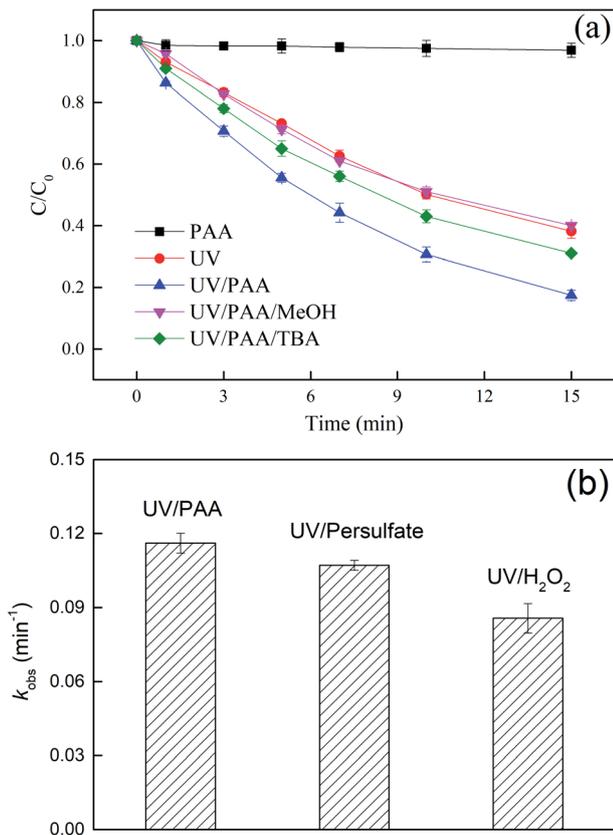
Fig. 1 Removal of DCF in different reaction systems (a) and the observed rate constants of DCF in UV/PAA, UV/persulfate and UV/H$_2$O$_2$ system (b). Experimental conditions: [DCF]$_0$ = 1 μM, [PAA]$_0$ = 50 μM, [persulfate]$_0$ = 50 μM, [H$_2$O$_2$]$_0$ = 50 μM, [MeOH]$_0$ = 5 mM, [TBA]$_0$ = 5 mM, 5 mM phosphate buffer at pH 7.0.

different systems (UV, UV/PAA, and UV/PAA/TBA), as shown in eqn (3)–(6). The result of the above calculation showed that the $k_{direct\ photolysis}$, $k_{HO^{\cdot}\ oxidation}$ and $k_{other\ radicals\ oxidation}$ of DCF were 0.0655, 0.0372, and 0.0134 min^{-1}, respectively. Therefore, the contribution of UV photolysis, HO$^{\cdot}$ oxidation and other radicals oxidation to DCF removal in UV/PAA system was 56%, 32% and 12%, respectively. To assess the superior performance of UV/PAA for DCF degradation, two control experiments were carried out, including UV/persulfate and UV/H$_2$O$_2$, to remove DCF at the same conditions, as shown in Fig. 1b. The degradation of DCF by UV/persulfate and UV/H$_2$O$_2$ also followed the pseudo first-order kinetic model. The result showed that the k_{obs} of different systems followed the order $k_{UV/PAA}$ (0.1161 min^{-1}) > $k_{UV/persulfate}$ (0.1071 min^{-1}) > k_{UV/H_2O_2} (0.0857 min^{-1}). Therefore, UV/PAA could be regarded as a promising process to degrade DCF.

$$CH_3COOH \xrightarrow{h\nu} CH_3COO^{\cdot} + HO^{\cdot} \qquad (2)$$

$$k_{UV/PAA} = k_{direct\ photolysis} + k_{HO^{\cdot}\ oxidation} + k_{other\ radicals\ oxidation} \qquad (3)$$

$$k_{direct\ photolysis} = k_{UV} \qquad (4)$$

$$k_{HO^{\cdot}\ oxidation} = k_{UV/PAA} - k_{UV/PAA/TBA} \qquad (5)$$

$$k_{other\ radicals\ oxidation} = k_{UV/PAA/TBA} - k_{UV} \qquad (6)$$

3.2. Effect of initial pH

As shown in Fig. 2a, no significant effect of pH was observed in the only UV system, indicating that although the deprotonation of DCF could occur when pH changed, the degradation of DCF by UV had nothing to do with whether DCF was deprotonation, which was due to the same UV absorbance for DCF under 254 nm at pH 3–11, as shown in Fig. 2b. However, the k_{obs} of DCF in UV system was only 0.065 min^{-1}. The optimal pH for DCF degradation in UV/PAA system was at 8.5, as shown in Fig. 2c. The k_{obs} increased gradually from 0.096 to 0.1902 min^{-1} in the range of pH 3.0–8.5, but it decreased to 0.1536 min^{-1} at pH 11.0. Since the pK_a value of PAA is 8.2, it was existed in two different forms at different pH, *i.e.*, protonated form (PAA^0) at acidic or neutral condition and deprotonated form (PAA$^-$) at alkaline pH. Furthermore the molar absorption coefficients (ε) of PAA^0 and PAA$^-$ at 254 nm were 8.0 M^{-1} cm^{-1} and 41.6 M^{-1} cm^{-1}, respectively.[32] PAA$^-$ had a faster photolysis rate than PAA^0 because of its higher UV absorption at 254 nm, leading to more formation of HO$^{\cdot}$ at alkaline pH condition. The effect of pH on photolysis of PAA within 15 min was shown in Fig. 2d. The photolysis of PAA in alkaline condition was higher than acidic or neutral condition, which was consist with the study of Cai *et al.*[32] At pH 11, possible explanations for the decrease of DCF removal rate included that: (1) the concentration of OH$^-$ was 1000 times higher than that of DCF, which could compete with DCF for HO$^{\cdot}$ ($k_{OH^-/HO^{\cdot}} = 1.2 \times 10^{10}$ M^{-1} s^{-1}),[41] and (2) the redox potential of HO$^{\cdot}$ is lower at basic pH than acid or neutral pH according to Nernst equation.[42] Combined with the above reasons, the k_{obs} was found to be the highest at pH 8.5.

3.3. Effect of PAA concentration

The oxidant dose is a significant parameter to evaluate whether the UV/PAA is economical and efficient for DCF degradation. The effect of initial PAA concentration on k_{obs} is shown in Fig. 3. The k_{obs} enhanced gradually from 0.0967 to 0.182 min^{-1} with increasing PAA concentration from 10 to 150 μM. When PAA concentration was below 50 μM, the k_{obs} increased linearly with the increase of PAA dose, which was probably attributed to the generation of more HO$^{\cdot}$ and CH$_3$COO$^{\cdot}$. Although k_{obs} was still increased in higher PAA concentration, its growth rate slowed down, which probably resulted from the scavenging effect of PAA on HO$^{\cdot}$, because excessive PAA could compete with DCF for HO$^{\cdot}$ ($k_{PAA/HO^{\cdot}} = (9.33 \pm 0.3) \times 10^8$ M^{-1} s^{-1}).[32] In addition, more PAA molecules in system probably absorbed more photons which inhibited the direct photolysis of DCF.

3.4. Effect of common water components

The composition of natural water is complex, which consists of various components such as inorganic ions and DOM. In order to apply UV/PAA to remove DCF from natural water, it is necessary to investigate their effects on DCF removal.
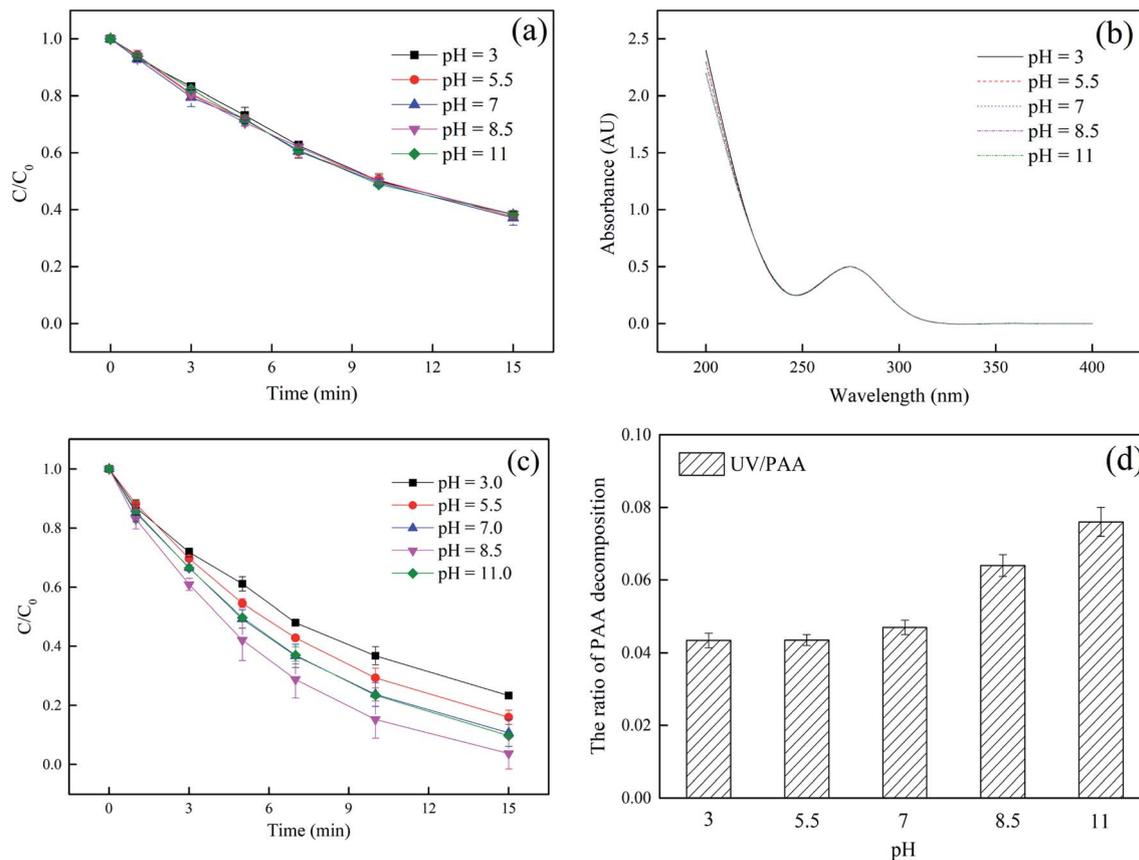
Fig. 2 Effect of initial pH on DCF removal by UV (a), absorption spectrum of DCF (b), DCF removal by UV/PAA (c) and photolysis of PAA (d). Experimental conditions: $[DCF]_0 = 1$ μM, $[PAA]_0 = 50$ μM, 5 mM phosphate buffer.
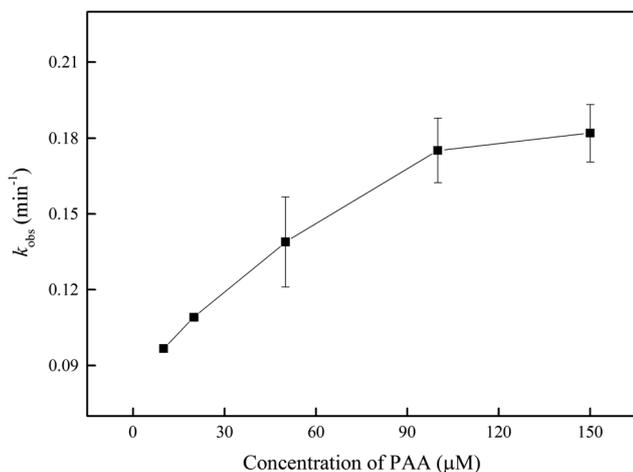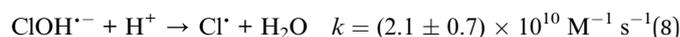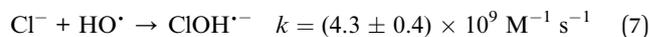

Fig. 3 Effect of PAA concentration on k_{obs} by UV/PAA. Experimental conditions: $[DCF]_0 = 1$ μM, 5 mM phosphate buffer at pH 7.0.

3.4.1 Effect of Cl⁻, SO₄²⁻ and NO₃⁻. The effect of Cl^- on DCF degradation is shown in Fig. 4a. Its existence had almost no influence on DCF removal with the changed concentration from 1 to 10 mM. Although Cl^- could react with $HO^{\bullet}$ to form $ClOH^{\bullet-}$ which could further transform to $Cl^{\bullet}$ and $Cl_2^{\bullet-}$, as

presented in eqn (7)–(9), eqn (8) was difficult to occur under neutral condition. Therefore, the formed $ClOH^{\bullet-}$ might mainly undergo self-decomposition to regenerate $HO^{\bullet}$ in current condition, as shown in eqn (10).[43] The presence of SO_4^{2-} showed no apparent influence on the degradation of DCF as shown in Fig. 4b, because it could not react with $HO^{\bullet}$.[44] The NO_3^-, as a well-known photosensitizer, probably had two effects on DCF removal in UV/PAA system. On one hand, NO_3^- could be excited to generate $HO^{\bullet}$ under UV, which promoted DCF removal, as presented in eqn (11)–(14).[45] On the other hand, NO_3^- also probably absorbed UV photons which inhibited the direct photolysis of DCF. Moreover, the NO_2^- produced during the NO_3^- photolysis process was a strong $HO^{\bullet}$ scavenger ($k_{NO_2^-/HO^{\bullet}} = 1.0 \times 10^{10}$ M^{-1} s^{-1}),[39] thus it could also compete with DCF for $HO^{\bullet}$. As shown in Fig. 4c, the removal efficiency of DCF was slightly improved by NO_3^-, especially at higher NO_3^- concentration, indicating that the positive effect of NO_3^- on DCF removal by UV/PPA was stronger than negative effects. Furthermore, further study was needed to estimate if mutagenic and carcinogenic nitrated byproducts were formed in the presence of nitrate.
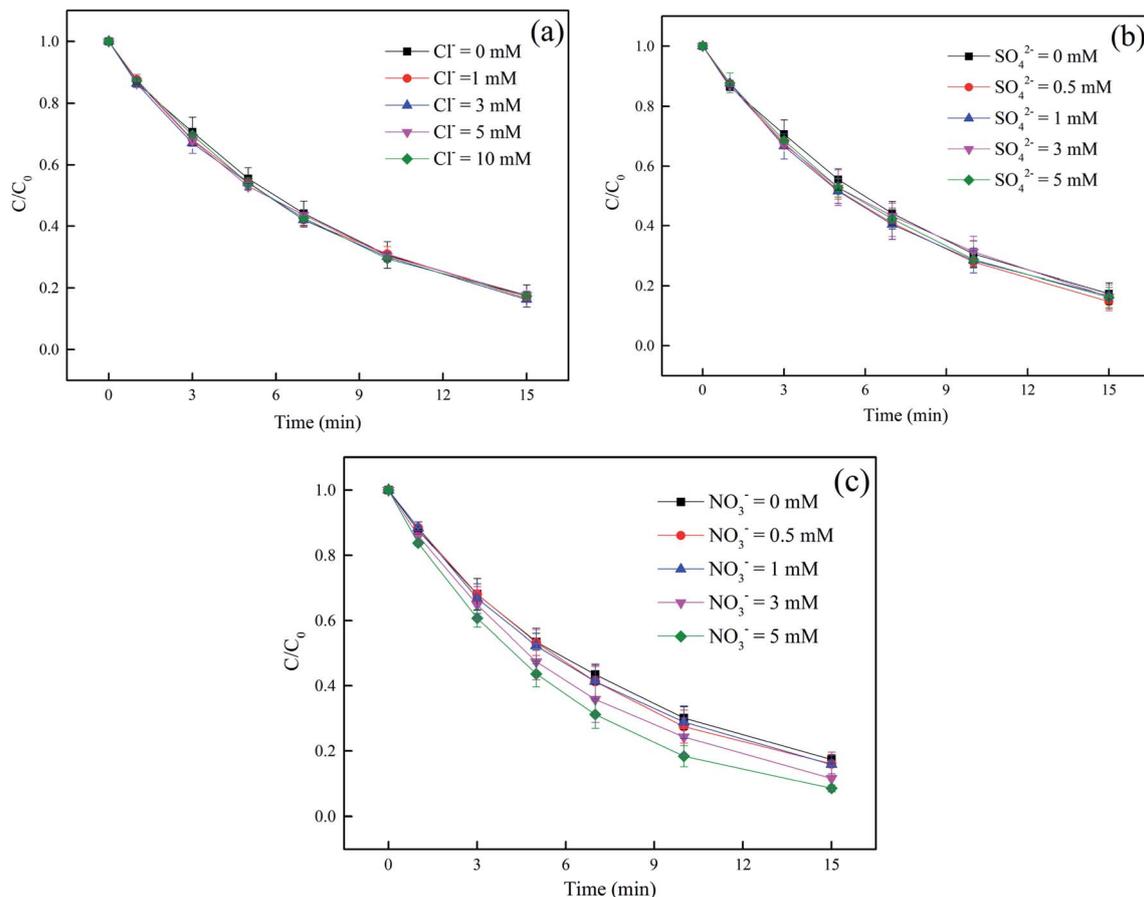
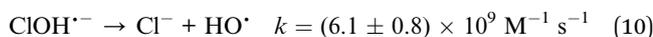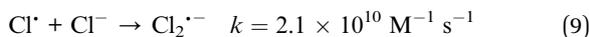$$Cl^- + HO^{\bullet} \rightarrow ClOH^{\bullet-} \quad k = (4.3 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (7)$$

$$ClOH^{\bullet-} + H^+ \rightarrow Cl^{\bullet} + H_2O \quad k = (2.1 \pm 0.7) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} (8)$$

Fig. 4 Effect of Cl^- (a), SO_4^{2-} (b) and NO_3^- (c) on DCF removal by UV/PAA. Experimental conditions: $[DCF]_0 = 1~\mu M$, $[PAA]_0 = 50~\mu M$, 5 mM phosphate buffer at pH 7.0.

$$Cl^\bullet + Cl^- \rightarrow Cl_2^{\bullet-} \quad k = 2.1 \times 10^{10}~M^{-1}~s^{-1} \tag{9}$$

$$ClOH^{\bullet-} \rightarrow Cl^- + HO^\bullet \quad k = (6.1 \pm 0.8) \times 10^9~M^{-1}~s^{-1} \tag{10}$$

$$NO_3^- \xrightarrow{h\nu} NO_2^\bullet + O^{\bullet-} \tag{11}$$

$$NO_3^- \xrightarrow{h\nu} NO_2^- + 0.5O_2 \tag{12}$$

$$NO_2^- \xrightarrow{h\nu} NO^\bullet + O^{\bullet-} \tag{13}$$

$$O^{\bullet-} + H_2O \rightarrow HO^\bullet + OH^- \tag{14}$$

3.4.2 Effect of CO_3^{2-}. Some studies reported that CO_3^{2-} could quench $HO^\bullet$ ($k_{CO_3^{2-}/HO^\bullet} = 3.9 \times 10^8~M^{-1}~s^{-1}$) as presented in eqn (15), leading to the inhibition on the degradation of organic pollutants in $HO^\bullet$ oxidation system.[46,47] However, no such inhibition was observed in our study. Conversely, the presence of CO_3^{2-} could promote the degradation of DCF by UV/PAA, as shown in Fig. 5. When the concentration of CO_3^{2-} increased from 0.5 to 5 mM, the pH of the solution enhanced from 9.9 to 10.8. To eliminate the influence of pH on DCF degradation, its removal by UV and UV/PAA in phosphate buffer at pH 9.9, 10.3, 10.6 and 10.8 was used as a control, respectively.

A similar degradation trend of DCF in UV system under different pH conditions (pH 9.9, 10.3, 10.6 and 10.8) was observed, which was consist with the previous results. Compared with the UV/PAA/buffer system, the degradation of DCF was faster in UV/PAA/CO_3^{2-} system, which was probably due to the generation of carbonate radical ($CO_3^{\bullet-}$) through the
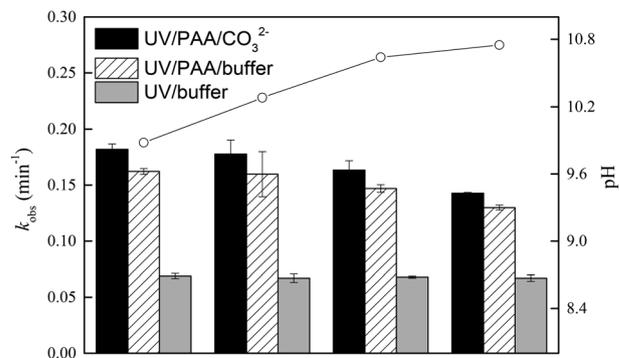

Fig. 5 The observed rate constants of DCF in UV/PAA system with the addition of CO_3^{2-}. Experimental conditions: $[DCF]_0 = 1~\mu M$, $[PAA]_0 = 50~\mu M$, no phosphate buffer. Degradation of DCF by UV and UV/PAA in phosphate buffer (5 mM) at pH 9.9, 10.3, 10.6 and 10.8 was used as a control, respectively.

reaction of CO_3^{2-} with $HO^{\bullet}$. Since $CO_3^{\bullet-}$ is an electrophilic single-electron oxidant with the oxidation potential of 1.78 V, it can react with electron-rich compounds, such as phenols, anilines, and sulfur-containing organic compounds, through electron transfer or hydrogen extraction.[48–50] Due to the presence of aniline group in DCF structure, it might react with $CO_3^{\bullet-}$ with the second-order rate constant of $2.7 \times 10^7 \ M^{-1} \ s^{-1}$,[51] which could result in the enhancement on DCF degradation in the presence of CO_3^{2-}. Liu et al.[52] also found $CO_3^{\bullet-}$ played a significant role on oxytetracycline removal in $UV/H_2O_2/CO_3^{2-}$ system.

$$HO^{\bullet} + CO_3^{2-} \rightarrow CO_3^{\bullet-} + OH^- \qquad (15)$$
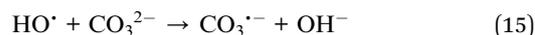
3.4.3 Effect of Fe^{3+} and Cu^{2+}. It was found that the removal of DCF was hardly affected by Fe^{3+} in this study, as shown in Fig. 6a. Although Fe^{3+} is a catalyst for Fenton-like reaction and $FeOH^{2+}$ can also produce $HO^{\bullet}$ under UV radiation, these reactions usually occur in acid condition.[53,54] In current condition (5 mM phosphate buffer at pH 7.0), Fe^{3+} was mainly existed in

the form of $Fe(OH)_3$ or $FePO_4$,[55] and consequently extra $HO^{\bullet}$ could hardly be generated by the above pathways. Unlike Fe^{3+}, the presence of Cu^{2+} significantly promoted DCF degradation and the higher the concentration of Cu^{2+} was, the better the promotion effect was, as shown in Fig. 6b. Cu^{2+} is also a kind of catalyst for Fenton-like reaction, which is adaptable to a wide range of pH, especially in near-neutral condition.[56,57] As a result, the improvement effect might be attributed to the formation of extra $HO^{\bullet}$ and $CH_3COO^{\bullet}$ in the decomposition of PAA catalyzed by Cu^{2+}, as shown in eqn (16).[57]

$$CH_3COOH \xrightarrow{Cu^{2+}} CH_3COO^{\bullet} + HO^{\bullet} \qquad (16)$$

3.4.4 Effect of DOM. In this work, fulvic acid was used as the representative of DOM. As shown in Fig. 7, the removal of DCF was inhibited in the presence of DOM and it was more obvious in higher concentration of DOM. There are two probable reasons to explain this phenomenon. Firstly, DOM is a kind of photosensitive substance that could compete with DCF and PAA for UV radiation, which would affect the direct photolysis of DCF and the formation of reactive radicals produced from the decomposition of PAA.[58] In addition, DOM is a well-known $HO^{\bullet}$ scavenger ($k_{DOM/HO^{\bullet}} = 2.23 \times 10^8 \ L \ (mol \ C)^{-1} \ s^{-1}$),[59] and it might compete with DCF for $HO^{\bullet}$. Zhang et al.[60] also found that the existence of DOM had a negative effect on azathioprine removal in UV and UV/H_2O_2 systems.

3.5. The elimination of TOC

As shown in Fig. 8, DCF was completely removed within 50 min. However, only 8.6% TOC was eliminated. There were two possible reasons for the low removal of TOC: (1) the aromatic ring of DCF might not be easily destroyed by UV/PAA, so that it could not be split into smaller molecular weight hydrocarbons or finally be mineralized to CO_2 and H_2O; (2) PAA itself was an organic peroxide and its addition also partially contributed to TOC of the reaction system. PAA could not be completely
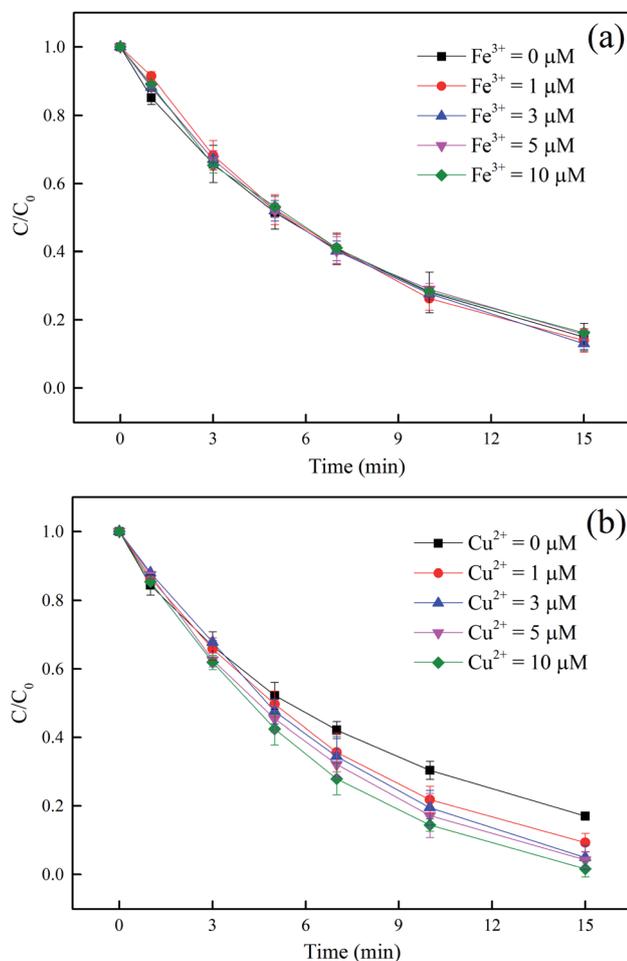

Fig. 6 Effect of Cu^{2+} (a) and Fe^{3+} (b) on DCF removal by UV/PAA. Experimental conditions: $[DCF]_0 = 1 \ \mu M$, $[PAA]_0 = 50 \ \mu M$, 5 mM phosphate buffer at pH 7.0.

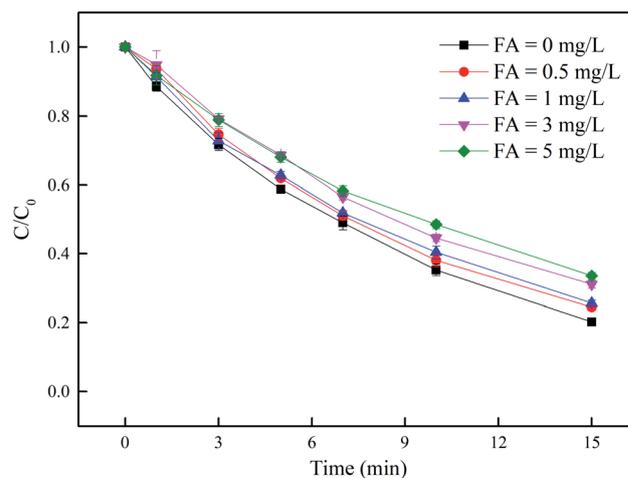**Fig. 7** Effect of DOM on DCF removal by UV/PAA. Experimental conditions: $[DCF]_0 = 1 \ \mu M$, $[PAA]_0 = 50 \ \mu M$, 5 mM phosphate buffer at pH 7.0.
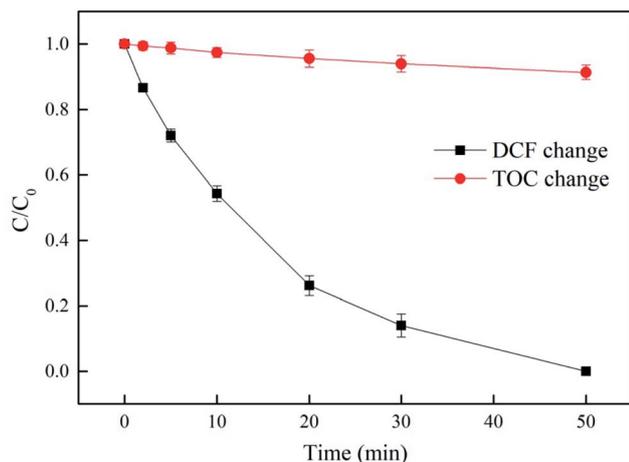
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Fig. 8 The removal of TOC in UV/PAA system. Experimental conditions: $[DCF]_0 = 10$ μM, $[PAA]_0 = 0.5$ mM, no phosphate buffer.

mineralized during DCF removal in UV/PPA system. Although DCF and PAA were not completely mineralized to CO_2 and H_2O during DCF treatment by UV/PAA, they were probably split to smaller or non-toxic molecules, which could be further treated by the combination of biodegradation process. This process was mainly used as a pro-treatment process. Further study is needed to calculate the respective contribution of the transformation products of DCF and PAA to TOC in UV/PAA system.

3.6. Identification of reaction products and degradation pathways

To investigate the transformation mechanism of DCF in UV/PAA system, its degradation products were detected by UPLC-QTOF/MS. Twelve transformation products of DCF were detected and identified in this system. Since direct photolysis might contribute significantly to DCF degradation in UV/PAA system, some products were probably derived from direct UV photolysis of DCF. Among these twelve transformation products, part of them were also detected by other researchers[61–65] in UV photolysis of DCF, as shown in Table 1. According to these

Table 1 Transformation products of DCF by UV/PAA or UV

Serial number	Mass to charge ratio (m/z)	The detected condition	The detected condition[61–65]
1	328	UV/PAA	—
2	312	UV/PAA	—
3	282	UV/PAA	—
4	280	UV/PAA	—
5	278	UV/PAA	—
6	268	UV/PAA	—
7	266	UV/PAA	UV
8	262	UV/PAA	UV
9	252	UV/PAA	UV
10	242	UV/PAA	UV
11	228	UV/PAA	UV
12	226	UV/PAA	UV

detected degradation products, the potential transformation mechanism of DCF by UV/PAA was proposed exhibiting eight different reaction pathways, i.e., hydroxylation, decarboxylation, formylation, dehydrogenation, dechlorination–hydrogenation, dechlorination–cyclization, dechlorination–hydroxylation, and amidation, as presented in Fig. 9.

(1) Hydroxylation. Hydroxylation was caused by the addition of HO⋅ to aromatic ring of DCF through electron transfer due to its electrophilic nature, leading to the generation of mono-hydroxylation product m/z 312 and di-hydroxylation product m/z 328. Madhavan et al.[66] also detected hydroxylation product m/z 312 in ultrasound assisted photocatalytic degradation of DCF in water.

(2) Decarboxylation. Decarboxylation referred to the removal of carboxyl group from acetic acid group in DCF structure, resulting in the formation of product m/z 252. It is well known that aromatic carboxylic acids are more prone to decarboxylate than saturated carboxylic acids. Under UV radiation, the molecule of DCF was in excitation state and then the C–C bond in acetic acid group was broken by HO⋅ attack. The generated product m/z 252 could further be hydroxylated to produce the product m/z 268 which might also be generated from hydroxylation product m/z 312 through decarboxylation.

(3) Formylation. Formylation was occurred during the decomposition of the products of DCF. The methyl group in product m/z 252 could be oxidized to produce formyl group under HO⋅ attack, leading to the production of formylation product m/z 266. It might undergo hydroxylation to generate product m/z 282 that could also be produced from the generated m/z 268 through this pathway. Similar formylation products were also detected in the degradation of DCF by ferrate.[67]

(4) Dehydrogenation. The structure of formed product m/z 282 contained not only phenol group but also aniline group, and both of them were electron-donating groups.[68] Therefore, these sites were readily attacked by HO⋅, yielding quinone-imine product m/z 280. Chong et al.[8] detected similar product in DCF removal by $FeCeO_x$ catalyzed H_2O_2. Bedner and Mac-Crehan[69] found that two quinone-imine byproducts in transformation of acetaminophen by chlorination were toxic compounds. However, further study was needed to estimate if the quinone-imine product (m/z 280) was also a toxic byproduct.

(5) Dechlorination–hydrogenation. Dechlorination–hydrogenation referred to the replacement a chlorine atom on the benzene ring with a hydrogen atom in DCF structure. During UV irradiation, the C–Cl bond was broken, resulting in the formation of carbocation through the transfer of an electron from carbon atom to chlorine radical, and subsequently it reacted with water molecule to generate dechlorination–hydrogenation products m/z 262 and 228.[70] Yu et al.[71] reported that dechlorination–hydrogenation was also an important pathway of DCF degradation by pulse radiolysis and γ-radiolysis.

(6) Dechlorination–cyclization. Dechlorination–cyclization was similar to dechlorination–hydrogenation except that the former underwent intramolecular electron transfer and subsequently cyclized producing the product m/z 260. Although this product was not detected in this work, it was found in others' studies where DCF was degraded by direct photolysis or
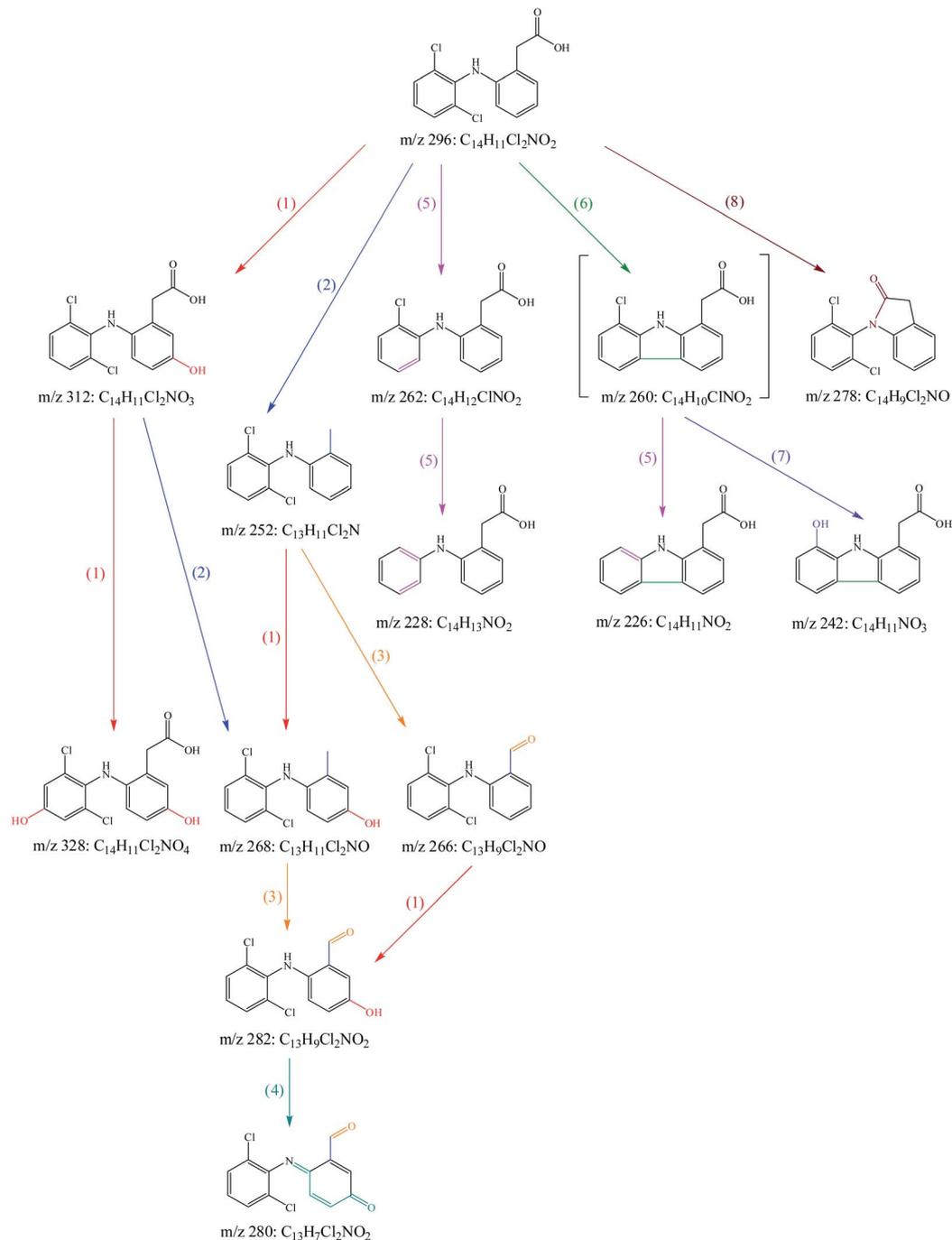
Fig. 9 Probable transformation pathways of DCF by UV/PAA: (1) hydroxylation, (2) decarboxylation, (3) formylation, (4) dehydrogenation, (5) dechlorination–hydrogenation, (6) dechlorination–cyclization, (7) dechlorination–hydroxylation, (8) amidation. Experimental conditions: $[DCF]_0$ = 10 μM, $[PAA]_0$ = 0.5 mM, no phosphate buffer.

photocatalysis.[63,65,72,73] Product m/z 226 was detected in this study, which might be formed from m/z 260 through dechlorination–hydrogenation.

(7) **Dechlorination–hydroxylation.** Dechlorination–hydroxylation was similar to dechlorination–hydrogenation mechanism except that chlorine atom was replaced by hydroxyl group possibly from water molecule.[70] It was probably occurred from the intermediate m/z 260 to form product m/z 242.

Lekkerkerker-Teunissen et al.[74] also detected this product in the transformation of DCF by UV/H_2O_2.

(8) **Amidation.** Amidation referred to the reaction of secondary amine with carboxylic acid to form carboxylic amine and then dehydrating to obtain the corresponding amide, which was probably occurred in the intramolecular structure of DCF, resulting in the production of amidation product m/z 278.

Salaeh et al.[75] also found this product in the photocatalytic degradation of DCF under simulated sunlight.

4. Conclusions

This study systematically investigated the degradation kinetics and transformation mechanism of DCF by UV/PAA. It was found that adding PAA into reaction solution could enhance DCF degradation in UV system, which was proved that the promotion effect was due to the role of HO$^\bullet$ and CH$_3$COO$^\bullet$ produced by the photolysis of PAA. In the pH range of 3–11, DCF had the best degradation efficiency at pH 8.5. When PAA dose increased, the observed degradation rate constant was enhanced gradually. Presence of Cl$^-$, SO$_4^{2-}$ and Fe^{3+} had almost no effect on DCF decomposition, while the existence of CO$_3^{2-}$ promoted DCF removal because of the contribution of CO$_3^{\bullet-}$ formed through the reaction of CO$_3^{2-}$ with HO$^\bullet$. Both NO$_3^-$ and Cu^{2+} improved the degradation of DCF and the enhancement effect increased with the increase in their concentrations. An inhibition effect was observed in DCF removal in the presence of DOM, which was possibly attributed to its light screening effect and competition for reactive radical. The elimination of TOC was low at only 8.6%. Degradation mechanism of DCF in UV/PAA system was evaluated exhibiting eight different transformation pathways, i.e., hydroxylation, decarboxylation, formylation, dehydrogenation, dechlorination–hydrogenation, dechlorination–cyclization, dechlorination–hydroxylation and amidation based on twelve detected degradation products. This study showed that UV/PAA as an AOP could remove pharmaceutical pollutants such as DCF from wastewater and provided some valuable information on the degradation of DCF for the potential application.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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