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Photodegradation of amoxicillin by catalyzed Fe^{3+}/H_2O_2 process

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Abstract

Three oxidation processes of UV-Fe^{3+}(EDTA)/H_2O_2 (UV: ultraviolet light; EDTA: ethylenediaminetetraacetic acid), UV-Fe^{3+}/H_2O_2 and Fe^{3+}/H_2O_2 were simultaneously investigated for the degradation of amoxicillin at pH 7.0. The results indicated that, 100% amoxicillin degradation and 81.9% chemical oxygen demand (COD_{Cr}) removal could be achieved in the UV-Fe^{3+} (EDTA)/H_2O_2 process. The treatment efficiency of amoxicillin and COD_{Cr} removal were found to decrease to 59.0% and 43.0% in the UV-Fe^{3+}/H_2O_2 process; 39.6% and 31.3% in the Fe^{3+}/H_2O_2 process. Moreover, the results of biodegradability (biological oxygen demand (BOD_5)/COD_{Cr} ratio) revealed that the UV-Fe^{3+} (EDTA)/H_2O_2 process was a promising strategy to degrade amoxicillin as the biodegradability of the effluent was improved to 0.45, compared with the cases of UV-Fe^{3+}/H_2O_2 (0.25) and Fe^{3+}/H_2O_2 (0.10) processes. Therefore, it could be deduced that EDTA and UV light performed synergetic catalytic effect on the Fe^{3+}/H_2O_2 process, enhancing the treatment efficiency. The degradation mechanisms were also investigated via UV-Vis spectra, and high performance liquid chromatography-mass spectra. The degradation pathway of amoxicillin was further proposed.

Key words: amoxicillin; catalytic oxidation; photodegradation
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Introduction

The occurrence of antibiotics in the aquatic environment has received considerable attention, which are regarded as the potential contaminations due to their continuous input into the ecosystem (Gulkowska et al., 2008; Huber et al., 2003; Kümmerer et al., 2000; Migliore et al., 1997). Another concern about antibiotic residues in the environment is the potential risk for aquatic and terrestrial organisms that exhibit resistance to some antibiotics. It has been reported that bacteria isolated from sewages showed resistance to antibiotics, such as ciprofloxacin, erythromycin and tetracycline (da Silva et al., 2006).

In the past decades, Fenton oxidation or Fenton like processes have been investigated for antibiotics degradation and biodegradability improvement, such as Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, Fe^{2+}/H_2O_2/UV and Fe^{3+}/H_2O_2/UV. Compared with Fenton process (Reaction (1), UV Fenton process is becoming attractive due to the decomposition of H_2O_2 and the photo-active $Fe(OH)^{2+}$ leading to additional HO· radicals in solution (Javier Benitez et al., 2002; Tokumura et al., 2006), which makes Fenton process improved by the participation of photo generated Fe^{2+} and HO· (Reactions (2)–(3).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO\cdot + HO^- \quad (1)$$

$$H_2O_2 + h\nu \longrightarrow 2HO\cdot \quad (2)$$

$$Fe(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + HO\cdot + H^+ \quad (3)$$

The above Fenton or photo-Fenton process for the degradation of antibiotics has been carried out at pH 3.0 (Alexy et al., 2004; Arslan-Alaton and Dogruel, 2004). However, the pH of real wastewater in many cases is neutral or alkaline, therefore pre-adjustment of pH is necessary with the added cost in chemicals and labor (Sabhi and Kiwi, 2001). Thus, it becomes an increasing concerned topic of improving the oxidation activity of Fenton or Fenton like process at ambient circumstance (Sun and Pignatello, 1992; Zhou et al., 2008).

EDTA used as catalyst for Fenton or Fenton like system to provide high efficiency for organics degradation, resulting from producing strong oxidants such as HO· radicals that can quickly and nonselectively decompose organic compounds (Noradoun and Cheng, 2005; Zhou et al., 2008). A previous investigation reported by our research group demonstrated that EDTA had a higher catalytic ability for the electro-Fe^{3+}/H_2O_2 process, enhancing the treatment efficiency of amoxicillin (Shen et al., 2009). To date, there is no information on antibiotics treatment

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with UV-Fe^{3+}(EDTA)/H_2O_2 process in either municipal or simulated antibiotics wastewater. Moreover, amoxicillin, as a semi-synthetic antibiotic, has been widely used as human and veterinary medicinal compounds for a long time, making livestock agriculture a major source of antibiotic pollution (Andreozzi et al., 2004). Therefore, it was selected as the model contamination.

This study, is expected to explore the applicability and mechanism of UV light and EDTA that contributed to the Fe^{3+}/H_2O_2 process. The UV-Fe^{3+}(EDTA)/H_2O_2 process was evaluated by the removal efficiency of amoxicillin and COD_{Cr}, biodegradability, UV-Vis spectra and high performance liquid chromatography-mass spectra (HPLC-MS).

1 Materials and methods

1.1 Materials

H_2O_2 (30%, *W*/*V*), 2-propanol (99%), Na_2SO_4, $K_2Ti(C_2O_4)_3$, $FeCl_3{\cdot}7H_2O$, Na_2EDTA (EDTA, 99.9%), H_2SO_4, NaOH, $HCOONH_4$ (99%), HCOOH, CH_3OH, CH_3CN (HPLC grade), N-Bromosuccinimide (NBS), tetrabutylammoniumbromide (TBA-Br) (AR), amoxicillin reference standard and amoxicillin capsule ($C_{16}H_{19}N_3O_5S{\cdot}3H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All of the reagents used without further purified. The water used in this work was deionized and purified by a pure water system (Milli-Q, Millipore, USA).

1.2 Experimental procedure

Reaction was conducted at 25 ± 0.2°C in a 1500-mL cylindrical Pyrex thermostatic cell having 1000 mL of working volume equipped with a magnetic stirrer. A UVA light tube (TLMINI6W, Philips) was used as light source, which was immersed into the reaction solution, providing a light intensity 6.0 mW/cm^2. The experiments were performed at different pH adjusted by 1.0 mol/L H_2SO_4 or 1.0 mol/L NaOH. Hydroxyl radical or H_2O_2 potential reactions in the collected effluents were quenched by 6.0 mol/L NaOH (Potter and Roth, 1993).

1.3 Analytic methods

The samples were taken out at certain intervals from the degraded solution. The pH of solution sample was adjusted to 10.0 to remove ferric/ferrous ion and then filtered by a Millipore filter (pore size of 0.22 μm) for COD_{Cr} measurement. The samples for UV-Visible spectra and HPLC detection were prepared by freeze-drying under vacuum at –45°C and then further dissolved in methanol and filtered by a Millipore filter (pore size of 0.22 μm).

Amoxicillin concentration was determined using a UV-Visible spectrophotometer (UV2550, Shimadzu, Japan) with a 1-cm quartz cell according to the methods presented by Saleh (1996), in which the oxidation of amoxicillin with N-bromosuccinimide (0.05%) in sodium hydroxide (0.1 mol/L) to give an intense yellow product (395 nm).

H_2O_2 solution was prepared with 30% H_2O_2 calibrated by $KMnO_4$ titration, which had been calibrated by $Na_2C_2O_4$ titration. The H_2O_2 concentration during the reaction was quantified by UV-vis spectra at 400 nm after color was developed with potassium titanium oxalate ($K_2Ti(C_2O_4)_3$) in 1.0 mol/L H_2SO_4 solution to prevent any interference caused by the organic disturbance (Sellers, 1980).

COD_{Cr} experiments were conducted according to APHA standard methods. Biological oxygen demand (BOD_5) was determined by a BOD system (OxiTop-IS6, WTW, Germany). In all biological analyses, hydrogen peroxide and iron in solution were previously removed to avoid errors in the measurement.

The concentration of Fe^{3+}(EDTA) in sample filtrates was determined by reverse phase high performance liquid chromatography (Agilent 1100, USA) with UV light detection (λ = 258 nm, Hewlett-Packard 1050 series), which referred to the method developed by Nowack (2002) and Noradoun and Cheng (2005). The mobile phase consisted of 92% 0.02 mol/L formate buffer (formic acid sodium salt 99%, formic acid 89.5%) and 8.0% acetonitrile containing 0.001 mol/L tetrabutylammoniumbromide (TBA-Br). pH was adjusted to 3.5. The standard Fe^{3+}(EDTA) complex was created by adding equivalent $FeCl_3{\cdot}7H_2O$ to the EDTA sample prior to HPLC analysis. Controls showed that neither EDTA nor Fe^{3+} salts alone gave UV absorbance at 258 nm. All samples were filtered using 0.22 μm nylon syringe filters prior to analysis.

HPLC-MS spectra of the degraded products were carried out on LCQ-Advantage (USA) equipped with an ODS C_{18} column (150 mm × 2.1 mm, i.d., 3.5 μm), referring to the methods reported by Nägele and Moritz (2005). The mobile phase consisting of A (water containing 10 mmol/L of ammonium formate)–B (acetonitrile containing 0.1% of formic acid) was delivered at 1.0 mL/min using a gradient elution as follows: 0–6 min of 15%–50% B; 6–17 min of 50% B; and 17–23 min of 50%–15% B. The auto-sampler was employed to make injections of 20 μL samples at room temperature. The mass spectrometers were operated under the following conditions: electrospray ionization (ESI) in positive mode with dual sprayer of ion trap MS source; 5.0 L/min of drying gas, 300°C of gas temperature; 1 kPa of nebulizer; 150,000 of ion current control; 50 msec of maximum accumulation time; 100–400 of scan; 55 L/hr of cone gas flow; 300°C of desolvation temperature; 100°C of ion source temperature; 400 L/hr of desolvation gas flow; and 3800 V of capillary.

1.4 HO· scavenging investigation

HO· scavenging investigation was conducted to determine whether the oxidation process was mediated by HO· in the UV-Fe^{3+}(EDTA)/H_2O_2 process. The molar ratio of 2-propanol (an effective scavenger of HO·) to Fe^{3+} was selected as 50:1 (Ndjou'ou et al., 2006). Amoxicillin removal efficiency was measured at selected time intervals to evaluate the oxidation efficiency.

2 Results and discussion

2.1 Role of initial pH

As shown in Fig. 1, the highest treatment efficiency occurred at pH 3.0 in the three processes. It was evident that a change in the pH of the solution to either side of 3.0 leads to a decrease in oxidation efficiency.

In the Fe^{3+}/H_2O_2 process, the following mechanisms likely explained the observations: at the strong acidic medium (pH < 3.0), the active species $Fe(H_2O)_5OH^{2+}$ was easily changed into $Fe(H_2O)_6^{2+}$, which had lower catalysis than that of $Fe(H_2O)_5OH^{2+}$, and thus the concentration of hydroxyl radicals HO· was relative lower, decreasing the treatment efficiency (Burbano et al., 2005). When the pH raised upon 3.0, the decrease in oxidation efficiency was due to the formation of $Fe(OH)_3$, leading to a decrease in Fe^{2+} concentration (Malik, 2004).

In the UV-Fe^{3+}/H_2O_2 process, H_2O_2 and the photoactive $Fe(OH)^{2+}$ could lead to additional HO· in solution (Reactions (2)–(3)) under the irradiation of UV light which could attack and initiate the oxidation of pollutant with relatively higher treatment efficiency than that in Fe^{3+}/H_2O_2 process.

In the UV-Fe^{3+}(EDTA)/H_2O_2process, 76.1% $TCOD_{Cr}$ (total COD_{Cr} that amoxicillin and EDTA contribute together) and 100% amoxicillin removal efficiency could be also achieved even though the pH was increased to 7.0, while the treatment efficiency decreased to 43.0% and 59.0% in the UV-Fe^{3+}/H_2O_2 process, and 31.3% and 39.6% in the Fe^{3+}/H_2O_2 process, respectively. The results could be ascribed that EDTA and Fe^{3+} formed stable complex therefore the solubility of Fe^{3+} was improved in the aqueous solution, facilitating the production of HO·; on the other hand, Fe^{3+}(EDTA) or Fe^{2+}(EDTA) could react with H_2O_2 quantitatively to form HO· when the pH ranged from 3.0 to 8.0 (Ndjou'ou et al., 2006; Sun and Pignatello, 1992), promoting the oxidation efficiency. In addition, when the pH was increased to 8.0–9.0, the UV-Fe^{3+}(EDTA)/H_2O_2 process still exhibited higher removal efficiency than those of UV-Fe^{3+}/H_2O_2 or Fe^{3+}/H_2O_2 process. The result should be ascribed that the formation of $Fe^{3+}(EDTA)O_2^{3-}$, which was a catalyst for the decomposition of hydrogen peroxide to form oxidation media, enhancing the extent of amoxicillin oxidation; whereas, when the pH raised beyond 10.5, H_2O_2 was cleanly decomposed to O_2 and water (Walling et al., 1970), which could not constitute an effective source of HO· in aqueous solution, leading to a poor degradation of amoxicillin. Therefore, the pH for this study was selected as 7.0

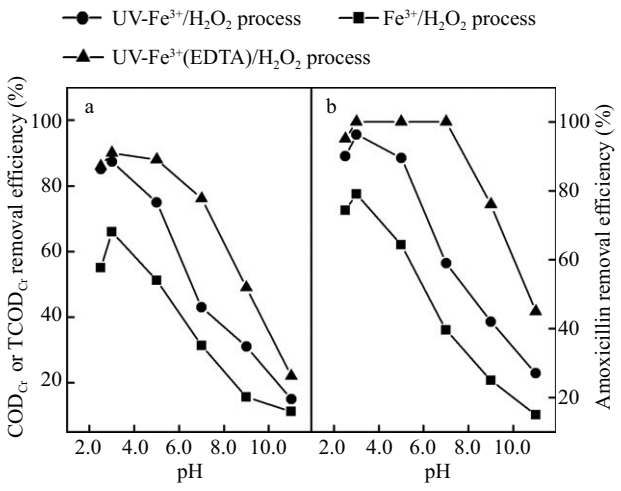

Fig. 1 Initial pH effect on COD_{Cr} removal efficiency in the UV-Fe^{3+}/H_2O_2 and Fe^{3+}/H_2O_2 processes; $TCOD_{Cr}$ removal efficiency in the UV-Fe^{3+}(EDTA)/H_2O_2 process (a); amoxicillin removal efficiency in the UV-Fe^{3+}/H_2O_2, UV-Fe^{3+}(EDTA)/H_2O_2 and Fe^{3+}/H_2O_2 processes (b). Experimental conditions: amoxicillin 250 mg/L, H_2O_2 64.7 mmol/L, Fe^{3+} 0.80 mmol/L, EDTA 0, 0.40 mmol/L, and temperature 25°C. $TCOD_{Cr}$ means the total COD_{Cr} that amoxicillin and EDTA contribute together.

2.2 Molar ratio of Fe^{3+} to EDTA

$TCOD_{Cr}$ and amoxicillin removal efficiency were generally enhanced when the molar ratio of Fe^{3+} to EDTA increased from 1:4 to 2:1 (Fig. 2). The results indicated that the molar ratio of Fe^{3+} to EDTA was responsible for the formation of Fe^{3+}-EDTA complex, which played a crucial role in the equilibrium among the oxidation, reduction and coordination reactions (Noradoun and Cheng, 2005). The excess EDTA would produce an extra contamination and also act as an antioxidant (Nicoli et al., 2000) that enhanced the activity of phenolic hydroxyl of amoxicillin, improving its anti-oxidation ability. Whereas, the treatment efficiency decreased when the molar ratio of Fe^{3+} to EDTA changed from 2:1 to 4:1 because the over dosage of Fe^{3+} acted as scavenger of H_2O_2 to form less reactive HO_2·. Another possible explanation was that the excess of Fe^{3+} would lead to the formation of $Fe(OH)_3$, destroying the complex and reducing the generation rate of HO·. Therefore, the optimal molar ratio of Fe^{3+} to EDTA was selected as 2:1. It should be noted that the dosage of EDTA was halved in the UV-Fe^{3+}(EDTA)/H_2O_2 process, compared with that in the previous investigation (Shen et al., 2009). The results should be attributed that Fe^{3+} or $Fe(OH)^{2+}$ was constantly photo-generated Fe^{2+} under irradiation of UV light (Reactions (3)–(4)) and inhibited the formation of $Fe(OH)_3$, resulting in the decrease of the

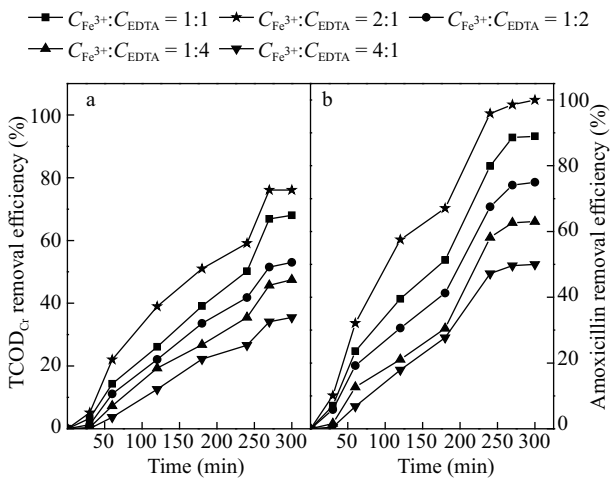

Fig. 2 $TCOD_{Cr}$ (a) and amoxicillin (b) removal efficiency under varying molar ratios of Fe^{3+} to EDTA in the UV-Fe^{3+}(EDTA)/H_2O_2 process. Experimental conditions: amoxicillin 250 mg/L, H_2O_2 64.7 mmol/L, Fe^{3+} 0.80 mmol/L, $EDTA_0$ 0.18 mol/L, pH 7.0, and temperature 25°C.

EDTA dosage. Therefore, the optimum molar ratio of Fe^{3+} to EDTA was selected as 2:1, and the concentration of EDTA was 0.40 mmol/L.

2.3 Molar ratio of H_2O_2 to Fe^{3+}

Figure 3 shows that $TCOD_{Cr}$ and amoxicillin removal efficiency increased when the molar ratio of H_2O_2 to Fe^{3+} increased from 36.0 to 108. However, when the molar ratio of H_2O_2 to Fe^{3+} was larger than 80.9, it could not lead to significant increase in the degradation efficiency. This might be attributed that the unconsumed H_2O_2 served as a scavenger for HO· and resulted in less reactive HO_2· (Zhou et al. 2007), decreasing amoxicillin degradation. Additionally, it should be noted that the residual H_2O_2 could create extra COD_{Cr}. Therefore, the optimum molar ratio of H_2O_2 to Fe^{3+} was selected as 80.9, and the concentration of H_2O_2 was 64.7 mmol/L.

2.4 COD_{Cr} distribution between EDTA and amoxicillin

As shown in Fig. 4, EDTA was degraded in the oxidation process due to the decreasing concentration of Fe^{3+}(EDTA) and its COD_{Cr} removal efficiency. It was

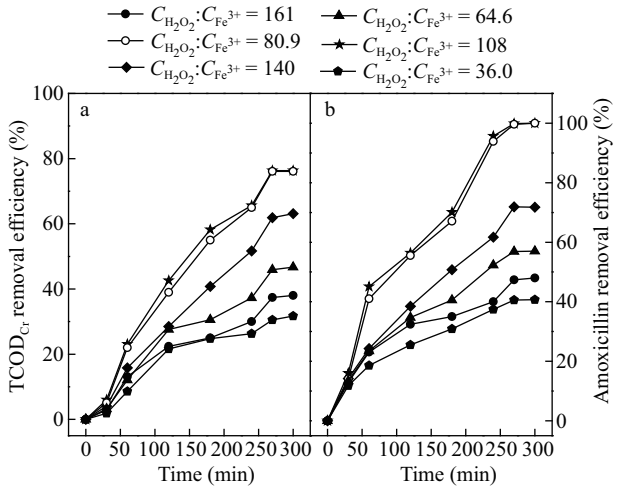

Fig. 3 $TCOD_{Cr}$ (a) and amoxicillin (b) removal efficiency under varying molar ratios of H_2O_2 to Fe^{3+}. Experimental conditions: amoxicillin 250 mg/L, $H_2O_2{}^0$ 32.3 mol/L, Fe^{3+} 0.80 mmol/L, EDTA 0.40 mmol/L, pH 7.0, and temperature 25°C.

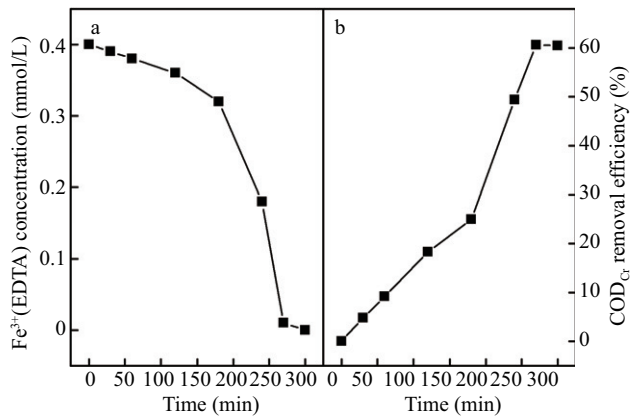

Fig. 4 Variation of Fe^{3+} (EDTA) concentration (a) and COD_{Cr} removal efficiency of EDTA (b) in the system that EDTA was selected as the sole contamination. Experimental conditions: Fe^{3+} 0.80 mmol/L, EDTA 0.40 mmol/L, H_2O_2 64.7 mmol/L, pH 7.0, and temperature 25°C.

therefore that both EDTA and amoxicillin contributed to COD_{Cr} removal efficiency ($TCOD_{Cr}$), yet which was difficult to be distinguished quantitatively only by the UV-Fe^{3+}(EDTA)/H_2O_2 process. Therefore, a control experiment that EDTA selected as the sole contamination was conducted under the same experimental conditions. The removal efficiency of $TCOD_{Cr}$ was found to be 76.1% at pH 7.0 and the initial COD_{Cr} of amoxicillin (0.25 g/L) and EDTA (0.40 mmol/L) were 360.0 and 135.0 mg/L, respectively. The total COD_{Cr} removal could be calculated as 376.7 mg/L according to the total COD_{Cr} multiplying by the total removal efficiency. Similarly, 81.7 mg/L of COD_{Cr} removal of EDTA could be obtained referring to 60.5% removal efficiency in Fig. 4b. Therefore, the COD_{Cr} removal of amoxicillin and the COD_{Cr} removal efficiency could be calculated as 295 mg/L and 81.9%, respectively.

2.5 Mechanisms investigation

2.5.1 Catalytic mechanisms of EDTA and UV light

In the UV-Fe^{3+}(EDTA)/H_2O_2 process, EDTA was employed to enhance iron cycles that catalyzed H_2O_2 to produce HO· or other activated media (Sun and Pignatello, 1992; Zhou et al., 2008). The efficiency of HO· formation increased by the photo-reaction of H_2O_2 and/or $Fe(OH)^{2+}$ that produced HO· directly or regenerated Fe^{2+} to feed back the chain reaction (Reactions (1)–(6)) (Javier Benitez et al., 2002; Tokumura et al., 2006). UV acceleration was most likely due to charge-transfer photoreduction of Fe^{3+}(EDTA) to give Fe^{2+}, which reacted with H_2O_2 to generate hydroxyl radical in the Fenton reaction (Sun and Pignatello, 1993). On the other hand, the enhancement of treatment efficiency might be ascribed to a photo-induced oxidation by an inner-sphere electron-transfer reaction of the ligands of various Fe(III) complexes such as Fe^{3+}(EDTA), $Fe(OH)_3$ with H_2O, the organic substrate, or its intermediates of degradation (Bossmann et al., 1998). Therefore, the following mechanisms could be further derived from the investigation.

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2\cdot + H^+ \quad (4)$$

$$H_2O_2 + Fe^{3+}(EDTA) \longrightarrow Fe^{2+}(EDTA) + HO_2\cdot + H^+ \quad (5)$$

$$H_2O_2 + Fe^{2+}(EDTA) \longrightarrow Fe^{3+}(EDTA) + HO\cdot + HO^- \quad (6)$$

$$\text{Amoxicillin} + h\nu \text{ or } HO\cdot \longrightarrow \text{degraded products} \quad (7)$$

$$\text{EDTA} + h\nu \text{ or } HO\cdot \longrightarrow \text{low weight molecules} \quad (8)$$

As shown in Fig. 5a, H_2O_2 concentration gradually decreased with the on-going oxidation process. It could be accounted that the large amount of H_2O_2 contributed to producing HO·/HO_2· under the irradiation of UV light or reacting with Fe^{3+} (EDTA)/Fe^{2+}(EDTA) (Eqs. (2), (4) and (5)).

Figure 5b presents that the pH decreased gradually from 7.0 to 3.0 in the oxidation process, which implied that low molecule weight organic acids or acidic media might be produced during the oxidation process. On the other hand, the decreasing pH was helpful for EDTA degradation because EDTA was subject to Fenton oxidation at acidic conditions (Walling et al., 1970). It was manifested that the initial higher pH inhibited the oxidation of EDTA during

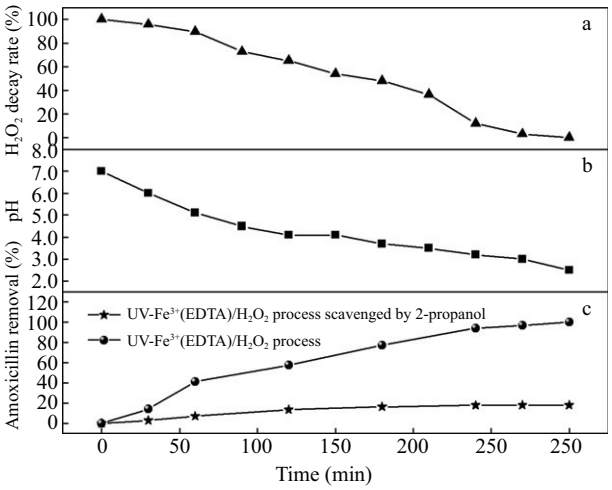

Fig. 5 H_2O_2 decay rate (a); pH changes (b); and amoxicillin removal efficiency (c) in the UV-Fe^{3+} (EDTA)/H_2O_2 process and UV-Fe^{3+} (EDTA)/H_2O_2 process scavenged by 2-propanol. Experimental conditions: amoxicillin 250 mg/L, H_2O_2 64.7 mol/L, Fe^{3+} 0.80 mmol/L, EDTA 0.40 mmol/L, pH 7.0, and temperature 25°C.

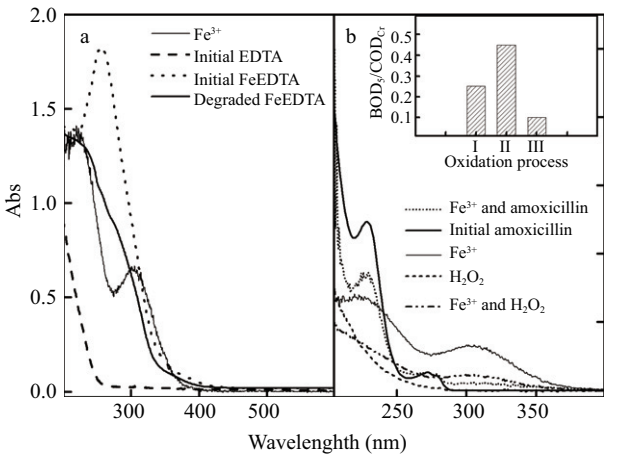

Fig. 6 UV-Vis spectra of Fe^{3+}, EDTA, initial Fe^{3+}(EDTA), and degraded Fe^{3+}(EDTA) (a); Fe^{3+}, amoxicillin, H_2O_2, the mixture of Fe^{3+} and amoxicillin, Fe^{3+} and H_2O_2 (b); BOD_5/COD_{Cr} in the UV-Fe^{3+} (EDTA)/H_2O_2 (I), UV-Fe^{3+}/H_2O_2 (II) and Fe^{3+}/H_2O_2 (III) processes (the insert plot in Fig. 6b). Experimental conditions: amoxicillin 250 mg/L, H_2O_2 64.7 mmol/L, Fe^{3+} 0.80 mmol/L, EDTA 0.40 mmol/L, pH 7.0, and temperature 25°C.

the initial reaction step, even though there was a large amount of HO·. Therefore, EDTA first acted as catalyst and then as reactant when the pH decreased to 3.0.

Figure 5c showed that the degradation of amoxicillin was dramatically decreased to 18.7% when 2-propanol (HO· scavenger) was added into the UV-Fe^{3+} (EDTA)/H_2O_2 process. These result demonstrated that HO· was a primary reactant in the oxidation process. It was also revealed that other activated media might exist in the oxidation process, leading to the tiny degradation of amoxicillin.

2.5.2 Potential activated media in the UV-Fe^{3+}(EDTA)/H_2O_2 process

The multi-staged degradation curves (Figs. 2, 3) proposed that EDTA, H_2O_2, and Fe^{3+} might build new activated media, which could be responsible for enhancing COD_{Cr} and amoxicillin removal, promoting the oxidation process. To confirm the resulted activated media, UV-Vis spectra of the following solutions were performed. As shown in Fig. 6a, only EDTA didn't exhibit any specific absorption at the range of 200–800 nm, and Fe^{3+} exhibited characteristic absorption at 223 and 301.5 nm, whereas Fe^{3+}(EDTA) led to a new maximum absorption at 258 nm. Figure 6b further shows that the mixture of Fe^{3+} and H_2O_2 led to a new maximum absorption at 303 nm, and alone H_2O_2 without any specific absorption. Amoxicillin caused maximum absorptions at 230 and 272 nm, whereas the mixture of Fe^{3+} and amoxicillin exhibited maximum absorptions at 229.5 and 278 nm. Therefore, these new absorptions likely contributed to the formation of new activated media, which cooperated with HO· for the degradation of amoxicillin.

The results of BOD_5/COD_{Cr} further revealed that the UV-Fe^{3+} (EDTA)/H_2O_2 process was a promising strategy to degrade amoxicillin as the biodegradability of the effluent was improved to 0.45, compared with the cases of UV-Fe^{3+}/H_2O_2(0.25) and Fe^{3+}/H_2O_2 processes (0.10) (Fig. 6c).

2.5.3 Degradation pathway of amoxicillin

The degraded products of amoxicillin were separated by HPLC at the retention time of 1.53, 2.63, and 16.13 min (Fig. 7), and each peak was characterized by its mass measurements (m/z), respectively (Fig. 8). The degradation of amoxicillin started with the opening of the fourmembered β-lactam ring and yielded the product amoxicillin penicilloic acid at m/z 383 ($C_{16}H_{22}N_3O_6S$) (Figs. 8b, 9a) which contained a free carboxylic acid group providing a higher polarity to this molecule (Nägele and Moritz, 2005). The structure of this degradation product was confirmed by the appearance of the characteristic fragment at m/z 340 ($C_{15}H_{22}N_3O_4S$) (Fig. 8b), which is the product of a decarboxylation reaction and the fragment at m/z 189 ($C_7H_{13}N_2O_2S$) was another important proof for the structure confirmation (Fig. 8b). Following by amoxicillin penicilloic acid, there were two possible pathways for the further degradation. The first one was based on the decarboxylation of the free carboxylic acid and demethyl

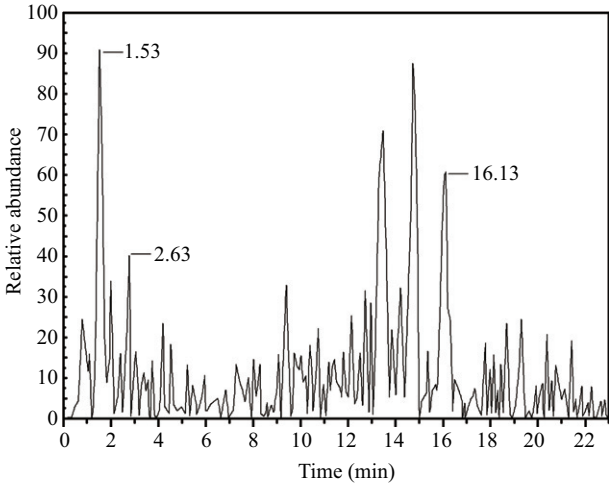

Fig. 7 HPLC chromatogram of the degraded amoxicillin.

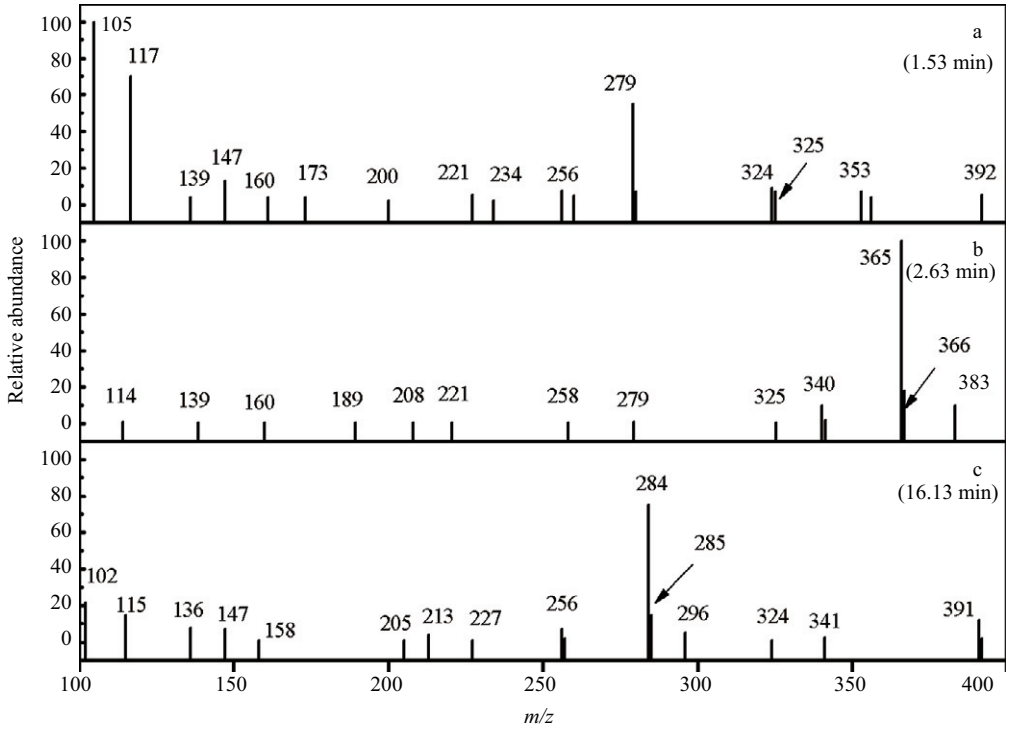

Fig. 8 Mass spectra of the degraded amoxicillin. Experimental conditions: ESI in positive model with scan of m/z 100–400.

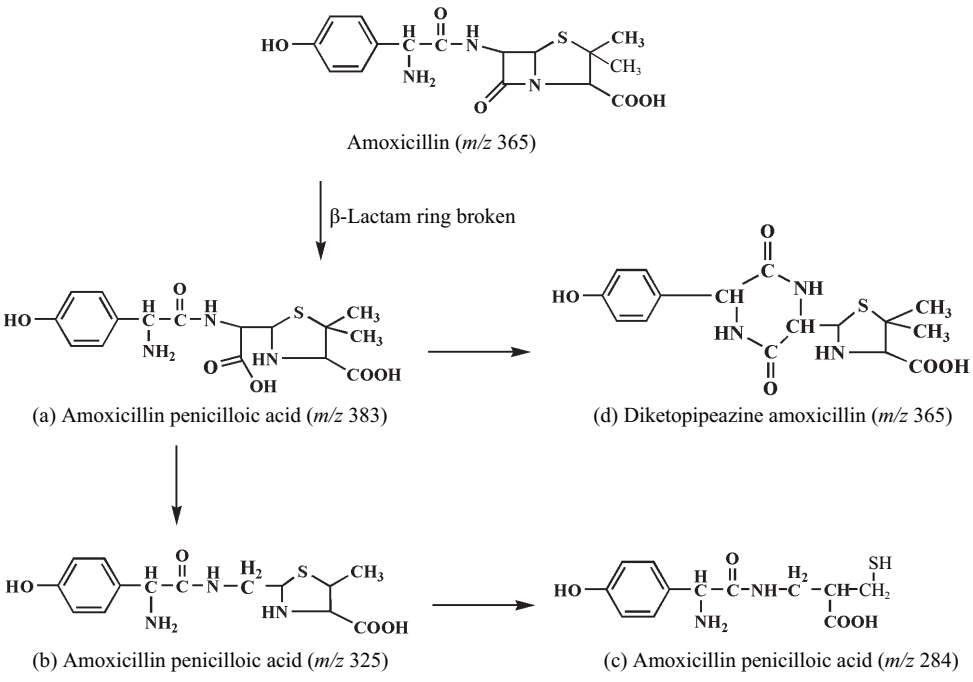

Fig. 9 Degradation pathway of amoxicillin.

reaction of the five-membered thiazolidine ring leading to the compound amoxicillin penilloic acid at m/z 325 ($C_{14}H_{19}N_3O_4S$) (Figs. 8a, 9b). The second one was undergone cleavage of the five-membered thiazolidine ring and decarboxylation yielding amoxicillin penicillamine at m/z 284 ($C_{12}H_{16}N_2O_4S$) (Figs. 8c, 9c). It was possible that another intermediate products was the formation of a new, stable, six-membered ring giving diketopiperazine amoxicillin (the isomeric compound of amoxicillin) at m/z 365 ($C_{16}H_{19}N_3O_5S$) (Figs. 8b, 9d).

3 Conclusions

In this work, a novel oxidation process of UV-Fe^{3+}(EDTA)/H_2O_2 has been investigated for the degradation of amoxicillin at pH 7.0, resulting in appreciable treatment efficiency. It was found that EDTA and UV light performed catalytic effect on the oxidation process synergistically, which involved in multi-step mechanisms of Fenton, Fenton like, photo-Fenton and Fe(III)-organic complexes. The results further revealed that EDTA acted

as catalyst and reactant as well.

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