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Oxidation of amitriptyline and nortriptyline by ferrate(VI): efficiency and reaction pathways

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ABSTRACT

The oxidation of amitriptyline (AMI) and nortriptyline (NOR), two typical tricyclic antidepressants, has been studied in ferrate(VI) (Fe(VI)) solution. The removal rate of AMI and NOR increased with increasing Fe(VI) dosage and was seen to be pH dependent in the order pH 7.0 < 10.0 < 8.0 < 9.0. UV irradiation at 254 nm was found to exert a synergistic effect on the Fe(VI) oxidation of AMI and NOR. By LC–ESI-MS/MS analysis, the main oxidation products of AMI and NOR by Fe(VI) have been identified. The exocyclic double bond is first oxidized to give the *exo*-epoxide, which is then hydrolyzed and finally oxidized to give dibenzosuberenone and 3-dimethylamino-propionaldehyde. The results suggest that Fe(VI) has a good ability to oxidize AMI and NOR in aqueous solution and could be an effective treatment method for the purification of waters containing these particular antidepressants.

Keywords: Ferrate(VI); Tricyclic antidepressants; Oxidation; Products; Water treatment

1. Introduction

In recent years, numerous articles have reported the presence of pharmaceuticals and personal care products, an important group of organic pollutants, in the aquatic environment throughout the world, including in the raw water sources of drinking water treatment plants [1]. Among these, psychiatric pharmaceuticals, such as anxiolytics, sedatives, hypnotics, and antidepressants, are the most prescribed active substances [2]. Antidepressants are drugs used for the treatment of clinical depression and other conditions such as neuropathic pain, and can mostly be classified into selective serotonin reuptake inhibitors, serotonin–norepinephrine reuptake inhibitors, tricyclic antidepressants (TAs), and monoamine oxidase inhibitors. A large number of antidepressants have already been identified in water, sludge, and the biological tissues of aquatic organisms at concentrations ranging from ng L^{-1} to μg L^{-1} [3–5]. They can not only affect the neuronal system, but also disrupt neuroendocrine signaling causing perturbations in reproductive behavior [2]. Hence, the widespread existence of antidepressants in the environment may pose a problem of toxicity and harmful effects. Two of the most widely used TAs of the dibenzocycloheptene type, amitriptyline (AMI) and nortriptyline (*N*-desmethyl amitriptyline) (NOR), which have been generally detected in wastewater, surface run-off, and effluents from sewage treatment plants (STPs) [6],

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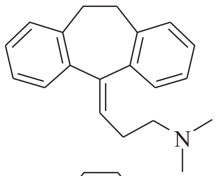
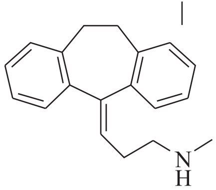
were selected as representative antidepressants in the present study. The structures of AMI (left side) and NOR (right side) are as shown below:





Even though concern about these emerging environmental pollutants is increasing, knowledge of the environmental fate of a large number of psychiatric pharmaceuticals is still very scarce, and further research on this topic is urgently needed [2]. Previous work has shown that AMI can be readily oxidized by permanganate in sulfuric acid medium [7]. In addition, the oxidation of three antidepressant compounds (duloxetine, venlafaxine, and bupropion) and their direct and indirect photochemical fate and treatment in humic acid solutions has been reported [8]. However, AMI has been shown to be nonbiodegradable under sewage treatment conditions [9], and cannot be efficiently removed by STPs [10]. Furthermore, uptake and retention by kaolinite has been shown to be effective for the adsorption and immobilization of a significant amount of AMI at low concentrations in natural water; the fast rate and large rate constant showed it to be a good adsorbent for contaminant removal [11]. On the other hand, the treatment of NOR in aquatic environments, such as wastewater, has seemingly been little reported.

As an emerging water treatment agent, Fe(VI) has received much recent attention [12,13]. Fe(VI) is a powerful oxidizing agent in water treatment, with an oxidation–reduction potential of 2.20 V under acidic pH conditions and 0.7 V under basic pH conditions [14]. During the oxidation process of organic pollutants and micro-organisms in water, Fe(VI) ions are reduced to Fe(III) ions or ferric hydroxide, simultaneously leading to coagulant and photocatalysis properties [15,16]. Due to its dual functions as an oxidant and as a subsequent coagulant/precipitant as ferric hydroxide, Fe(VI) is regarded as an environmentally friendly oxidant in water and wastewater treatment [17,18]. However, only a few studies have hitherto been performed on the Fe(VI) oxidation of pharmaceuticals [19–23], and to the best of our knowledge there has been no report on the oxidation of antidepressants by this species. In addition, it was noteworthy that UV irradiation, as an important reaction condition, exerted a great synergistic effect in the treatment of municipal landfill leachate with the Fe(VI)/UV system in our previous work [24].

Therefore, the aim of the current work has been to investigate the oxidation of representative antidepressants, namely AMI and NOR, by Fe(VI). The varied ferrate dosages, pH effect, and UV irradiation were studied. Moreover, the oxidation products (OPs) have been identified by LC–ESI-MS/MS.

2. Materials and methods

2.1. Materials

AMI hydrochloride (≥98%) and NOR hydrochloride (≥98%) were purchased from Sigma (USA) and were used as received. Stock solutions of AMI and NOR were prepared by dissolving the solid compound in 10 mM Na_2HPO_4 buffer solution prepared with distilled water. Potassium ferrate (K_2FeO_4) (≥97%) was obtained from Aldrich (USA) and was used without further purification. The Fe(VI) solutions were prepared by addition of solid K_2FeO_4 to 1 mM $Na_2B_4O_7{\cdot}10H_2O$/5 mM Na_2HPO_4 buffer solution at pH 9.0. All other chemicals used were of at least analytical reagent grade.

2.2. Degradation analysis

The oxidation effect on AMI and NOR by Fe(VI) was quantified by degradation analysis of AMI and NOR at different Fe(VI) doses and solution pH values. The concentrations of AMI and NOR were analyzed on a Shimadzu Essentia LC–15C HPLC system with an Agilent HC-C18 column (5 μm, 150mm × 4.6 mm). The mobile phase was a 40:60 mixture of acetonitrile and pH 2.5 phosphate buffer solution at a flow rate of 1.0 mL/min. The detection wavelength was 240 nm, and an injection volume of 20 μL was used in isocratic elution mode.

The Fe(VI) content in the solution was determined by an UV/vis spectrophotometer (Hitachi U3100, Japan) at a wavelength of 510 nm. A molar absorption coefficient of $\varepsilon_{510\text{nm}} = 1{,}150$ M/cm was used to determine the Fe(VI) concentration at pH 9.0 [25].

2.3. Irradiation experiments

UV irradiation experiments were carried out in a Pyrex photoreactor under illumination by a low-pressure UV lamp with light intensity 48.4 $\mu W/cm^2$

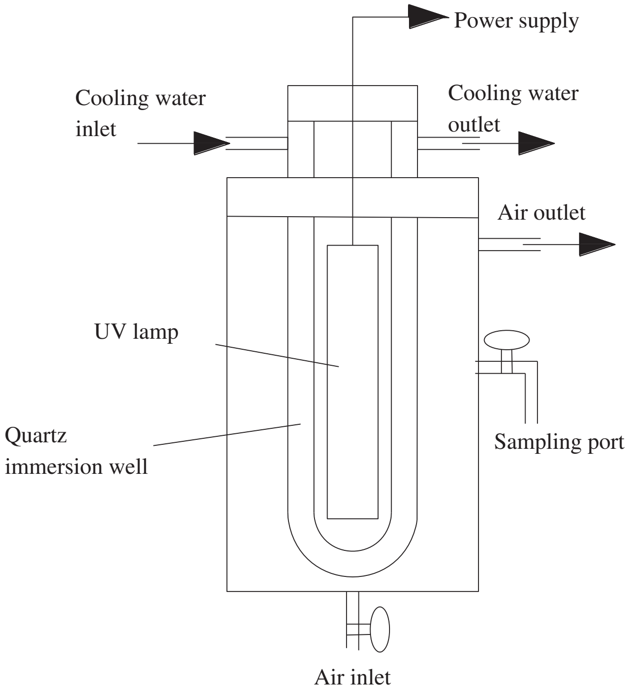


Fig. 1. Diagram of the UV irradiation reactor.

(254 nm, 15 W). An immersion well made of high-purity quartz was placed inside the glass reactor and fitted with a standard joint at the top. The UV lamp was fixed inside the immersion well. Water was passed through the thin annular zone of the immersion well to prevent overheating of the reaction solution (Fig. 1). In order to achieve a stabilized radiation emission, the lamp was always switched on for 30 min before being fitted into the reactor. Air was bubbled through the reaction system in order to homogenize the solution throughout the experiment. Each result is an average of triplicate runs. The standard errors of measurement were within 5%.

2.4. *Product identification*

The OPs from the reaction of Fe(VI) with AMI and NOR were analyzed on an Agilent Technologies 1100 series LC/MSD Trap XCT (Palo Alto, CA, USA) with electrospray ionization in positive-ion mode in full-scan mode (*m/z* 50–350). An Agilent HC-C18 column (5 µm, 150mm × 4.6 mm) was used to achieve chromatographic separation of AMI and NOR and OPs by isocratic elution. The binary mobile phases were: (i) acetic acid; (ii) acetonitrile containing 0.1% formic acid. The MS conditions were set as follows: HV capillary 3,000 V; drying gas (N_2) temperature 300℃; drying gas (N_2) flow of 10 L/min; nebulizer pressure at 30 psi; trap drive 30.3; skimmer 40.0 V; octopole RF amplitude 145.5 V; capillary exit 110.8 V; max. accumulation time 200 ms; and ion charge control 200,000.

3. Results and discussion

3.1. *Effect of Fe(VI) dose*

The effect of initial Fe(VI) dose on the oxidation of AMI and NOR was investigated with varied doses and the results are shown in Fig. 2. It has been reported that the oxidation effect by Fe(VI) depends on the molar ratio of Fe(VI) to substrates and solution pH [13,14]. Here, the reaction was primarily determined by Fe(VI) dose since the initial concentration of AMI and NOR and solution pH were fixed at 20 µM and 9.0, respectively. Fig. 2 reveals that the removal

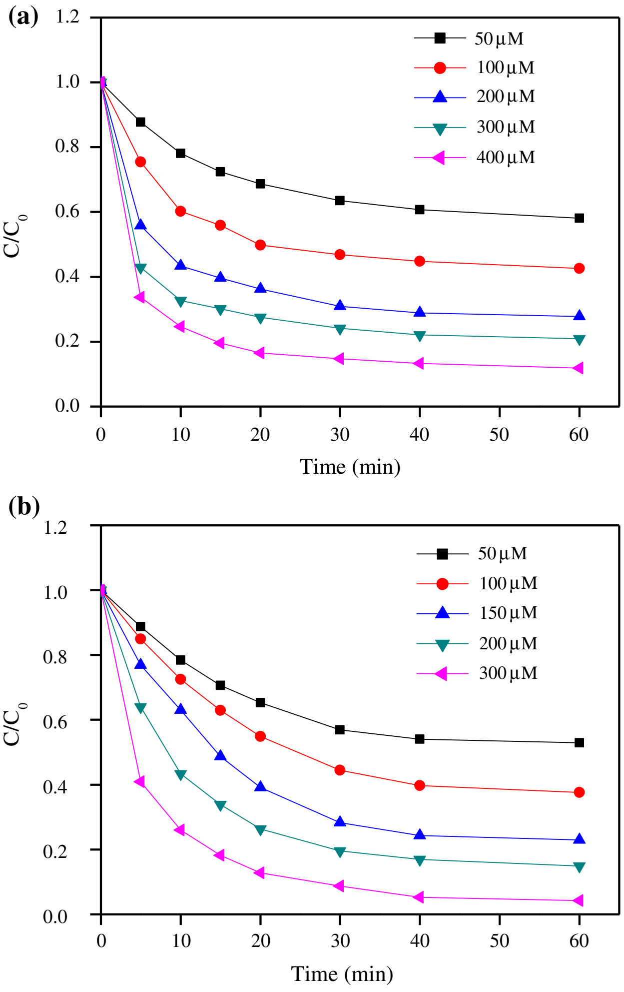


Fig. 2. Degradation of (a) AMI and (b) NOR at pH 9.0 with different Fe(VI) doses ($[AMI]_{initial}$ and $[NOR]_{initial}$ = 20 µM).

rate of AMI and NOR increased with increasing initial Fe(VI) dose at pH 9.0. When 400 μM Fe(VI) was added to the solution, up to 88.1% removal of AMI was achieved after 60 min. Meanwhile, the NOR concentration decreased by 95.7% with 300 μM Fe(VI), reflecting the strong oxidation ability of the Fe(VI) system.

In addition, Fig. 2 suggests that almost 50% of the AMI and NOR could be removed by 100 μM Fe(VI) (i.e. five times the concentration of the substrates). Removal of the remaining 50% of AMI and NOR needed 300 and 200 μM Fe(VI), respectively, indicating that Fe(VI) not only reacted with the AMI and NOR but also with OPs in the solution. A similar phenomenon was also observed for the oxidation of propranolol by Fe(VI) [26].

3.2. Effect of pH

Fig. 3 shows the effect of solution pH on the removal of AMI and NOR by Fe(VI) within the pH range 7.0–10.0 in 10 mM phosphate-buffered solutions. The degradation of AMI and NOR increased in the order pH 7.0 < 10.0 < 8.0 < 9.0. Fe(VI) is a very strong oxidant, as can be seen from the reduction potentials of reactions (1) and (2) in acidic and alkaline solutions, respectively [27].

$$\mathrm{FeO_4^{2-}} + 8\mathrm{H^+} + 3e^- \rightarrow \mathrm{Fe^{3+}} + 4\mathrm{H_2O} \qquad E^0 = 2.2\ \mathrm{V} \tag{1}$$

$$\mathrm{FeO_4^{2-}} + 4\mathrm{H_2O} + 3e^- \rightarrow \mathrm{Fe(OH)_3} + 5\mathrm{OH^-} \qquad E^0 = 0.72\ \mathrm{V} \tag{2}$$

Owing to their strong oxidizing ability, when ferrate salts are dissolved in water, oxygen is evolved and ferric hydroxide is precipitated, thus accounting for the instability of Fe(VI) in aqueous solution (Eq. (3)).

$$4\mathrm{K_2FeO_4} + 10\mathrm{H_2O} \rightarrow 4\mathrm{Fe(OH)_3} + 8\mathrm{KOH} + 3\mathrm{O_2}\uparrow \tag{3}$$

This spontaneous decomposition strongly depends on the coexisting ions, the pH, and the temperature of the solution [28]. On the other hand, the effect of pH on the oxidation is also related to the protonation of ferrate ion ($\mathrm{FeO_4^{2-}}$), with protonated Fe(VI) having a much stronger oxidizing ability than $\mathrm{FeO_4^{2-}}$, as expressed by Eqs. ((4)–(6)) [29].

$$\mathrm{H_3FeO_4^+} \leftrightarrow \mathrm{H^+} + \mathrm{H_2FeO_4} \qquad \mathrm{p}K_{\mathrm{a1}} = 1.6 \tag{4}$$

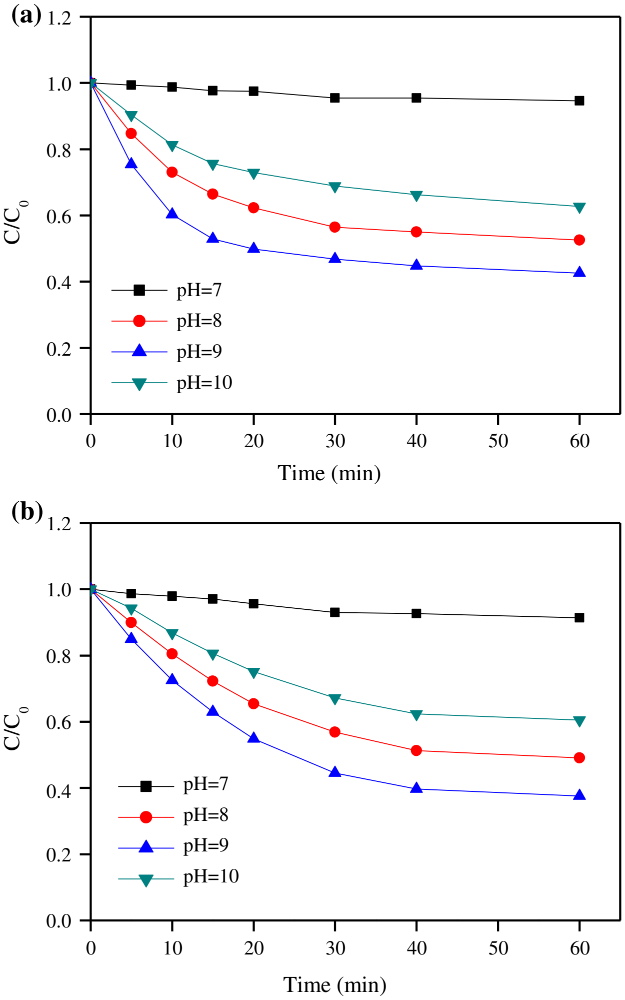


Fig. 3. Degradation of (a) AMI and (b) NOR by Fe(VI) at different pH values ($[\mathrm{AMI}]_{\mathrm{initial}}$ = 20 μM with [Fe(VI)] = 400 μM, $[\mathrm{NOR}]_{\mathrm{initial}}$ = 20 μM with [Fe(VI)] = 300 μM).

$$\mathrm{H_2FeO_4^+} \leftrightarrow \mathrm{H^+} + \mathrm{HFeO_4^-} \qquad \mathrm{p}K_{\mathrm{a2}} = 3.5 \tag{5}$$

$$\mathrm{HFeO_4^-} \leftrightarrow \mathrm{H^+} + \mathrm{FeO_4^{2-}} \qquad \mathrm{p}K_{\mathrm{a3}} = 7.3 \tag{6}$$

Therefore, the pH dependence behavior in Fig. 3 may be explained in terms of two components, the first being the protonation, i.e. oxidizing ability of Fe(VI), and the second being its stability [30]. During oxidation, protonation and decomposition occurred simultaneously, but the dominant reaction varied according to the pH range. It has been reported that the lowest rate of decomposition occurs at pH 9.4–9.7, and that the rates increase below and above this pH range [31]. In alkaline solutions, at pH < 9.0, the stability of Fe(VI) is enhanced with increasing pH and becomes the

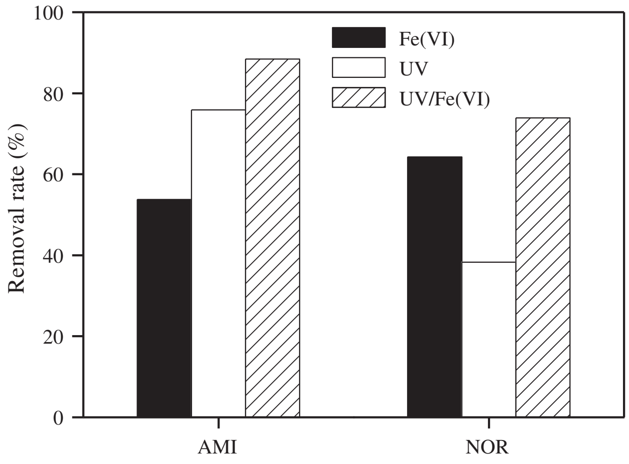


Fig. 4. Degradation of (a) AMI and (b) NOR by Fe(VI) at pH 9.0 with and without UV irradiation ($[AMI]_{initial}$ and $[NOR]_{initial}$ = 20 μM, [Fe(VI)] = 100 μM and UV intensity = 48.4 W/cm^2).

dominant factor, which is in agreement with the pH-dependence behavior of the removal rate. At pH > 9.0, the protonation and stability of Fe(VI) decrease simultaneously, but protonation becomes the dominant factor, leading to a relatively lower removal rate of AMI and NOR at pH 10.0 than at pH 8.0 or 9.0. Hence, the maximum removal rates of AMI and NOR with 100 μM Fe(VI) were achieved at pH 9.0 (57.4 and 62.4%, respectively), as shown in Fig. 3.

3.3. Effect of UV irradiation

Fig. 4 shows the effect of UV_{254} irradiation on the degradation of AMI and NOR by Fe(VI) at pH 9.0. The degradation of AMI was significant under UV irradiation alone, with a degree of removal of 75.8%, presumably due to the absorption of UV light at 254 nm [32]. Several studies have indicated that pollutants can be degraded by direct UV photolysis

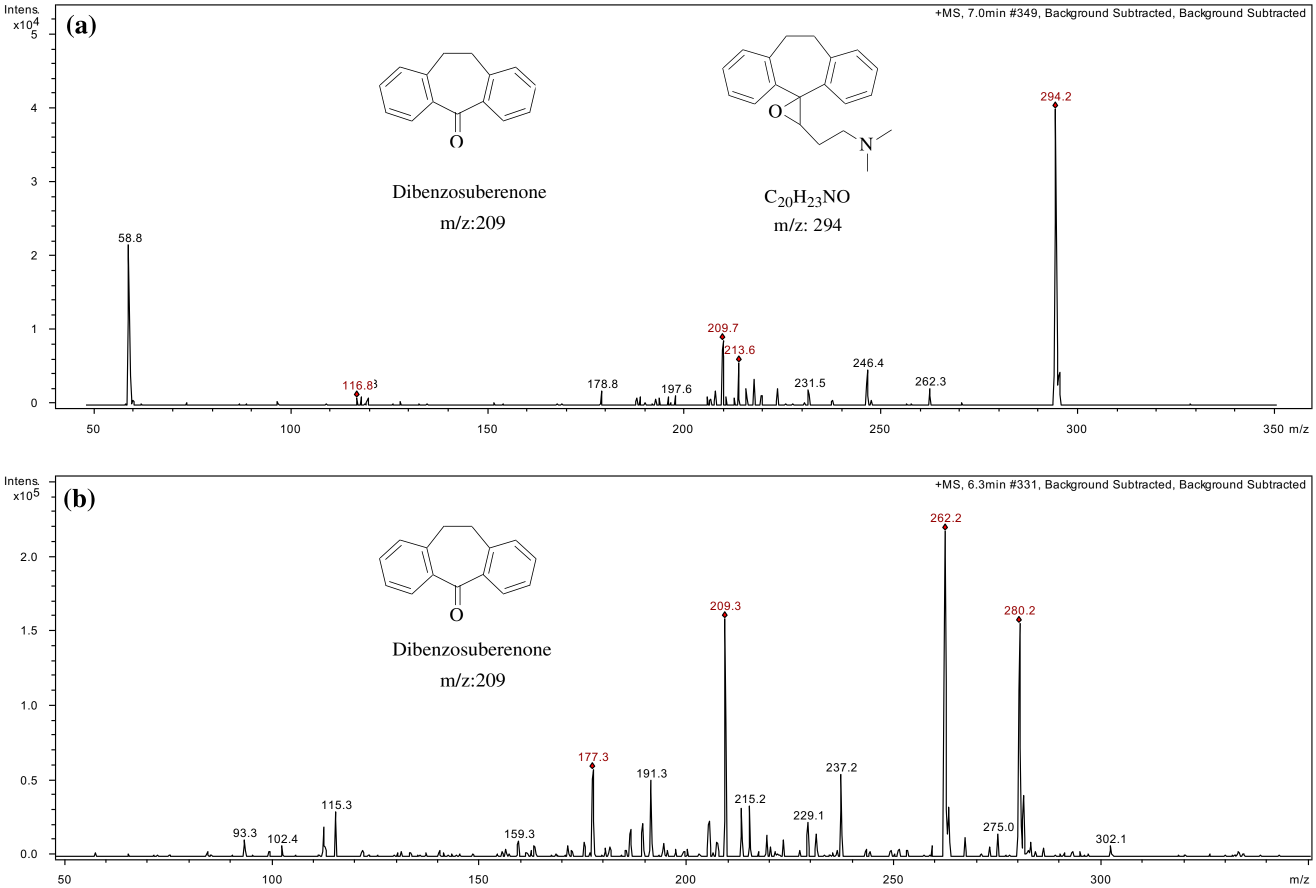


Fig. 5. Full-scan (+)-ESI-mass spectra of the main OPs of (a) AMI and (b) NOR in Fe(VI) solutions at pH 9.0.

through electronic excitation of organic substrates, leading to the transfer of an electron from the excited state of the substrate to the ground state of molecular oxygen, or to homolysis to form organic radicals that can then react with oxygen [33–35]. In contrast, only 38.3% of NOR was removed by UV irradiation without Fe(VI). Despite similar absorptions of UV light at 254 nm, a large difference in the degrees of removal was observed for AMI and NOR, highlighting the fact that the degradation of pollutants by direct UV photolysis is highly dependent on the target compound being studied [36].

Compared with direct UV photolysis, the degrees of removal of AMI with Fe(VI), with and without UV irradiation, were 88.5 and 53.7%, respectively. Therefore, a significant synergistic effect of UV light on the oxidation of AMI by Fe(VI) was observed, which was most likely attributable to easier reduction of Fe(VI) under UV irradiation [37]. FeO_4^{2-} in the photoexcited state is closely related to the generation of Fe(V), as expressed in Eq. (7).

$$\mathrm{HFeO_4^- + e^- \leftrightarrow HFeO_4^{2-}} \qquad (7)$$

Fe(V) is 103–105 times more reactive towards pollutants than Fe(VI), resulting in a stronger oxidation ability of Fe(VI) solution under UV light irradiation. The spontaneous decomposition of Fe(V) is another an important aspect with the release of Fe(III) ion and hydrogen peroxide in alkaline medium illustrated in Eq. (8) [38,39].

$$\mathrm{FeO_4^{3-} + 4H_2O \rightarrow Fe(OH)_3 + H_2O_2 + 3OH^-} \qquad (8)$$

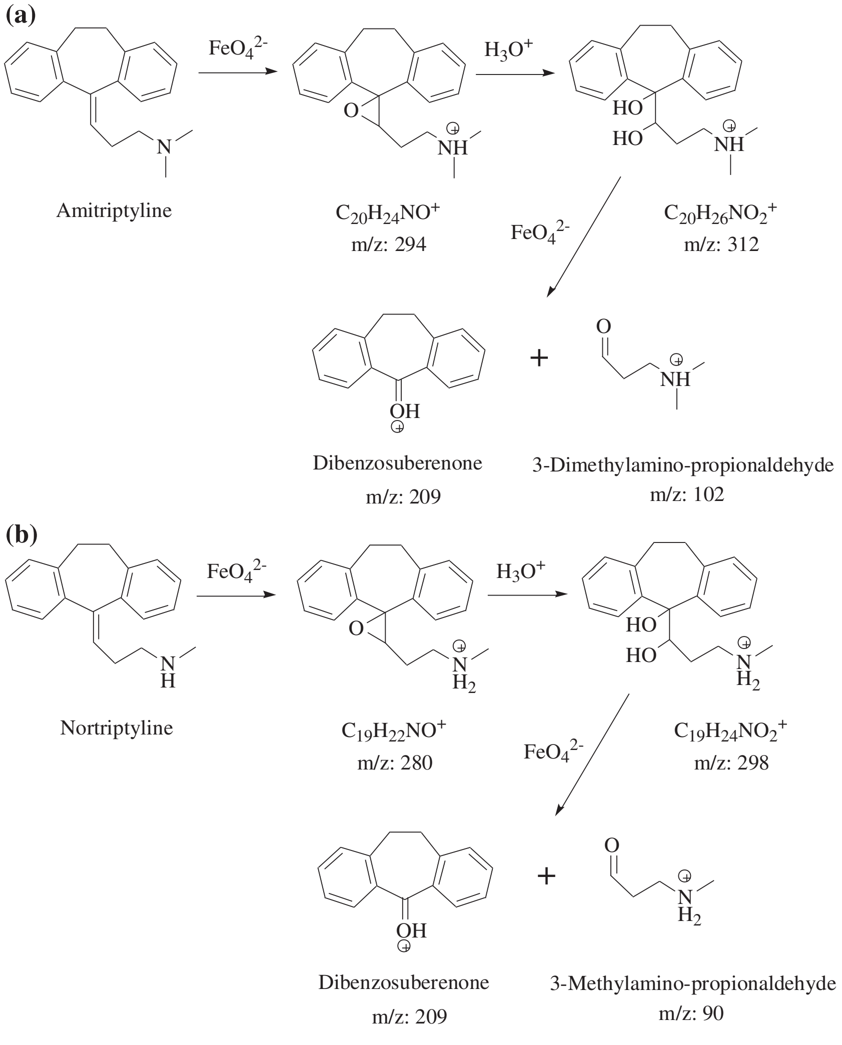


Fig. 6. Proposed oxidation pathway of (a) AMI and (b) NOR by Fe(VI).

Ferric hydroxide can cause coagulation and hydrogen peroxide also has a strong oxidabillity, leading to a higher degradation of AMI and NOR with UV irradiation. In addition, it is possible that the initial products derived from AMI absorb UV light and thus accelerate the degradation.

It is noted that the degree of removal of AMI in the UV/Fe(VI) system was less than the sum of those with the Fe(VI) alone and UV alone systems because the reduction product $Fe(OH)_3$ interfered with the absorption of UV by both AMI and Fe(VI). The detailed synergistic effect needs further investigation. A similar phenomenon was observed in the reaction between NOR and Fe(VI), with degrees of removal of 73.9 and 64.2% with the UV/Fe(VI) and Fe(VI) alone systems, respectively. These experimental results indicated that UV light contributed to the oxidation of refractory organic contaminants by Fe(VI).

3.4. Oxidation products and pathway

The OPs derived from AMI and NOR by treatment with Fe(VI) in aqueous solution at pH 9.0 were identified by LC–ESI-MS/MS to gain further insight into the oxidation mechanism of these molecules in the Fe(VI) system. The MS data were used to identify the main OPs. As shown in Fig. S1, three main OPs of AMI (m/z 102, 294, and 209) were identified at 3.2, 7.0, and 7.9 min, respectively, in the total ion chromatogram. Based on the ESI-MS/MS spectra (Figs. 5(a) and S2), these products were assigned as OP-102 ($C_5H_{11}NO$, 3-dimethylamino-propionaldehyde), OP-294 ($C_{20}H_{23}NO$, 5-(3-dimethylamino-1-hydroxypropyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol), and OP-209 ($C_{15}H_{12}O$, dibenzosuberenone). Moreover, the main oxidation product from NOR, i.e. dibenzosuberenone, was also identified on the basis of the LC–ESI-MS/MS data in Figs. 5(b), S3, and S4. This suggests that no attack of Fe(VI) on benzene ring occurred and oxidation took place at the side chain of target molecules.

Thus, the possible oxidation pathways of AMI and NOR are shown in Fig. 6. The results suggest that AMI may degrade through a pathway involving three major reaction steps. Firstly, the exocyclic double bond is oxidized to the *exo*-epoxide ($C_{20}H_{23}NO$). Secondly, the *exo*-epoxide is hydrolyzed to $C_{20}H_{25}NO_2$ (5-(3-dimethylamino-1-hydroxypropyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol), which can then be oxidized to dibenzosuberenone and 3-dimethylamino-propionaldehyde (Fig. 6(a)). Analogously, the oxidation pathway of NOR by Fe(VI) is shown in Fig. 6(b). Similar key steps in the mechanism have been proposed in earlier studies [40–42].

4. Conclusions

(1) The oxidation of AMI and NOR has been shown to be strongly dependent on the Fe(VI) dosage and pH. The degree of removal of AMI and NOR followed the order pH 7.0 < 10.0 < 8.0 < 9.0. At pH 9.0, up to 88.1% of AMI and 95.7% of NOR were degraded after 1 h of reaction with 20:1 and 15:1 M ratios of Fe(VI) to AMI and NOR, respectively. UV irradiation at 254 nm was found to exert a synergistic effect on the oxidation of AMI and NOR by Fe(VI).

(2) For AMI, the exocyclic double bond is first oxidized to the *exo*-epoxide ($C_{20}H_{23}NO$). This *exo*-epoxide is then hydrolyzed to 5-(3-dimethylamino-1-hydroxypropyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol ($C_{20}H_{25}NO_2$), which can then be oxidized to dibenzosuberenone and 3-dimethylamino-propionaldehyde. A similar pathway can be proposed for the reaction between NOR and Fe(VI). Fe(VI) could be an effective water treatment method for these particular antidepressants.

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Supplementary material

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