Oxidative removal of acetaminophen using zero valent aluminum-acid system: Efficacy, influencing factors, and reaction mechanism

Honghua Zhang[1], Beipei Cao[1], Wanpeng Liu[1], Kunde Lin[1,*], Jun Feng[2]

1. College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310032, China. E-mail: zhh124@zjut.edu.cn
2. Shangyu Environmental Monitoring Station, Shaoxing 312300, China

Abstract

Commercial available zero valent aluminum under air-equilibrated acidic conditions (ZVAl/H$^+$/air system) demonstrated an excellent capacity to remove aqueous organic compounds. Acetaminophen (ACTM), the active ingredient of the over-the-counter drug Tylenol®, is widely present in the aquatic environment and therefore the treatment of ACTM-contaminated water calls for further research. Herein we investigated the oxidative removal of ACTM by ZVAl/H$^+$/air system and the reaction mechanism. In acidic solutions (pH < 3.5), ZVAl displayed an excellent capacity to remove ACTM. More than 99% of ACTM was eliminated within 16 hr in pH 1.5 reaction solutions initially containing 2.0 g/L aluminum and 2.0 mg/L ACTM at 25 ± 1°C. Higher temperature and lower pH facilitated ACTM removal. The addition of different iron species Fe^0, Fe^{2+} and Fe^{3+} into ZVAl/H$^+$/air system dramatically accelerated the reaction likely due to the enhancing transformation of H$_2$O$_2$ to HO· via Fenton's reaction. Furthermore, the primary intermediate hydroquinone and the anions formate, acetate and nitrate, were identified and a possible reaction scheme was proposed. This work suggested that ZVAl/H$^+$/air system may be potentially employed to treat ACTM-contaminated water.

Key words: acetaminophen; advanced oxidation processes (AOPs); aluminum; Fenton reaction

DOI: 10.1016/S1001-0742(11)60769-9

Introduction

Acetaminophen [*N*-(4-hydroxyphenyl)ethanamide, ACTM], the active ingredient of various over-the-counter analgesic and antipyretic drugs such as Tylenol®, is commonly available alone or in combination with other medications in households. The amount of ACTM through prescription in 2000 was estimated to be more than 400 tons, ranking as one of the top three mediations prescribed in England (Sebastine and Wakeman, 2003). In China, the export quantity of ACTM was up to 15,348 tons in 2001 (An et al., 2009). Because of the widespread use and the low removal efficiency in the traditional wastewater treatment, ACTM has become one of the most frequently detected pharmaceuticals in the aquatic environment, with concentrations ranging from several ng/L to dozens of μg/L (Kolpin et al., 2002; Kim et al., 2007; Lin and Tsai, 2009; Nikolaou et al., 2007; Rosal et al., 2010; Santos et al., 2009; Sim et al., 2010).

Recent advents in advanced oxidation processes (AOPs) offer a wide variety of choices for ACTM removal. For example, TiO$_2$-based photocatalysis displayed an outstanding capacity to oxidize ACTM to innocuous CO$_2$, H$_2$O and NO$_3^-$ (Yang et al., 2008, 2009; Zhang et al., 2008). More recently, Klamerth et al. (2010a, 2010b) used

photo-Fenton process to treat ACTM-spiked municipal wastewater and a complete removal was obtained in several minutes to a few hours. In addition, ozonation and H$_2$O$_2$/UV system exhibited powerful oxidative capacity to destroy the aromatic ring in ACTM with a partial conversion (30% to 40%) of the organic carbon into carbon dioxide (Andreozzi et al., 2003).

Each process mentioned above has its own advantages and disadvantages with respect to simplicity, efficacy, ease of use, and cost. Continuous improvements in treatment processes are still in demand. Recently, ZVAl/H$^+$/air system, a simple AOP like zero valent iron was developed by Bokare and Choi (2009) to eliminate organic compounds. The excellent oxidative powder of ZVAl/H$^+$/air system is mainly due to the formation of hydroxyl radical (Bokare and Choi, 2009). Figure 1 illustrates the formation of HO· in ZVAl/H$^+$/air system. First, the oxide layer is removed through acid dissolution (pathway i). Second, the corrosive dissolution of aluminum and the simultaneous reduction of oxygen occurs on the aluminum surface forming the radical HO$_2$· (pathway ii). Third, the rapid disproportionation of HO$_2$· yields H$_2$O$_2$ (pathway iii, Reaction (1)), which serves as the precursor of hydroxyl radical. Finally, HO is generated via electron transfer from ZVAl to H$_2$O$_2$ (pathway iv, Reaction (2).

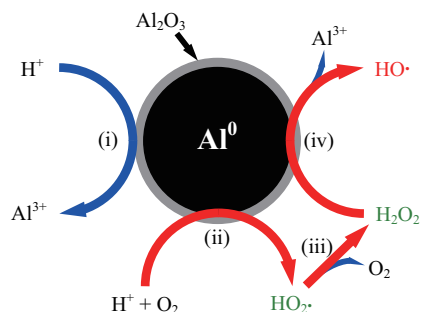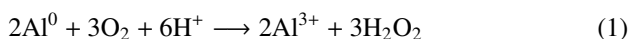* Corresponding author. E-mail: lin.kunde@gmail.com

Fig. 1 Schematic diagram for the formation of hydroxyl radicals in ZVAl/H$^+$/air system.

$$2Al^0 + 3O_2 + 6H^+ \longrightarrow 2Al^{3+} + 3H_2O_2 \tag{1}$$

$$Al^0 + 3H_2O_2 \longrightarrow Al^{3+} + 3HO\cdot + 3OH^- \tag{2}$$

The objective of the present work was to investigate the removal of aqueous ACTM using ZVAl/H$^+$/air system by exploring the reaction efficacy, influencing factors and reaction mechanism. Furthermore, we evaluated the enhancing ACTM removal by introducing different iron species Fe^0, Fe^{2+} and Fe^{3+} into ZVAl/H$^+$/air system.

1 Materials and methods

1.1 Chemicals

Acetaminophen standard (purity > 99%) and *N*, *O*-bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane (BSTFA + TMCS, 99:1) were purchased from Sigma-Aldrich (USA). Aluminum powder (purity > 99%, particle size 75–150 μm, surface covered with native aluminum oxide layer), iron powder (purity > 98%), anhydrous ferric chloride (purity > 97%) and ferrous chloride tetrahydrate (purity > 98%) were purchased from Sinopharm Chemical Reagent (China). Other chemicals and solvents used in this study were of analytical grade or high performance liquid chromatography (HPLC) grade. All chemicals were used as received. Ultrapure water (18.2 MΩ cm resistivity) was prepared using a Millipore purification system. Stock solution of 5.0 g/L ACTM was prepared in acetone. Ferric chloride and ferrous chloride solutions (0.05 mol/L) were prepared in 0.1 mol/L HCl solution. Ferrous chloride solution was freshly prepared prior to use. All solutions were stored at 4°C before use.

1.2 Reaction setup

All reactions were carried out in 250-mL glass Erlenmeyer flasks with a total suspension volume of 100 mL under air-equilibrated conditions and in the absence of light. Unless otherwise noted, temperature was fixed at 25 ± 1°C. The initial pH (pH$_i$) of the solutions was adjusted to the designated value with 1 mol/L HClO$_4$ standard solution. A 40-μL aliquot of 5.0 g/L ACTM stock solution was added to make a nominal initial concentration of 2.0 mg/L. Re-action mixtures were constantly stirred with Teflon-coated magnetic stir bars at 200 r/min in a thermostat. Reactions were initiated by adding a predetermined amount of ZVAl into the pre-equilibrated and constantly mixed solutions. Aliquots of 1.0 mL sample were periodically withdrawn and transferred to 2-mL centrifuge tubes containing 10 μL of methanol (as HO· scavenger). The samples were immediately vortexed for 10 sec and centrifuged at 8000 r/min for 5 min. The supernatant was transferred to 2-mL vials and subjected to HPLC analysis to determine ACTM residue. All samples were stored at 4°C and analyzed within 24 hr.

Specific treatments were also included to evaluate the effect of Fe^0, Fe^{2+} and Fe^{3+}. A predetermined amount of iron powder, FeCl$_2$ and FeCl$_3$ were separately added into the reaction solutions. Except for the ZVAl-free control, all treatments were carried out in triplicates.

1.3 Chemical analysis

Acetaminophen concentrations in reaction samples were determined using a reverse-phase HPLC coupled with a variable wavelength ultraviolet (UV) detector (Jasco Technologies, Japan). The detection wavelength was 243 nm. A Waters Symmetry® C18 column (250 × 4.6 mm, 5 μm, Waters, USA) was employed for the separation. The isocratic mobile phase consisted of 25% methanol and 75% water at a flow rate of 1.0 mL/min. The injection volume was 20 μL. Under these conditions, the typical retention time for ACTM was 5.2 min.

For reaction product identification, 8.0 mg/L ACTM and 2.0 g/L aluminum were reacted at pH$_i$ 1.5 (4 replicates), and the reaction was quenched by adding 1.0 mL methanol at 0, 8, 12, and 24 hr, respectively. Fifty mL of the solution was filtered through a 0.22-μm syringe filter. The filtrate was freeze-dried and the residue was redissolved in 2 mL of acetone. The resulting samples were evaporated to dryness under nitrogen and were derivatized with 200 μL BSTFA + TMCS at 60°C for 2 hr and diluted to 1 mL with ethyl acetate. Aliquots (2 μL) of the silylated samples were injected into an Agilent 7890A gas chromatograph (GC) coupled with an Agilent 5975C mass spectrometer (MS) (USA) for chemical structural elucidation. An HP-5MS column (30 m × 0.25 mm × 0.25 μm, Agilent) was used for separation. The inlet temperature was 250°C, and the detector temperature was 325°C. The column temperature was fixed at 80°C for 1 min, then programmed to 150°C at 7°C/min and held for 5 min, then from 150 to 200°C with the same rate, the final temperature was maintained for 5 min. The flow rate of the carrier gas (helium) was 1.0 mL/min. The temperatures of transfer line, ion source, and MS detector were 170, 230, and 150°C, respectively. The MS detector was operated in EI mode at 70 eV and the mass spectra were acquired in the full scan mode with *m/z* ranging from 40 to 600.

The formation anions formate, acetate and nitrate was verified using an ICS-2000 iron chromatography (Dionex, USA) with an IonPac AS 19 anion column (4.0 × 250 mm, Dionex) and a 10 mmol/L KOH eluent at a flow rate of 1.0 mL/min.

2 Results and discussion

2.1 Efficacy of ACTM removal by ZVAl/H⁺/air system

In the absence of ZVAl, ACTM remained stable in the acidic solutions. However, ACTM concentration steadily decreased as the reaction proceeded when ZVAl was added into the acidic solutions (Fig. 2). For instance, nearly all ACTM (> 99%) was removed in 16 hr by a ZVAl/H⁺/air system containing 2.0 mg/L of ZVAl. Higher ZVAl loadings apparently enhanced the removal. The removal percentages of ACTM in 16 hr were 14.5%, 74.0%, and 99.8% for reaction solutions initially containing 0.5, 1.0 and 2.0 g/L ZVAl, respectively (Fig. 2). As described above, hydroxyl radicals, the actual oxidant for the decomposition of ACTM, were generated via direct electron transfer from the ZVAl surface to H_2O_2 in the ZVAl/H⁺/air system. Therefore, the enhanced ACTM removal with higher aluminum loadings may be attributable to both the increase of hydrogen peroxide produced from aluminum corrosion and the total surface area of the metal.

The removal of ACTM was obviously dependent on the solution pH (Fig. 3). In the pH range 1.5–3.5, ACTM removal decreased with increasing pH_i, suggesting that acidic conditions facilitated ACTM removal. For example, ACTM removal at 16 hr was decreased from 99% for solutions with pH_i 1.5 to 46% for those with pH_i 2.5. No appreciable degradation was observed in 16 hr when pH_i was further increased to 3.5. The oxidative potential of ZVAl toward other organic compounds such as 4-chlorophenol (Bokare and Choi, 2009) and bisphenol A (Liu et al., 2011), was also found to be pH-dependent. Both ZAVl-induced H_2O_2 production Reaction (1) and the following reaction Reaction (2) are highly favored under acidic conditions. First, pH governs the corrosion of ZVAl which induces the generation of H_2O_2. On the other hand, the neutralization of OH^- produced by Reaction (2) with H^+ facilitates the formation of HO·. However, ACTM
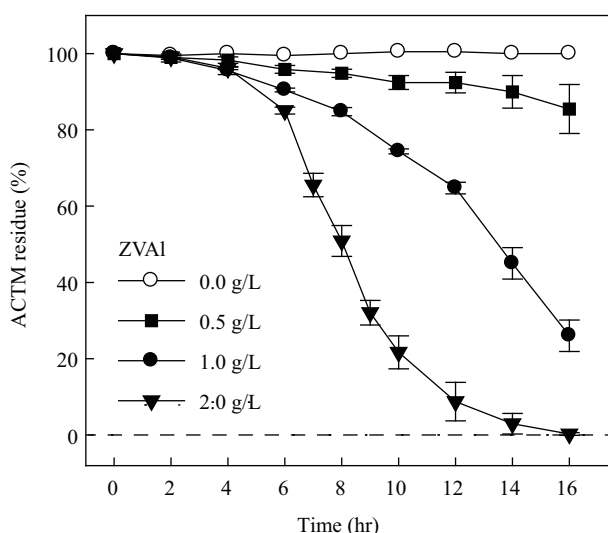

Fig. 2　Effect of initial aluminum loading on acetaminophen (ACTM) removal at 25 ± 1°C in pH 1.5 reaction solutions initially containing 2.0 mg/L ACTM. Data for aluminum-free treatment were from single measurement, while the other data points are means ± standard deviations (n = 3).
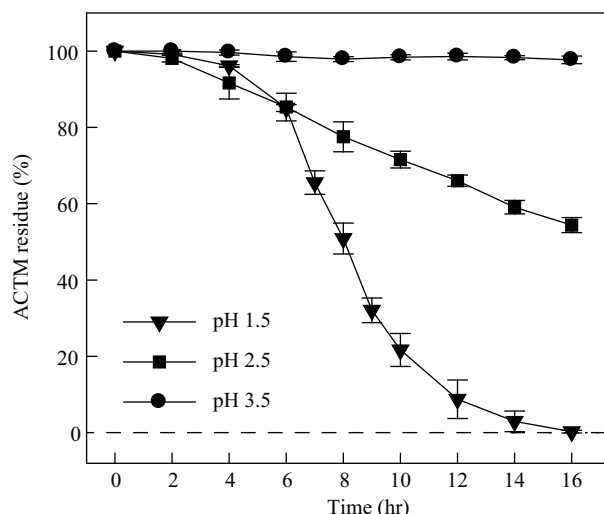

Fig. 3　Effect of pH on ACTM removal in reaction solutions initially containing 2.0 mg/L ACTM and 2.0 g/L aluminum at 25 ± 1°C. Data points are given as means ± standard deviations (n = 3).

remained fairly stable in the whole reaction period in pH 3.5 solutions. The similar result was also observed in our previous study (Liu et al., 2011). The possible reason is that both H_2O_2 generation and HO· formation consumed H^+. Therefore, ZVAl/H⁺/air system is more effective under pH < 3.5 acidic conditions.

2.2 Removal of ACTM by iron-enhanced ZVAl/H⁺/air system

It is well known that Fe^{2+} is highly active to decompose H_2O_2, generating hydroxyl radicals as Reaction (3) (Walling, 1975).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + HO\cdot \qquad (3)$$
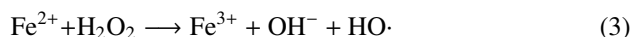
Similar to our previous study (Liu et al., 2011), Fe^{2+} at μmol/L level dramatically accelerated the removal of ACTM (Fig. 4a). For example, the time for complete removal of ACTM was reduced from 16 hr for solutions without Fe^{2+} to 5 hr for those with 100 μmol/L Fe^{2+}. It can be speculated that the primarily pathway of HO· formation in a ZVAl/H⁺/air system fortified with Fe^{2+} was largely replaced by a more efficient way of Fenton reaction, which was more efficient than the electrons transfer from aluminum surface.

Similarly, Fe^{3+} displayed comparatively capacity in accelerating the removal of ACTM in ZVAl/H⁺/air system. For instance, the time for complete removal of ACTM was shortened from 16 hr for solutions without Fe^{3+} to 3 hr for solutions with 100 μmol/L Fe^{3+} (Fig. 4b). A suite of reactions may occur as Fe^{3+} was added into ZVAl/H⁺/air system. For example, Fe^{3+} may be reduced to Fe^{2+} or even to Fe^0 by aluminum. On the other hand, H_2O_2 generated in ZVAl/H⁺/air system may complex with Fe^{3+} forming a $Fe\text{-}OOH^{2+}$ (Reaction (4)), which tends to decompose into Fe^{2+} and HOO· (Reaction (5)).

$$Fe^{3+} + H_2O_2 \longrightarrow Fe\text{-}OOH^{2+} + H^+ \qquad (4)$$

$$Fe\text{-}OOH^{2+} \longrightarrow Fe^{2+} + HOO\cdot \qquad (5)$$
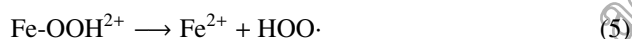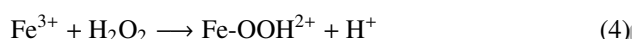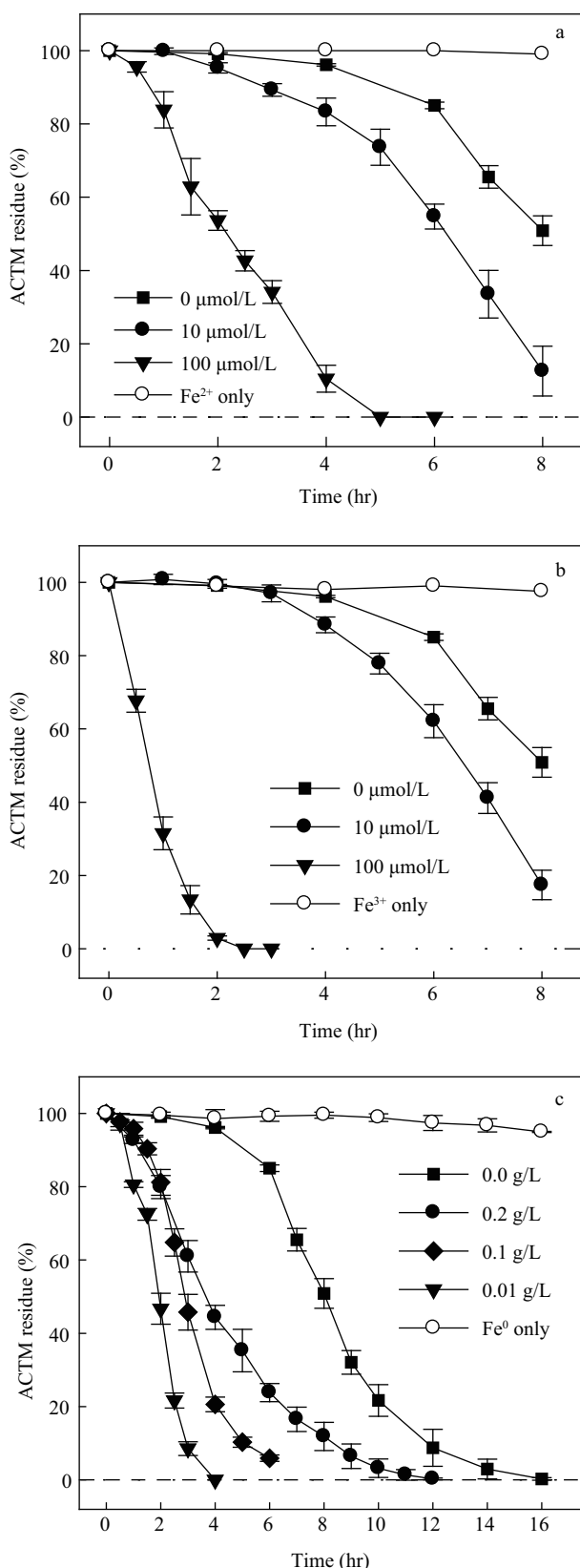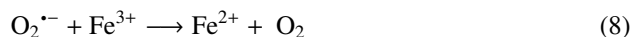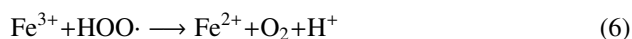
Fig. 4 Effect of Fe^{2+} (a), Fe^{3+} (b) and Fe^0 (c) on ACTM removal in pH 1.5 reaction solutions initially containing 2.0 mg/L ACTM and 2.0 g/L aluminum at $(25 \pm 1)°C$. Data for Fe^{2+}-only and Fe^{3+}-only treatment were from single measurement, while the other data points were means $\pm$ standard deviations ($n = 3$).

Besides, the generated radicals such as HOO· and $O_2^{•-}$ also participate in the speciation of Fe^{3+} as Reactions (6)–(8) (Walling, 1975).

$$Fe^{3+} + HOO· \longrightarrow Fe^{2+} + O_2 + H^+ \qquad (6)$$

$$HO_2· \longrightarrow H^+ + O_2^{•-} \qquad (7)$$

$$O_2^{•-} + Fe^{3+} \longrightarrow Fe^{2+} + O_2 \qquad (8)$$

All these factors could promote the reaction of ACTM with Fe^{3+}-fortified ZVAl/H^+/air system.

In addition, zero valent iron also greatly improved the removal of ACTM in ZVAl/H^+/air system. As shown in Fig. 4c, ACTM removal achieved >90% in only 3 and 5 hr when the solutions were fortified with 0.01 and 0.1 g/L iron, respectively. Although zero valent iron-acid system may also generate HO· to oxidize ACTM, the removal efficiency was relatively low and no significant ACTM was removed in 16 hr. Therefore, ACTM removal in Fe-fortified ZVAl/H^+/air system mainly resulted from HO· generated from ZVAl/H^+/air system. Iron accelerated the removal mainly through its transformation to Fe^{2+} in the acidic solution, which subsequently triggered Fenton reaction. It is worth mentioning that the stimulative effect did not increased when iron loadings were increased from 0.01 to 0.1 and 0.2 g/L. A plausible explanation for this result may be attributable to the fact that the reduction of Fe consumed H^+, which resulted in the increase of solution pH.

2.3 Reaction products and suggested scheme

The reaction intermediates or products were identified through GC-MS or ion chromatography (IC) analysis. In the early oxidation stages (8 hr), GC-MS analysis showed that hydroquinone was the main intermediate in the reaction solution (Fig. 5). Based on the total ion chromatogram in GC-MS analysis at 8, 12, and 24 hr (data not shown), hydroquinone concentrations were found to decrease as the reaction proceeded, suggesting that the intermediate was further oxidized to other products. In addition, ion chromatography (IC) analysis (data not shown) verified the formation anions acetate, formate and nitrate. On the basis of the identified products, a possible reaction scheme is given in Fig. 6. Generally, hydroxylation was considered as the primary initial step for the oxidation of ACTM by hydroxyl radical (Andreozzi et al., 2003; Zhang et al., 2008). It was demonstrated that HO· tends to attack the *ortho-* or *meta*-position with respect to the –OH group in ACTM (Zhang et al., 2008; Yang et al., 2009). However, none of such products was detected in this study. Only hydroquinone was found in the reaction solution, indicating that the reaction of HO· with ACTM mainly occurred at the *para*-position and formed hydroquinone by releasing acetamide (Fig. 6). The intermediate hydroquinone may be subjected to further oxidation by HO·, leading to ring cleavages and yielding carboxylate acid and finally carbon dioxide (Scheck and Frimmel, 1995; Zhang et al., 2008; Yang et al., 2009). On the other hand, the intermediate acetamide may also undergo HO· oxidation forming acetate acid, formic acid NH_4^+ and NO_3^- (pathways (b) in Fig. 6). Although oxamic acid was reported to be a possible HO· oxidation product of acetamide (Leitner et
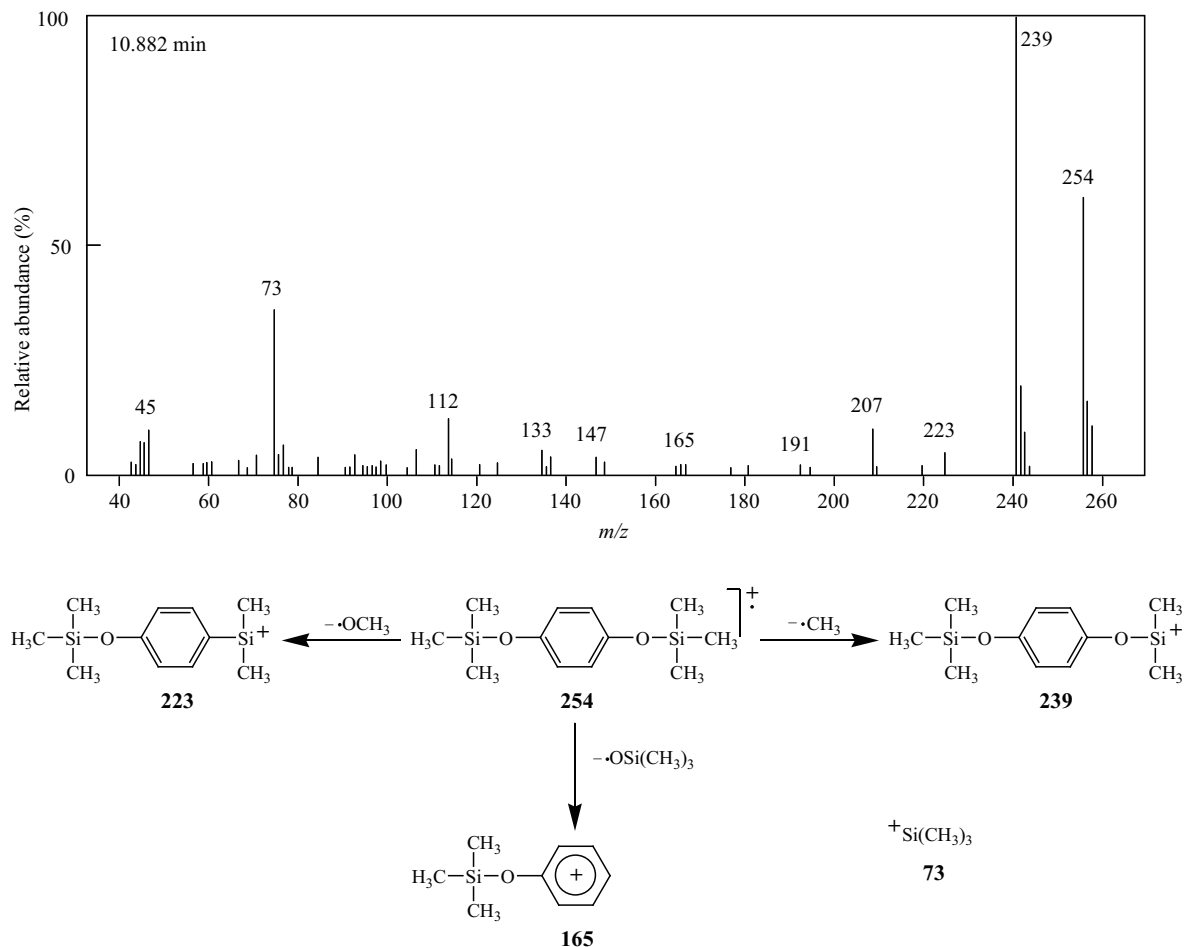
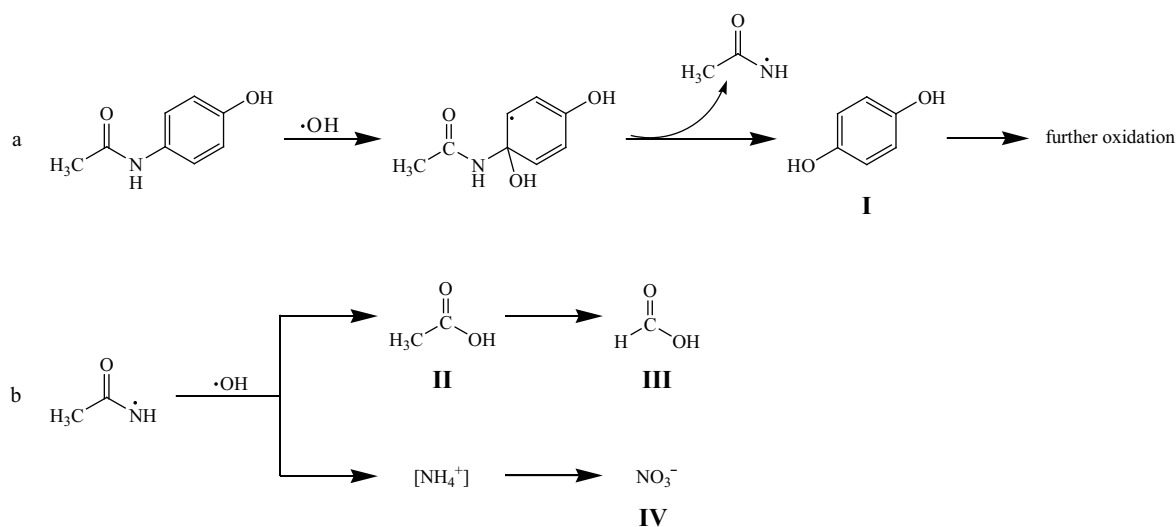**Fig. 5** Mass spectra and ion fragment of the identified intermediate hydroquinone.

Fig. 6 Proposed reaction scheme for the oxidation of acetaminophen by ZVAl/H$^+$/air system. The symbols of I–IV represent formation intermediates or products.

al., 2002), it was not detected in this study.

3 Conclusions

This study demonstrated that ZVAl/H$^+$/air system under pH < 3.5 acidic conditions possesses a high capacity in removing aqueous ACTM. The addition of different iron species Fe^0, Fe^{2+} and Fe^{3+} into ZVAl/H$^+$/air system dra-

matically accelerated ACTM removal. This work suggests that iron-enhanced ZVAl/H$^+$/air system may be potentially employed to treat ACTM-contaminated water.

2011R10075).

References

An J, Zhou Q X, Sun F H, Zhang L, 2009. Ecotoxicological effects of paracetamol on seed germination and seedling development of wheat (*Triticum aestivum* L.). *Journal of Hazardous Materials*, 169(1-3): 751–757.

Andreozzi R, Caprio V, Marotta R, Vogna D, 2003. Paracetamol *oxidation* from aqueous solutions by means of ozonation and H_2O_2/UV system. *Water Research*, 37(5): 993–1004.

Bokare A D, Choi W, 2009. Zero-valent aluminum for oxidative degradation of aqueous organic pollutants. *Environmental Science and Technology*, 43(18): 7130–7135.

Kim S D, Cho J, Kim I S, Vanderford B J, Snyder S A, 2007. Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water Research*, 41(5): 1013–1021.

Klamerth N, Malato S, Maldonado M I, Agüera A, Fernández-Alba A R, 2010a. Application of photo-Fenton as a tertiary treatment of emerging contaminants in municipal wastewater. *Environmental Science and Technology*, 44(5): 1792–1798.

Klamerth N, Rizzo L, Malato S, Maldonado M I, Agüera A, Fernández-Alba A R, 2010b. Degradation of fifteen emerging contaminants at μg L^{-1} initial concentrations by mild solar photo-Fenton in MWTP effluents. *Water Research*, 44(2): 545–554.

Kolpin D W, Furlong E T, Meyer M T, Thurman E M, Zaugg S D, Barber L B et al., 2002. Response to comment on "Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance". *Environmental Science and Technology*, 36(18): 4007–4008.

Leitner N K V, Berger P, Legube B, 2002. Oxidation of amino groups by hydroxyl radicals in relation to the oxidation degree of the α-carbon. *Environmental Science and Technology*, 36(14): 3083–3089.

Lin A Y C, Tsai Y T, 2009. Occurrence of pharmaceuticals in Taiwan's surface waters: Impact of waste streams from hospitals and pharmaceutical production facilities. *Science of the Total Environment*, 407(12): 3793–3802.

Liu W P, Zhang H H, Cao B P, Lin K D, Gan J, 2011. Oxidative removal of bisphenol A using zero valent aluminum-acid system. *Water Research*, 45(4): 1872–1878.

Nikolaou A, Meric S, Fatta D, 2007. Occurrence patterns of pharmaceuticals in water and wastewater environments. *Analytical and Bioanalytical Chemistry*, 387(4): 1225–1234.

Rosal R, Rodríguez A, Perdigón-Melón J A, Petre A, García-Calvo E, Gómez M J et al., 2010. Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. *Water Research*, 44(2): 578–588.

Santos J L, Aparicio I, Callejón M, Alonso E, 2009. Occurrence of pharmaceutically active compounds during 1-year period in wastewaters from four wastewater treatment plants in Seville (Spain). *Journal of Hazardous Materials*, 164(2-3): 1509–1516.

Scheck C K, Frimmel F H, 1995. Degradation of phenol and salicylic acid by ultraviolet radiation/hydrogen peroxide/oxygen. *Water Research*, 29(10): 2346–2352.

Sebastine I M, Wakeman R J, 2003. Consumption and environmental hazards of pharmaceutical substances in the UK. *Process Safety and Environmental Protection*, 81(B4): 229–235.

Sim W J, Lee J W, Oh J E, 2010. Occurrence and fate of pharmaceuticals in wastewater treatment plants and rivers in Korea. *Environmental Pollution*, 158(5): 1938–1947.

Walling C, 1975. Fenton's reagent revisited. *Accounts of Chemical Research*, 8(4): 125–131.

Yang L M, Yu L E, Ray M B, 2008. Degradation of paracetamol in aqueous solutions by TiO_2 photocatalysis. *Water Research*, 42(13): 3480–3488.

Yang L M, Yu L E, Ray M B, 2009. Photocatalytic oxidation of paracetamol: Dominant reactants, intermediates, and reaction mechanisms. *Environmental Science and Technology*, 43(2): 460–465.

Zhang X, Wu F, Wu X W, Chen P Y, Deng N S, 2008. Photodegradation of acetaminophen in TiO_2 suspended solution. *Journal of Hazardous Materials*, 157(2-3): 300–307.