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Influencing factors and degradation products of antipyrine chlorination in water with free chlorine

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Abstract

Owing to its low cost, free chlorine is one of the most common disinfectants for wastewater and drinking water treatment. However, the formation of disinfection byproducts has been found to occur after free chlorine disinfection in recent decades. Antipyrine (ANT), an anti-inflammatory analgesic, has been frequently detected in the aquatic environment. In this work, the removal efficiency of ANT by free chlorine oxidation in ultrapure water was investigated with batch experiments. The influencing factors on the removal of ANT were explored at initial concentrations of ANT from 0.04 to 0.64 mg/L, free chlorine dosage from 0.30 to 1.31 mg/L, and pH from 1.5 to 9.0. The main degradation products were identified by solid phase extraction-gas chromatography-mass spectrometry. The results showed that ANT reacted rapidly with free chlorine in ultrapure water systems and up to 90.6% removal efficiency of ANT was achieved after 25 sec (initial free chlorine 1 mg/L, ANT 0.5 mg/L, pH 7.0). Higher oxidant dosage, lower ANT initial concentration and low pH favor the ANT removal. The main degradation product in ANT chlorination was a monochlorine substitution product (4-chloro-1,2-dihydro-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one), which can be further chlorinated by free chlorine. In addition, the total organic carbon result indicated that ANT is difficult to be mineralized using chlorine.

Key words: antipyrine; chlorination; disinfection byproduct

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Introduction

Richardson and Bowron (1985) first confirmed that micropollutants (e.g., pharmaceutical and personal care products (PPCPs), endocrine disruptors (EDs)) from domestic, industrial and medicinal applications are present at trace level (μg/L–ng/L) in the effluents of wastewater treatment plants (WWTPs). Since then, PPCPs have been frequently reported in effluents and sludge from WWTPs, as well as in surface water, ground water, and even in drinking water, across the world (Kim et al., 2007; Sui et al., 2010; Ternes 1998; Vieno et al., 2007; Wang et al., 2010; Watkinson et al., 2009). In view of the increase of PPCPs' species and usage and their persistence in aquatic environments, the potential risk of PPCPs to the ecosystem and human health cannot be ignored.

Due to the widely varying types and physical-chemical properties of these compounds, conventional drinking water treatment methods (coagulation/flocculation, filtration and disinfection) cannot effectively remove all the PPCPs. Many studies have documented that the removal efficiency of PPCPs by coagulation, flocculation and filtration processes is poor, and the removal capacity is related to physical-chemical properties of compounds, such as hydrophilicity (Kim et al., 2007; Kosma et al., 2010; Simazaki et al., 2008; Vieno et al., 2007). By comparison, disinfection processes (e.g., Cl_2, ClO_2, O_3) are more favorable for the removal of PPCPs (Kosma et al., 2010; Simazaki et al., 2008; Vieno et al., 2007).

As a low-cost disinfectant, free chlorine is the most-used chemical oxidant in drinking water and wastewater disinfection (Gibs et al., 2007; Glassmeyer and Shoemaker, 2005; Lee and von Gunten, 2010; Sharma, 2008). Free available chlorine (FAC) in water includes hypochlorous acid (HOCl) and hypochlorite (OCl^-). FAC can react with micropollutants (e.g., NOM, PPCPs, EDCs) to form uncharacterized chlorinated byproducts during the disinfection process (Acero et al., 2010; Bedner and MacCrehan, 2006; Dodd and Huang, 2004, 2007; Dodd et al., 2005; Li et al., 2011; Shah et al., 2006; Xagoraraki et al., 2008). Some investigations reported the transformation of certain PPCPs and found that some products have biotoxicity (e.g., acetaminophen) (Bedner and MacCrehan,

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2006; Chamberlain and Adams, 2006; Dodd and Huang, 2004, 2007; Dodd et al., 2005; Li et al., 2011; Shah et al., 2006). But there are still many PPCPs that need to be investigated concerning their fate in the process of disinfection.

Antipyrine (ANT) is a kind of anti-inflammatory analgesic, belonging to the category of non-prescription drugs, which is applied extensively in clinics to relieve headache, fever, and general pain. It has toxicity towards lungs and mucosas, leading to target organ damage for long-term exposure. According to investigations, ANT and its metabolites were measured at up to the μg/L level in municipal sewage effluents, ground water and drinking water in the northwestern districts of Berlin, Germany (2.5–0.05 μg/L) (Reddersen et al., 2002; Wiegel et al., 2004; Zuehlke et al., 2004, 2007). In China, Yu et al. (2010) also found that the concentration of ANT in drinking water plant influent was 1.34–2.22 ng/L. In addition, Ternes (1998) observed relatively low removal efficiency of ANT (33%) in WWTPs with preliminary and final clarification and aeration, and a significant percentage of this compound is thus able to reach receiving natural waters. Zuehlke et al. (2007) also determined a removal efficiency of 89% for ANT in a drinking water plant (aeration and filtration). Therefore, ANT is commonly present in environments and cannot be removed completely after general water and wastewater treatments. Some oxidation technologies have good removal efficiency for ANT, such as ClO_2, ozone, and UV (Huber et al., 2005; Rivas et al., 2011a, 2011b). However, the removal of ANT in disinfection processes is still not clear.

In the present study, the removal efficiency of ANT by FAC oxidation was determined. The influencing factors including initial ANT concentration, oxidant dosage and pH during chlorination were investigated. In addition, the main products of ANT from its reaction with FAC were identified.

1 Materials and methods

1.1 Materials

ANT with purity > 99% was obtained from WAKO (Japan). A stock solution of ANT (50 mg/L) was prepared using ultrapure water after dissolution in 1 mL methanol, and then was protected from light and stored at 4°C. Sodium hypochlorite solution (NaOCl) was purchased from Sigma-Aldrich at 13% available chlorine concentration. All other reagents ($Na_2S_2O_3$, NaOH, H_2SO_4, Na_2SO_4, phosphate, etc.) were analytical reagents or better and used without further purification. Methanol and acetonitrile were HPLC grade (Fisher Scientific). Dichloromethane was pesticide grade (DUKSAN). All solutions were prepared using ultrapure water (18 MΩ·cm) from a Water Purification System (ELGA Purelab Classic, Veolia).

1.2 Analytical methods

ANT was analyzed by a Rapid Resolution Liquid Chromatography system (RRLC 1260, Agilent, USA) which included a Quatpump, automatic liquid sampler, thermoregulation column compartment and variable wavelength UV detector. A sample volume of 5 μL was injected onto a Poroshell 120 EC-C18 column (4.6×50 mm 2.7 Micron, Agilent, USA). The column was maintained at 30°C with a flow rate of 1.0 mL/min. The composition of the mobile phase was 10% acetonitrile, 5% methanol and 85% acetic acid (0.02 vol.%, pH 4). ANT was detected at 242 nm with an isocratic flow for 10 min. The limit of quantitation for ANT was approximately 5 ng/L.

Free chlorine stock solution was prepared at 100 mg/L Cl_2 and quantified by the DPD (N,N-diethyl-p-phenylenediamine, Sigma-Aldrich, > 99%) colorimetric method. Identification of chlorinated products was carried out using an Agilent 7890 gas chromatograph (GC) with an Agilent 5975C MSD mass spectrometer (MS) (Agilent, USA). The capillary column was a DB-5ms (30 m × 0.25 mm × 0.25 μm film thickness, 5% phenyl methylpolysiloxane, Agilent, USA). The sample (1 μL) was injected into the GC/MS in splitless mode at an inlet temperature 280°C, using helium (99.999%) as the carrier gas which maintained at a constant flow rate of 0.8 mL/min. The column temperature was programmed as follows: from 80°C (20 min) to 300°C (1 min) at 3.5°C/min. The MS interface temperature was kept at 300°C. The MS ion source and quadrupole temperatures were set at 230 and 150°C, respectively. Qualitative analysis was carried out using SCAN mode with the National Institute of Standards and Technology (NIST) mass spectral data library.

1.3 Chlorination experiments in ultra-pure water

Batch experiments were conducted in 250-mL amber borosilicate bottles with glass stoppers under continuous magnetic stirring at room temperature (25 ± 0.5°C). ANT solution (10 mg/L) was prepared by diluting stock solution (50 mg/L) using ultrapure water. The methanol concentration of each experiment was less than 0.05 vol.% and should have a negligible impact on the oxidation of ANT (Dodd et al., 2005). pH was controlled by using 0.05 mol/L phosphate and 0.25 mol/L acetate buffer, and NaOH and H_2SO_4 were used to adjust the pH of the buffer solution to the desired values. The sample pH did not vary by more than 0.05 at the initial and final point of each experiment. In addition, experiments without oxidant to assess the potential acid- and base-catalyzed hydrolysis of ANT showed only 5.5% loss of ANT in 528 hr confirmed that the hydrolysis of ANT is extraordinarily weak and can be considered to be negligible over a wide pH range (1.5–9.0).

The volume of reaction solution for each experiment was 150 mL. The reaction time was 30 min. Each sample (2 mL) was obtained at constant time intervals,

and quenched with 0.1 mL sodium thiosulfate (0.3 g/L). The residual concentration of ANT was analyzed by RRLC/UV.

The effects of the initial concentrations of ANT (0.04–0.64 mg/L), chlorine dosage (0.30–1.31 mg/L), and pH (1.5–9.0) on the removal efficiency of ANT were investigated. All experiments were conducted in duplicates or triplicates, and the averaged data are presented.

1.4 Products identification

ANT (50 mg/L) was added to phosphate buffer (0.05 mol/L, pH 7.0) to achieve starting concentrations of 1 mg/L in 500 mL volume. After adding FAC, 5 g/L sodium thiosulfate (1.5 mL) was used to quench the reaction at different reaction times for each sample (0, 10 sec, 60 sec, 10 min, 30 min, 1 hr, 4 hr and 8 hr). Samples (500 mL) for products identification were pre-concentrated by solid-phase extraction equipment (Mediwax 12-ports Vacuum SPE manifold) at a speed of 3 to 5 mL/min. Oasis HLB SPE cartridges (500 mg, 6 mL, Waters, USA) were conditioned with 2×5 mL methanol and 2×5 mL ultrapure water prior to use. After loading samples and washing with 3 mL ultrapure water, the cartridges were flushed with air for 10 min and eluted using 4×2 mL methanol. The eluents were evaporated under a gentle nitrogen stream until complete dryness, dehydrated by anhydrous sodium sulfate and then dissolved in 0.5 mL dichloromethane. Final extracts were filtered through a 0.45 μm membrane filter, transferred into 2 mL amber glass vials and analyzed by GC/MS.

Total organic carbon (TOC) over 21 hr of reaction time was analyzed to confirm whether FAC can mineralize ANT or not, using a Shimadzu TOC-V analyzer (Japan). UV-Vis spectroscopic scans by an evolution 300 UV-Vis spectrophotometer (Thermo, USA) and RRLC/UV were also used as a supplementary tool to illustrate the changes of ANT in chlorination.

2 Results and discussion

2.1 Effects of initial ANT concentration on ANT chlorination

Figure 1a shows a good removal efficiency of ANT (> 85%) by FAC oxidation in around 4 min (25 ± 0.5°C, pH 7.0, initial chlorine 0.52 ± 0.02 mg/L). Moreover, the residual ANT declined with decreasing initial ANT concentration at constant oxidant dosage, pH and temperature. Using pseudo first-order kinetics (Dodd and Huang, 2004, 2007; Dodd et al., 2005; Shah et al., 2006) to plot the natural logarithm of the normalized concentration versus time, the results show good correlation coefficients (**Fig. 1b**), $R^2 > 0.96$ in all the experiments except the case of 0.64 mg/L initial ANT concentration because of the shortage of free chlorine (data not shown in **Fig. 1b**). Therefore, under an excess of FAC, ANT chlorination exhibited a pseudo first-order dependence on the concentration of ANT. Meanwhile, pseudo first-order reaction rate constants (k_{obs}, sec^{-1}) of ANT with chlorine under these conditions also can be determined from the absolute value of the slope (**Fig. 1b**). The rate constant increased from 0.018 sec^{-1} (initial ANT 0.44 mg/L) to 0.049 sec^{-1} (initial ANT 0.04 mg/L).

2.2 Effects of chlorine dosage

As shown in **Fig. 2a** and **Table 1**, with increasing chlorine dosages from 0.30 to 1.31 mg/L, the removal rates were enhanced from 42% to 95% in 25 sec. Moreover, the

Table 1 k_{obs} at different chlorine dosages

Chlorine dosage (mg/L)	k_{obs} (sec^{-1})	R^2
0.57	0.018	0.9651
0.82	0.059	0.9956
1.01	0.097	0.9964
1.31	0.121	0.9966

Experimental condition: 25.0 ± 0.5°C, pH 7.0, initial ANT concentration 0.45 ± 0.02 mg/L.

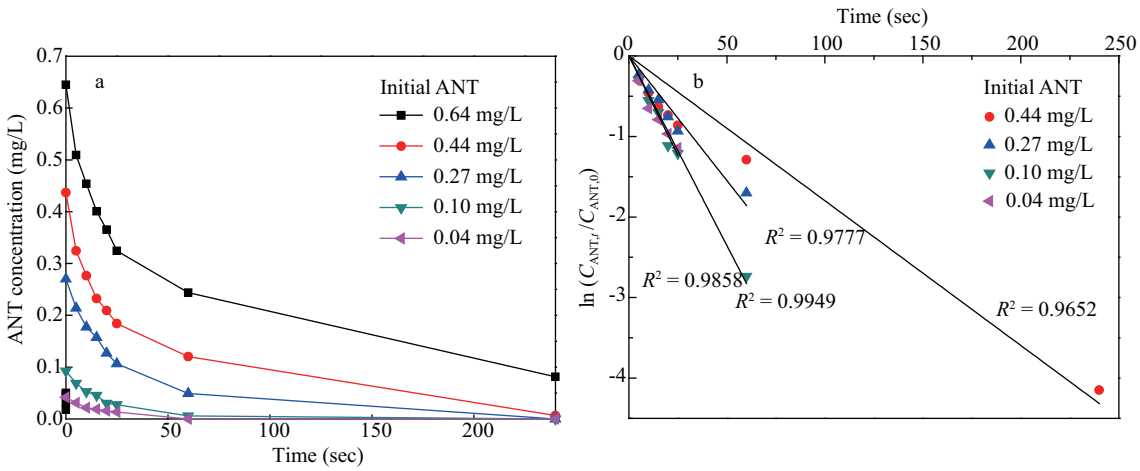


Fig. 1 ANT chlorination at different initial ANT concentrations. (a) ANT removal efficiency; (b) Pseudo first-order kinetic plot. Experimental condition: 25.0 ± 0.5°C, pH 7.0, chlorine dosage 0.52 ± 0.02 mg/L.

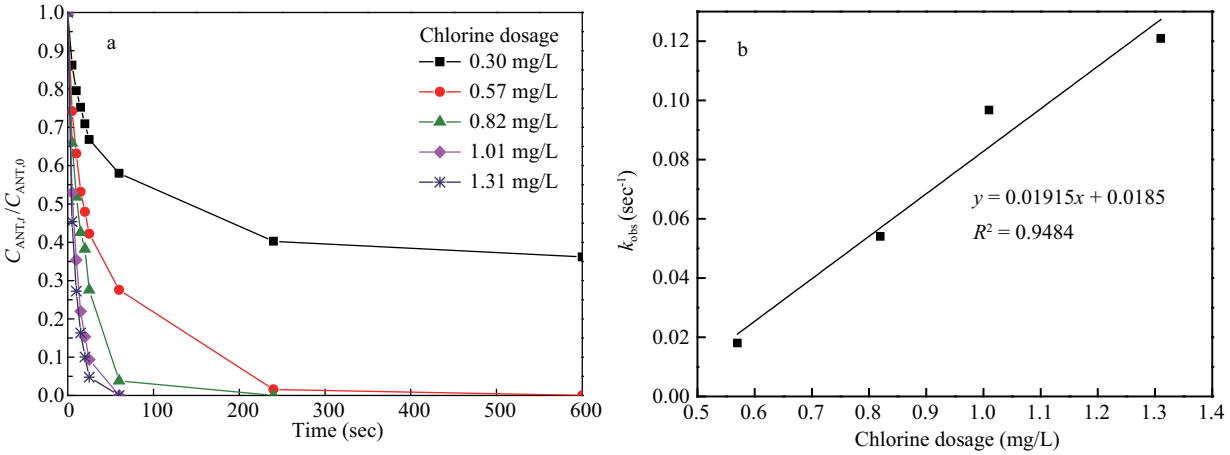


Fig. 2 ANT chlorination at different chlorine dosages. (a) removal efficiency; (b) effect on k_{obs}. Experimental condition: 25.0 ± 0.5°C, pH 7.0, initial ANT concentration 0.45 ± 0.02 mg/L.

effects of chlorine dosage on the extent of ANT elimination (0.45 mg/L) at pH 7.0 were positive. This indicates that the chlorine dosage applied in WWTPs (5–20 mg/L) and drinking water plants (0.5–2.0 mg/L) can remove ANT effectively in a short time (Glassmeyer and Shoemaker, 2005; Acero et al., 2010). As shown in **Table 1**, k_{obs} positively correlated with chlorine dosage (Deborde et al., 2004) and increased from 0.018 sec^{-1} (chlorine 0.57 mg/L) to 0.121 sec^{-1} (chlorine1.31 mg/L). The linear correlation between k_{obs} and initial chlorine dosage was confirmed from **Fig. 2b** with $R^2 = 0.9484$.

2.3 Effects of pH

Lower pH is favorable to the removal of ANT. Removal rates of ANT were higher than 98% at pH < 7.0, while only up to 72 % and 29% in 4 min at pH 8.0 and 9.0, respectively (data not shown). **Table 2** shows that k_{obs} decreased two orders of magnitude as pH increase. The results indicated that reactions between ANT and FAC were fast and ANT was more readily transformed by FAC at pH < 7.0.

Figure 3 shows the variation tendency of k_{obs} over the pH range 1.5–9.0. The k_{obs} decreased slowly with pH increasing from 5.0 to 9.0, while at pH < 4.5 k_{obs} decreased sharply. These trends can be attributed to the varying importance of specific reactions amongst the individual acid-base species of ANT and FAC. FAC may be present as HOCl or as OCl^- with an associated $pK_{a,HOCl}$ of 7.5 (Chamberlain and Adams, 2006; Wang et al., 2011) at 25°C (Reaction (1)) and ANT has two species, cationic ANT (ANT^+) and neutral ANT, with $pK_{a,ANT}$ of 1.4

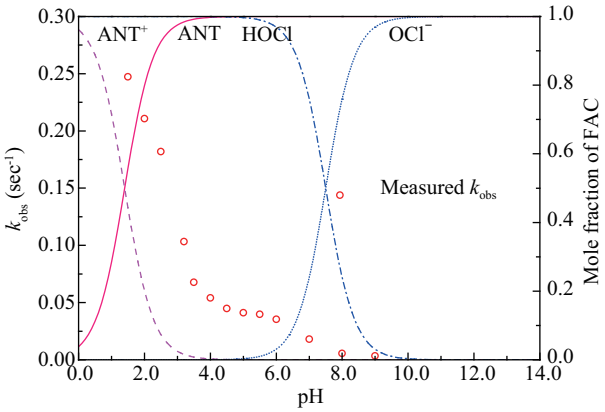


Fig. 3 Influence of pH on k_{obs} and FAC mole fraction. Experimental condition: 25.0 ± 0.5°C, chlorine dosage 0.51 ± 0.03 mg/L, ANT 0.45 ± 0.04 mg/L.

(Rimmer et al., 1986; Staiger et al., 1980; Taylor and Blaschke, 1984) (Reaction (2)).

$$HOCl \overset{K_{a,HOCl}}{\longleftrightarrow} H^+ + OCl^- \quad (1)$$

$$ANT^+ \overset{K_{a,ANT}}{\longleftrightarrow} ANT + H^+ \quad (2)$$

The distribution coefficient of cationic ANT species is less than 10^{-4} at pH 6.0–9.0 and neutral ANT is the main species undergoing oxidation (**Fig. 3**). Meanwhile, the HOCl distribution coefficient decreases from 0.96 (pH

Table 2 k_{obs} at different pH levels

pH	k_{obs} (sec^{-1})	R^2	pH	k_{obs} (sec^{-1})	R^2	pH	k_{obs} (sec^{-1})	R^2
1.5	0.247	0.9996	4.0	0.054	0.9977	6.0	0.035	0.9773
2.0	0.211	0.9995	4.5	0.044	0.9938	7.0	0.018	0.9652
2.5	0.187	0.9975	5.0	0.041	0.9931	8.0	0.006	0.9543
3.2	0.103	0.9989	5.5	0.040	0.9839	9.0	0.003	0.9992
3.5	0.068	0.9986						

Experimental condition: 25.0 ± 0.5°C, chlorine dosage 0.51 ± 0.03 mg/L, ANT 0.45 ± 0.04 mg/L.

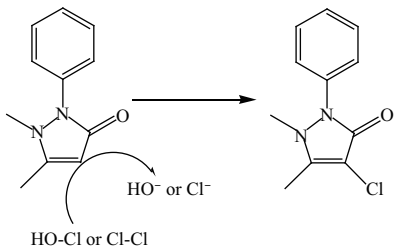
6.0) to 0.024 (pH 9.0). However, lower reactivity can be obtained at pH more than 8.0, and it can be inferred that the possibility of reaction between OCl^- and ANT is very small. Therefore, in these conditions, ANT chlorination may be mainly the reaction of ANT with HOCl. When pH < 4.5, the OCl^- distribution coefficient (< 0.0013) is small enough to be neglected. Besides the potential reaction of ANT and ANT^+ with HOCl, the rapid increase of k_{obs} could be explained by the form of Cl_2 (Reactions (3)) and high reactivity between Cl_2 and PPCPs has been reported (Acero et al., 2010; Deborde et al., 2004; Rebenne et al., 1996).

$$HOCl + Cl^- + H^+ \overset{K_1}{\longleftrightarrow} Cl_2 + H_2O \quad (3)$$

2.4 Products identification in ANT chlorination

Products from ANT chlorination were investigated by GC/MS at 1.0 mg/L chlorine dosage, pH 7.0. The total ion chromatograms (TICs) of mass spectra (**Fig. 4**) at different reaction times showed that a main product (m/z 222) was formed in chlorination at 55.6 min. Sampling at the triggering of the reaction was missed because of the rapid chlorination of ANT, and the TIC at 0 sec slightly lagged behind the beginning of reaction.

Matching with the NIST library, the product at m/z 222 was identified as a monochlorine substitution product (4-chloro-1,2-dihydro-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one) with 66% probability (**Fig. 5**). As a two-electron electrophile, FAC can react with some electron-rich organic moieties, and mainly results in substitution and addition reactions (Lee and von Gunten, 2010). In the process of ANT chlorination, free chlorine can attack ANT to bring about halogenation (Reaction (4)). As shown in **Fig. 4**, the peak area of the m/z 222 product increased with time at first, and then decreased. This indicated that the m/z 222 product was further chlorinated by FAC and is a main intermediate in the ANT chlorination reaction.



(4)

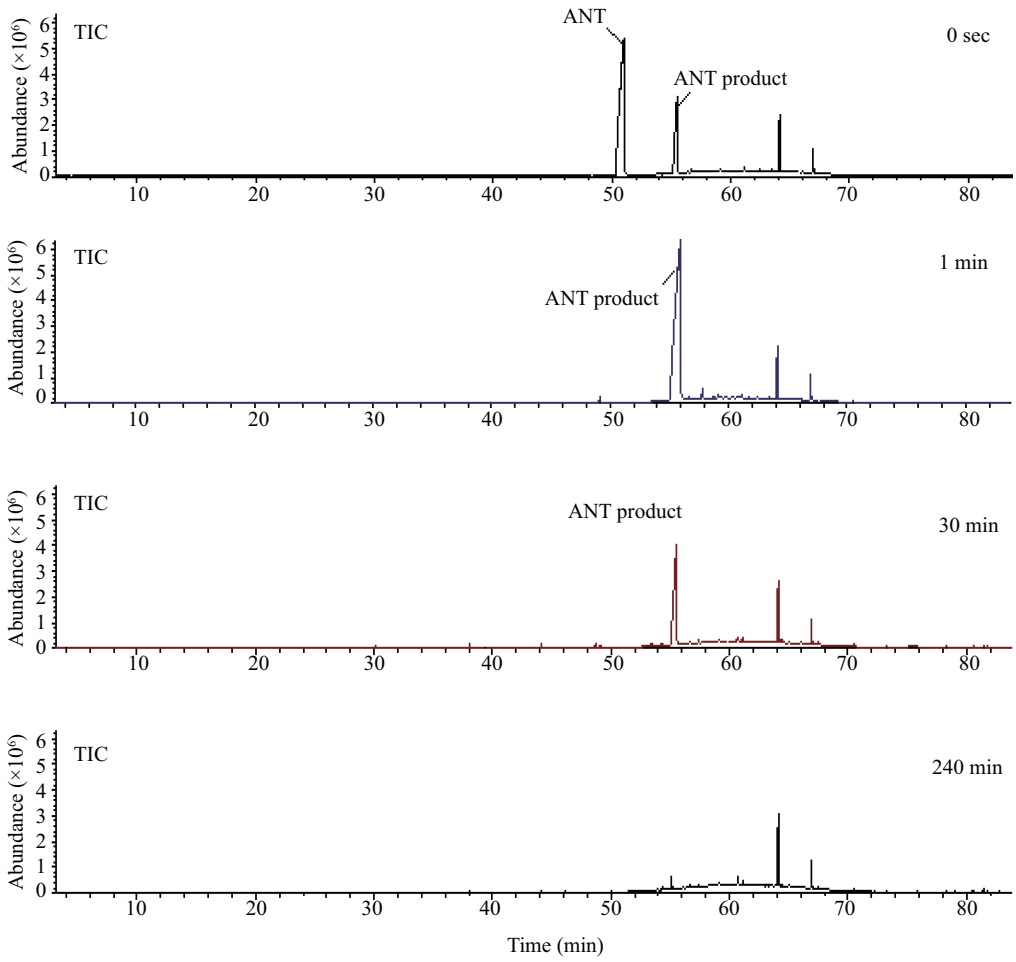


Fig. 4 Total ion chromatograms (TIC) of ANT chlorination at different reaction time (0 sec, 1 min, 30 min, 240 min).

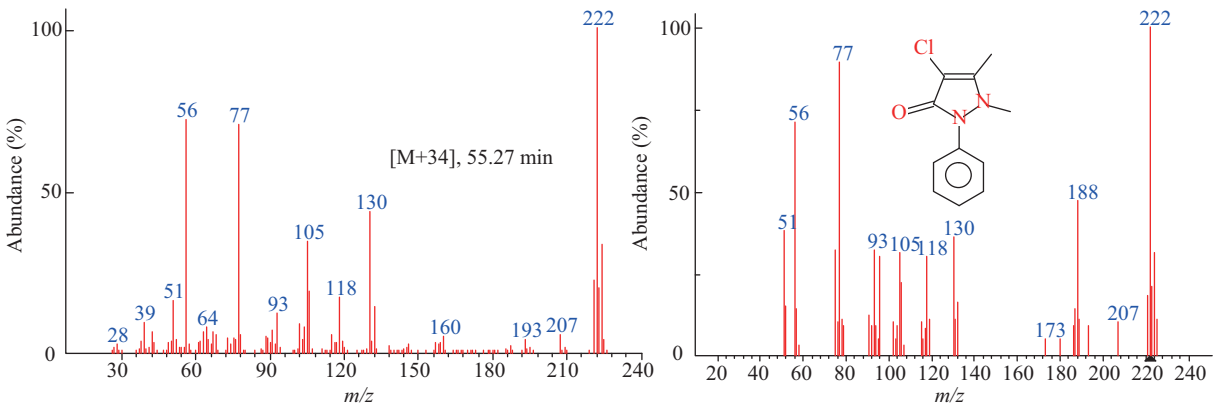


Fig. 5 Mass spectrogram of byproduct (m/z 222) and the reference standard from NIST.

The variation of TOC over 21 hr reaction was less than 0.4% (data not shown). It can be inferred that FAC is transforming ANT into other compounds instead of mineralizing ANT due to the lower oxidation-reduction potential of free chlorine. From the result of UV-Vis spectroscopy scans over 190 to 600 nm (**Fig. 6a**), the absorption in the range from 250 to 280 nm was notably weakened with reaction time while the absorption band from 300 to 390 nm appeared and was enhanced with time. The peak around 250–280 nm at 0 sec suggests that there exist chromogenesis groups, including conjugations of phenyl and between carbonyl and double bonds of carbon. The intensity of this peak diminished with time and a new peak over 300–390 nm appeared. This indicates that a chlorine substitution reaction occurs in ANT chlorination, and creates a stronger conjugation between carbonyl and double bonds of carbon because hydrogen atoms are replaced by chlorine atoms as auxochromic groups.

The samples over 21 hr reaction were also analyzed by RRLC/UV and the chromatograms at 242 nm show that ANT transformed into some unknown compounds, and one of them is the main intermediate (ANT byproduct 1, **Fig. 6b**) which was identified via qualitative analysis by GC/MS. **Figure 6b** further illustrates that ANT byproduct 1 was a main intermediate, and byproducts 2, 3 were also intermediates. After 8 hr of reaction, the generated amount of all byproducts was close to constant on account of the limitation of residual oxidant. It is difficult to determine whether byproducts 4, 5 were intermediates or not. Identification of all products and the specific pathway of chlorination require further investigation.

3 Conclusions

This investigation shows ANT can be removed effectively by free available chlorine oxidation and exhibits rapid reactivity with free chlorine in an ultrapure water system. As might be expected, the removal efficiency of ANT increases with decreasing initial ANT concentration and increasing chlorine dosage. Moreover, low pH is favorable for increasing the ANT removal efficiency and k_{obs}. With the increase in pH, k_{obs} decreases to 0.034 sec^{-1} (pH 9.0) from 0.247 sec^{-1} (pH 1.5). The main intermediate product of ANT in chlorination is identified as a chlorine substitution product by GC/MS, which can be further chlorinated by free chlorine. Moreover, ANT was found to be difficult to be mineralized by chlorine with TOC analysis.

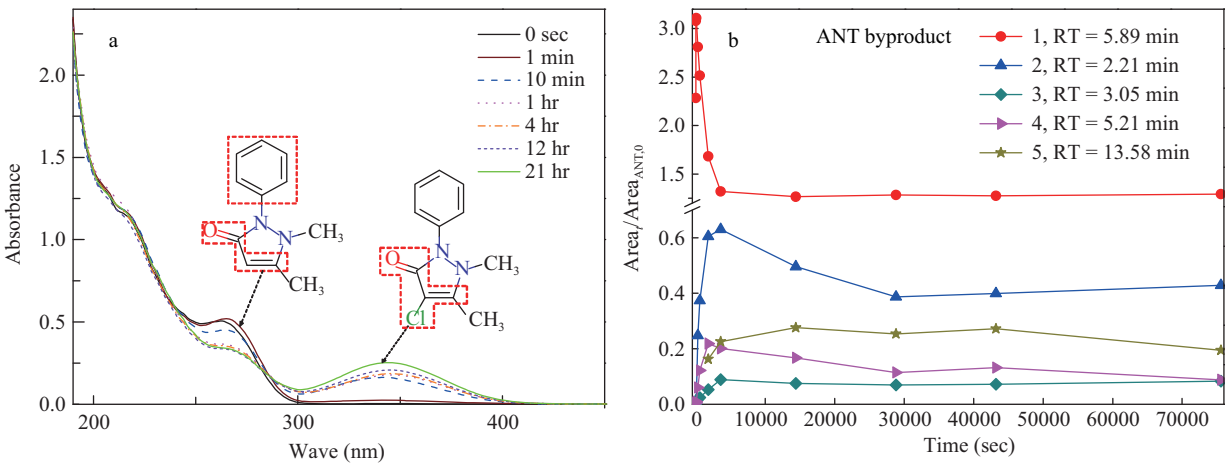


Fig. 6 UV-Vis spectroscopy of ANT chlorination (a) and product transformation of chlorination ANT (b) over 21 hr reaction. Experimental condition: 25.0 ± 0.5°C, initial ANT concentration 10 mg/L, chlorine dosage 10 mg/L, pH 7.0.

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