Fenton degradation of Cartap hydrochloride: identification of the main intermediates and the degradation pathway
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ABSTRACT
The advanced oxidation of Cartap hydrochloride (Cartap) promoted by the Fenton system in an aqueous medium was investigated. Based on total organic carbon, chemical oxygen demand and high-performance liquid chromatography, the oxidation of Cartap is quite efficient by the Fenton system. Its long chain is easily destroyed, but the reaction does not proceed to complete mineralization. Ion chromatography detection indicated the formation of acetic acid, propionic acid, formic acid, nitrous acid and sulfuric acid in the reaction mixtures. Further evidence of nitrogen monoxide and sulfur dioxide formation was obtained by using a flue gas analyzer. Monitoring by gas chromatograph-mass spectrometer demonstrated the formation of oxalic acid, ethanol, carbon dioxide, and L-alanine ethylamide. Based on these experimental results, plausible degradation pathways for Cartap mineralization in an aqueous medium by the Fenton system are proposed.

Key words | Cartap hydrochloride, degradation pathway, Fenton oxidation, intermediates

INTRODUCTION
The presence of organic pollutants in the environment is an issue that is receiving increasing attention worldwide (Sarathy et al. 2009). The main source of discharge of these compounds into the environment is from sewage treatment plants.

Cartap hydrochloride (Cartap, S,S’-(2-dimethylaminotrimethylene) bis(thiocarbamate) CAS# 15263-53-3) is a nereistoxin derivative that has been widely used as a pesticide in agriculture since it was first introduced in Japan in 1964 (Ray 1991; Tomlin 2000). Cartap is widely used for controlling Lepidoptera, Hemiptera, Coleoptera and Orthoptera insect pests, and rice insect pests, such as Plutella xylostella, the rice stem borer, rice shell pests and leafhoppers. In the Mekong Delta, Vietnam, Cartap comprises 19% of the insecticide usage in rice and rice–fish farms (Berg 2001). In China and Japan, it is also one of the most frequently used pesticides for controlling insect pests. Therefore, Cartap is an important pesticide in agriculture and cannot be replaced at present.

A large amount of wastewater is produced during the process of Cartap production, i.e., mixing, cyaniding, alcoholysis and desolventizing, and the concentration of poisonous and harmful substances is high. Therefore, Cartap wastewater may present serious health hazards to humans and animals. A study reported that a patient ingested Cartap and subsequently developed multiple symptoms and finally died (Kurisaki et al. 2010). It is therefore necessary to reduce the concentration of Cartap in aqueous environments. Currently, national and international studies on Cartap are mainly focused on crop and soil residue contamination (Wu et al. 2011), insect resistance, resistance mechanisms (Siqueira et al. 2000), inheritance of resistance (Cheng et al. 2000) and toxicological studies of organisms (Zhou et al. 2009), but they hardly study Cartap wastewater treatment. Successful application of an advanced oxidation process (AOP) has been reported for the degradation of Cartap wastewater (Choi et al. 2004), but the degradation mechanism of Cartap is still not clear. To the best of our knowledge, there have been few reports indicating the oxidative degradation of Cartap. Considering the extensive application of Cartap, it is very easy to cause environmental pollution and hazardous accidents during usage. To avoid further accumulation of Cartap compounds in aquatic environments, and to destroy these contaminants in water, it is necessary to perform degradation studies of Cartap.
In recent years, the application of AOPs has been gaining attention. Different groups of pharmaceutical compounds have been treated with AOPs, and the results show its suitability for organic pollutants (Oller et al. 2011). An important AOP is Fenton oxidation, which is a mixture of hydrogen peroxide and ferrous iron (Fe²⁺). Compared with other oxidation techniques (Lin & Leu 1999; Rao & Chu 2008), Fenton oxidation is relatively inexpensive because of the instantaneous availability of hydrogen peroxide and the abundance of iron (Canizares et al. 2008). In contrast, its operation is simple, and it possesses a strong oxidizing ability (Kang & Hwang 2000). Fenton oxidation has been successfully applied to the treatment of recalcitrant contaminants, such as aromatic amines, aromatic hydrocarbons, phenols, pesticides and nuclear waste wastewater (Nam et al. 2001; Kavitha & Palanivelu 2004). Fan and Tsui demonstrated the effective removal of Parathion via the Fenton process in a neutral environment (Fan et al. 2014). In studies by Chen et al. (2007) and Martín et al. (2009), the Fenton process was utilized as a pretreatment technology, which is beneficial to subsequent treatments.

Our group has verified that Fenton oxidation is an economical and effective option to treat Cartap wastewater (Ming et al. 2017); now we are carrying out a further study of the degradation mechanism. In this study, we use Cartap as a probe, and many methods to investigate its degradation intermediates. According to the intermediates, the plausible degradation pathway in the Fenton system was deduced to more completely understand the Cartap degradation process.

**EXPERIMENT**

**Materials and reagents**

Cartap hydrochloride (Figure 1) was obtained from the Hunan Haohua Chemical Co., Ltd (Hunan, China). The FeSO₄·7H₂O, sodium hydroxide, 1,10-phenanthroline monohydrate, ferrous ammonium sulfate, silver sulfate, sodium carbonate, acetonitrile and sodium sulfate were purchased from Tianjin, China. The FeCl₂·4H₂O, H₂O₂ (30%), mercury(II) sulfate, dichloromethane, formic acid, acetic acid, propionic acid, sodium nitrite and 0.22-μm cellulose membranes were purchased from Guangdong Xilong Chemical Factory, Guangdong, China. Sulfuric acid and hydrochloric acid were purchased from Hunan Kaixin Chemical Reagent Co., Hunan, China. Sodium 1-heptanesulfonate was purchased from Shanghai Zhenpin Chemical Co., Shanghai, China. All of these reagents are analytically pure, and the acetonitrile is chromatographically pure. Ultrapure water (>18 MΩ) was used throughout.

**Instruments**

The following instruments were used: a gas chromatograph-mass spectrometer (GC–MS, QP2010 Plus, Shimadzu, Kyoto, Japan), an ion chromatograph (IC, Anhui Wanyi Technology Co., Anhui, China), a total organic carbon (TOC) analyzer (TOC-L series, Shimadzu, Kyoto, Japan), a flue gas analyzer (Testo 340 ECO, SET 1, Testo, Germany), a constant temperature oscillator (ZD-85A, Jiangsu Changzhou Ruipin Precision Instrument Co., Jiangsu, China), a versatile refrigerated centrifuge (CT15RT, Jiangsu Changzhou Ruipin Precision Instrument Co., Shanghai, China) and a watertight portable CyberScan pH (300/310, Eutech/Oakton, Vernon Hills, IL, USA).

**Fenton oxidation experiments**

In these experiments, 100 mL of artificial Cartap wastewater was used every time. The Cartap concentration was 720 mg/L and the wastewater quality was chemical oxygen demand (COD) 676.8 mg/L, biochemical oxygen demand (BOD₅) 50.5 mg/L, total organic carbon (TOC) 215 mg/L. Based on our previous research, the optimum conditions of degradation in the Fenton system were determined to be 1 g FeSO₄·7H₂O + 4 mL H₂O₂, pH 3, bed rotation speed 160 r/min, and reacting for 60 min at 25 °C. This unit was configured with a beaker flask reactor (250 mL); samples were intermittently collected to monitor the progress of the reaction using different analytical techniques. Before IC analysis, all reaction mixtures were filtered through 0.22-μm cellulose membranes. The aqueous mixture was extracted twice with water saturated butyl alcohol or dichloromethane, and the extraction liquid was consolidated. The solvent was dried with anhydrous sodium sulfate for subsequent analysis by GC–MS.

**Figure 1** The structure of Cartap hydrochloride.
Analytical methods

In the determination of Cartap, intermediate compounds were analyzed by TOC, COD, IC, Testo340 flue gas analyzer and GC–MS. The TOC studies were performed under the following conditions: the oxygen pressure was 0.2 MPa, the electric furnace temperature was 680 °C, and the air pressure was 200 kPa. The IC studies were performed on an anionic column (250 × 4.6 mm i.d., dp = 5 m). The eluting agent was an Na2CO3 solution with a concentration of 0.3816 g/L and a flow rate of 0.8 mL/min. The oven temperature was 50 °C, the suppressor was 40 mA, and the conductivity cell temperature was 45 °C. High-performance liquid chromatography (HPLC) analyses were performed using a ZORBAX SB-C18 column, 150 × 4.6 mm, 0.25-mm film thickness. According to GB 22612-2008 (The National Standards of the People’s Republic of China), the HPLC detection condition of Cartap is as follows: the mobile phase was a mixture of a 90% aqueous solution (3.64 g sodium 1-heptanesulfonate + 900 mL ultrapure water + 16 mL phosphoric acid + triethylamine to reach pH 2) and 10% methanol, and the flow rate was 1.0 mL/min. The column temperature was room temperature, the detection wavelength was 225 nm, the injection volume was 10 μL, and the retention time was 7.4 min. GC–MS analyses were performed on an HP-5 capillary column (Agilent), 30 m, 0.25-mm i.d., and 0.25-μm thick film using a split–splitless injector under the following conditions: injection volume 1 μL, injector temperature 280 °C, split flow 10 mL/min and split ratio 50. The helium carrier gas flow was 3 mL/min. The oven temperature program was 2.0 min at 60 °C and 5 °C/min to 230 °C (20 min). Electron impact mass spectra were monitored; the ion source and inlet line temperatures were set at 200 °C and 290 °C, respectively.

RESULTS AND DISCUSSION

COD and TOC studies

The experiment was performed to study the Fenton oxidation of Cartap in aqueous solutions (720 mg/L) with FeSO4·7H2O and H2O2. The reaction changes in the mixture were monitored by COD and TOC (Figure 2). HPLC was used to determine the concentration of Cartap and compare the Cartap degradations. The experimental HPLC results indicate that Cartap is oxidized into other organic species within 2 min; this result is due to the strong oxidizing ability of the Fenton system, and the long chain of Cartap is easily destroyed. However, the TOC and COD results show that the intermediate organic compounds are hard to degrade because they can remain in the solution for a long time; Figure 2 shows that the reaction does not achieve complete mineralization. When comparing COD, TOC and HPLC studies, because of Kapp (COD) = 0.045, Kapp (TOC) = 0.040 and Kapp (HPLC) ≈ 1, it is apparent that Cartap degrades much faster than the intermediate species. This result agrees with the previous literature reports (Moctezuma et al. 2012).

Degradation mechanisms

IC studies

Five intermediate ions were identified by IC. The results indicate that the peak eluting times at 6.327 min, 6.508 min, 7.615 min, 13.899 min and 26.527 min are the acetate ion, propionate ion, formic ion, nitrite ion and sulfate ion, respectively. In addition, the decrease of solution pH from 3 to 2.2 suggests the formation of ionic compounds (Chiron et al. 1998). Cartap degradation is similar to most other organic matter, which all form small molecule organic acid (Guivarch et al. 2005).

Figure 3 shows the time profile of Cartap degradation and the major intermediate ions detected by IC. The determination of the sulfate ion was substituted for ferrous chloride to eliminate the interference from ferrous sulfate. Cartap gradually degraded (substituted for TOC) via HO• radical attack, and the major intermediates simultaneously
formed and evolved. The degradation process of the five intermediates follows: they all increase during the early stages, and then begin to decrease until they completely disappear or remain stable. This phenomenon is due to the strong oxidizing ability of HO\(^{-}\): it can oxidize the amino group at the end of the Cartap chain into a nitro group. Some pharmaceutical compounds have degradation intermediates with similar structures to Cartap (Brillas \textit{et al.} 1998; Sires \textit{et al.} 2007). The nitro group subsequently forms nitrous acid, and the C-S chemical bond is destroyed to produce sulfuric acid in solution. The result is the production of sulfate ions and nitrite ions, which support the breaking of the sulfur–carbon and carbon–nitrogen chemical bonds as the predominant process during the initial stage; this result is in agreement with the result previously reported in the literature (Sakkas & Albanis 2003). The next carbonyl group oxidizes into carboxyl; the rest of the Cartap molecule is converted into acetic acid, propionic acid and formic acid. It can be observed from Figure 3 that formic acid changes markedly because Cartap decomposes rapidly to produce formic acid in the early stages. Acetic acid and propionic acid may be oxidized into formic acid and, then, under the action of volatility and mineralization, rapidly be reduced. The IC studies demonstrate that the long alkane chain is more easily degraded into small molecule organic acids.

\textbf{Testo 340 flue gas analyzer studies}

The experiment was performed in an enclosed beaker flask. There were some gases during the reaction. Therefore, to better investigate the process of Cartap degradation by Fenton oxidation, the released gases were detected using a Testo 340 flue gas analyzer. The species and concentration changes are shown in Figure 4. The expected intermediates, nitrogen monoxide and sulfur dioxide, were detected in the reaction process. These studies showed that Cartap rapidly liberates nitrogen monoxide and sulfur dioxide. Figure 4(a) shows that the oxygen concentration increased rapidly within 1 minute, followed by a rapid decrease to a stable concentration. This observation is due to the addition of hydrogen peroxide, which releases oxygen instantaneously; however, the formation of nitrogen monoxide and sulfur dioxide will consume oxygen, which causes the oxygen concentration to be reduced gradually. Figure 4(b) indicates that Cartap rapidly liberates nitrogen monoxide and sulfur dioxide, and the concentration of nitrogen monoxide reaches 0.3 ppm at 0.5 min, and the concentration of sulfur dioxide reaches its highest point of 22 ppm at 11 min.
GC–MS studies

The reaction intermediates were further examined by GC–MS based on the molecular ion measurement. Figure 5 shows the GC–MS chromatogram obtained from liquid–liquid extraction of Cartap solution after Fenton oxidation. The extraction conditions of two identifications follow: Figure 5(a) shows Cartap (7,200 mg/L) degradation products after 8 min using water saturated butyl alcohol for extraction, Figure 5(b) shows Cartap (720 mg/L) degradation products after 3 min using dichloromethane for extraction. The GC-MS analysis of the Fenton process of Cartap degradation shows the formation of several intermediate products. Figure 5 shows that the peaks eluting at 1.408 min, 1.517 min, 20.511 min and 30.950 min during GC–MS are oxalic acid, ethanol, carbon dioxide and L-alanine ethylamide with fit values of 76%, 96%, 99% and 93%, respectively. The volatilities of some intermediates are likely too small to be eluted out under the gas chromatographic conditions, and some compounds have
Figure 6 | The formation and evolution of the major intermediates of Cartap degradation by the Fenton system and possible pathways of the oxidation mechanism.
significant polarity such that the GC–MS cannot obtain all of the intermediates (Fan et al. 2009).

Formation and evolution of the degradation intermediates and degradation pathways

Based on the IC, flue gas analyzer and GC–MS analyses for the various process intermediates, a plausible degradation pathway for Cartap mineralization is proposed in Figure 6.

First, because Cartap is an ionic compound, the molecule of HCl is freely liberated into the solution, consequently Cartap changed into compound A in the solution. Amino oxidation into a nitro group forms substance B due to the action of HO•, followed by two nitro group eliminations to generate nitrous acid and the oxidation of the carbonyl group to generate compound C. Compound C is attacked by the HO• radicals at the C–S chemical bond, which leads to the formation of methanol, sulfur dioxide or sulfate ions, oxalic acid and compound D. In fact, the sulfate ion production pathway of C–S chemical bond destruction has been reported in the oxidation of the pesticide Thiram, which has a similar structure to Cartap with an S–C=O functional group attached to the long chain structure (Kaneco et al. 2009). Oxalic acid is cleaved to formic acid and carbon dioxide, and the intermediate D finally generates propanedioic acid and nitrous acid. The second route is for compound D to generate L-alanine ethylamide (H) from intermediates F and G, and a portion of the F and G intermediates may produce acetic acid and propionic acid. The HO• attack on the amino of L-alanine ethylamide (H) generates compound I, followed by -NO2 elimination and the formation of acetic acid and propionic acid.

CONCLUSIONS

HPLC studies indicated that the degradation of Cartap wastewater by the Fenton system is a highly efficient process. However, COD and TOC studies implied that the reaction does not reach complete mineralization. IC analysis of the reaction mixture at different reaction times indicated the formation of several intermediate compounds, such as acetic acid, propionic acid, formic acid, nitrous acid and sulfuric acid. The formation of nitrogen monoxide and sulfur dioxide was also supported by the flue gas analyzer. Furthermore, the GC–MS analysis further demonstrated the formation of oxalic acid, ethanol, carbon dioxide, and L-alanine ethylamide. Based on this experiment, the plausible degradation pathways for Cartap mineralization in an aqueous medium by the Fenton system are proposed.

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