



## Ametryn degradation by aqueous chlorine: Kinetics and reaction influences

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### ABSTRACT

The chemical oxidation of the herbicide ametryn was investigated by aqueous chlorination between pH 4 and 10 at a temperature of 25 °C. Ametryn was found to react very rapidly with aqueous chlorine. The reaction kinetics can be well described by a second-order kinetic model. The apparent second-order rate constants are greater than  $5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  under acidic and neutral conditions. The reaction proceeds much more slowly under alkaline conditions. The predominant reactions were found to be the reactions of HOCl with neutral ametryn and the charged ametryn, with rate constants equal to  $7.22 \times 10^2$  and  $1.58 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. The ametryn degradation rate increases with addition of bromide and decreases with addition of ammonia during the chlorination process. Based on elementary chemical reactions, a kinetic model of ametryn degradation by chlorination in the presence of bromide or ammonia ion was also developed. By employing this model, we estimate that the rate constants for the reactions of HOBr with neutral ametryn and charged ametryn were  $9.07 \times 10^3$  and  $3.54 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. These values are 10- to  $10^3$ -fold higher than those of HOCl, suggesting that the presence of bromine species during chlorination could significantly accelerate ametryn degradation.

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### 1. Introduction

In order to improve agricultural production by destroying pests and weeds, many different kinds of synthetic pesticides have been extensively applied in most countries. These include insecticides, larvacides, miticides, molluscides, nematocides, fumigants, fungicides, herbicides, defoliant, etc. [1]. In recent years, considerable attention has been focused on these chemicals because they have become ubiquitous environmental pollutants and show potential risk to human health due to their mutagenicity, toxicity and carcinogenicity [2,3]. Ametryn, also known as (2-ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine, is a selective methylthio-triazine herbicide widely used for the control of broadleaf and weeds in the cultivation of sugarcane, corn, citrus, pineapple, tea and other crops [4]. It tends to leach from the

soil both vertically and laterally with high persistence in the environment because of its relatively high water solubility (209 mg/L, 25 °C) [5–7]. Thus, this chemical shows wide occurrence in surface and ground waters [3,8,9]. Because these waters are often used as source of drinking water, it is necessary to identify the ultimate fate of this chemical.

Chlorination is used worldwide for pre-oxidation and finished water disinfection to eliminate microorganisms such as bacteria and viruses. However, chlorine is also a strong oxidant and may react with organics in water to form disinfection by-products such as trihalomethanes (THMs), haloacetic acids (HAAs), and other chlorine derivatives [11]. Due to potential carcinogenic activity, formation and control of THMs and HAAs have been investigated thoroughly in the last few decades. Some chlorine derivatives of organic contaminants are more toxic than their parent compounds, such as chlorinated bisphenol A (BPA) [12,13]. Recently, many studies have focused on chlorination of specific organic chemicals including phenols [14], endocrine disruptors [15–17], cyanobacteria-produced toxins [18], substituted dihydroxybenzenes [19] and antibacterials [20]. However, limited literature exists on chlorination kinetics of herbicides. Acero et al. [21] reported the chlorination of diuron and isoproturon with a second-order rate constant of less than  $0.45 \text{ M}^{-1} \text{ s}^{-1}$  at pH 5–9 and 20 °C. Addition of bromine during chlorination significantly increases the reaction

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rate, especially with isoproturon, but pH increase exerts a negative effect. Mascolo et al. [22] and Lopez et al. [23] investigated the oxidation of s-triazines (prometryne, terbutryne, ametryn and desmetryne) and isoproturon by sodium hypochlorite and chlorine dioxide. The main degradation products were identified and pathways for degradation were proposed. However, both studies were mainly concerned with the percentage oxidation and by-products identification for a given oxidant dose. Limited quantitative information on the reaction pathways and the kinetic parameters on chlorination of herbicides was reported. Such information is useful for predicting degradation during the water treatment process.

The objectives of this study were to (1) investigate the chlorination kinetics of ametryn over a wide range of pH conditions and calculate the rate constants in chlorination reactions, (2) develop a mechanistic kinetic model to describe the chlorination rate of ametryn in the presence of bromine and ammonia, and (3) examine the influence of temperature and thus calculate the reaction activation energy.

## 2. Experimental

### 2.1. Material and analysis

Ametryn (>99%) was obtained from Sigma–Aldrich (St. Louis, MO, USA) and used as received. NaOCl, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, NaBr, NH<sub>4</sub>Cl, phosphate, NaOH, and HCl were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) without further purification. Stock solutions of chlorine were prepared by diluting a commercial solution of NaOCl. Sodium hypochlorite was standardized by iodometry. All solutions were prepared with Milli-Q water.

A Shimadzu 2010 AHT high performance liquid chromatograph (HPLC) system (Kyoto, Japan) with an autosampler and a Shimadzu VP-ODS column (150 mm × 4.6 mm) was used to analyze ametryn. The mobile phase consisted of 80%/20% (v/v) acetonitrile (Fisher, Pittsburgh, PA, USA) and Milli-Q water at a flow rate of 0.80 mL/min. The injection volume was 10 μL and ametryn was detected by an UV detector at the wavelength of 220 nm. At least two replicates of each measurement were carried out and more replicates were executed in cases where the variation between the two measurements exceeded 5%.

Chlorine was analyzed by the *N,N*-diethyl-*p*-phenylenediamine (DPD) colorimetric method [24]. The pH was measured with a SenSion4 pH-meter (HACH, USA).

### 2.2. Experiments

All experiments were performed in a batch reactor at room temperature (25 ± 2 °C). The batch reactor consisted of a 500 mL bottle equipped with a dispenser. Typical experiments were initiated by adding an aliquot of a concentrated chlorine solution to the reactor containing buffered ametryn solution (1 mg/L, 4.40 μM in all cases). The solutions were buffered using 10 mM phosphate buffer for pH range 5–9. For pH < 5 and pH > 9, pH was adjusted with small volumes of H<sub>2</sub>SO<sub>4</sub> or NaOH solutions, respectively. Variation of solution pH during the experiments was negligible. At different reaction times, 3 mL of solution was rapidly transferred into a HPLC vial containing 100 μL Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (100 g/L) to quench the reaction. Samples were then analyzed by HPLC.

The kinetic experiments were carried out over a pH range between 4 and 10 and were monitored until more than 50% of ametryn degradation occurred. The effects of bromine and ammonia were evaluated under similar conditions with buffered ametryn solutions (4.40 μM, pH 7, phosphate buffer) and chlorinated using the same chlorine dose (28.2 μM Cl<sub>2</sub>). The temperature dependence

of the rate constant was determined at 10, 20, 25, and 30 °C in experiments performed at pH 7.

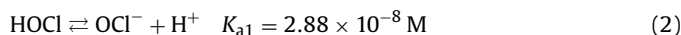
### 2.3. Kinetic modeling

The evolution of ametryn and other substances in the solution was simulated with Matlab 7.4.0 (R2007a). Optimization of the kinetic parameter values was conducted through non-linear least squares fitting of the experimental data using the function *nlinfit*. The simultaneous ordinary differential equations that result from the substitution of the rate equations were solved by function *ode45*. Function *nlparci* was employed to determine the 95% confidence interval of the estimated parameters.

## 3. Results and discussion

### 3.1. Effect of applied chlorine doses

Fig. 1 shows the impact of applied chlorine dose on ametryn degradation. Ametryn disappeared rapidly during chlorination and the removal rate increased steadily with chlorine dose as the total chlorine concentration was increased from 14.1 to 56.4 μM. It is well known that NaOCl rapidly hydrolyzes in water, forming hypochlorous acid (HOCl), hypochlorite (OCl<sup>-</sup>) and sodium ion (Na<sup>+</sup>) [10,25]:



The ratio between hypochlorous and hypochlorite depends on solution pH. HOCl is a strong oxidant with a high oxidation potential ( $E^0 = 1.44 \text{ V}$ ), while hypochlorite ion is generally a weak oxidant [10]. The increase in ametryn degradation with the applied chlorine dose is obviously caused by the presence of higher level of HClO in the reactor.

### 3.2. Effects of pH on ametryn chlorination

It has been reported that chlorination reactions of different types of organic chemicals generally follow second-order kinetics [14]. The overall reaction rate of ametryn degradation in chlorination can be expressed as

$$\frac{d[\text{Ametryn}]_T}{dt} = -k_{\text{app}}[\text{Ametryn}]_T[\text{HOCl}]_T \quad (3)$$

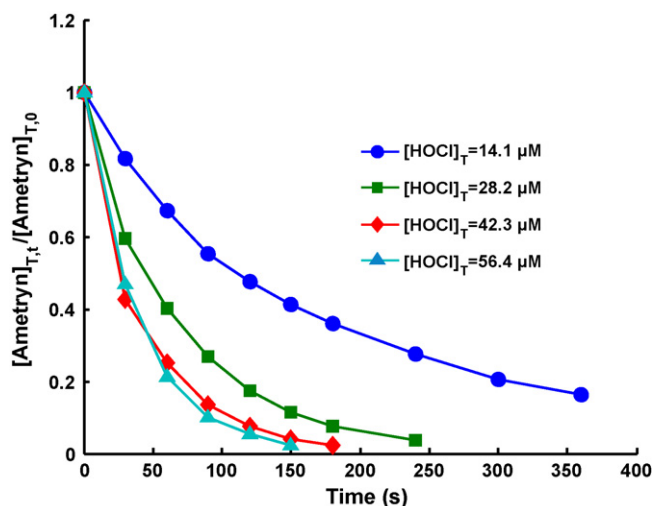


Fig. 1. Effect of applied chlorine doses on ametryn degradation in chlorination at 25 °C, pH 7, [Ametryn]<sub>T,0</sub> = 4.40 μM.

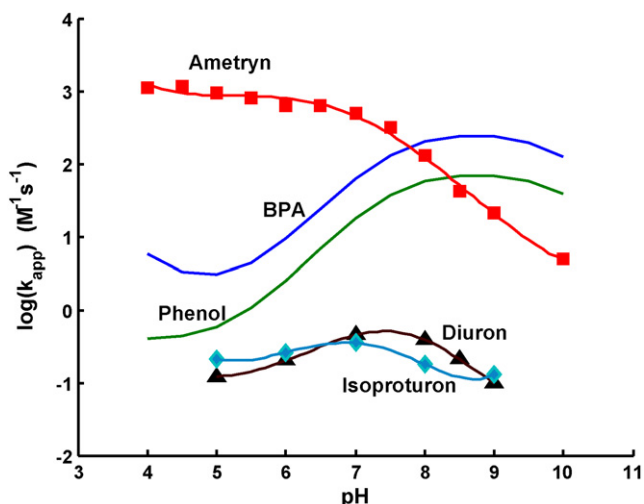


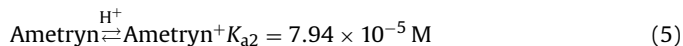
Fig. 2. Experimental pH dependence of the apparent second-order rate of ametryn degradation in chlorination. Phenol and BPA data were obtained from Gallard and Gunten [14] and Gallard et al. [16], respectively. Diuron and isoproturon data were obtained from Acero et al. [21].

$$[\text{HOCl}]_{\text{T}} = [\text{HOCl}] + [\text{OCl}^-] \quad (4)$$

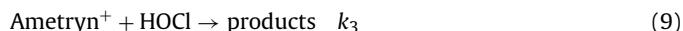
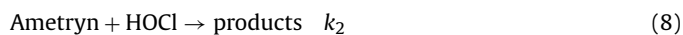
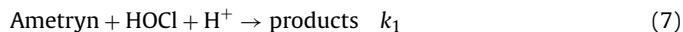
where  $k_{\text{app}}$  is the apparent second-order rate constant at specific pH and  $[\text{HOCl}]_{\text{T}}$  is the total concentration of chlorine species.

It is well documented that the dissociation reactions of chlorine and ionizable organic compounds are highly dependent on the solution pH [16,17,20]. Fig. 2 shows the pH dependence of  $k_{\text{app}}$  for ametryn chlorination. The  $k_{\text{app}}$  value decreased gradually as the solution pH increased from 4 to 10. This trend is quite different from the results observed during chlorination of BPA and phenols [14,16]. As shown in Fig. 2, chlorination rate of ametryn is about 1–3 orders of magnitude higher than those of BPA and phenol under acidic conditions, but 1–2 orders of magnitude lower under alkaline conditions. Compared with the herbicides diuron and isoproturon, ametryn shows significantly higher reactivity with chlorine. The major chemical reactions during ametryn degradation in chlorina-

tion include the following [18]:



$$[\text{Ametryn}]_{\text{T}} = [\text{Ametryn}] + [\text{Ametryn}^+] \quad (6)$$



Ametryn ( $\text{p}K_{a1} = 4.1$ ) exists almost entirely in the uncharged form under neutral and basic conditions [5]. No acid-catalyzed reaction occurred in chlorination as shown in Fig. 2, which is different from previous research on chlorination of phenols, endocrine disruptors and pharmaceuticals [14,16]. Thus, the variation of  $k_{\text{app}}$  under acid conditions can be attributed to the uncatalyzed reactions (8) and (9). Similarly, the decrease of  $k_{\text{app}}$  under neutral and basic conditions can be attributed to the conversion of HOCl to  $\text{OCl}^-$ , where the neutral ametryn predominates. The rate expression for pH-dependent ametryn chlorination can be written as

$$-\frac{d[\text{Ametryn}]_{\text{T}}}{dt} = k_1[\text{Ametryn}][\text{HOCl}][\text{H}^+] + k_2[\text{Ametryn}][\text{HOCl}] + k_3[\text{Ametryn}^+][\text{HOCl}] \quad (10)$$

After replacing  $[\text{HOCl}]$ ,  $[\text{Ametryn}]$ , and  $[\text{Ametryn}^+]$  with the respective expression as the ratio of  $[\text{HOCl}]_{\text{T}}$  or  $[\text{Ametryn}]_{\text{T}}$ ,  $\alpha_1 = [\text{H}^+]/(K_{a1} + [\text{H}^+])$  for  $[\text{HOCl}]$  and  $\beta_1 = K_{a2}/([\text{H}^+] + K_{a2})$  for  $[\text{Ametryn}]$ , the rate of ametryn disappearance becomes:

$$-\frac{d[\text{Ametryn}]_{\text{T}}}{dt} = \frac{(k_1 K_{a2} + k_3)[\text{H}^+]^2 + k_2 K_{a2}[\text{H}^+]}{[\text{H}^+]^2 + (K_{a1} + K_{a2})[\text{H}^+] + K_{a1} K_{a2}} [\text{Ametryn}]_{\text{T}} [\text{HOCl}]_{\text{T}} \quad (11)$$

Thus,

$$k_{\text{app}} = \frac{(k_1 K_{a2} + k_3)[\text{H}^+]^2 + k_2 K_{a2}[\text{H}^+]}{[\text{H}^+]^2 + (K_{a1} + K_{a2})[\text{H}^+] + K_{a1} K_{a2}} \quad (12)$$

Table 1  
Specific rate constant for the reaction of ametryn, BPA, phenol and trimethoprim.

Compounds	Chemical structures	$\text{p}K_{\text{a}}$	Rate constants ( $\text{M}^{-1} \text{s}^{-1}$ )		Reaction temp. ( $^{\circ}\text{C}$ )	Reference
			$k_2^{\text{a}}$	$k_3^{\text{b}}$		
Ametryn		4.1	$7.22(\pm 0.90) \times 10^2$	$1.58(\pm 0.34) \times 10^3$	25	Present study
BPA		9.6	1.84	$3.1 \times 10^4$	20	[16]
Phenol		9.99	$0.36(\pm 0.28)$	$2.19(\pm 0.08) \times 10^4$	23	[14]
Trimethoprim		3.2	$1.6(\pm 0.1) \times 10^2$	$6.0(\pm 1.4)$	25	[20]

<sup>a</sup>  $k_2$  refers to the reaction of specific compounds with HOCl.

<sup>b</sup>  $k_3$  refers to the reaction of charged species with HOCl.

Since the acid-catalyzed reaction is negligible, Eq. (12) can be further simplified to

$$k_{app} = \frac{k_3[H^+]^2 + k_2K_{a2}[H^+]}{[H^+]^2 + (K_{a1} + K_{a2})[H^+] + K_{a1}K_{a2}} \quad (13)$$

The individual rate constants  $k_2$  and  $k_3$  were determined by a non-linear least-square regression of the experimental  $k_{app}$  in Fig. 2. The values used for  $K_{a1}$  and  $K_{a2}$  were  $2.88 \times 10^{-8}$  M and  $7.94 \times 10^{-5}$  M, respectively [5,21]. The model fitted values of the rate constants are presented in Table 1. For comparison, the corresponding parameters of several other compounds are also listed. The value of  $k_2$  for ametryn is  $10^2$ – $10^3$  times higher than BPA and phenol while their  $k_3$  values are comparable. This result indicates that ametryn inclines to react with chlorine and exerts fast consumption of HOCl in chlorine during drinking water treatment compared to the other three compounds. In contrast to what happens to trimethoprim, it is observed that the rate constant  $k_3$  (reaction between HOCl and ametryn<sup>+</sup>) is about two times that of  $k_2$  (reaction between HOCl and ametryn). Protonation of ametryn leads to transfer more electron cloud towards –NH–C<sub>2</sub>H<sub>5</sub> group and thus weakens the CH<sub>3</sub>S–R interactions. As a result, ametryn<sup>+</sup> becomes more reactive than the neutral ametryn.

### 3.3. Effects of bromide on ametryn chlorination

In the water treatment process, hypobromous acid (HOBr) may be formed during chlorination when bromide is present. The reactivity of HOBr to organic compounds is much higher than that of HOCl, and thus the presence of bromide increases the yield and the formation rate of THMs during chlorination [17]. In our experiment, the effect of bromide on ametryn chlorination was investigated and a kinetic model based on the generally accepted elementary reactions was established to evaluate the rate constants for reaction of ametryn and HOBr. The results of ametryn chlorination in the presence of bromide at different concentrations are shown in Fig. 3. As expected, the introduction of bromide significantly increased the removal rate of ametryn.

The following chemical reactions occurred during ametryn chlorination in the presence of bromide:

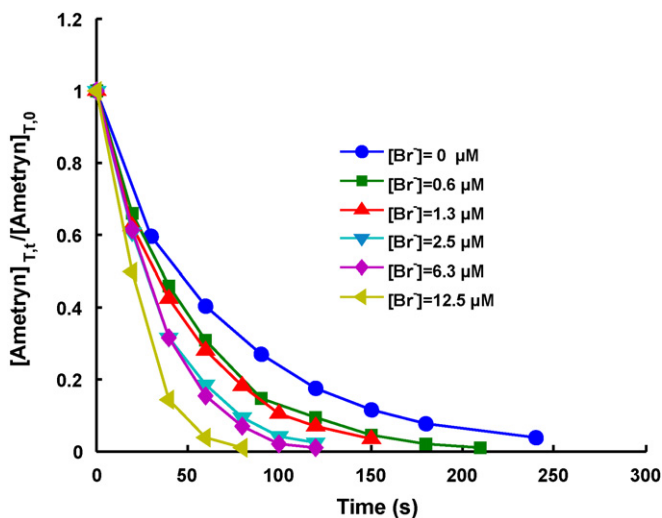
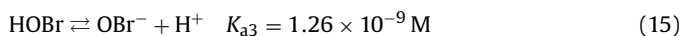
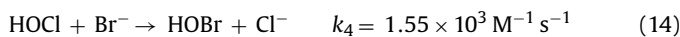
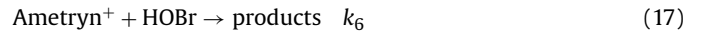
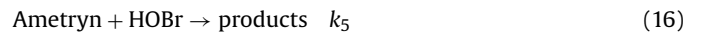


Fig. 3. Effect of Br<sup>-</sup> on ametryn degradation in chlorination, where pH 7, [HOCl]<sub>T,0</sub> = 28.2 μM and [Ametryn]<sub>T,0</sub> = 4.40 μM.



Under neutral conditions, the rate expressions for HOCl, HOBr, ametryn and Br<sup>-</sup> can be written as

$$\gamma_1 = \frac{[H^+]}{K_{a3} + [H^+]} \quad (18)$$

$$\frac{d[HOCl]_T}{dt} = -k_4\alpha_1[Br^-][HOCl]_T - k_2\alpha_1\beta_1[HOCl]_T[Ametryn]_T - k_3\alpha_1(1 - \beta_1)[HOCl]_T[Ametryn]_T \quad (19)$$

$$\frac{d[HOBr]_T}{dt} = k_4\alpha_1[Br^-][HOCl]_T - k_5\gamma_1\beta_1[HOBr]_T[Ametryn]_T - k_6\gamma_1(1 - \beta_1)[HOBr]_T[Ametryn]_T \quad (20)$$

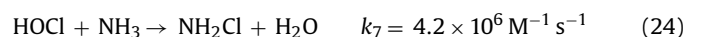
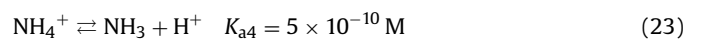
$$\frac{d[Ametryn]_T}{dt} = -k_2\alpha_1\beta_1[HOCl]_T[Ametryn]_T - k_3\alpha_1(1 - \beta_1)[HOCl]_T[Ametryn]_T - k_5\gamma_1\beta_1[HOBr]_T[Ametryn]_T - k_6\gamma_1(1 - \beta_1)[HOBr]_T[Ametryn]_T \quad (21)$$

$$\frac{d[Br^-]}{dt} = -k_4\alpha_1[Br^-][HOCl]_T \quad (22)$$

The fraction HOBr in [HOBr]<sub>T</sub> is given by  $\gamma_1$ . The values for  $K_{a3}$  and  $k_4$  are  $1.26 \times 10^{-9}$  M and  $1.55 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , respectively [26]. Values of  $9.07 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and  $3.54 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  were obtained for  $k_5$  and  $k_6$ . Both values are comparable to the rate constants reported for 4-chlorophenol and 4-acetylphenol oxidation by HOBr [27]. As expected, HOBr is a more reactive oxy-halide and rate constants of HOBr with ametryn species are about one to three orders of magnitude higher than those of HOCl.

### 3.4. Effects of ammonia on ametryn chlorination

Ammonia in water tends to react with chlorine and form three different inorganic chloramines: monochloramine (NH<sub>2</sub>Cl), dichloramine (NHCl<sub>2</sub>) and trichloramine (NCl<sub>3</sub>). Trichloramine is negligible under neutral and basic conditions [10]. The chloramine formation reactions and corresponding rate constants are given in Eq. (23)–(25) [26]. Since chloramine is a relatively weak oxidizer, reaction between chloramine and various ametryn species are relatively unimportant during chlorination:



The rate expressions for HOCl, ametryn, NH<sub>2</sub>Cl, and NHCl<sub>2</sub> based on the elementary reactions in the presence of ammonia can be written as

$$\frac{d[HOCl]_T}{dt} = -k_2\alpha_1\beta_1[HOCl]_T[Ametryn]_T - k_3\alpha_1(1 - \beta_1)[HOCl]_T[Ametryn]_T - k_7\alpha_1(1 - \lambda_1)[HOCl]_T[NH_4^+]_T - k_8\alpha_1[HOCl]_T[NH_2Cl] \quad (26)$$

$$\frac{d[\text{NH}_4^+]_T}{dt} = k_7\alpha_1(1 - \lambda_1)[\text{HOCl}]_T[\text{NH}_4^+]_T \quad (27)$$

$$\begin{aligned} \frac{d[\text{NH}_2\text{Cl}]}{dt} &= k_7\alpha_1(1 - \lambda_1)[\text{HOCl}]_T[\text{NH}_4^+]_T \\ &\quad - k_8\alpha_1[\text{HOCl}]_T[\text{NH}_2\text{Cl}] \end{aligned} \quad (28)$$

$$\frac{d[\text{NHCl}_2]}{dt} = k_8\alpha_1[\text{HOCl}]_T[\text{NH}_2\text{Cl}] \quad (29)$$

$$\begin{aligned} \frac{d[\text{Ametryn}]_T}{dt} &= -k_2\alpha_1\beta_1[\text{HOCl}]_T[\text{Ametryn}]_T \\ &\quad - k_3\alpha_1(1 - \beta_1)[\text{HOCl}]_T[\text{Ametryn}]_T \end{aligned} \quad (30)$$

where  $\lambda_1 = [\text{H}^+]/(K_{a4} + [\text{H}^+])$  represents the fraction of  $[\text{NH}_4^+]_T$  in the  $\text{NH}_4^+$  form. The proposed model was evaluated by measuring the ametryn degradation at varying concentrations of ammonia in chlorination systems under the same pH, chlorine dose, and initial ametryn concentration. Fig. 4 shows the experimental and model predicted results for ametryn degradation. The experimental data showed that the degradation rate of ametryn decreased very quickly with increasing ammonia concentration and is well predicted by the model. These results not only indicate that ammonia plays an important role in the performance of the oxidation and shows a negative effect, but also verify the accuracy of the rate constants between HOCl and ametryn species calculated in the kinetics studies.

### 3.5. Effect of temperature and activation energy

Temperature is critical to the reaction rate, the product yield and species distribution. In order to determine the effect of reaction temperature on the chlorination of ametryn, a series of experiments were conducted at 10, 20, 25 and 30 °C. As illustrated in Fig. 5, temperature exerts a strong effect on the degradation rate of ametryn and is accelerated by a rise in temperature. A good linear fit between  $\ln(k_{\text{app}})$  and  $1/T$  ( $R^2 = 0.99$ ) was observed, and an activation energy of 14.42 kJ/mol was estimated according to the Arrhenius equation. This value is lower than the activation energy of microcystin-LR at 20.1 kJ/mol [28] and cylindrospermopsin at 32.7 kJ/mol [18]. Thus, temperature does not exert an important effect of ametryn degradation in chlorination.

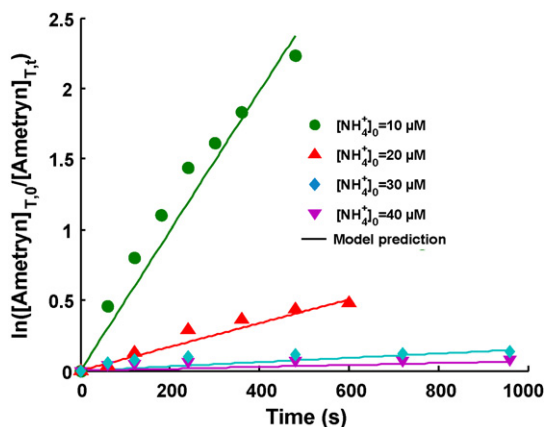


Fig. 4. Effect of ammonia on ametryn degradation in chlorination and the corresponding model predictions, where pH 7,  $[\text{HOCl}]_{T,0} = 28.2 \mu\text{M}$  and  $[\text{Ametryn}]_{T,0} = 4.40 \mu\text{M}$ .

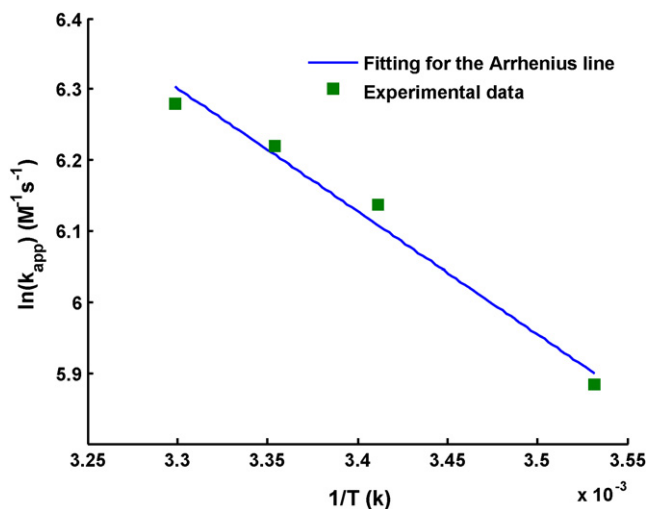


Fig. 5. Effect of temperature on ametryn degradation in chlorination and the Arrhenius line, where pH 7,  $[\text{HOCl}]_{T,0} = 28.2 \mu\text{M}$  and  $[\text{Ametryn}]_{T,0} = 4.40 \mu\text{M}$ .

### 3.6. Oxidation products during ametryn chlorination

The results obtained from the HPLC analysis (Fig. 6) show one major peak of oxidation product eluted before ametryn, which indicates that the product has a more hydrophilic structure than ametryn. Lopez et al. [23] reported that in the oxidation of ametryn by sodium hypochlorite, ametryn-derivatives including the sulphoxide (R-SO-CH<sub>3</sub>), the sulphone (R-SO<sub>2</sub>-CH<sub>3</sub>), sulphonate ester (R-O-SO<sub>2</sub>-CH<sub>3</sub>) and alcohol (R-OH) were detected as main intermediates/products by HPLC-MS. Accordingly, the proposed pathways during ametryn chlorination are shown in Fig. 7 [23]. The degradation of ametryn in chlorination mainly occurred via cleavage of the weakened R-S-CH<sub>3</sub> bond rather than the addition chlorine, which is reported in chlorination of BPA and trimethoprim. This may also explain the behavior that ametryn<sup>+</sup> reacts with hypochlorous acid is faster than neutral ametryn.

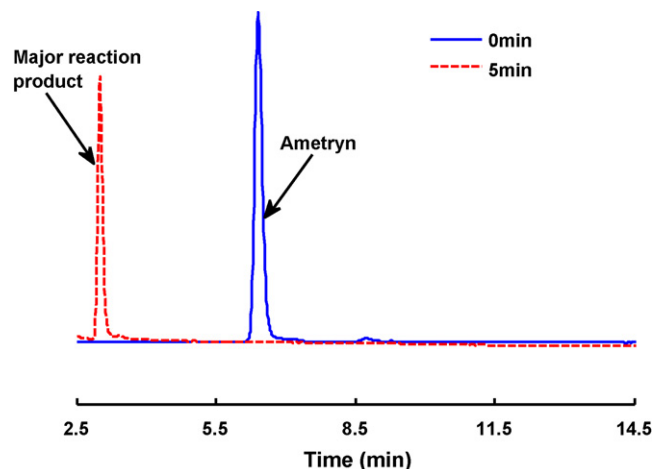


Fig. 6. HPLC spectral changes of ametryn degradation in chlorination, where pH 7,  $[\text{HOCl}]_{T,0} = 28.2 \mu\text{M}$  and  $[\text{Ametryn}]_{T,0} = 4.40 \mu\text{M}$ .

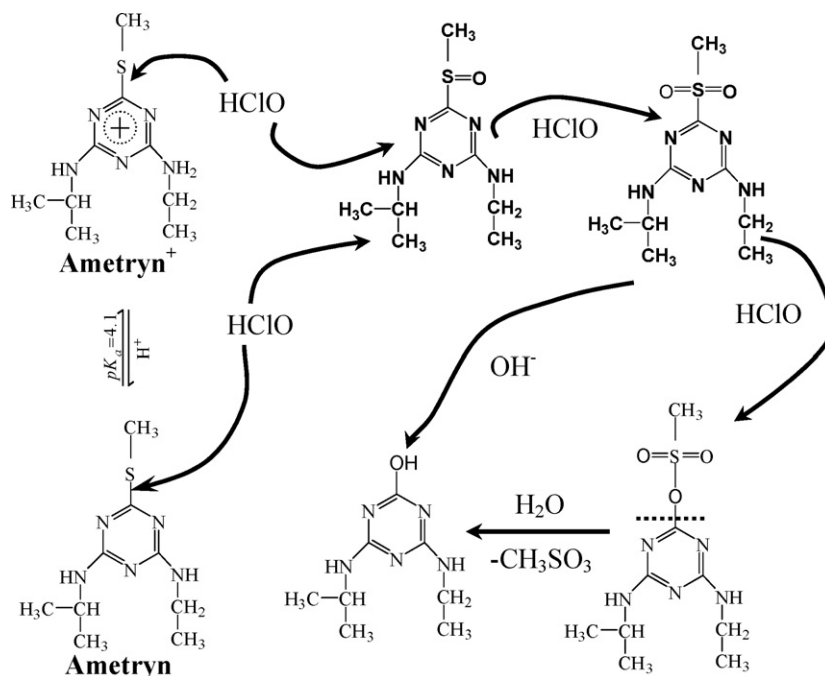


Fig. 7. Proposed pathways for ametryn degradation in chlorination (modified from Lopez et al. [23]).

#### 4. Conclusions

- (1) Chlorination of ametryn follows second-order kinetics and is first-order with respect to the concentration of chlorine and ametryn. The reactivity is relatively high under acidic and neutral conditions with the apparent second-order rate constant larger than  $5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ . Increasing pH leads to a decrease in the chlorination rate, since the overall reaction is controlled by HOCl speciation. Based on model fitting of experimental data, the rate constant for the reaction between HOCl and neutral ametryn and charged ametryn was determined as  $7.22 \times 10^2$  and  $1.58 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.
- (2) Chlorination of ametryn is accelerated by the presence of bromide, and the effect of bromide could be accounted for in the kinetic model after incorporating the corresponding elementary chemical reactions. The estimated rate constant for the reaction between neutral ametryn and charged ametryn with HOBr was  $9.07 \times 10^3$  and  $3.54 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. These values are one to three orders of magnitude higher than the corresponding reactions with HOCl.
- (3) Ammonia exerts a strong negative effect on the chlorination rate of ametryn due to the formation of chloramines. This effect was also well described by the kinetic model after accounting for the formation of chloramines. The good agreement between experimental data and model predictions verifies the accuracy of the rate constants between HOCl and ametryn species obtained.
- (4) The activation energy for ametryn chlorination was estimated to be 14.42 kJ/mol. It indicates that temperature does not exert an important effect on ametryn degradation in chlorination.

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