



Ametryn degradation in the ultraviolet (UV) irradiation/hydrogen peroxide (H₂O₂) treatment

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ABSTRACT

Ultraviolet (UV) irradiation (253.7 nm) in the presence of hydrogen peroxide (H₂O₂) was used to decompose aqueous ametryn. The concentrations of ametryn were measured with time under various experiment conditions. The investigated factors included H₂O₂ dosages, initial pH, initial ametryn concentrations, and a variety of inorganic anions. Results showed that ametryn degradation in UV/H₂O₂ process was a pseudo-first-order reaction. Removal rates of ametryn were greatly affected by H₂O₂ dosage and initial concentrations of ametryn, but appeared to be slightly influenced by initial pH. Furthermore, we investigated the effects of four anions (SO₄²⁻, Cl⁻, HCO₃⁻, and CO₃²⁻) on ametryn degradation by UV/H₂O₂. The impact of SO₄²⁻ seemed to be insignificant; however, Cl⁻, HCO₃⁻, and CO₃²⁻ considerably slowed down the degradation rate because they could strongly scavenge hydroxyl radicals (OH•) produced during the UV/H₂O₂ process. Finally, a preliminary cost analysis revealed that UV/H₂O₂ process was more cost-effective than the UV alone in removal of ametryn from water.

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1. Introduction

Massive application of herbicides in agriculture has been causing great concern about the environment pollution. The pollution greatly threatens the quality of groundwater overlaid by permeable soil. Among these herbicides used, ametryn is one widely used to control broadleaf and grass weeds in fields planted with maize, popcorn, pineapple, and sugarcane. This herbicide is applied mainly by groundboom but also by aerial application in Florida, USA [1]. Ametryn is a water soluble (185 mg/L) sulfur-containing triazine, and its chemical structure is shown in Fig. 1. The organic compound is highly toxic to crustaceans and mollusks [2]. Once residues of ametryn are introduced into wastewater treatment plants, they are difficult to remove. Farre et al. [3] reported that 18 days were required to achieve 94% removal efficiency of ametryn with an initial concentration of 168.3 mg/L in activated sludge simulation tests, and four metabolites after its biodegradation exhibited high toxicity in terms of inhibition of *V. fischeri*.

Up to now, various physicochemical methods have been investigated to remove aquatic ametryn. Lopez et al. [4] applied sodium hypochlorite (NaClO) and chlorine dioxide (ClO₂) to oxidize ametryn. They found that, at pH 7 and molar ratio of ametryn to

oxidant = 0.05 × 10⁻², 100% of ametryn was removed by NaClO within 2 min, while only 40% was removed by ClO₂ within 48 h. Mascolo et al. [5] reported that hypochlorite acid (HClO) oxidation of ametryn led to three oxidation by-products: sulfoxide, sulfone and sulfone's hydrolysis product, but oxidation with ClO₂, instead, gave rise to a sole oxidation by-product—sulfoxide. Yang et al. [6] found that a commercial activated carbon had an adsorption capacity of 230 mg ametryn adsorbed/g activated carbon at pH 6.07 when aqueous equilibrium concentration of ametryn was around 36 mg/L. McMartin et al. [7] investigated ametryn decomposition by several advanced oxidation processes (AOPs). Ametryn degradation was a pseudo-first-order reaction under photoradiation. At ambient pH, half-lives of ametryn (0.1–1.0 mg/L) degradation under artificial solar irradiation were 10.60–10.76 min in groundwater and 30.72–32.85 min in ocean water, respectively. In the presence of Fe(II), the degradation was significantly accelerated due to photo-Fenton reaction, and exhibited a biphasic kinetics—the half-lives of ametryn (0.1–1.0 mg/L) degradation ranged 2.06–2.08 min in the first phase, and 4.81–6.22 min in the second phase, under artificial solar or UV₂₅₄ irradiation. However, H₂O₂/ultraviolet light (UV), one of AOPs, has not been used to treat ametryn-containing water. Introduction of H₂O₂ is able to enhance photochemical oxidation, and a H₂O₂ molecule is cleaved to generate two hydroxyl radicals (OH•) as follows [8]:



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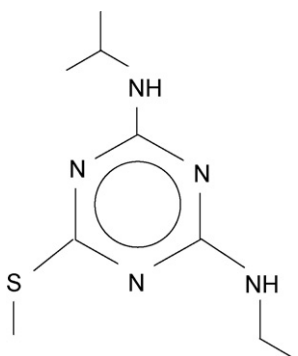


Fig. 1. Chemical structure of ametryn.

Hydroxyl radical is a highly reactive and non-selective oxidizing agent, with an oxidation potential between 2.8 V (pH 0) and 1.95 V (pH 14) vs. saturated calomel electrode (SCE) [9]. It can rapidly react with numerous species with the rate constants typically on the order of 10^8 – 10^{10} L mol⁻¹ s⁻¹. The reactions of OH• and organic compounds produce carbon-centered radicals (R• or R•-OH). In the presence of O₂, these carbon-center radicals may be transformed to organic peroxy radicals (ROO•). All the radicals may further react, accompanied with formation of reactive species such as super oxide (O₂^{•-}), finally leading to decomposition and mineralization of these organic compounds [10].

Stefan et al. [11] have proposed the primary advantages of the UV/H₂O₂ method for treatment of contaminated water, including: (1) high oxidation rates of pollutants; (2) large range of applicability, regardless of the water quality; and (3) convenient dimensions of the required equipment. However, UV/H₂O₂ process, a potential effective technology, has not been well investigated for control of ametryn contamination. The purpose of this study is to measure the kinetics of ametryn removal by UV/H₂O₂ process, and investigate the effects of H₂O₂ dose, initial ametryn concentration, initial pH, and various inorganic anions on removal rate of ametryn.

2. Materials and methods

2.1. Reagents

All chemicals were at least analytical grade, except as noted. Ametryn was purchased from Aldrich. Acetonitrile (HPLC grade, ≥99.9%) was purchased from Sigma. Hydrogen peroxide (H₂O₂, Sinopharm Chemical Reagent Co., Ltd., China) was used as a 30% (w/w) solution. Sodium sulfate (Na₂SO₄ ≥99.0%), sodium chloride (NaCl ≥99.0%), sodium bicarbonate (NaHCO₃ 99.7–100.3%), and sodium carbonate (Na₂CO₃ ≥99.5%) were purchased from Sinopharm Chemical Reagent Co. And 0.1N of sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH) were obtained through diluting stock solutions of H₂SO₄ (1.0M) and NaOH (5.0M) (Sinopharm Chemical Reagent Co., China), respectively.

2.2. Experimental procedure

All runs were conducted at room temperature and atmospheric pressure in a UV/H₂O₂ reactor shown in Fig. 2. A UV lamp (30 W, 253.7 nm) (GPH287T5L/4P UV Lamp, Bulbtronics Ltd., USA) surrounded by a quartz tube was inserted into a 3-L complete-mixing glass cylinder reactor wrapped with foil. Two liters of sample solution were dispensed to the reactor and stirred thoroughly at 100 rpm with a magnetic stirrer (Meiyingpu Instrument Company Ltd., China) in each experiment. A thermometer was suspended into the solution to monitor the reaction temperature.

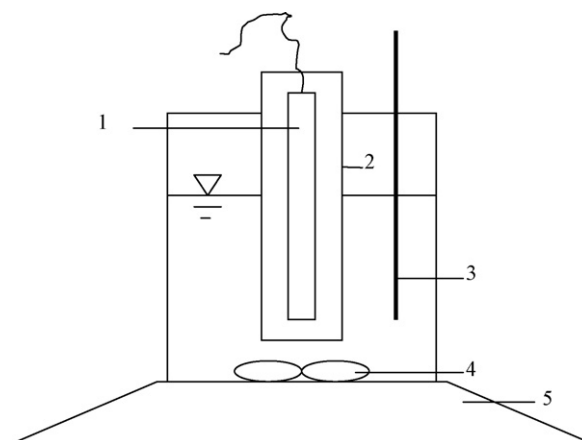


Fig. 2. Schematic of UV/H₂O₂ reactor ((1) UV lamp; (2) quartz tube; (3) thermometer; (4) stirring bar; (5) magnetic stirrer).

In a typical run, the reaction was initiated by addition of the designated amount of H₂O₂ and turning on the UV lamp. At each sampling time, 1 mL of sample was pipetted to a 25 mL glass test tube for measurement of ametryn. In the experiments to investigate effect of initial pH, 0.1 N sulfuric acid and sodium hydroxide solution were used to adjust the initial solution pH to the designated value before reaction, except in the experiment to investigate the effect of anions in which the initial pH was not controlled. The designated initial pH was 7.0 in the experiments to investigate effects of H₂O₂ dosages and initial ametryn concentration; and the designated initial pH were 4.0, 5.0, 6.0, 7.0, and 8.0, respectively, in the experiments to investigate the effect of pH. In the experiments to investigate effect of anions, the designated amount of salt (Na₂SO₄, NaCl, NaHCO₃, or Na₂CO₃) was added to form 1 mM initial concentration of anions, prior to the reaction. All samplings were measured at least in duplicates. The standard deviations of all measurements were less than 5%. The symbols in Figs. 3–9 showed the mean values.

2.3. Analytical method

Water sample was filtered through 0.45 μm HA membrane. Ametryn in the filtrate was measured through high performance liquid chromatography (HPLC) method. HPLC operative conditions were as follows. A LC-2010HT series HPLC chromatography (Shimadzu Scientific) was equipped with a shim-pack VP-ODS column (150 mm × 4.6 mm i.d.). The mobile phase (flow rate = 0.8 mL/min) was a mixture of acetonitrile/deionized water solution with a composition of 60/40 (v/v). The wavelength of the ultraviolet light detector was set at 240 nm and analysis time was 7.5 min. The equilibrium compositions of carbonate and bicarbonate in testing the effects of the both anions on ametryn removal were estimated using Visual Minteq ver. 2.53.

3. Results and discussion

3.1. Effect of H₂O₂ dosages

The effect of H₂O₂ dosages on ametryn degradation in the UV/H₂O₂ treatment is shown in Fig. 3(a) and (b). At an ametryn concentration of 10 mg/L and H₂O₂ concentrations of 0–150 mg/L, the removal of ametryn showed a pseudo-first-order kinetic behavior. Increasing H₂O₂ dosage caused increasing removal of ametryn. Within 45 min, the introduction of 0–150 mg/L H₂O₂ resulted in the residual ametryn ranging from 0.14 to 0.07 mg/L accordingly,

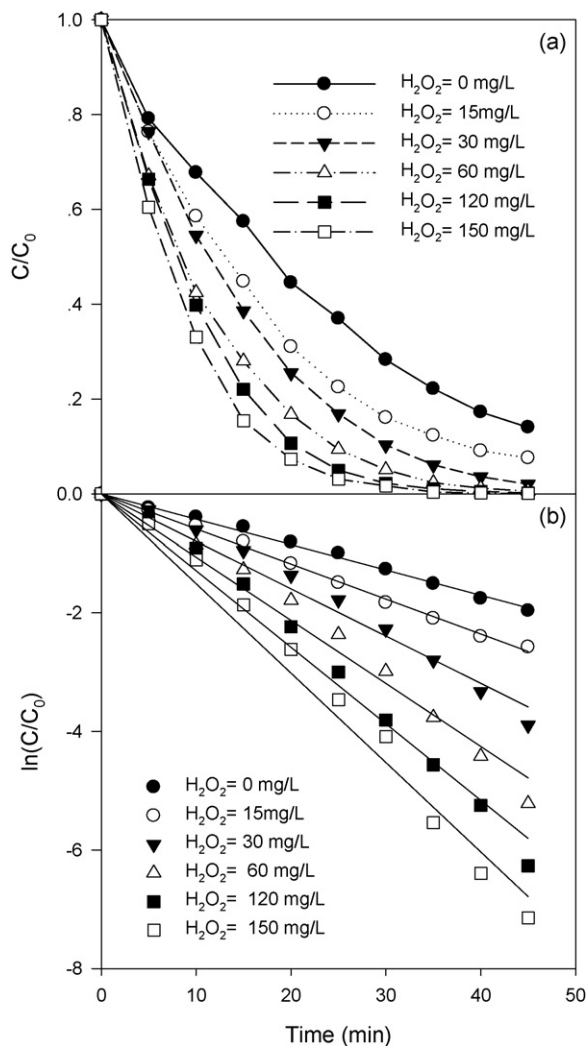


Fig. 3. Ametryn degradation under different H_2O_2 dosages: (a) C/C_0 vs. time; and (b) $\ln(C/C_0)$ vs. time ($C_0 = 10$ mg/L; and initial pH 7).

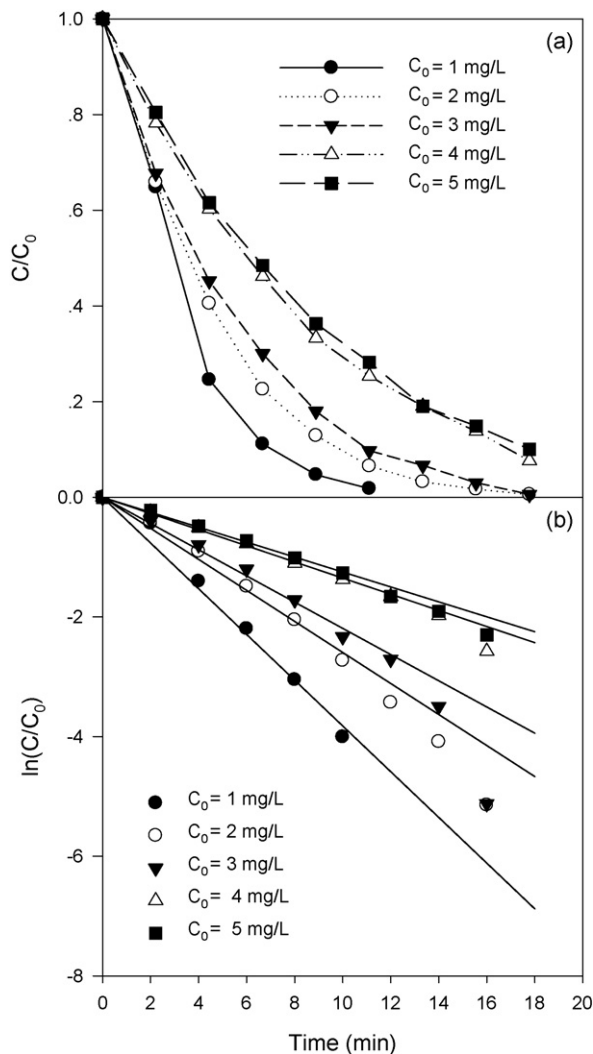


Fig. 5. Ametryn degradation under different initial concentrations: (a) C/C_0 vs. time; and (b) $\ln(C/C_0)$ vs. time ($H_2O_2 = 5$ mg/L; and initial pH 7).

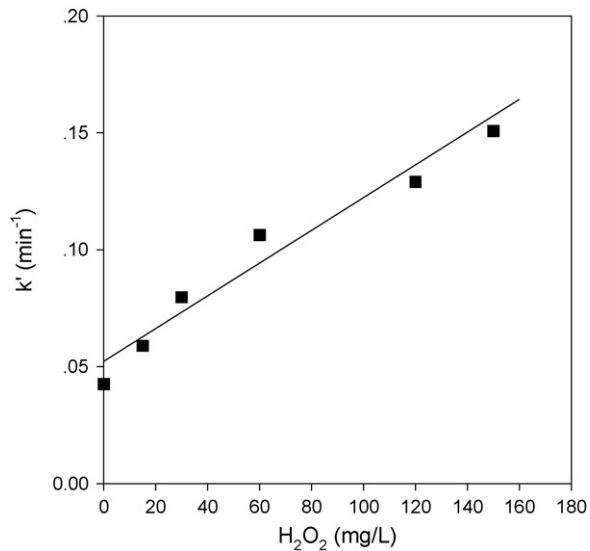


Fig. 4. Pseudo-first-order rate constants k' of ametryn degradation vs. H_2O_2 dosages ($C_0 = 10$ mg/L; and initial pH 7; k' shows a linear relationship with $[H_2O_2]$; $k' = 0.0007[H_2O_2] + 0.0523$, $r^2 = 0.9578$).

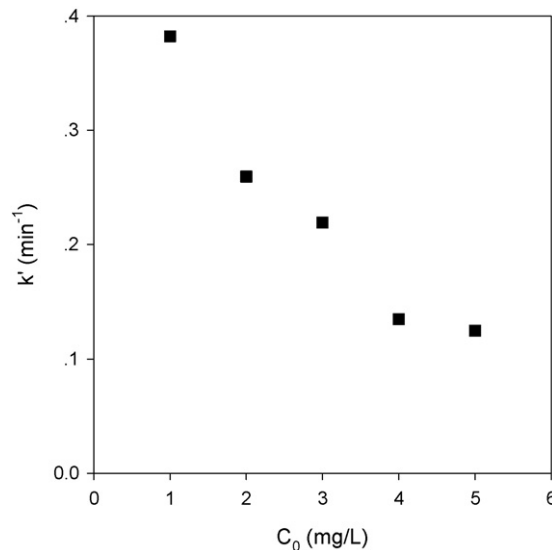


Fig. 6. Pseudo-first-order rate constants k' of ametryn degradation vs. initial concentrations ($H_2O_2 = 5$ mg/L; and initial pH 7).

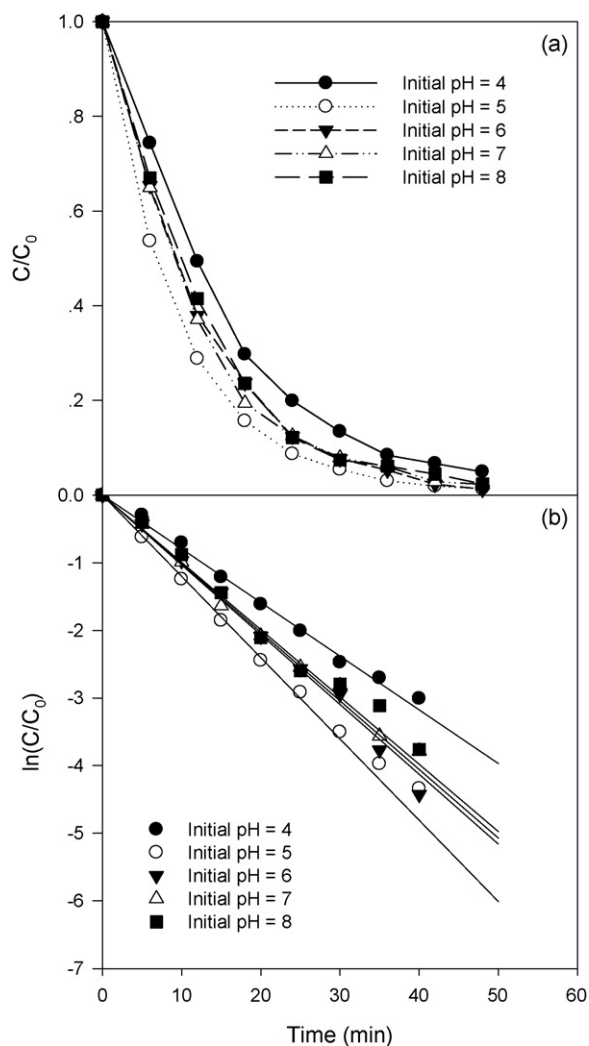


Fig. 7. Ametryn degradation under different initial pH: (a) C/C_0 vs. time; and (b) $\ln(C/C_0)$ vs. time ($H_2O_2 = 5 \text{ mg/L}$; and ametryn = 1 mg/L).

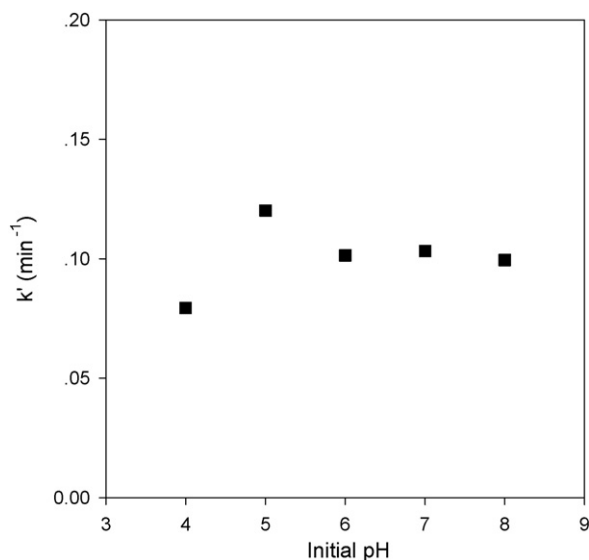


Fig. 8. Pseudo-first-order rate constants k' of ametryn degradation vs. initial pH ($H_2O_2 = 5 \text{ mg/L}$; and ametryn = 1 mg/L).

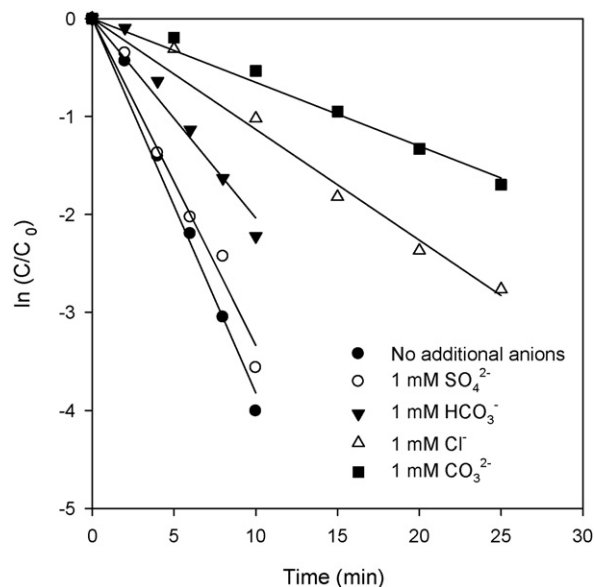


Fig. 9. Ametryn degradation in the presence of different anions.

indicating that UV/ H_2O_2 was superior to UV alone in terms of the removal efficiency. The reason is that UV/ H_2O_2 was able to rapidly generate more hydroxyl radicals under UV irradiation than UV alone. Difference in the pseudo-first-order rate constants (k') was statistically significant ($p < 0.05$). And k' of $0.04\text{--}0.15 \text{ min}^{-1}$ appeared to increase linearly with the increasing H_2O_2 dosages of $0\text{--}150 \text{ mg/L}$, as shown in Fig. 4.

Optimal ratios of H_2O_2 dosage to the concentration of a target organic compound [12,13] were reported in UV/ H_2O_2 treatment of organic pollutants, below or above which the treatment efficiency was decreased. The reason was that H_2O_2 , as a OH^\bullet scavenger, could compete for OH^\bullet to inhibit oxidation of the target organic compound, as shown in Reaction (2). The scavenging effect became dominant particularly at a high H_2O_2 dosage.



However, such an optimal ratio was not observed in our study. The removal efficiency of ametryn at an initial concentration of 10 mg/L continuously increased with the increasing H_2O_2 dosage within $0\text{--}150 \text{ mg/L}$ (the ratio of H_2O_2 dosage to ametryn concentration = $0\text{--}15$). The reason may be that the optimal ratio was greater than 15, the maximum one used in this study.

3.2. Effect of initial ametryn concentration

The effect of initial ametryn concentration on ametryn degradation in the UV/ H_2O_2 process was shown in Fig. 5(a) and (b). At a fixed H_2O_2 dosage of 5 mg/L and ametryn concentrations of $1\text{--}5 \text{ mg/L}$, all the reactions exhibited pseudo-first-order kinetic behaviors. And more than 90% of ametryn was removed within 18 min. As expected, an increase in the initial ametryn concentration caused a decrease in the ametryn removal efficiency. The reason was that the amount of OH^\bullet generated in the UV/ H_2O_2 process was limited due to a fixed dosage of H_2O_2 , and the amount of ametryn decomposed by the OH^\bullet was relatively lower against a higher initial concentration. These pseudo-first-order rate constants (k') were statistically significantly different ($p < 0.05$), and the k' decreased from 0.38 to 0.12 min^{-1} with the increasing initial concentration from 1 to 5 mg/L as shown in Fig. 6.

Table 1
Rate constants for reactions of OH• and the anions (HCO₃⁻, Cl⁻, and CO₃²⁻)

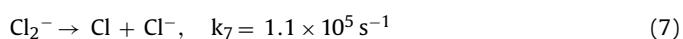
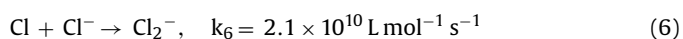
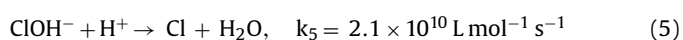
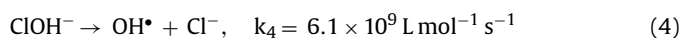
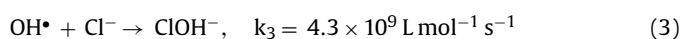
Anion species	Rate constants (L mol ⁻¹ s ⁻¹)	Reference
HCO ₃ ⁻	8.5 × 10 ⁶	[14]
CO ₃ ²⁻	3.9 × 10 ⁸	[14]
Cl ⁻	4.3 × 10 ⁹	[15]

3.3. Effect of initial pH

The effect of initial pH on ametryn degradation in the UV/H₂O₂ process was shown in Fig. 7(a) and (b). At a H₂O₂ dosage of 10 mg/L and an ametryn concentration of 1 mg/L, all the reactions followed pseudo-first-order kinetics at pH 4–8. Within 50 min, more than 95% of ametryn was removed by the UV/H₂O₂ process. As shown in Fig. 8, the pseudo-first-order rate constant (*k'*) varied slightly within the range of 0.08–0.12 min⁻¹ at pH 4–8.

3.4. Effect of different inorganic anions

The effects of four inorganic anions on ametryn degradation were investigated (Fig. 9). Their inhibiting effect on ametryn decomposition followed the order of SO₄²⁻ < HCO₃⁻ < Cl⁻ < CO₃²⁻. Hydroxyl radicals were the dominant oxidative species in the UV/H₂O₂ process, and these anions were able to compete with ametryn for OH• at various rates. Among these anions, SO₄²⁻ only slightly slowed down the decomposition of ametryn, compared with the degradation rate in the control group (no additional anions), because SO₄²⁻ itself almost did not react with OH•. However, HCO₃⁻, Cl⁻, and CO₃²⁻ greatly inhibited the decomposition rate of ametryn due to their high rate constants with OH• (>10⁶ L mol⁻¹ s⁻¹) as shown in Table 1. HCO₃⁻ or CO₃²⁻, once added, would proceed to react and eventually reach the equilibration of carbonate system. In the solutions with 1 mM initial concentration of HCO₃⁻ and with 1 mM initial concentration of CO₃²⁻, the primary compositions at equilibrium were 0.98 mM HCO₃⁻/0.01 mM CO₃²⁻ and 0.35 mM HCO₃⁻/0.63 mM CO₃²⁻, respectively. On the other hand, in the sodium chloride solution, NaCl was almost completely ionized into Na⁺ and Cl⁻. The reactions between hydroxyl radical and chloride are as follows:



Hydroxyl radicals reacted with chloride ions to initially form ClOH⁻. And ClOH⁻ was dissociated back to OH radicals and chloride ions. Moreover, ClOH⁻ could react with hydrogen ion (H⁺) to form chlorine atoms, and the generated chlorine atoms combined with chloride ions to form Cl₂⁻ and Cl₂⁻ could dissociate back to chlorine atoms and chloride ions [14]. As a result, alkalinity (HCO₃⁻ and CO₃²⁻) and Cl⁻ present in water could significantly inhibit the degradation rate of ametryn.

3.5. Preliminary cost analysis

A comparison of the projected operating costs for the UV alone and for the UV/H₂O₂ process for removal of ametryn was conducted as shown in Table 2, based on the results in Section 3.1. The operating costs per unit mass removed ametryn (dollar/g ametryn removed) consist of expenditures for power consumption and purchasing H₂O₂. The estimated unit cost of H₂O₂ and

Table 2
Cost comparison of UV alone and UV/H₂O₂ processes for treatment of ametryn^a

Process	Added H ₂ O ₂ (mg/L)	Estimated reaction time (min)	Cost per unit mass removed ametryn (dollars/g) ^b
UV alone	0	45	0.131
UV/H ₂ O ₂	15	33	0.100
	30	27	0.086
	60	22	0.079
	120	18	0.083
	150	15	0.082

^a Initial ametryn concentration = 10 mg/L, reaction times were those when 86% of ametryn removal efficiencies were achieved (86% was the highest removal achieved by UV alone process), and the volumes of ametryn-containing samples were 2 L.

^b Assume 0.00218 dollars/g H₂O₂, and 0.10 dollar/kWh [16,17].

power are 0.00218 dollars/g (0.495 dollars/lb for 50% purity) [16], and 0.10 dollars/kWh [17], respectively. To compare the two individual processes, 86% of ametryn removal efficiency, the highest one achieved by UV alone within 45 min, was selected as the final removal efficiency. The estimated reaction times required for UV/H₂O₂ treatment with 15, 30, 60, 120, and 150 mg/L H₂O₂ were 33, 27, 22, 18, and 15 min, respectively. Obviously, introduction of H₂O₂ shortened the reaction times due to production of more hydroxyl radicals. As shown, the projected operating cost of the UV/H₂O₂ process ranged within 0.079–0.100 dollars/g ametryn removed, below the projected cost of the UV alone, 0.131 dollars/g ametryn removed. Therefore, the UV/H₂O₂ appeared to be more cost-effective than the UV alone in terms of the projected operating costs.

4. Conclusion

Ametryn degradation in UV/H₂O₂ process exhibited a pseudo-first-order kinetic behavior. Removal rates of ametryn were strongly affected by H₂O₂ dose and initial concentrations of ametryn, but appeared to be slightly influenced by initial pH. Within 1 h, 10 mg/L ametryn could be almost all removed. Cl⁻ or high alkalinity present in water could significantly slow the rate of ametryn degradation due to the strong OH• scavenging effect. Therefore, removal of these anions from water may be necessary prior to UV/H₂O₂ process in practice. Our experimental results showed UV/H₂O₂ exhibited high removal efficiency of ametryn, similar to other advanced oxidation processes such as UV-catalytic and photo-Fenton processes. Furthermore, based on a preliminary cost analysis, UV/H₂O₂ process was more cost-effective than the UV alone. Therefore, it appears to be a promising technology in the removal of aqueous ametryn.

Acknowledgments

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