Degradation of herbicide (ametryn) in water by UV-H_2O_2 combinated process

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Abstract—**The removal performances of ametryn in drinking water using UV-H_2O_2 combined process was investigated in this paper. The results showed that ametryn cannot be effectively removed by UV radiation and H_2O_2 oxidation alone, while UV-H_2O_2 combination process could achieve quite good removal efficiency. As the initial concentration of ametryn about 0.901mg/L, its removal efficiency reached 97.68% under the condition that the intensity of UV radiation, the dosage of H_2O_2, reaction time, pH and residual concentration were 85.7μW/cm^2, 5mg/L, 40minutes, 7.0 and 0.021mg/L, respectively. The kinetic effects of H_2O_2 dosage, pH values and ametryn initial concentration on the conversion of ametryn were examined respectively. Analysis of factors showed that UV radiation intensity, H_2O_2 dosage, pH values and ametryn initial concentrations have important effect on the degradation of ametryn.**
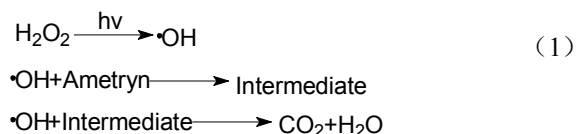
Keywords-advanced oxidation process; ametryn; drinking water; UV radiation; kinetics

I. INTRODUCTION

Ametryn is an herbicide used to control broadleaf and grass weeds in fields planted with field corn, popcorn, pineapple, and sugarcane. There is only one formulation, an 80% water dispersible granule. Ametryn is applied mainly by groundboom but also by aerial application in Florida. Ametryn was first registered as a pesticide in the U.S. in 1964. Due to their wide application and potential high toxicity, several generic Data Call-Ins (DCIs) were issued that required a full range of testing on ametryn's chemistry, toxicology, and environmental fate [1, 2].

Ametryn is one of the most frequently identified herbicide with high water solubility and short-chain in diverse environmental samples including surface water, drinking water, and sea water and so on. Since ametryn is difficult to biologically and photo-chemically degrade [3, 4], there is a strong need to look for effective treatment processes for such pollutants.

Homogeneous advanced oxidation process (AOPs) employing hydrogen peroxide with UV-light has been found to be very effective in the degradation of endocrine disruptors [5, 6]. In UV–H_2O_2 process the photolysis of hydrogen peroxide generates effective oxidizing species hydroxyl radical (Equation 1), which can oxidize a broad range of organic pollutants quickly and non-selectively [7, 8].

$$H_2O_2 \xrightarrow{\ h\nu\ } \cdot OH$$
$$\cdot OH + Ametryn \longrightarrow Intermediate \qquad (1)$$
$$\cdot OH + Intermediate \longrightarrow CO_2 + H_2O$$

The purpose of the present study was to investigate the oxidation behavior of ametryn by UV–H_2O_2 process and thus the possibility of removal form waters polluted by ametryn. The results of effects, influencing factors, degradation mechanism and also theoretically perform a kinetic on the degradation of ametryn were presented in this paper.

II. EXPERIMENTAL

A. Material and analysis

Ametryn, chromatographical purity, obtained from Sigma Chemical Company (purity>99%). H_2O_2 (30%, w/w) was obtained from Sinopharm Chemical Reagent Co. Ltd., China. AR grade NaOH and HCl were used to adjust the pH value. The double distilled water was used to prepare experimental solution.

A high performance liquid chromatograph (HPLC 2010 AHT, Shimadzu, Japan) was used to analyze ametryn. The HPLC system consisted of an SIL-auto-injector auto-sampler with the volume injection set to l0μL, Shimadzu VP-ODS column (150mm×4.6mm), UV detector at 240nm. The mobile phase consisted of methanol (Fisher, USA) and Milli-Q water (Millipore, Mosheim, France), acetonitrile /H_2O= 60/40(ratio by volume) and the applied flow rate was 0.8mL/min. A UV–vis spectrophotometer UV2550 (Shimadzu) was used to scan the spectrum of ametryn. The standard curve and detectabilities of ametryn are shown in Table I.

B. Photoreactor

The irradiation set-up was a completely mixed batch reactor (CMB made of stainless steel) shown in Fig.1. The UV lamp (emitting wavelength = 253.7nm, 30W) with quartz sleeves was fixed in circularity in the reactor. Meanwhile, the UV light intensity, controlled by turning on or off the lamps, was monitored by light intensity meter and the value had been shown in Table II. In order to homogenize the solution, a mechanical stirrer was provided at the centre. All the reactions were carried out at room controlled temperature.

TABLEI. STANDARD CURVE AND DETECTABILITIES OF AMETRYN BY HPLC

Standard curve	R^2	Range (mg/L)	LOD (µg/L)
$Y=1.39417\times10^{-2}X$	0.999997	0.05-15	1
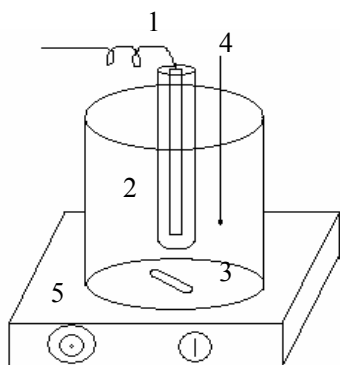
1. UV lamps 2. Quartz sleeve 3. Stirrer
4. Thermograph 5. Magnetic force stirrer

Figure 1. The schematic diagram of experiment system

TABLEII. THE INTENSITY OF UV RADIATION

UV lamps	Intensity (µW/cm²)
1	15.5
2	21.2
3	42.3
4	51.0
5	68.0
6	77.2
7	85.7
8	107.6
10	133.9

III. RSELUTS AND DISCUSSION

A. *Degradation effect of ametryn by UV radiation or H_2O_2 oxidation alone*

With the maximum intensity of UV radiation about intensity as 133.9µW/cm², concentration of ametryn versus reaction time for experiments were carried out with UV radiation only and different initial concentrations of ametryn. The removal rate was found to be as low as 12.7% after 90min with the initial concentration ametryn 1.0mg/L.

To investigate the performance of ametryn oxidation by H_2O_2, the solution of ametryn with concentration of 1.0 mg/L and H_2O_2 (100mg/L) were added to the reactor simultaneously without UV radiation and then mixed by a mechanical stirrer. It could be found that ametryn concentration after 3h reaction was not changed, which implied that ametryn is extremely inert and difficult to be degraded by H_2O_2 oxidation alone.

B. *Degradation effect of ametryn by UV-H_2O_2*

The degradation effect of ametryn by UV-H_2O_2 has been investigated by varying the UV radiation intensities（15.5, 42.3, 68.0, 85.7 and 133.9µW/cm²）under the condition that the

initial H_2O_2 concentration and initial concentration were 100mg/L and 10mg/L. Fig.2 shows the concentration of ametryn declined with increasing UV radiation intensity with the value from 2.97 to 0.02mg/L at the time of 40 min. It can be deduced that the enhancement of removal efficiency is also due to the increase of hydroxyl radical concentration. According to Equation (1), the efficiency of photolysis of H_2O_2 depends directly on the UV intensity. At low UV intensity the photolysis of H_2O_2 is limited. At high UV intensity more hydroxyl radicals are formed, which directly results in the high removal rate of ametryn.
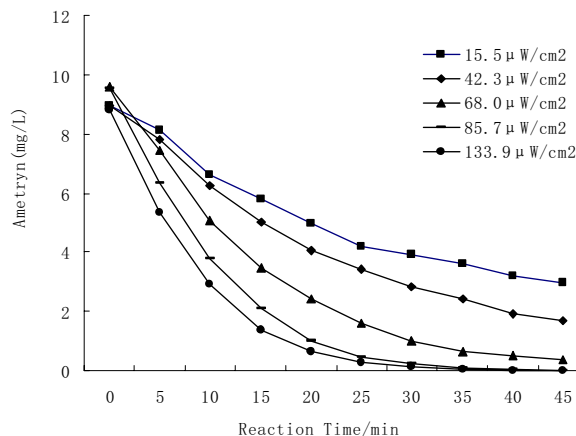

Figure 2. Degradation effect of ametryn by UV-H_2O_2

C. *Effect of addition of H_2O_2*

The effect of addition of H_2O_2 (15, 30, 60, 120 and 150mg/L) on the photochemical degradation has been investigated under the condition that the intensity of UV radiation and initial concentration were 85.7µw/cm2 and 10mg/L. It can be shown in Fig.3. As it can be seen in Fig.3, the removal rate of ametryn increases with increasing H_2O_2 concentration, the addition of 15–120mg/L increases the degradation from 52.6% to 95.8% at time of 15 min. Moreover, the increment is also limited above 60 mg/L at time of 35 min.
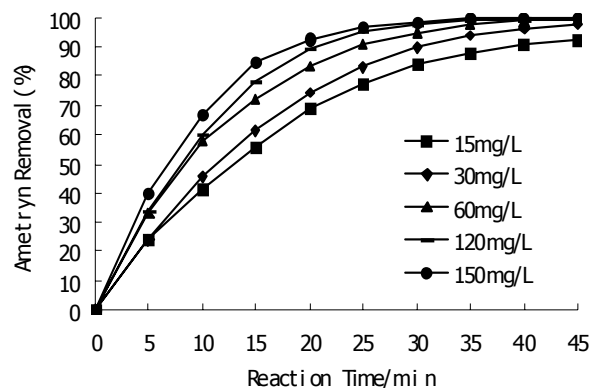

Figure 3. Effect of initial concentration of H_2O_2 in ametryn degradation

The enhancement of degradation by addition of H_2O_2 is due to the increase in the hydroxyl radical concentration. At low concentration H_2O_2 can not generate enough hydroxyl radical and the removal rate is limited. However, it was reported that high concentration of H_2O_2 could restrain the

reaction[9]. This phenomenon did not happen in our experiment for the reason that the dosage did not reach the restrain point.

D. Effect of initial ametryn concentration

Concerning contamination of ametryn from different water varies from locations. It is important to investigate the impact of different initial ametryn concentrations in oxidation process. With the same initial concentration of H_2O_2 and UV intensity, the processes with different initial ametryn concentrations were carried out 0.959、1.884、3.014、3.932 and 4.982mg/L in the experiments with the UV irradiation time was 16min. The results are shown in Fig.4. As shown in the fig.4, photooxidation effect became worse and worse as initial concentration of ametryn is increased in reaction time. It can be explained that by considering that both the ametryn and H_2O_2 absorb UV radiation in the range emitted by the lamp. An increase in ametryn concentration induces a rise of the internal optical density and the solution becomes more and more impermeable to UV radiation. By this way, hydrogen peroxide can only be irradiated by a smaller portion of UV light to form lower free radicals and the degradation rate decrease [10].
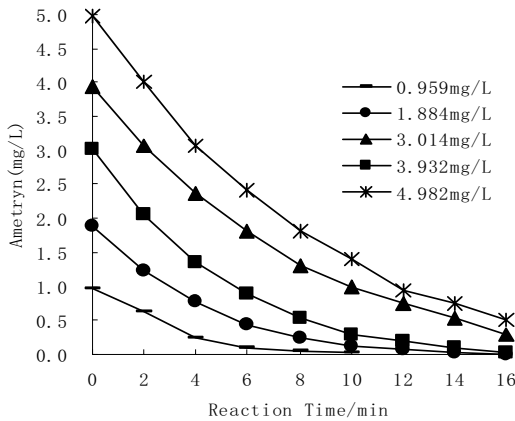

Figure 4.　Degradation effect of different initial concentration of ametryn

E. Effect of initial pH value

The effect of different initial pH values (4, 5, 6, 7,8 and 9) on the photochemical degradation has been investigated under the condition that the intensity of UV radiation and initial concentration were $85.7\mu w/cm^2$ and 5mg/L. The results are shown in Fig.5. As it can be seen, the best removal efficiency of ametryn was reached when pH=7; the worst removal efficiency was reached when pH=8; the removal efficiency were similar on pH from 4 to 7.

F. Kinetic Study

As shown in Fig.6, experimental data was fitted according to pseudo-first order kinetics. The values are shown in Table IV. According to Table III, the apparent reaction rate constant (k) for degradation of ametryn is a function of H_2O_2 concentration. The results also reveal that k increases with increasing the amount of H_2O_2. A linear relation exists between pseudo-first order reaction rate and initial H_2O_2 concentration, which indicated that employed H_2O_2 dosage in
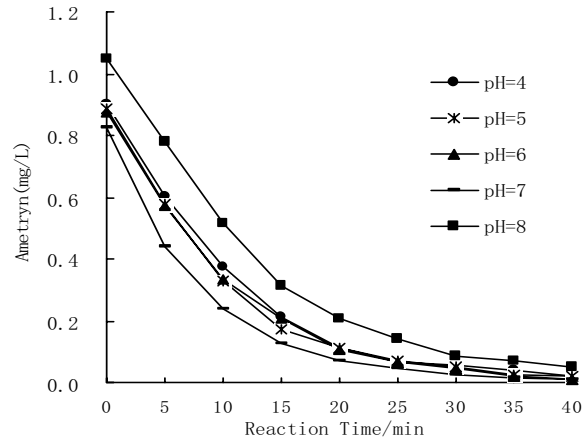
this study are in the low range.

Figure 5.　Effect of different initial pH values in ametryn degradation

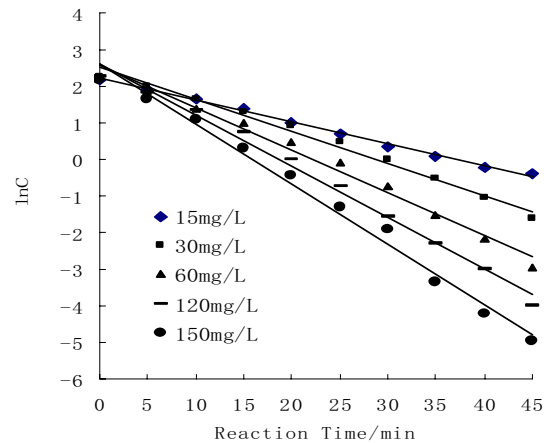
Figure 6.　Pseudo-first order decay curves of ametryn degradation with different H2O2 initial concentration

TABLEIII.　PSEUDO-FIRST ORDER RATE CONSTANTS OF AMETRYN DEGRADATION WITH DIFFERENT H2O2 INITIAL CONCENTRATION

H_2O_2 （mg/L）	Pseudo-first order equation	k(min^{-1})	R^2
15	lnC=-0.0597t+2.2176	0.0597	0.9973
30	lnC=-0.0870t+2.5021	0.0870	0.9885
60	lnC=-0.1156t+2.5534	0.1156	0.9866
120	lnC=-0.1408t+0.2246	0.1408	0.9910
150	lnC=-0.1640t+2.5904	0.1640	0.9884

TABLEIV.　PSEUDO-FIRST ORDER RATE CONSTANTS OF AMETRYN DEGRADATION WITH DIFFERENT INITIAL AMETRYN CONCENTRATION

Ametryn （mg/L）	Pseudo-first order equation	k(min^{-1})	R^2
0.959	lnC=-0.4096t+0.1577	0.4096	0.9922
1.884	lnC=-0.3157t+0.9089	0.3157	0.9871
3.014	lnC=-0.2896t+1.4475	0.2896	0.9432
3.932	lnC=-0.1534t+1.4640	0.1534	0.9866
4.982	lnC=-0.1429t+1.6857	0.1429	0.9942

TABLE V. PSEUDO-FIRST ORDER RATE CONSTANTS OF AMETRYN DEGRADATION WITH DIFFERENT INITIAL PH VALUE

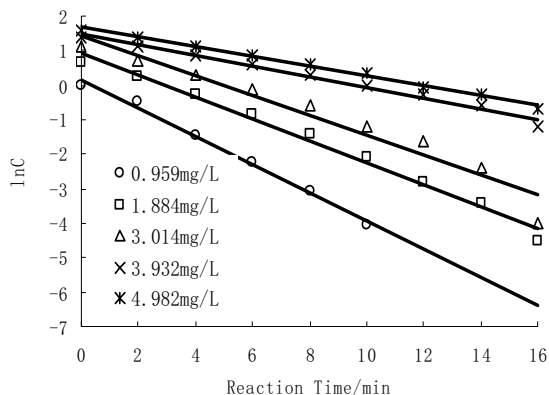| Ametryn (mg/L)	Pseudo-first order equation	$k(min^{-1})$	R^2
4	$\ln C = -0.0939t - 0.1263$	0.0939	0.9888
5	$\ln C = -0.0969t - 0.1664$	0.0969	0.9929
6	$\ln C = -0.1094t - 0.0149$	0.1094	0.9943
7	$\ln C = -0.1100t - 0.3161$	0.1100	0.9955
8	$\ln C = -0.0786t + 0.0614$	0.0939	0.9888

Figure 7. Pseudo-first order decay curves of ametryn degradation with different initial ametryn concentration
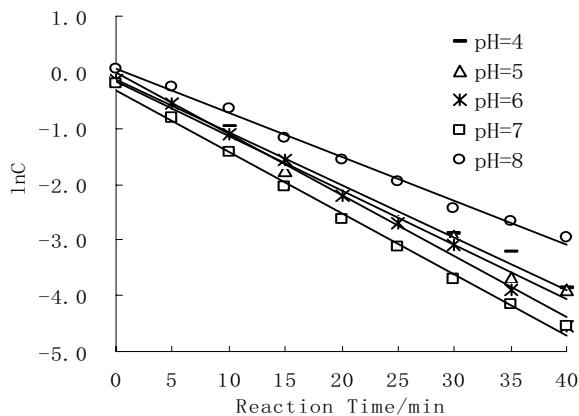

Figure 8. Pseudo-first order decay curves of ametryn degradation with different initial pH values

Concerning the effect of initial ametryn concentration and pH value on ametryn degradation, the linear method by the kinetics model also is used to analyze the relationship of the pseudo-first order reaction rate with initial ametryn concentration and pH value. The results are shown in Fig.7,8 and Table IV,V.

As it can be seen from Fig.7 and Table IV, Pseudo-first order rate constants k increases with increasing initial ametryn concentration; the addition of 0.959–4.982mg/L increases the pseudo-first order rate constants k from 0.4096 to 0.1429. It is obvious that initial concentration has considerable influence on reaction rate.

As it can be seen from Fig.8 and Table V, degradation rates of ametryn, in neutral and acidity condition are similar.

Degradation rates of ametryn, in alkalinity, is lower because HO^{2-} restricts the formation of ·OH [11].

In this study, as shown in Table III, IV and V, R^2 are all more than 0.980, which can denote the better relativity between removal efficiency of ametryn and relative effect factor. H_2O_2 dosage, pH value and ametryn initial concentrations have important effect on degradation of ametryn.

IV. CONCLUSION

The results obtained in this study clearly indicate that single UV radiation process and H_2O_2 oxidation process can hardly remove ametryn from water and the UV–H_2O_2 process is very promising for complete removal of ametryn from contaminated water. The degradation rate and removal efficiency of ametryn can be affected by initial H_2O_2 concentration, initial ametryn concentration and initial pH value, et al. The degradation follows pseudo-first order kinetics. Pseudo-rate constant (k) is affected with varying H_2O_2 concentration, initial concentration of ametryn and initial pH value. There have linear relationship between rate constant k and H_2O_2 concentration and initial ametryn concentration, which indicated higher removal capacity can be achieved by improvement of both factors.

REFERENCES

[1] M. Shechter, B. Xing, D. Kopinke, B. Chefetz, "Competitive sorption-desorption behavior of triazine herbicides with plant cuticular fractions," Journal of Agricultural and Food Chemistry, vol. 54, pp.7761-7768, 2006.

[2] A. Lopez, G. Mascolo and G. Tiravanti, "Degradation of herbicides (ametryn and isoproturon) during water disinfection by means of two oxidants (hypochlorite and chlorine dioxide)," Water Science and Technology, vol. 35, pp. 129-136, 1997

[3] M. P. Ormad, N. Miguel, and A. laver, "Pesticides removal in the process of drinking water production," Chemosphere, In Press.

[4] D. D. Zhao, N. Y. Gao, M. Rui, B. Xu, J.F. Zhao and L.S. Le, "Degradation of DMP by combination of UV- H_2O_2 and impact factors," Environment Chemistry, vol. 25, pp. 477-480, 2006.

[5] W. Chu, "Modeling the quantum yields of herbicide 2, 4-D decay in UV/ H_2O_2 process," Chemosphere, vol. 44, pp. 935–941, 2001.

[6] A.M. Fares, S. Carmen and E. Santiago, "A comparative study of the advanced oxidation of 2, 4-dichlorophenol," Journal of Hazardous Materials, vol.107, pp. 123–129, 2004.

[7] B. Xu, N. Y. Gao, X.F. Sun, S.J. Xia, M. Rui, "Photochemical degradation of diethyl phthalate with UV/H_2O_2," Journal of Hazardous Materials, vol. 139, pp.132-139, 2007.

[8] O. M. Alfano, R.J. Brandi and A.E. Cassano, "Degradation kinetics of 2,4-D in water employing hydrogen peroxide and UV radiation," Chemical Engineering Journal, vol.82, pp.209–218, 2001.

[9] M. Muruganandham, M. Swaminathan, "Photochemical oxidation of reactive azo dye with UV–H_2O_2 process," Dyes Pigments, vol.62, pp. 269–275, 2004.

[10] A. Aleboyeh,Y. Moussa and H. Aleboyeh, "The effect of operational parameters on UV/ H_2O_2 decolourisation of Acid Blue 74," Dyes Pigments, vol.66, pp.129–134, 2005.

[11] M. Patrick, B. Cécile, D. Anne, D.L. Joseph, "A comparison of fenuron degradation by hydroxyl and carbonate radicals in aqueous solution," Water Research, vol.41, pp.4585-4594, 2007.