

## KINETICS OF ATRAZINE OXIDATION BY UV RADIATION AND OXALATE ASSISTED H<sub>2</sub>O<sub>2</sub>/UV PROCESSES

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**Abstract** : The degradation of atrazine was explored using UV alone, H<sub>2</sub>O<sub>2</sub>/UV, oxalate/UV and oxalate-assisted H<sub>2</sub>O<sub>2</sub>/UV. The addition of oxalate to the H<sub>2</sub>O<sub>2</sub>/UV (oxalate-assisted H<sub>2</sub>O<sub>2</sub>/UV) process was the most effective method for the degradation of atrazine. The overall kinetic rate constant was split into the direct oxidation due to photolysis and that by the radicals from hydrogen peroxide or oxalate. In semi-empirical terms, the initial concentration of hydrogen peroxide had a greater contribution than that of oxalate for atrazine oxidation.

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**Key Words** : photolysis, oxalate, hydrogen peroxide, atrazine

### INTRODUCTION

Atrazine, a very popular herbicide, was introduced about 35 years ago, and has subsequently been applied to a variety of crops. It shows a relatively high persistence in soils, and in aquatic systems, atrazine is known to behave almost conservatively except for its proposed degradation due to the photochemically produced OH radicals.<sup>1,2)</sup>

It has been known that advanced oxidation processes (AOPs), such as ozonation, TiO<sub>2</sub> photocatalysis, H<sub>2</sub>O<sub>2</sub>/UV and O<sub>3</sub>/UV, lead to extensive mineralization of the target pollutant.<sup>3~11,13,14)</sup> The mechanisms and products formed by the reaction of atrazine have been carefully studied in experimental systems related to the photolysis<sup>3)</sup> or different pathways in which OH radicals are formed.<sup>4,5)</sup>

Recently, research focused on the combined

photo-assisted Fenton system, or oxalate-assisted Fenton system, for the mineralization of some organics due to their synergic effect,<sup>7)</sup> but the processes are not widely accepted in reality because of the formation of the iron-complex and precipitates. Another approach, the oxalate-assisted H<sub>2</sub>O<sub>2</sub>/UV process, was found to be a viable alternative option for the oxalate-assisted photo-Fenton oxidation, as no iron complex and precipitates form.<sup>12)</sup>

In this work, the kinetics of the transformation of a probe pollutant in the H<sub>2</sub>O<sub>2</sub>/UV and oxalate-assisted H<sub>2</sub>O<sub>2</sub>/UV process were investigated in the presence of different concentrations of hydrogen peroxide or oxalate. Furthermore, the enhancement in the levels of degradation in the presence of free radicals was also investigated and compared to the single photo reaction, with the evaluation of the partial contribution of the radical pathway to the overall oxidation process.

### MATERIALS AND METHODS

The experiments with the UV alone, H<sub>2</sub>O<sub>2</sub>/UV,

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Oxalate/UV and oxalate-assisted H<sub>2</sub>O<sub>2</sub>/UV processes were carried out in a 7 cm diameter round glass cylinder, equipped with a low-pressure lamp (Hankuk TUV 15W), at the irradiation range of 100-280 nm. The radiation source was located axially, and held in a quartz sleeve. The reactor was kept at room temperature (30 ± 2 °C) by a cooling system positioned at the top of the reactor (Figure 1).

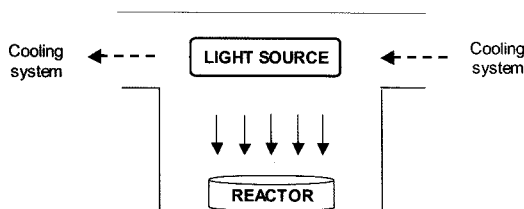


Figure 1. A schematic diagram of the photo-assisted oxidation reactor. The irradiation power was  $6.00 \times 10^{-7}$  E/s and the light source was located at 15 cm above the round glass reactor.

All solutions were prepared using double-distilled water, with an initial pH of 4.0. Samples were taken at regular time intervals, and rapidly analyzed. The concentrations of the substrates were measured by HPLC (KNAUER, Germany). For this purpose the HPLC apparatus equipped with a UV-VIS detector (254 nm) and a Waters C-18 reverse column was used. The mobile phase was composed of a methanol:water (70:30 by volume), with a flow rate of 1 cm<sup>3</sup>/min. The atrazine (>98% purity Aldrich, USA), H<sub>2</sub>O<sub>2</sub> (30 % W/V, Samchun chemical) and sodium oxalate (>99% purity, Junsei chemical) were all of analytical grade.

## RESULT AND DISCUSSION

In order to demonstrate the greater oxidizing power of a combination of oxidizing agents, atrazine oxidation experiments were carried out using a combination of UV radiation and hydrogen peroxide or oxalate. The hydrogen peroxide or oxalate molecules, when irradiated at 254 nm, undergo photolysis to produce OH or organic

radicals, which readily attack organic species in solution.<sup>12)</sup>

Similar to previous photochemical processes, the reaction can be considered to follow first order kinetics with respect to the atrazine concentration. Then, the disappearance rate can be represented by an expression similar to Equation 1.

$$r_T = \frac{dC_s}{dt} = -k_T \cdot C_s \quad (1)$$

where  $C_s$  is the concentration of atrazine at reaction time.

By integrating this kinetic rate equation, we obtain:

$$\ln \frac{C_s}{C_{so}} = -k_T \cdot t \quad (2)$$

where  $C_{so}$  is the initial concentration of atrazine, and  $k_T$  is the overall rate constant.

### Influence of Operating Variables

Experiments were performed at different initial hydrogen peroxide (0, 5, 20, 50 and 200 mg/L) and oxalate (0, 0.8, 1.5 and 2 mM) concentrations under UV irradiation. It can be observed that increasing hydrogen peroxide concentration lead to a parallel increase in the conversion of atrazine, as seen from Figure 2. These results clearly reflect

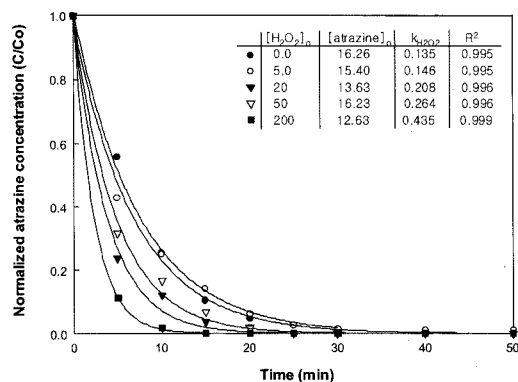


Figure 2. Influence of the initial hydrogen peroxide concentration on the evolution of atrazine in the UV/H<sub>2</sub>O<sub>2</sub> process. Units: [H<sub>2</sub>O<sub>2</sub>]=mg/L, [atrazine]=mg/L.

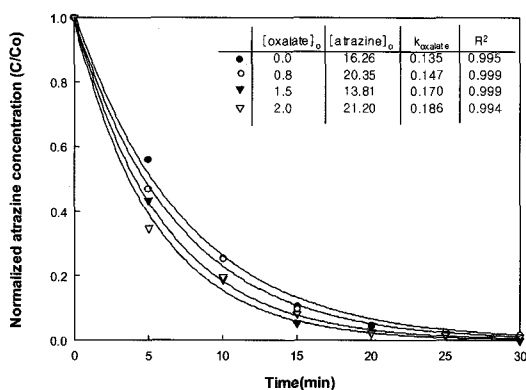


Figure 3. Influence of the initial oxalate concentration on the evolution of atrazine in the UV/H<sub>2</sub>O<sub>2</sub> process. Units: [oxalate]=mmol/L, [atrazine]=mg/L.

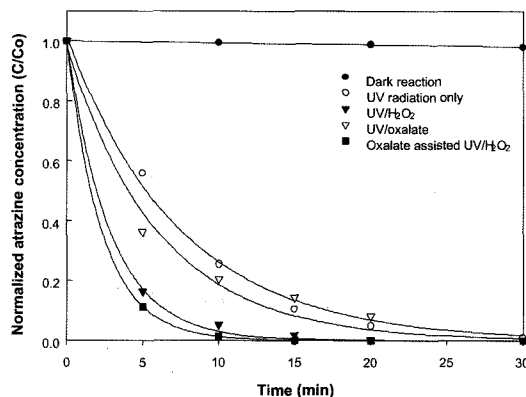


Figure 4. The influence of oxalate on the UV/H<sub>2</sub>O<sub>2</sub> process for atrazine degradation. [oxalate]<sub>0</sub>=2.0 mmol/L, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>=100 mg/L; k<sub>dark</sub>=0.001, k<sub>UV</sub>=0.135, k<sub>UV/H2O2</sub>=0.353, k<sub>T</sub>=0.437.

the role of hydrogen peroxide in the H<sub>2</sub>O<sub>2</sub>/UV process. The hydroxyl radicals generated in photolysis might be an additional contribution to the overall oxidation process.

The degradation rate of atrazine in this irritated system gradually increased with increase of oxalate concentrations as seen from Figure 3. This indicated that the organic radical species generated by the oxalate molecules should attack atrazine molecules in the solution.

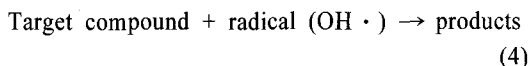
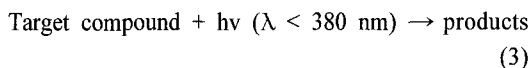
The photolysis of atrazine was undertaken in the presence of oxalate and hydrogen peroxide. As seen in Figure 4, the addition of oxalate to the H<sub>2</sub>O<sub>2</sub>/UV (oxalate-assisted H<sub>2</sub>O<sub>2</sub>/UV) process helped improve the atrazine degradation, but the

degradation did not take place in the dark reaction.

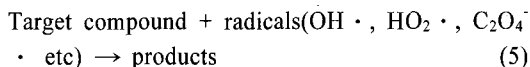
### Kinetic Studies

The consistency of the transformation curve fits in Figures 2, 3 and 4 confirms the assumption of the kinetic regime, in that the reaction mechanism of these combined systems is highly complex, involving numerous individual reactions. At a first approximation; however, one may assume with the oxalate-assisted photooxidation that the reaction mechanism consists of the following individual stages:

- 1) The reaction of the target compound with UV radiation emitted by the polychromatic source and OH radical generated by UV radiation:



- 2) Reaction between the target compound and the radicals generated by the photolysis and homolysis of the hydrogen peroxide and oxalate.



In accordance with this simple mechanism, one can therefore assume that the overall rate of disappearance of the target compound,  $r_T$ , is due to the sum of the contributions of the different individual oxidation stages:

$$r_T = -k_T \cdot C_s = -(k'_{UV} + k'_r) \cdot C_s \quad (6)$$

where  $k'_{UV}$  and  $k'_r$  represent the photochemical and radical reaction rate constants, respectively. This last expression can be expressed as functions of known variables:

$$r_T = -k_T \cdot C_s = -(k'_{UV} + k_r [H_2O_2]_0^m [oxalate]_0^n) \cdot C_s \quad (7)$$

Table 1. Values of the apparent kinetic constants for each reaction pathway

Experiment (mmol/L)		Combined reaction		Photochemical reaction		Radical reaction
H <sub>2</sub> O <sub>2</sub>	oxalate	$k_T$	Std. Error	$k'_{UV}$	Std. Error	$k'_r$
0	1.0	0.160	0.018	0.135	0.008	0.025
0.59	1.0	0.186	0.012	0.135	0.008	0.051
2.94	1.0	0.410	0.001	0.135	0.008	0.275
11.7	1.0	0.528	0.006	0.135	0.008	0.393
2.94	0.0	0.353	0.015	0.135	0.008	0.218
2.94	0.2	0.382	0.028	0.135	0.008	0.247
2.94	2.0	0.437	0.002	0.135	0.008	0.302

: Std. Error represents the standard error of the first order reaction constant for the statistical analysis.

According to Equation 6, the contribution of the radical reaction to the overall reaction rate may be quantified as the difference between the rates of the total and photochemical reactions. Also, the value of the pseudo-first order reaction constant for the radical reaction may be easily calculated by subtracting the determined value of  $k'_{UV}$  from that of the overall constant determined for the process,  $k_T$ .<sup>7)</sup> The values of  $k'_r$  are shown in Table 1.

The apparent radical constant,  $k'_r$ , should be directly proportional to both the initial hydrogen peroxide concentration and the initial oxalate concentration in the solution. The corresponding plots of  $-\ln k'_r$  versus  $-\ln[H_2O_2]_0$  or  $-\ln[oxalate]_0$  were straight lines, with slopes of 0.69 and 0.09, which denote the values of  $m$  and  $n$ , respectively (see Figures 6 and 7). One can see from the above values that, in the combined process, the initial concentration of hydrogen peroxide had a greater contribution than that of oxalate in the atrazine transformation.

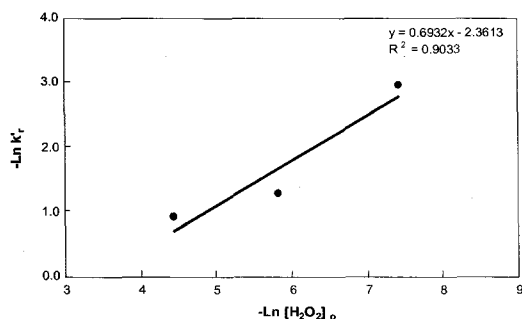


Figure 5. Effect of the initial hydrogen peroxide concentration on the apparent radical reaction constant,  $k'_r$ .

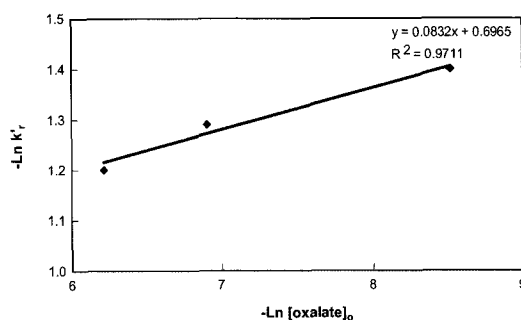


Figure 6. Effect of the initial oxalate concentration on the apparent radical reaction constant,  $k'_r$ .

## CONCLUSIONS

The experimental results indicated that the oxidation kinetics for the oxalate-assisted photolysis in the presence of hydrogen peroxide were a good pseudo first order fit ( $R^2 > 99.5\%$ ). The effect of the initial hydrogen peroxide or oxalate concentration on the oxidation of atrazine was positive. The addition of oxalate to the H<sub>2</sub>O<sub>2</sub>/UV (oxalate-assisted H<sub>2</sub>O<sub>2</sub>/UV) process was the most effective method for the degradation of atrazine. The overall kinetic rate constant contains two elements: the direct oxidation due to UV radiation and that by radicals from the hydrogen peroxide and oxalate. In the combined process (in the presence of hydrogen peroxide and oxalate), the contribution of radical oxidation to the atrazine transformation was as much as 74.4% of the overall oxidation process. This means that the atrazine transformation was due mainly to radical oxidation pathways rather than a photolysis

process. From the empirical analysis, hydrogen peroxide was found to have a greater contribution than oxalate in the radical oxidation of atrazine. For the further study, it is recommended to identify the individual reaction taking place in these complex system because oxalate could act as a scavenger of hydroxyl radicals that are produced in the photolysis reaction and hence competes with the atrazine for OH radical. Also, the degradation products of the photolysis should be identified to determine the environmental persistence and ecological significance of atrazine decomposition.

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