

Kinetics of the UV degradation of atrazine in aqueous solution in the presence of hydrogen peroxide

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Abstract

The kinetics of degradation of atrazine were studied using UV radiation in combination with hydrogen peroxide at different pH values. The influence of the initial concentration was also considered. The dark reactions were negligible. The kinetic constants were determined following a proposed first-order kinetic model.

The photochemical treatment of water contaminated with atrazine is conditioned by the toxicity of the decomposition products, since the treatment is unable to degrade all of these products.

Keywords: UV radiation; Hydrogen peroxide; Photo-oxidation; Kinetic study; Atrazine; Pesticides

1. Introduction

The widespread use of pesticides has led to public health concerns, increases in the resistance of many pests and the contamination of water, air and soil [1]. Many pesticides are toxic and some are carcinogenic or mutagenic. Many also have great persistence in the environment. Therefore a knowledge of how to degrade these compounds into environmentally compatible products is required. One of the most powerful methods is treatment with UV radiation. The simultaneous use of UV light and an oxidant—usually ozone [2] or hydrogen peroxide [3]—is more powerful. However, hydrogen peroxide has the advantage that it does not need to be generated in situ.

The need to design new powerful wastewater treatment plants requires a new set of parameters. These constants and relationships cannot always be found in the literature. The aim of this study is to determine the photodegradation kinetic constants of atrazine.

Atrazine is a 1,3,5-triazine used as a selective herbicide in grassland, maize, pineapple, sorghum, sugarcane and non-crop areas [4]. According to the US Environmental Protection Agency (EPA), atrazine shares the characteristics of other triazine herbicides, such as high

leaching potential, high persistence in soils, slow hydrolysis, low vapour pressure, moderate solubility in water and moderate adsorption to organic matter and clay [5]. The toxicity of atrazine is quite high for aquatic organisms and lower for mammals.

A tentative photodegradation pathway (Fig. 1) in aqueous solution containing 3%–4% methanol has been presented in Ref. [6]. The photodegradation of atrazine has been studied using ozonation [7] and photocatalytic degradation [8].

2. Materials and methods

Atrazine (purity, 99%) was obtained from Chem Service (USA) and hydrogen peroxide (30% v/v) was purchased from Panreac (Spain).

The experiments were carried out in a stirred annular photoreactor. A diagram of the experimental device is shown in Fig. 2. It consists of an annular photoreactor, a jacket, a lamp and a filter solution circuit.

The annular photoreactor is a hollow cylinder of 1.62 l capacity with the following dimensions: height, 6.20 cm; internal radius, 3.0 cm; external radius, 9.65 cm. The inner wall is made of quartz and the outer wall is made of Pyrex (Corning 7740). There are two stirrers to guarantee good mixing in the reactor. Between the

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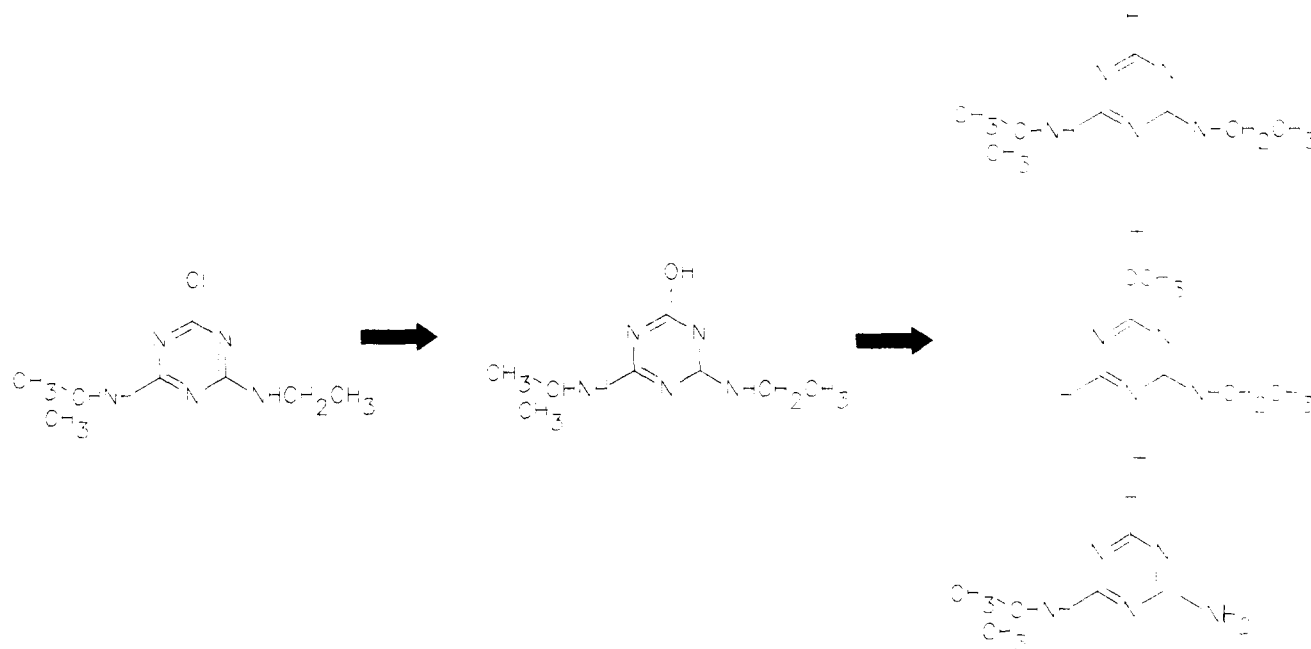


Fig. 1. Possible pathway of photodegradation of atrazine.

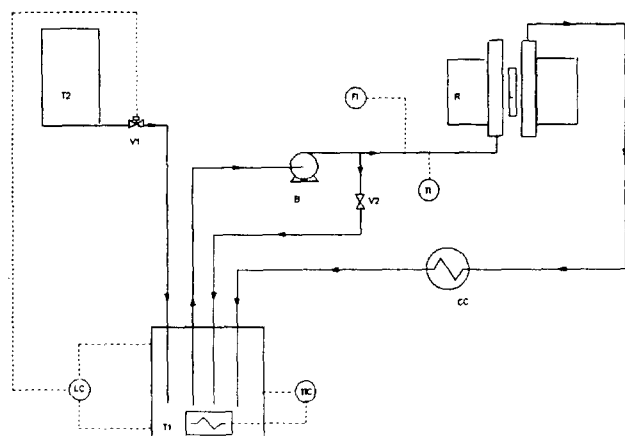


Fig. 2. Diagram of the experimental device.

lamp and the photoreactor chamber there is an annular space (jacket) through which a filter solution flows to maintain constant temperature and to eliminate certain wavelengths.

The jacket is a cylinder of annular section made of quartz. The radius of the internal cylinder is 1.7 cm and the radius of the external cylinder is 3.0 cm. This latter measure also corresponds to the inner radius of the reaction chamber.

The radiation source is a mercury lamp (Philips HPK 125 W) of 3.0 cm in length, with a radius of 0.6 cm and a wavelength range of 240–540 nm (Fig. 3). The photon flow emitted by the lamp is $78.2 \mu\text{einsteins}^{-1}$, as determined using uranyl oxalate actinometry.

The filter solution is circulated continuously through the annular space of the photoreactor by a recycle

pump. The valves (V) are used to regulate the flow rate, which is measured by a rotameter (FI). Temperatures in the filter solution circuit and in the reactor chamber are measured by thermometers (TI). A temperature controller (TIC), heat exchanger and filter solution tank keep the temperature in the filter circuit constant.

All the experiments were carried out in batch operation at 28 °C. Millipore quality water was used as cooling fluid in the experiments without hydrogen peroxide, but a filter solution of $\text{UO}_2(\text{NO}_3)_2$ ($6 \times 10^{-4} \text{ M}$) was used for the experiments with oxidants. The absorption spectrum is shown in Fig. 4. The filter solution was used to reduce the rate of the reaction.

The samples were analysed by high performance liquid chromatography (HPLC). The equipment used was a Waters model 510 apparatus equipped with a variable wavelength UV detector. A Supelcosil LC-18 column ($5 \mu\text{m}$, $250 \text{ mm} \times 4.6 \text{ mm}$) was employed. The mobile phase was a mixture of 70% (v/v) methanol and 0.01 M aqueous sodium hydrogenphosphate [9]. The eluent was delivered at a rate of 1.0 ml min^{-1} and the wavelength for detection was 235 nm. For these operating conditions, the retention time was 10.5 min.

A spectrophotometer (Beckman model 25) was used to measure the absorbance of the solutions.

All the experiments were buffered except those labelled A1, B1, AP1 and BP1 (Tables 1 and 2). In these experiments, the pH was allowed to vary from pH 5.5 to pH 4.8. The buffer solution of pH 4.8 was prepared with acid and sodium acetate. The pH 7.0 buffer contained potassium dihydrogenphosphate and sodium hy-

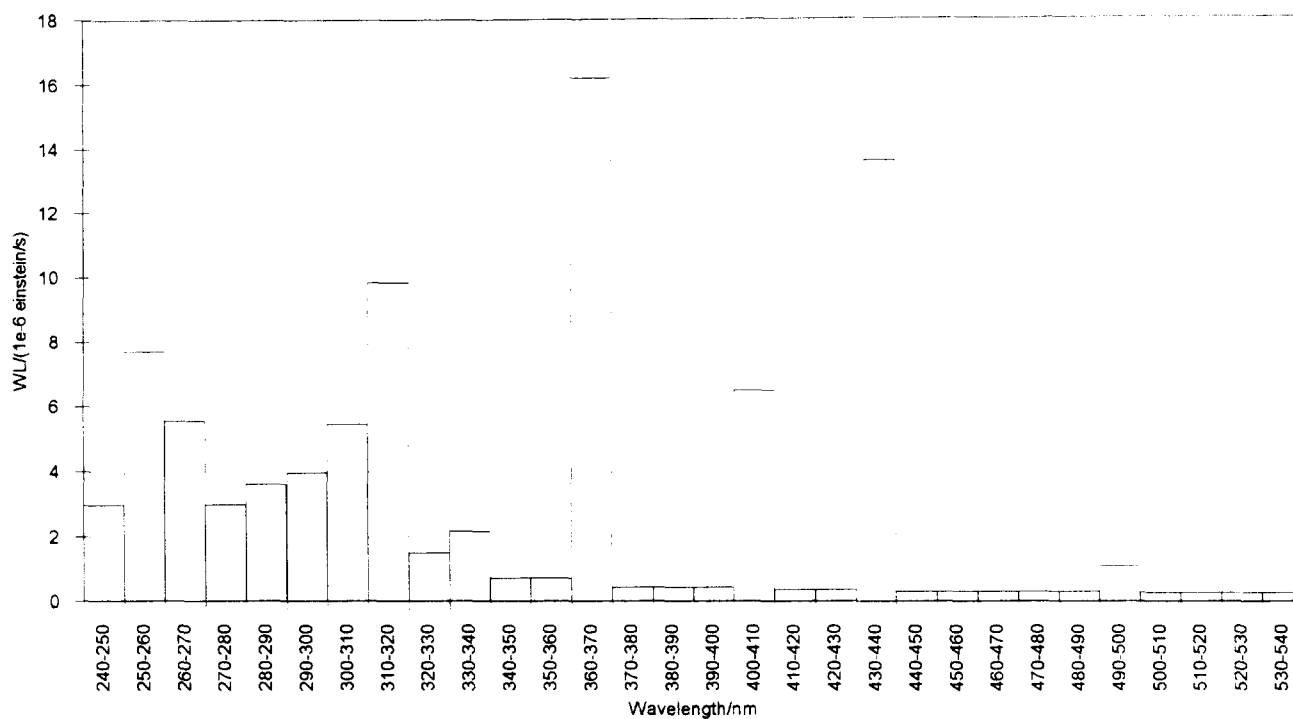


Fig. 3. Emission spectrum of the radiation source (Philips HPK 125 W).

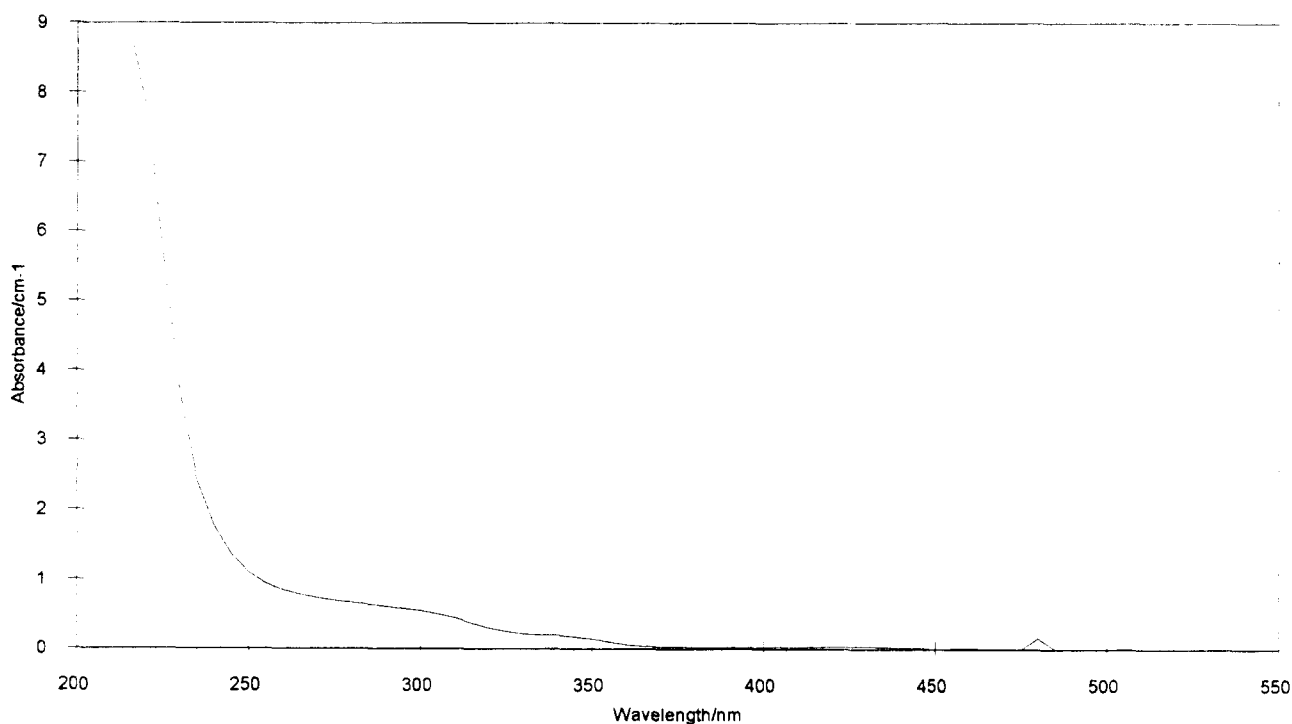


Fig. 4. Absorption spectrum of a $\text{UO}_2(\text{NO}_3)_2$ (6×10^{-4} M) solution used as filter solution.

drogenphosphate; the pH was brought to pH 9.0 by adding sodium hydroxide to this buffer. A run with the same initial conditions as B1 was also performed using filter solution. The reason for this run was to compare the dynamic variation of the total organic carbon (TOC) between experiments B1 and BP1.

3. Mathematical model

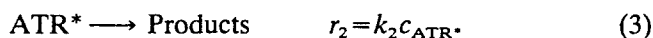
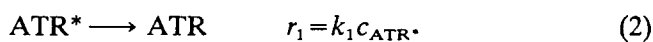
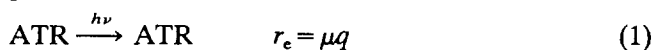
3.1. Experiments with UV radiation

The photodegradation of pesticides is very complex, since many subproducts can be obtained and many reactions may take place. Due to the need to obtain

Table 1
Initial conditions and quantum yields of the experiments carried out without oxidant

No.	C_{ATR}^0 (ppm)	c_{ATR}^0 ($\mu\text{mmol l}^{-1}$)	W_{abs}^0 ($\mu\text{einstein s}^{-1}$)	pH	ϕ
A1	16.6	77.0	4.02	5.5–4.8	0.100
A2	16.1	74.6	3.99	7.0	0.103
A3	16.1	74.6	3.99	9.0	0.104
A4	17.0	78.8	4.04	4.8	0.075
B1	10.8	50.1	3.59	5.5–4.8	0.100
B2	11.7	54.2	3.68	7.0	0.103
B3	13.6	63.1	3.82	9.0	0.106
B4	13.1	60.7	3.79	3.8	0.076

a kinetic equation, a simple mechanism has been proposed



where ATR denotes atrazine, k_1 includes the constants of the molecular deactivation process, radiative and non-radiative, and the pseudo-first-order constants of the bimolecular deactivation process and k_2 includes the constants of the primary photodegradation process.

Applying the pseudo-steady state hypothesis to the activated atrazine ($r_{\text{ATR}^*} = 0$), the rate of decomposition of the pesticide is

$$r_{\text{ATR}} = -\mu q \frac{k_2}{k_1 + k_2} = -\phi \mu q \quad (4)$$

where ϕ is the quantum yield, which indicates the amount of atrazine degraded per mole of absorbed photons.

Assuming perfect mixing in the liquid phase and batch operation, the mass balance of atrazine in the reactor is

$$V \frac{dc_{\text{ATR}}}{dt} = -\frac{k_2}{k_1 + k_2} W_{\text{abs}} \quad (5)$$

Table 2
Initial conditions and kinetic constants of the experiments carried out with oxidant

No.	c_{ATR}^0 (ppm)	c_{ATR}^0 ($\mu\text{mol l}^{-1}$)	$W_{\text{abs,ATR}}^0$ ($10^{-2} \mu\text{einstein s}^{-1}$)	pH	K_1 (10^{-5}s^{-1})	K_2 ($10^{-2} \mu\text{mol l}^{-1} \text{s}^{-1}$)	k ($\text{l}^{1/2} (\text{einstein}^{-1/2} \text{s}^{-1/2})$)
AP1	16.3	75.6	2.39	5.5–4.8	–2.09	–2.70	1.26
AP2	19.13	89.5	2.83	7.0	–2.17	–4.54	2.12
AP3	19.9	92.3	2.92	9.0	–2.21	–7.68	0.36
AP4	12.5	58.0	1.85	4.8	–1.60	–1.79	0.84
BP1	14.0	64.9	2.06	5.5–4.8	–2.10	–1.25	0.58
BP2	13.5	62.6	1.99	7.0	–2.18	–2.69	1.26
BP3	13.0	60.3	1.92	9.0	–2.12	–5.57	0.26
BP4	13.8	64.0	2.03	4.8	–1.60	–1.62	0.76

where

$$W_{\text{abs}} = \int_V \mu q dV \quad (6)$$

The photon flow absorbed by the reaction system W_{abs} can be estimated by the linear spherical model [10,11] (Fig. 5)

$$q = W_L \sum_{\lambda} \frac{F_{\lambda}}{4\pi L} \int_x^{x+L} \frac{\exp(-\mu_{\lambda} B)}{r^2 + (z-l)^2} dl \quad (7)$$

where

$$B = \left(1 - \frac{R_1}{r}\right) [r^2 + (z-l)^2]^{1/2} \quad (8)$$

The absorbed photon flow varies with the concentration of atrazine (Fig. 6) and with the presence of the products of degradation, and so changes as atrazine reacts. It can be considered to be constant with time for the beginning of the reaction, and can be derived from the absorbance by atrazine by applying the Lambert–Beer law

$$\frac{W_{\text{abs}}}{W_{\text{abs}}^0} = \frac{\mu}{\mu_0} = \frac{c_{\text{ATR}}}{c_{\text{ATR}}^0} \quad (9)$$

Integrating Eq. (5), considering Eq. (9) and using the boundary condition $c_{\text{ATR}}(t=0) = c_{\text{ATR}}^0$, the dependence of the concentration of atrazine on time is

$$c_{\text{ATR}} = c_{\text{ATR}}^0 \exp\left(-\frac{k_2}{k_1 + k_2} \frac{W_{\text{abs}}^0}{c_{\text{ATR}}^0 V} t\right) \quad (10)$$

The value of W_{abs}^0 was calculated on the basis of the absorption spectrum of atrazine and the emission spectrum of the lamp using the following equation

$$W_{\text{abs}}^0 = \sum_{\lambda} \frac{W_{\text{abs},\lambda}^0}{W_{L,\lambda}} W'_{L,\lambda} \quad (11)$$

The values of $W_{\text{abs},\lambda}^0/W_{L,\lambda}$ were calculated by a computational program [12]. The value of $W'_{L,\lambda}$ was obtained from actinometry using uranyl oxalate. In the wavelength range 240–540 nm, W'_L was $78.2 \mu\text{einstein s}^{-1}$.

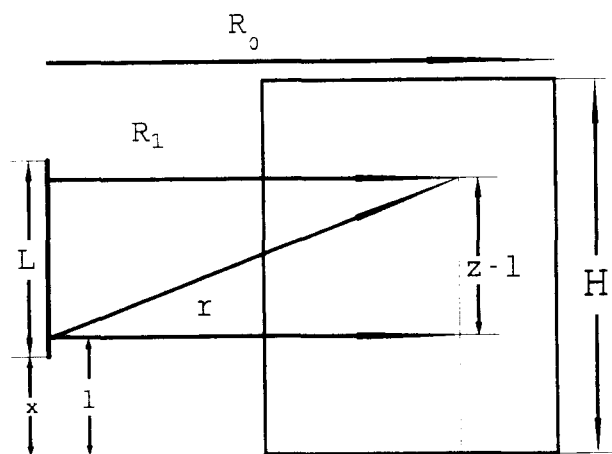
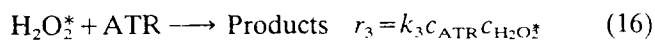
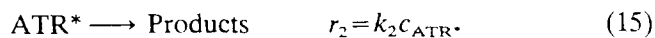
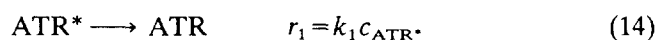
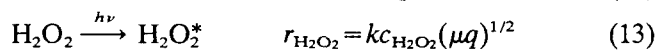
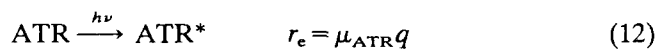


Fig. 5. Variables of the linear spherical model.

3.2. Experiments with hydrogen peroxide and UV radiation

A simple degradation pathway can be written for the decomposition of atrazine in the presence of hydrogen peroxide and UV radiation



All the radicals formed by the collision of one photon and one molecule of H_2O_2 are included in the term H_2O_2^* .

The rate of decomposition of a solution of H_2O_2 with a concentration of less than 0.2 M was taken from Ref. [13].

Applying the hypothesis of pseudo-steady state ($r_{\text{ATR}^*} = 0$ and $r_{\text{H}_2\text{O}_2^*} = 0$), we have

$$r_{\text{ATR}} = - \frac{k_2}{k_1 + k_2} \mu_{\text{ATR}} q - k c_{\text{H}_2\text{O}_2} (\mu_{\text{H}_2\text{O}_2} q)^{1/2} \quad (17)$$

The mass balance of atrazine in the reactor assuming perfect mixing and batch operation is as follows

$$V \frac{dc_{\text{ATR}}}{dt} = \int_V r_{\text{ATR}} dV \quad (18)$$

The concentration of H_2O_2 remains constant, and assuming that the absorbance of the sample does not change with time, the atrazine mass balance is

$$V \frac{dc_{\text{ATR}}}{dt} = - \phi \frac{c_{\text{ATR}}}{c_{\text{ATR}_0}} W_{\text{abs, ATR}}^0 - k c_{\text{H}_2\text{O}_2}^m \int_V (\mu_{\text{H}_2\text{O}_2} q)^{1/2} dV \quad (19)$$

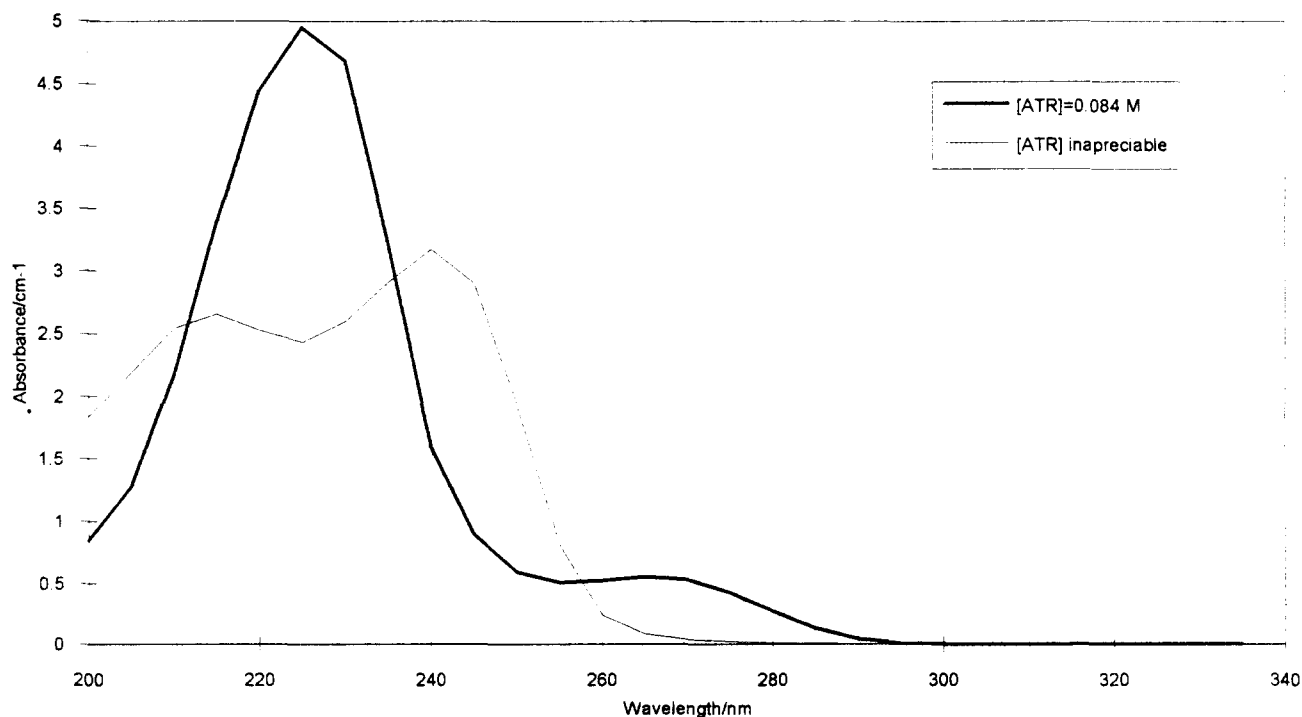


Fig. 6. Absorption spectra of a solution of atrazine and the same solution photodegraded until the concentration of atrazine was inappreciable (note that the broken line shows the initial emission wavelength of the lamp).

The value of $W_{\text{abs},\lambda}^0$ was calculated in the same way as for the mechanism without H_2O_2 but using

$$\mu_\lambda = \mu_{\text{ATR},\lambda} + \mu_{\text{H}_2\text{O}_2,\lambda} \quad (20)$$

Integrating Eq. (19), we obtain

$$c_{\text{ATR}} = \frac{(K_1 c_{\text{ATR}}^0 + K_2) \exp(K_1 t) - K_2}{K_1} \quad (21)$$

where

$$K_1 = - \frac{\phi W_{\text{abs},\text{ATR}}^0}{c_{\text{ATR}}^0 V} \quad (22)$$

$$K_2 = - \frac{k c_{\text{H}_2\text{O}_2}^m}{V} \int_V (\mu_{\text{H}_2\text{O}_2} q)^{1/2} dV \quad (23)$$

4. Results and discussion

No dark reaction was observed. No concentration change was observed, although the concentration of atrazine was measured in several samples at different pH values for many weeks. Moreover, dark degradation was not observed in the presence of hydrogen peroxide.

The proposed photodegradation pathway shows that atrazine cannot be completely degraded by UV radiation. This conclusion can also be reached by examination of Fig. 7. This figure shows how the TOC changes as a function of the irradiation time in a run with only

UV radiation. A lower limit to the TOC concentration is achieved, which cannot be decreased by this method. Even treatment with UV radiation and hydrogen peroxide cannot eliminate the decomposition products entirely. However, the TOC limit concentration obtained is lower because of the presence of new degradation pathways.

A synergistic effect is shown in Fig. 7, which compares two experiments with the same initial conditions. There was no reaction with the samples treated with only hydrogen peroxide. The sample treated with UV radiation and hydrogen peroxide was decomposed four times faster. The reason for this behaviour is a radical mechanism. New reactions occur as a consequence of the presence of radicals (especially OH^\cdot and HO_2^\cdot) from the decomposition of hydrogen peroxide by UV radiation.

4.1. Experiments with UV radiation

The initial conditions of the experiments and the calculated kinetic constants are shown in Table 1.

To maintain the hypothesis of constant absorbance in the reaction medium during irradiation, only the initial points of the experiments, conversions below 65%, were fitted to Eq. (10).

The experiments shown in Fig. 8 had the same initial pH but different initial concentrations of pesticide. The experiment with the lowest initial concentration showed

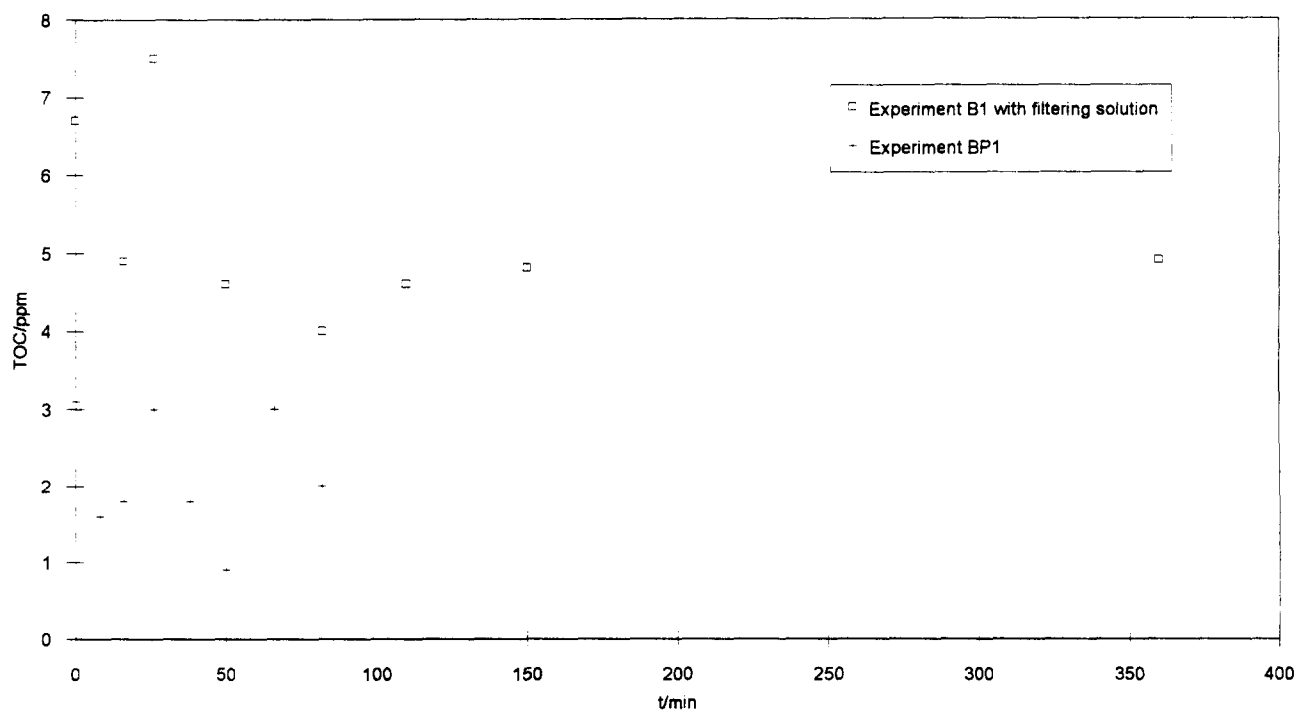


Fig. 7. Experiments carried out with the same initial conditions. A TOC limit concentration is reached in all cases (note that the experiment with oxidant (BP1) was carried out with a filter solution).

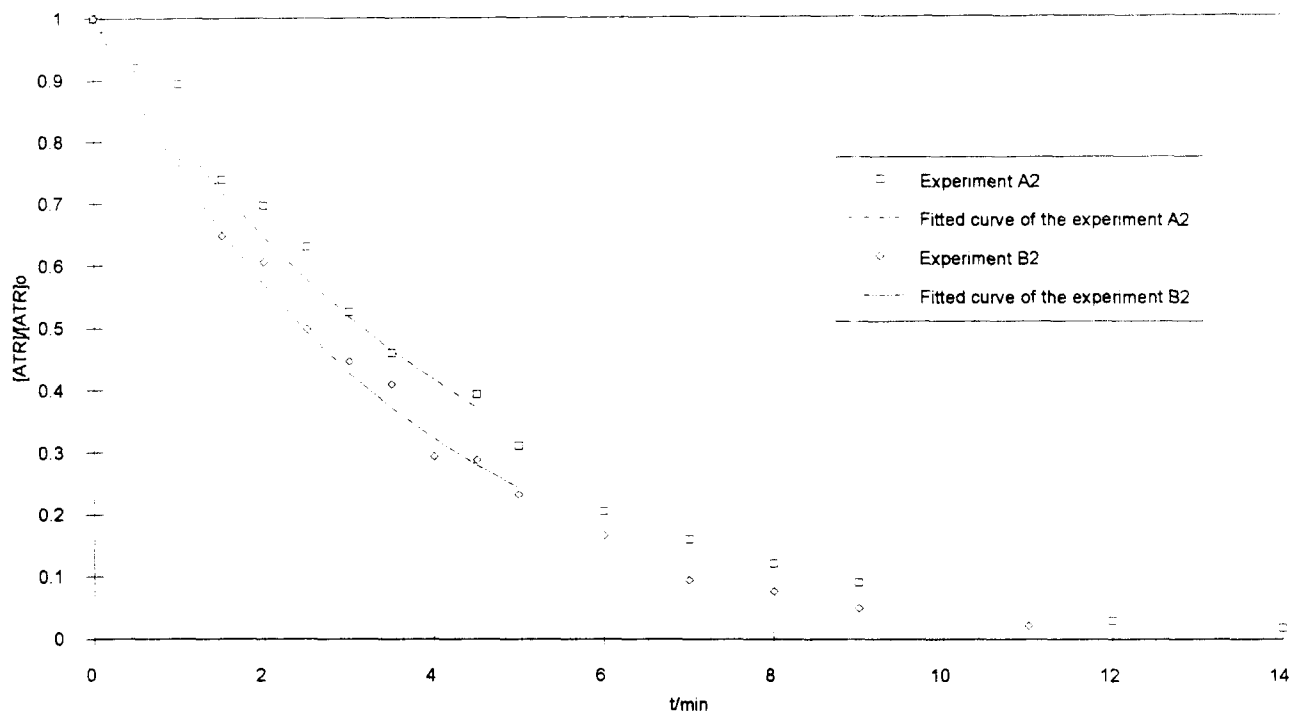


Fig. 8. Experiments carried out at the same pH and different concentrations of atrazine.

the highest rate. This tendency occurred in all the experiments with the same pH and different initial concentrations of pesticide.

The influence of the pH is shown in Fig. 9. The presented experiments have the same initial concentration of atrazine and different pH values. The kinetic

rates of the experiments at pH 7.0 and 9.0 are the same within experimental error. The experiment at acidic pH (pH 4.8) presented the lowest photodecomposition rate. The same behaviour was observed for the other experiments with different concentrations of atrazine.

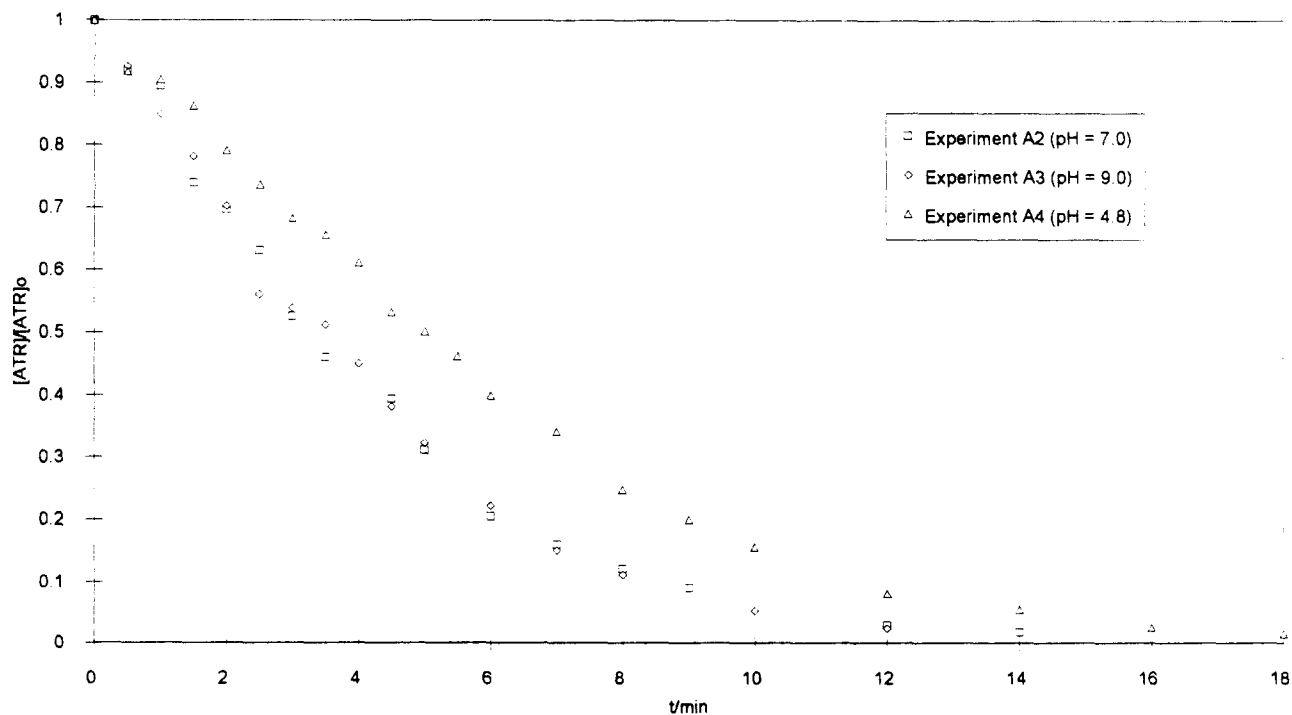


Fig. 9. Experiments carried out with the same initial atrazine concentration but different pH values.

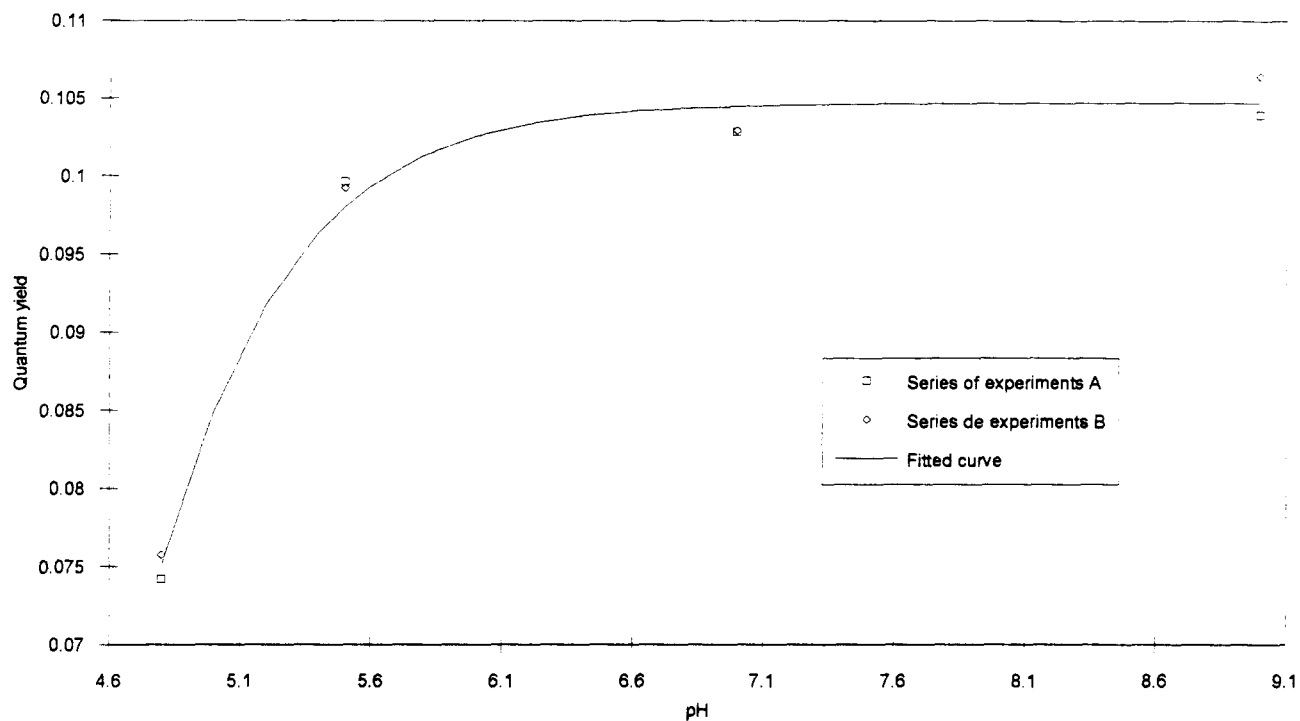


Fig. 10. Empirical fit of the quantum yield with the pH.

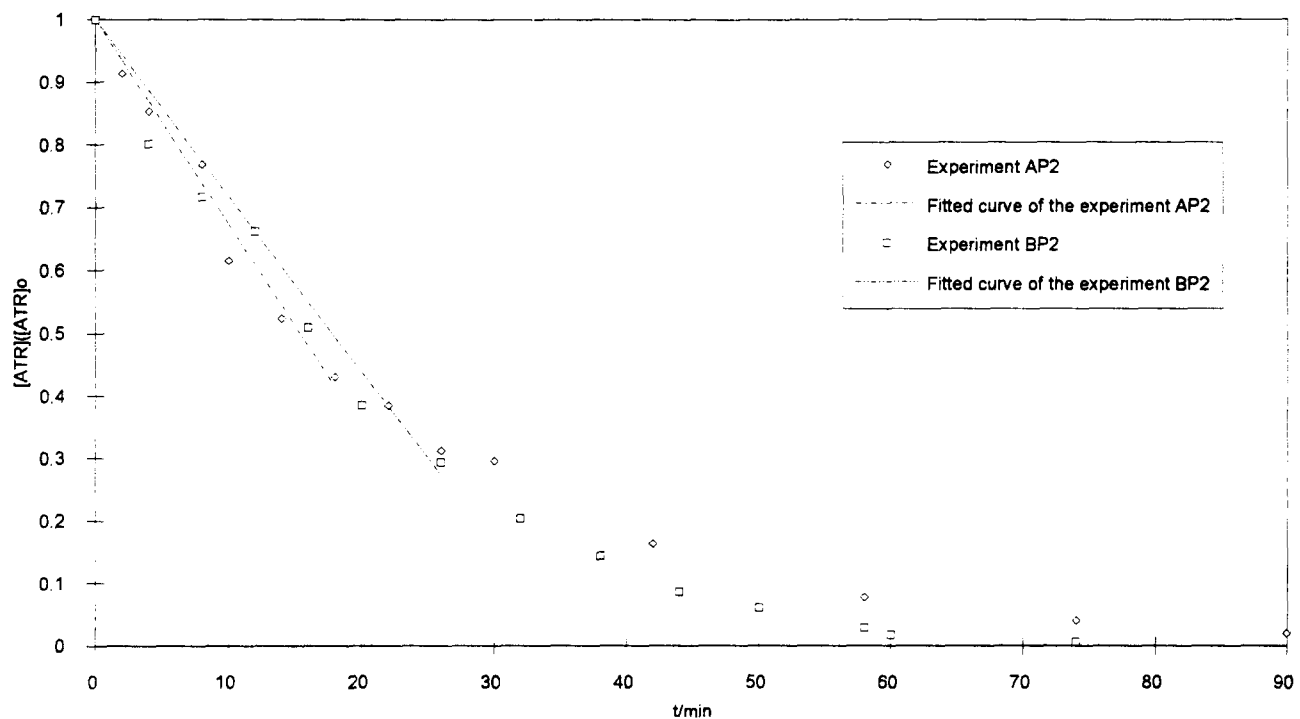


Fig. 11. Experiments at the same pH and different initial concentrations of atrazine treated with UV radiation and H_2O_2 (note that a filter solution was used in these experiments).

The quantum yield was fitted empirically to the pH, as shown in Fig. 10. Considering 95% threshold intervals, the resulting equation is

$$\phi = 10^{(-9.80 \pm 0.13) \times 10^{-1} \text{pH}^{(-9.08 \pm 0.71) \times 10^3}} \quad (24)$$

with a correlation coefficient $r = 0.9951$.

4.2. Experiments with hydrogen peroxide and UV radiation

The initial conditions of the experiments and the calculated kinetic constants are given in Table 2.

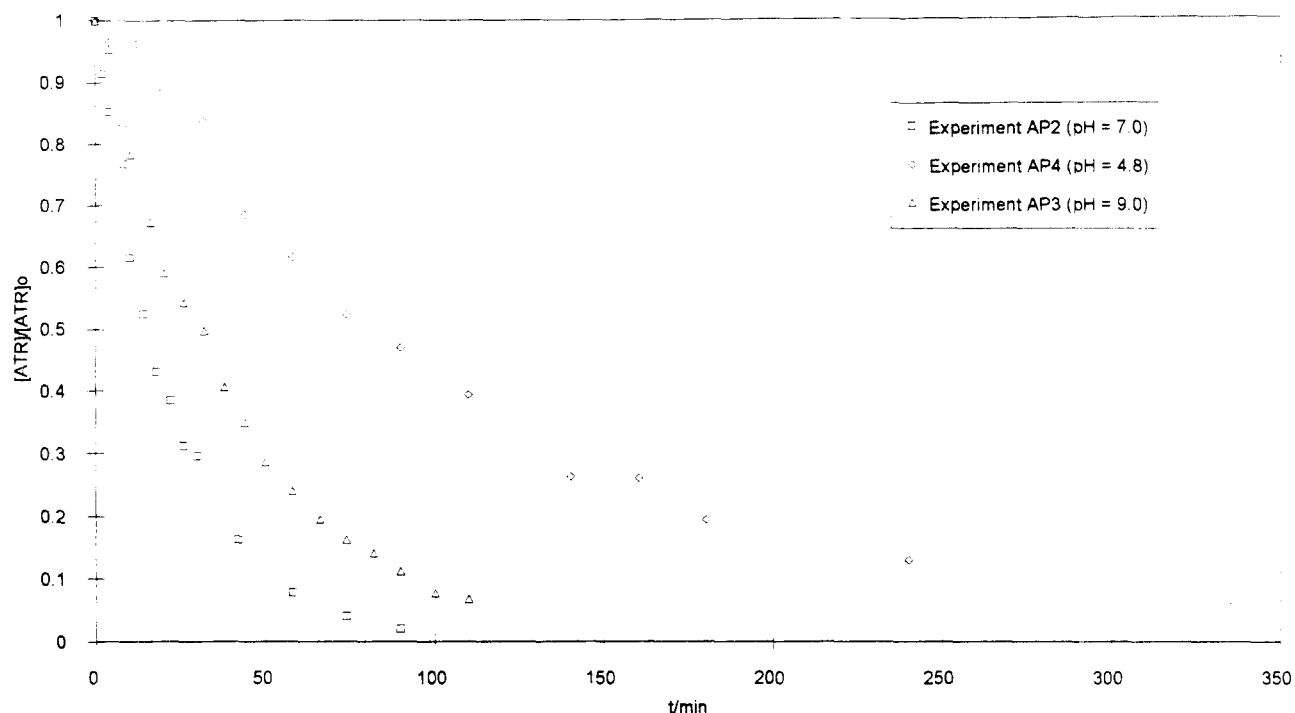


Fig. 12. Experiments at the same initial concentration of atrazine and different pH values carried out with UV radiation and H_2O_2 (note that a filter solution was used in these experiments).

The experiments carried out with hydrogen peroxide and UV radiation could only be fitted for the initial time of the reaction as observed for the samples treated with UV radiation only. The reason for this behaviour is that the absorption of the system is dependent on time because products of decomposition are produced as atrazine is degraded.

No influence of the initial concentration of atrazine on the rate of decomposition was observed, within experimental error, in the pH buffered experiments carried out with H_2O_2 and UV. For example, the experiments shown in Fig. 11 demonstrate that the rate is the same for all experiments performed at pH 7.0.

When comparing experiments at the same initial concentration of atrazine but different pH values, no simple relationship was obtained between the rate of photo-oxidation and the pH. As shown in Fig. 12, the experiment at pH 7.0 has the highest rate and the experiment at pH 4.8 the lowest.

As in the series of experiments with UV radiation, an empirical equation has been calculated for the dependence of the constant K_1 in the kinetic model on the pH

$$K_1 = -10^{(4.66 \pm 0.02)} \text{pH}^{(8.6 \pm 1.0) \times 10^3} \quad (25)$$

with a correlation coefficient $r=0.9935$, considering confidence intervals of 95%.

5. Conclusions

- (1) The dark decomposition of atrazine in aqueous solution is negligible with respect to the photochemical decomposition and photo-oxidation.
- (2) The rate of photodecomposition and photo-oxidation of aqueous solutions of atrazine at short times of irradiation follows first-order kinetics with respect to the radiation absorbed in the range of concentrations and pH studied. The quantum yield depends on the pH of the medium.
- (3) In the case of the use of hydrogen peroxide and UV radiation, a synergistic effect is observed.
- (4) The treatment of atrazine in water with UV radiation is conditioned by the toxicity of the decomposition products, and alternative methods are needed to degrade them. On the other hand, the use of UV radiation and H_2O_2 is a more powerful method that further reduces the TOC concentration. This treatment can eliminate the TOC concentration.

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Appendix: Nomenclature

B	optical path of the linear spherical model (m)
c_i	concentration of compound i (mol l ⁻¹)
F	factor of the lamp
h	Planck's constant (J s)
k	kinetic constant of the photodecomposition of H ₂ O ₂ (l ^{1/2} einstein ^{-1/2} s ^{-1/2})
k_1	kinetic constant of the deactivation processes (s ⁻¹)
k_2	kinetic constant of the photodegradation processes (s ⁻¹)
k_3	kinetic constant of the photodegradation of atrazine in the presence of H ₂ O ₂ (l mol ⁻¹ s ⁻¹)
K_1	kinetic constant defined in Eq. (22) (s ⁻¹)
K_2	kinetic constant defined in Eq. (23) (mol l ⁻¹ s ⁻¹)
l	axial coordinate of one point of the lamp (m)
L	length of the lamp (m)
q	modulus of the flux density of the radiant energy vector
r	radical coordinate (m)
r_e	rate of the excitation step (mol l ⁻¹ s ⁻¹)
r_i	rate of reaction of compound i (mol l ⁻¹ s ⁻¹)
r_1	rate of the deactivation processes (mol l ⁻¹ s ⁻¹)
r_2	rate of the photodegradation processes (mol l ⁻¹ s ⁻¹)
r_3	rate of the photodegradation of atrazine in the presence of H ₂ O ₂ (mol l ⁻¹ s ⁻¹)
R_1	internal radius of the reaction chamber (m)
t	time (s)
V	volume (l)
W_{abs}	absorbed photon flow (einstein s ⁻¹)
W_L	photon flow emitted by the lamp (einstein s ⁻¹)
W'_L	photon flow corrected for the effect of the radiation filter (einstein s ⁻¹)
x	axial coordinate (m)
z	axial coordinate (m)

Greek symbols

λ	wavelength (nm)
μ	absorbance (cm ⁻¹)

ν	radiation frequency (s ⁻¹)
ϕ	quantum yield

Subscripts and superscripts

ATR	atrazine
H ₂ O ₂	hydrogen peroxide
m	medium
*	activated
0	initial

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