ADVANCED OXIDATION PROCESSES FOR ENVIRONMENTAL PROTECTION

Photolysis of atrazine in aqueous solution: role of process variables and reactive oxygen species

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Abstract Photochemical advanced oxidation processes have been considered for the treatment of water and wastewater containing the herbicide atrazine (ATZ), a possible human carcinogen and endocrine disruptor. In this study, we investigated the effects of the photon emission rate and initial concentration on ATZ photolysis at 254 nm, an issue not usually detailed in literature. Moreover, the role of reactive oxygen species (ROS) is discussed. Photon emission rates in the range 0.87×10^{18}–3.6×10^{18} photons L^{-1} s^{-1} and $[ATZ]_0 = 5$ and 20 mg L^{-1} were used. The results showed more than 65 % of ATZ removal after 30 min. ATZ photolysis followed apparent first-order kinetics with k values and percent removals decreasing with increasing herbicide initial concentration. A fivefold linear increase in specific degradation rate constants with photon emission rate was observed. Also, regardless the presence of persistent degradation products, toxicity was efficiently removed after 60-min exposure to UV radiation. Experiments confirmed a noticeable contribution of singlet oxygen and radical species to atrazine degradation during photolysis. These results may help understand the behavior of atrazine in different UV-driven photochemical degradation treatment processes.

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Introduction

Persistent organic pollutants (POPs) have been identified as an emerging problem in drinking water supplies. Many herbicides and other pesticides have been included amongst POPs due to their resistance to natural degradation processes and hence their capacity to remain in the environment for long periods of time (McMurray et al. 2006).

Atrazine (ATZ), 2-chloro-4-ethylamino-6-isopropylamino-S-triazine, is one of the most commonly used herbicides in the world (Hleli et al. 2006). For example, about 40 million kilograms were consumed in the USA in 2005 (US 2005). ATZ is currently used in pre and postemergent control of broad-leaved herbs, mainly in maize, sugar cane, and soybean cultures (González-Barreiro et al. 2006), and can be present in wastewaters from industrial synthesis processes and agro-industry, rinse water from spray equipment and pesticide containers, spills due to improper handling and disposal, agricultural runoff, etc. Due to its relatively high solubility in water of 33 mg L^{-1} (Lin and Chu 2011) and high mobility, atrazine can be transported to groundwater or to surface waters and therefore easily reach the aquatic environment (Chen et al. 2009). It is more frequently detected in groundwater and surface water than any other herbicides in many countries (Ta et al. 2006).

ATZ is classified as a possible human carcinogen by the Environmental Protection Agency of the USA. Several studies suggest that ATZ can act as an endocrine disruptor and cause sexual abnormalities in aquatic animals (Lin and Chu 2011). It is therefore a matter of concern that ATZ has been detected in many rivers and water reservoirs in Brazil and around the world (Curini et al. 2000; Carabias-Martinez et al. 2006) at concentrations between 0.6 to 2.46 $\mu g\ L^{-1}$ (Carabias-Martinez et al. 2006; Hildebrant et al. 2008). Some countries established maximum limits of ATZ in water for human consumption like 2 $\mu g\ L^{-1}$ in Brazil (Directive 518 of the Brazilian Ministry of

Health 2004), 3 μg L^{-1} in the USA (US 2003), and 0.1 μg L^{-1} in countries of the European Union (Baranda et al. 2012).

Several authors have studied the feasibility of ATZ degradation in aqueous medium by different advanced oxidation processes (AOPs) as H_2O_2/UV (Beltrán et al. 1995), TiO_2/UV (Pérez et al. 2006), Fenton (Chan and Chu 2005) and photo-Fenton (De Luca et al. 2013) reactions, and oxidation by ozone (Farre et al. 2007). However, studies devoted to exploring ATZ photolysis considering the effects of radiant power and herbicide concentration are scarce in the literature.

In this study, the effects of the photon emission rate and ATZ initial concentration during photolysis under 254-nm UV radiation on degradation rate are discussed. Furthermore, the role of reactive oxygen species (ROS) in ATZ photolysis and the toxicity of irradiated samples were investigated. These studies combined are not usually found in the literature and therefore configure an original contribution.

Experimental

Chemicals

All solutions were prepared using water purified by reverse osmosis (Mili-Q). Technical grade atrazine (ATZ, MM=215.68 g mol^{-1}, minimum purity 92 %) was supplied by Syngenta Brazil and was used as a standard in ultra-fast liquid chromatography (HPLC) analysis and in photochemical experiments. Sodium azide and isopropanol were used as described later. For HPLC analysis, acetonitrile (HPLC quality) and glacial acetic acid (100 %) were purchased from Merck.

Equipment and procedures

Hydrolysis experiments were performed in the dark in flasks of 20 mL at 25 °C, at pH 3, 5, 7, and 9, in a shaker. Samples were taken at 0, 6, and 24 h and analyzed by HPLC.

Photolysis experiments were performed in batch in a tubular photochemical reactor (Fig. 1) which consists of a borosilicate glass tube equipped with a concentric low-pressure (LP) mercury vapor lamp (TUV Philips, 36 W), emitting UV radiation with a peak at 253.7 nm. According to the lamp supplier, the glass of this lamp filters out the 185-nm line. By homogenously covering different fractions of the lamp surface with an opaque material, four different photon emission rates on a per unit reactor volume basis ($E_{P,0}$, photons L^{-1} s^{-1}) could be obtained, namely 3.6×10^{18}, 1.9×10^{18}, 1.1×10^{18}, and 8.7×10^{17}. These values were measured by ferrioxalate actinometry according to a procedure detailed elsewhere (Braun et al. 1991). The radiation field inside the photochemical reactor is considered to be uniform along the axial direction, but not along the radial coordinate.
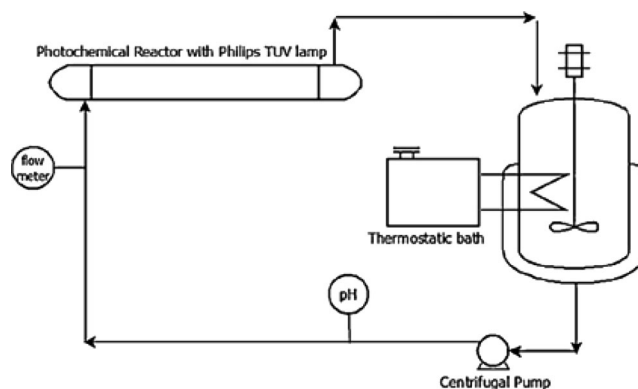

Fig. 1 Simplified diagram of the apparatus used in the photolysis experiments

The reactor is connected to a circulation vessel, from which samples were withdrawn. Two ATZ initial concentrations were used, 5 and 20 mg L^{-1}. All experiments were carried out at 25 °C and pH 6, which was adjusted in the beginning but not corrected over time. At this pH, the neutral form of the ATZ molecule dominates (pKa=1.7, Salvestrini et al. 2010). The solution was recirculated at a flow rate of 0.4 L min^{-1} through the reactor and the vessel by means of a centrifugal pump, which enabled the oxygenation of the reaction medium. The flow rate was adjusted by using a needle valve and read with a rotameter. The total and irradiated volumes of ATZ solutions were 5.00 and 3.93 L, respectively. The monitoring time started when the system was completely filled and the lamp was switched on. In this study, three replicates of the experiments at each experimental condition were carried out.

Additional experiments were performed in the presence of sodium azide (NaN_3, suppressor of singlet oxygen) or 2-propanol (C_3H_8O, suppressor of hydroxyl radicals), at concentrations of 7.7 and 14 mg L^{-1}, respectively. These concentrations were chosen in order that the azide would not compete with ATZ for photon absorption and from the literature, respectively. To further investigate the effect of dissolved oxygen on ATZ degradation, photolysis experiments were performed in flasks in the absence of dissolved oxygen, by bubbling nitrogen (Air Products, 99.5 %) for 60 min before and during irradiation using an 11-W lamp; another experiment was carried out in O_2-saturated solution by bubbling oxygen (Air Products, 99.5 %).

Chemical analysis

High performance liquid chromatography (HPLC)

An HPLC system (Shimadzu), equipped with a two-solvent delivery pump, UV/VIS diode array detector (SPD 20A model), and an auto sampler, was used to follow ATZ concentration-time profiles. The pesticide was analyzed using a C18 column (Phenomenex, 250 mm×4.6 mm; 5 μm). The

ATZ detection wavelength was 220 nm. The oven temperature and sample injection volume were 40 °C and 50.0 μL, respectively. The analyses were performed in isocratic mode. The eluents were (a) H2O+0.2 % acetic acid and (b) acetonitrile at 50:50 ratio (*v*/*v*) and 1.0 mL min^{-1} flow rate. Under these conditions, the retention time of atrazine was 8 min, and the detection and quantification limits were 0.025 and 0.075 mg L^{-1}, respectively.

Ion chromatography

Selected irradiated samples of ATZ were analyzed by ion chromatography to determine the concentration of nitrate and chloride ions in solution. The equipment used was a Metrohm 881 Compact IC Pro with a conductivity detector and a Metrosep A Supp 5 column (150 mm×4 mm; 5 μm). Solutions of Na_2CO_3 (3.2 mmol L^{-1}) and $NaHCO_3$ (1.0 mmol L^{-1}) were used as eluent at a flow rate of 0.7 mL min^{-1}. The analyses were performed at 9.38 MPa and 24 °C.

TOC

The total organic carbon (TOC) of the samples was measured with a Shimadzu TOC-5000A equipment. The TOC was determined indirectly by the difference between total carbon (TC) content of the sample and inorganic carbon (IC) content.

UV-visible spectrophotometry

UV-Vis absorption spectra were measured with a Varian Cary 50 UV-Vis spectrophotometer using a 1-cm path-length quartz cuvette.

Toxicity test

Samples taken at 0, 8, and 60 min during photolysis of the experiment that showed the best performance for ATZ removal were examined for acute toxicity to *Daphnia similis* according to the method 8711 of the Standard Methods (Clesceri et al. 2005).

Results and discussion

Hydrolysis experiments

Before studying the UV degradation of atrazine, dark control experiments performed in aqueous solution at 25 °C showed that the hydrolysis of ATZ over 24 h was found to be insignificant regardless of pH. The stability of ATZ in aqueous solution in the absence of light has been previously reported (Ye et al. 2006). Therefore, in the photolysis experiments described in the present study, ATZ degradation occurred under the effect of UVC radiation only.

Photolysis experiments

Figure 2a, b shows time-concentration profiles for atrazine initial concentrations of 5 and 20 mg L^{-1}, as a function of the photon emission rate. Table 1 summarizes the results obtained in the photolysis experiments. ATZ molecules achieved more than 80 and 65 % removals after 30 min of irradiation, for $[ATZ]_0$=5 and 20 mg L^{-1}, respectively. ATZ removal followed apparent first-order decay during the first 10 min, as indicated by the linear time behavior of $ln([ATZ]/[ATZ]_0)$ over time (Figs. 2c, d). Except for $E_{P,0}$=8.7×10^{17} photons L^{-1} s^{-1}, in all experiments, ATZ concentrations below the detection limit were achieved after 60 min of irradiation.

The primary event for a photochemical process is the absorption of photons at a specific wavelength; hence, ATZ photolysis is related to a high molar absorption coefficient (ε) at 254 nm. UV-Vis absorption spectrum of atrazine exhibit an intense band around 220 nm and another weak band around 265 nm, which have been assigned to the transitions of π and n electrons to the π* excited state, respectively (Chen et al. 2009). In our study, a high ε of 3,270 L mol^{-1} cm^{-1} was measured for ATZ at 254 nm, which is similar to previously reported values (Prosen and Zupancic-Kralj 2005). It is worth mentioning that no ozone was produced in the system, owing to the lamp glass which filters out the ozone-forming line at 185 nm. From the initial degradation rates for the experiments carried out at $[ATZ]_0$=20 mg L^{-1}, the quantum yield of atrazine photolysis was estimated as Φ(ATZ, 254 nm)= 0.035±0.009, which is in good agreement with previously reported values for the same concentration range (De Laat et al. 1999; Parsons 2005).

Figure 3 shows that the values of the apparent first-order rate constants increase linearly with $E_{P,0}$. The calculated proportionality constants (units not shown) are 0.085 and 0.056 for 5 and 20 mg L^{-1}, respectively. This suggests the direct relationship between ATZ degradation and the photon emission rate.

The results in Table 1 show that the rate of ATZ photolysis is influenced by the initial concentration of the pesticide. The higher the initial ATZ concentration, the lower the values of the apparent first-order rate constants k, the higher the pesticide half-lives and the lower the percent removals after 30 min of irradiation. Beltrán et al. (1993) report increasing atrazine conversion from 45 to 70 % with decreasing initial ATZ concentration in the range 2–25 mg L^{-1} for a photon emission rate (254 nm) of 9.63×10^{17} photons L^{-1} s^{-1}; their results also indicate decreasing apparent degradation constants with increasing $[ATZ]_0$. Hessler et al. (1993) report a decrease in the quantum yield of ATZ photolysis at 254 nm (photon emission rate of about 4×10^{17} photons L^{-1} s^{-1}) with increasing initial
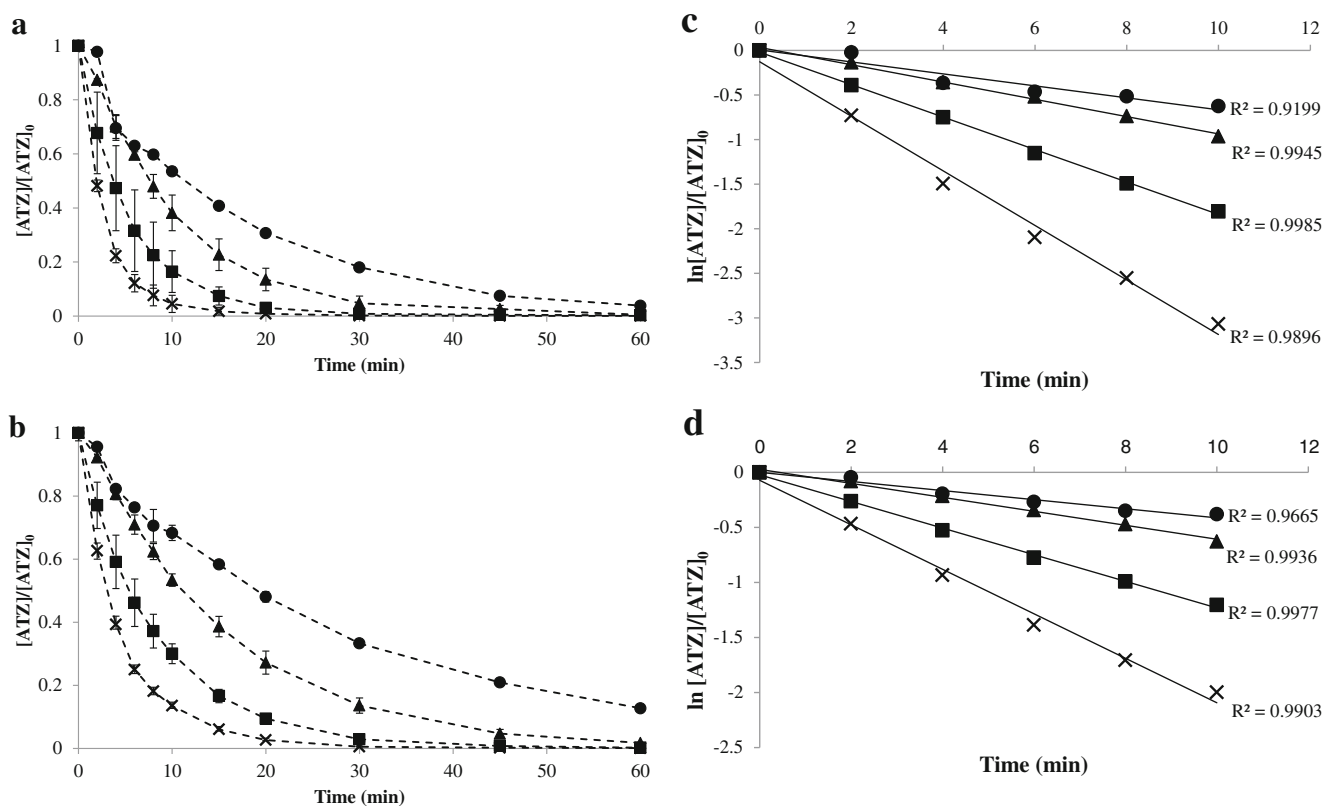
Fig. 2 Atrazine (ATZ) degradation during photolysis for different initial concentrations and photon emission rates (—✖— 3.6×10^{18} photons L^{-1} s^{-1}; —■— 1.9×10^{18} photons L^{-1} s^{-1}; —▲— 1.1×10^{18} photons L^{-1} s^{-1} and —●— 8.7×10^{17} photons L^{-1} s^{-1}). **a, c** $[ATZ]_0 = 5$ mg L^{-1}. **b, d** $[ATZ]_0 = 20$ mg L^{-1}

herbicide concentration in the range 0.65 to 34.5 mg L^{-1}. For first-order concentration decay of a pollutant, the rate constant of photolysis is directly proportional to the quantum yield (Parsons 2005). The dependence of the amount of substrate destroyed and apparent first-order rate constants with $[ATZ]_0$ can be explained by the fact that the higher the ATZ initial concentration, the higher the amount of degradation products formed; as a result, competition by incident photons increase.

The results of ion chromatography analysis (Fig. 4) reveal that the amount of chloride anions measured in solution reached an almost steady state value after 30 min (corresponding to a steady concentration of about 20 μmol L^{-1}), when ATZ concentration was below its detection limit. The increase in the amount of Cl^- anions with time closely followed ATZ

degradation, while the difference may suggest the persistence of very small amounts of chlorinated degradation products, as previously reported by other authors (Chen et al. 2009; Hequet et al. 2001). The relatively long bond length (1.734 Å) and low polarity (0.293) of the C–Cl bond in atrazine molecule (Chen et al. 2009) make this bond easier to break than any other bonds during ATZ photolysis under irradiation at 254 nm (Ye et al. 2006). Dehalogenation followed by hydroxylation to give the 2-OH derivative could result either from (1) the homolytic cleavage of the C–Cl bond, followed by electron transfer from the carbon to the chlorine radical and hydrolysis of the carbocation, or (2) the heterolytic cleavage in the excited state of ATZ molecules (Hequet et al. 2001).

Despite the efficient ATZ removal for all conditions studied, the results of TOC with time showed that virtually no

Table 1 Results of the photolysis experiments: k, apparent first-order rate constant; $t_{1/2}$, half-life; and percent removal after 30 min of irradiation

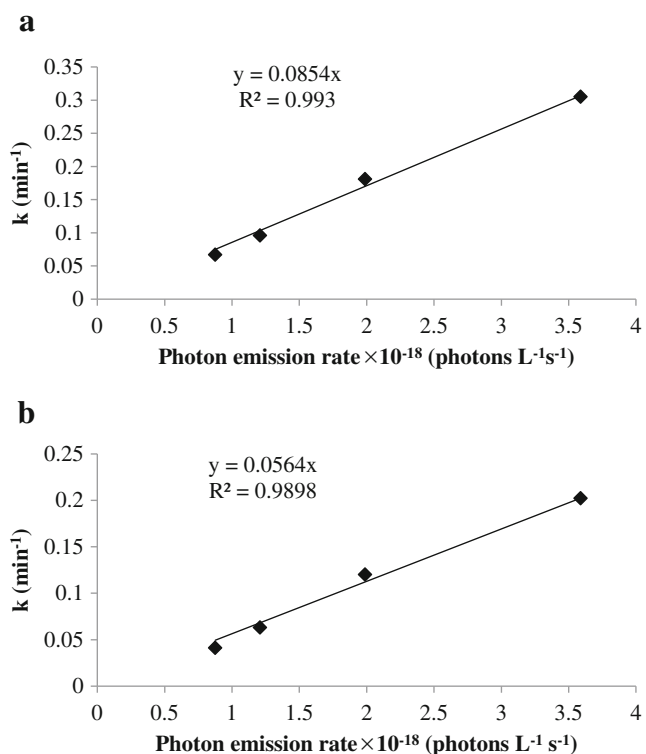| Photon emission rate (photons L^{-1} s^{-1})	5 mg L^{-1}			20 mg L^{-1}		
	k (min^{-1})	$t_{1/2}$ (min)	% removal	k (min^{-1})	$t_{1/2}$ (min)	% removal
3.6×10^{18}	0.305	3.0	99.8	0.202	5.0	99.5
1.9×10^{18}	0.181	5.0	99.1	0.120	6.0	97.1
1.1×10^{18}	0.096	9.0	95.3	0.063	12.0	86.4
0.87×10^{18}	0.067	12.0	82.0	0.041	20.0	66.7

a

b

Fig. 3 Correlation between apparent first-order rate constants and photon emission rates for different initial concentrations. **a** [ATZ]$_0$=5 mg L^{-1}. **b** [ATZ]$_0$=20 mg L^{-1}

carbon removal occurred (results not shown), which is associated with the formation of persistent degradation products and is due to the stability of the *s*-triazine ring toward oxidation (Chen et al. 2009). These findings are in agreement with the results of Seema et al. (2009) and Klementova and Zlamal (2013). Finally, a variation in pH from 6.5 to 4.5 in average was observed in the experiments performed in this study, probably due to the formation of more acidic species.

Table 2 presents the results of acute toxicity assays performed with *D. similis* for the best condition studied ($E_{P,0}$= 3.6×10^{18} photons L^{-1} s^{-1}). According to the classification of Bulich (1992), for [ATZ]$_0$=5 mg L^{-1} untreated and treated samples are considered as nontoxic. In contrast, the untreated

Table 2 Results of the acute toxicity assays with *Daphnia similis*. Values of EC50 in parentheses

Experiments	Degradation time (min)		
	0	8	60
5 mg L^{-1}	Nontoxic (100 %)	Nontoxic (89.1 %)	Nontoxic (75.7 %)
20 mg L^{-1}	Toxic (47.6 %)	Toxic (39.5 %)	Nontoxic (76.7 %)

sample with [ATZ]$_0$=20 mg L^{-1} is classified as toxic (EC50= 47.6 %), with a decrease in EC50 after 8 min of irradiation, i.e., with an increase in toxicity. Despite the presence of persistent degradation products, photolysis was efficient in order to reduce toxicity after 60 min of exposure to UV radiation.

Role of reactive oxygen species (ROS) in ATZ photolysis

A contaminant must absorb incident radiation at an appropriate wavelength to be degraded by direct photolysis. The most common steps in chemical reactions initiated by excited states are summarized by Eqs. (1) through (6) (Parsons 2005).
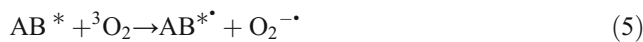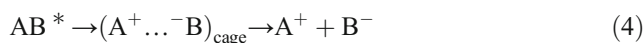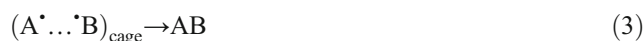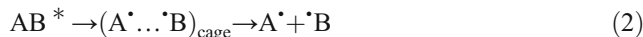
$$AB + h\nu \rightarrow AB^* \tag{1}$$

$$AB^* \rightarrow (A^{\bullet} \dots {}^{\bullet}B)_{cage} \rightarrow A^{\bullet} + {}^{\bullet}B \tag{2}$$

$$(A^{\bullet} \dots {}^{\bullet}B)_{cage} \rightarrow AB \tag{3}$$

$$AB^* \rightarrow (A^+ \dots {}^-B)_{cage} \rightarrow A^+ + B^- \tag{4}$$

$$AB^* + {}^3O_2 \rightarrow AB^{*\bullet} + O_2{}^{-\bullet} \tag{5}$$

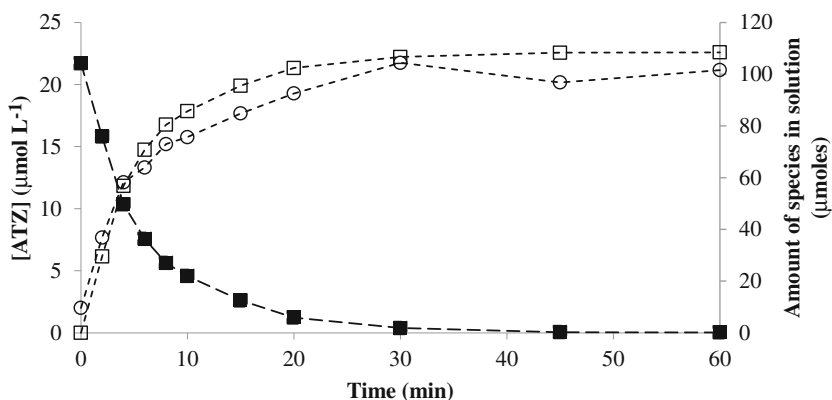**Fig. 4** Comparison between the release of chloride ions in solution and ATZ photolytic degradation. [ATZ]$_0$=5 mg L^{-1} and $E_{P,0}$=3.6× 10^{18} photons L^{-1} s^{-1}. –■– [ATZ]; - ⊖ - amount of Cl$^-$ released; –⊟– amount of ATZ degraded

$$AB^* + {}^3O_2 \rightarrow AB + {}^1O_2 \qquad (6)$$

The electronically excited state AB* generated from light absorption is highly energetic. The homolytic cleavage of the chemical bond (2) corresponds to the predominant reaction step. When the radicals escape of the solvent cage, they undergo oxidation/reduction reactions. The recombination of the primary radicals (3) has a high probability to occur, which explains the low quantum yield observed in some cases. An alternative to the homolytic scisson is the heterolytic scission in the excited state (4), which is favored in polar solvents, such as water (Nick et al. 1992). Electron and energy transfer to O_2 is possible, but need a long-lived excited state as the triplet state. Many reactive oxygen species (ROS) such as the superoxide radical (5) and singlet oxygen (6) are generated (Parsons 2005).

To qualitatively investigate the role of ROS, solutions containing ATZ were irradiated in the presence of sodium azide, a selective quencher for ${}^1O_2$, according to Razavi et al. (2011) and other authors, or 2-propanol, a well-known radical scavenger (Xu et al. 2011). The results are shown in Fig. 5.

The addition of the azide anion resulted in a decrease in the rate of ATZ degradation ($k = 1.09 \times 10^{-1}$ min^{-1}, $t_{1/2} = 7$ min), therefore suggesting that energy transfer to ${}^3O_2$ molecules from excited ATZ molecules seems to be effective for generating ${}^1O_2$ species, according to reaction (6). In a previous study, Oliva et al. (2005) have obtained the ATZ phosphorescence spectrum and the lifetime of its triplet excited state in water. The existence of such state is a prerequisite for photosensitization reactions. Hence, although the excited state is expected to be short-lived at room temperature, ATZ degradation promoted by ${}^1O_2$ cannot be discarded. As shown by Fig. 5, the addition of 2-propanol also resulted in a decrease of ATZ degradation rate ($k = 1.1 \times 10^{-1}$ min^{-1}, $t_{1/2} = 8$ min), thus suggesting that the excited state of the ATZ molecule can transfer electrons to dissolved oxygen and induce the
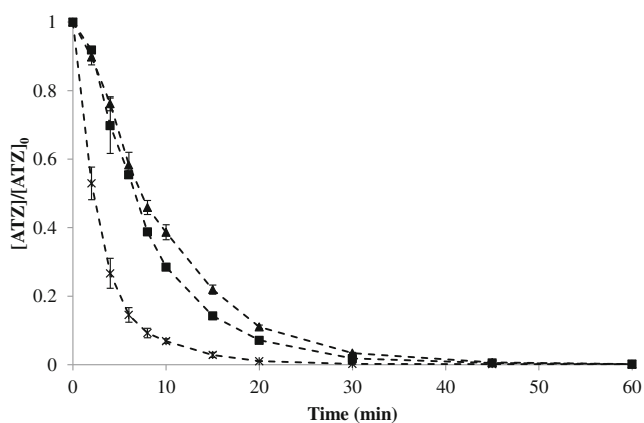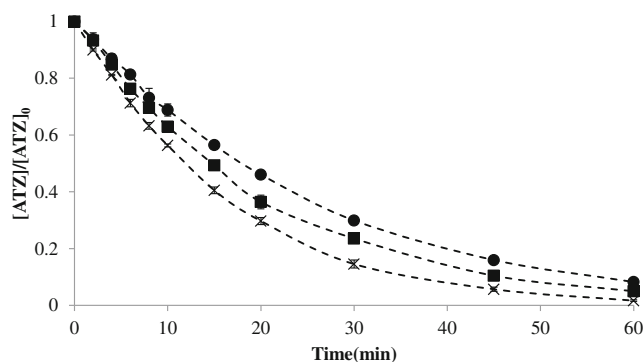
Fig. 6 Atrazine (ATZ) degradation during the photo-induced degradation process at pH 6, [ATZ]$_0$=5 mg L^{-1}. —✖— UV; —■— UV+solution purged with nitrogen; —●— UV+solution saturated with oxygen

formation of radical species which can oxidize the target pollutant as well, cf. reaction (5).

Further experiments were performed in deoxygenated (nitrogen purged) and oxygen-saturated solutions. The results in Fig. 6 show that in an oxygen-free medium, the degradation rate was lower ($k = 5 \times 10^{-2}$ min^{-1}, $t_{1/2} = 15$ min) than that observed under ordinary conditions due to the impossibility of ROS formation, indicating that these species play an important role in photo-induced ATZ degradation. The fact that the UV photodegradation of ATZ was not completely inhibited by oxygen removal from the reaction medium indicates the importance of photolysis on ATZ degradation at 254 nm. When the reaction medium was saturated with oxygen, ATZ degradation was also decreased ($k = 4.1 \times 10^{-2}$ min^{-1}, $t_{1/2} = 19$ min). A possible explanation is that oxygen in excess quenches the excited state of atrazine, in such a way that reactions (5) and (6) replace reactions (2) and (4). Similar results were obtained by Nick et al. (1992), who reports that saturation of ATZ aqueous solutions with oxygen reduces the quantum yield of ATZ degradation by 30 % as compared to the photolysis in oxygen-free solutions.

Conclusions

In this study, the photolysis of atrazine (ATZ) under 254-nm UV radiation in aqueous solution, using a photochemical reactor, was detailed. We focused on the effects of the photon emission rate and initial concentration on ATZ degradation rate.

ATZ degradation followed apparent first-order kinetics, with a fivefold linear increase in specific degradation rate constants with photon emission rates in the range 0.87×10^{18}–3.6×10^{18} photons L^{-1} s^{-1}. High percent removals were obtained after 30 min of irradiation, with more than 80 and 65 % for initial concentrations of 5 and 20 mg L^{-1}, respectively. For all photon emission rates studied, the results show that the higher the initial ATZ concentration, the lower the

Fig. 5 Atrazine (ATZ) degradation during the photo-induced degradation process at pH 6, [ATZ]$_0$=5 mg L^{-1} and $E_{P,0}$=3.6×10^{18} photons L^{-1} s^{-1}. —✖— UV; —▲— UV+2-propanol; —■— UV+NaN$_3$

values of the apparent first-order rate constants, the higher the pesticide half-lives, and the lower the percent removals obtained.

The results confirmed that dechlorination, which occurred almost stoichiometrically relative to ATZ degradation, was the dominant mechanism during the initial steps of ATZ photolysis. However, no appreciable carbon removal was observed. Despite the presence of persistent degradation products, toxicity was efficiently removed after 60 min of exposure to UV radiation.

Additional experiments performed in the presence of a suppressor of singlet oxygen, using a radical scavenger and by varying the amount of dissolved oxygen in reaction medium, qualitatively pointed out reactive oxygen species (ROS) as important actors during the photolytic degradation of atrazine.

These results may help understand the behavior of atrazine in different UV-driven photochemical degradation process, in which photolysis and oxidation by ROS can occur simultaneously and therefore should be adequately quantified.

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