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Journal of Photochemistry and Photobiology A: Chemistry 155 (2003) 215–222

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photocatalytic degradation of imazaquin in an aqueous suspension of titanium dioxide

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Received 8 October 2002; accepted 17 October 2002

Abstract

The photocatalytic degradation of imazaquin, a herbicide of the imidazolinone class, in an aqueous suspensions of titanium dioxide as catalyst was investigated. A pseudo-first-order kinetic model was used to describe the results. The effect of sonication time, catalyst loading, initial concentration of imazaquin, hydrogen peroxide and pH, temperature and radiation source were examined. The disappearance of imazaquin and the increase of nitrate ion content as a function of irradiation time were analyzed by HPLC. The ammonium ion formation was determined spectrophotometrically at 694 nm. A lower solution pH in the 3–11 range was found to be favorable to degradation. The addition of H_2O_2 up to 10^{-3} mol l^{-1} enhanced the degradation rate and decreased it at higher concentrations. The photocatalytic effect was more efficient in a suspension containing 2.0 g l^{-1} TiO_2 with 1 h sonication in the dark rather than with 20 min sonication before irradiation. Solar radiation decomposed the herbicide faster than an artificial source. The activation energy was estimated through the variation of temperature in the range 20–40 °C.

Keywords: Photocatalytic degradation; Titanium dioxide; Imazaquin

1. Introduction

Industrial, agricultural, and urban development has caused great damage to human health and to biodiversity due to the high pollution rates, especially involving water. Since drinking water is becoming increasingly scarce, investigations concerning the decontamination of these environments have grown substantially, because several pollutants such as surfactants [1], herbicides [2,3], dyes [4,5], polychlorinated biphenyls [6,7] have been degraded by advanced oxidative processes. Therefore, TiO_2 photocatalysis has been widely established as an alternative physical–chemical process for environmental remediation in the last two decades [8,9]. The use of low energy UV light and semiconductor photocatalysts such as the anatase form of TiO_2, in suspension [10–12] or immobilized [13–16], can degrade and even mineralize these herbicides.

The photochemical process begins when the TiO_2 particle absorbs light at a wavelength smaller than 400 nm and the valence band electron jumps through the bandgap to the conduction band, leaving a positive hole behind, generating an electron–hole (e^-–h^+) pair. These pairs are able to initiate oxidation and reduction reactions on the TiO_2 surface. The positive hole can oxidize the organic molecules sorbed on the surface either directly or indirectly, through the formation of $^\bullet OH$ radicals. On the other hand, the photogenerated electron can produce radical species such as peroxyl ($O_2{}^{2-}$) and hydroperoxyl ($HO_2{}^-$). These radicals and hydrogen peroxide oxidize the substrate, producing an intermediate compound that, through subsequent oxidation, reaches mineralization [17]. This means that the increase of these species in the reaction medium is a path leading to the improvement of the mineralization level. Thus, several researchers have studied the effect of other oxidants such as H_2O_2 [3,18], Fe^{3+} [19] and $S_2O_8{}^{2-}$ [20,21] on the semiconductor surface.

In this paper, we report the results of the photocatalytic degradation of imazaquin ((*RS*)-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)quinoline-3-carboxylic acid) (Fig. 1) by TiO_2 in aqueous suspension. The effects of initial concentration and pH on the degradation rate were investigated because the contaminant concentration and the pH are relevant parameters in wastewater treatment. The effect of TiO_2 amount, of hydrogen peroxide addition, of radiation source and of temperature were also examined for enhancement of imazaquin degradation and mineralization.

Imazaquin is a herbicide used for pre- or post-emergence control of the broadleaf weeds and grasses in soybeans

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PII: S1010-6030(02)00370-2

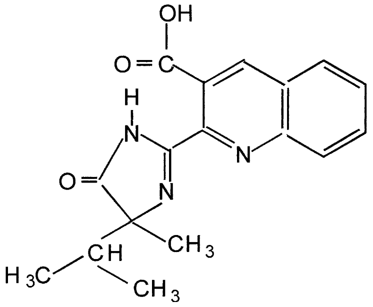

Fig. 1. The chemical structure of imazaquin.

tillage applied to plant foliage. It is vulnerable to foliar washoff and herbicide washed off from foliage could promote surface water run off due to shorter contact time with soil for sorption [22].

2. Experimental procedure

2.1. Materials

Imazaquin ($C_{17}H_{17}O_3N_3$, 98%) was kindly supplied by Milênia Agroindústria (Londrina, Paraná, Brazil). Titanium dioxide (P-25, 80% anatase, 20% rutile, specific surface of $50\,m^2\,g^{-1}$) was a gift from Degussa and was used as the photocatalyst without further purification. Hydrogen peroxide (30%, P.A.) was purchased from Nuclear. Acetonitrile was chromatographic grade and purchased from Mallinckrodt. All other chemicals were analytical grade and employed without previous purification. The water used in all the experiments was purified with a Milli-Q-Plus system.

2.2. Photodegradation

Illuminations were carried out in three cylindrical 70 ml borosilicate glass reactors (ID 5.0 cm) with aqueous suspensions containing the desired amounts of TiO_2 and imazaquin under ambient conditions. A stock aqueous solution of imazaquin ($50.0 \times 10^{-6}\,mol\,l^{-1}$) was prepared by dissolving the herbicide in an ultrasonic bath. The natural pH for imazaquin is about 4.7. Three reactors, each containing 100 mg TiO_2 in 50 ml ($2.0\,g\,l^{-1}$) of herbicide solution were kept inside an ultrasonic bath for 1 h in the dark to achieve a complete adsorption prior to irradiation. These reactors were placed on a magnetic stirring plate with the suspension surface at a fixed distance of 15 cm from a 125 W mercury lamp without a bulb. This radiation source was attached vertically to the internal top of a wood box (50 cm × 50 cm × 50 cm). Two fans were positioned on the lateral walls at different heights in order to minimize the heat effect generated by the lamp. During irradiation, the temperature varied by ±3.0 °C.

When irradiation was performed with temperature control, we used a cylindrical 70 ml borosilicate glass vessel containing 50 ml imazaquin solution in a TiO_2 suspension, surrounded by a recirculating water-jacket and positioned inside the chamber described above. During irradiation, the temperature was maintained constant in the range of ±0.1 °C.

2.3. Analytical determination

Changes in imazaquin concentration as a function of irradiation time were monitored by HPLC with a diode array at 210 nm (Shimadzu LC-10AD with UV detector, Supelco, Waters Spherisorb-ODS2 pre-column and C18 column, 5 μm porosity, 4.6 mm × 50 mm and 4.6 mm × 150 mm, respectively). A 30:70 mixture of acetonitrile–phosphate buffer (v/v) at pH 4 was used as eluant, with an injection volume of 20 μl, a flow rate of $0.8\,ml\,min^{-1}$ at 35 °C and a retention time of 4.5 min. $NO_3{}^{-}$ formation was monitored by ion chromatography (Sycam 3110 with a Sycam1100 conductivity detector, an AG11 Dionex Ionpac pre-column, 4 mm × 50 mm, and an AS11 Dionex Ionpac column, 4 mm × 250 mm, 5 μm porosity). NaOH ($11.0 \times 10^{-3}\,mol\,l^{-1}$) was used as eluant and $12.0 \times 10^{-3}\,mol\,l^{-1}$ H_2SO_4 as suppressor with a flow of $1\,ml\,min^{-1}$ at 35 °C giving a retention time of 3.1 min. The ammonium ion was determined spectrophotometrically at 694 nm by the modified Berthelot method [23]. The calibration curves were prepared for a concentration range of $(4.0–100) \times 10^{-6}\,mol\,l^{-1}$. This procedure was repeated whenever this ion was determined. The validation method was based on the absorption spectra of the blue compound recorded at pH 3.0, 7.0, and 11.0 from 350 to 800 nm, whose maximum absorption occurred between 690 and 700 nm.

3. Results and discussion

3.1. Kinetics of imazaquin degradation

The disappearance of imazaquin from an initial concentration of $50.0 \times 10^{-6}\,mol\,l^{-1}$ is shown in Fig. 2 under different conditions. The degradation fitted well the exponential decay curve, following a first-order behavior. There was a negligible effect on imazaquin when the irradiation occurred in the absence of TiO_2 using a 125 W mercury lamp without a bulb ($k = 0.503 \times 10^{-2}\,min^{-1}$). However, the rate constant was doubled when solar radiation was used ($k=1.1\times10^{-2}\,min^{-1}$). In the presence of hydrogen peroxide, $1.0 \times 10^{-2}\,mol\,l^{-1}$, the rate constant was enhanced to $1.44 \times 10^{-2}\,min^{-1}$. In the presence of TiO_2 ($2.0\,g\,l^{-1}$), the rate constant increased to $4.94 \times 10^{-2}\,min^{-1}$ when the artificial radiation source was used and to $27.8\times10^{-2}\,min^{-1}$ with solar radiation.

3.2. Effect of sonication time

Experiments were undertaken to investigate the effect of sonication time in the dark on the degradation of

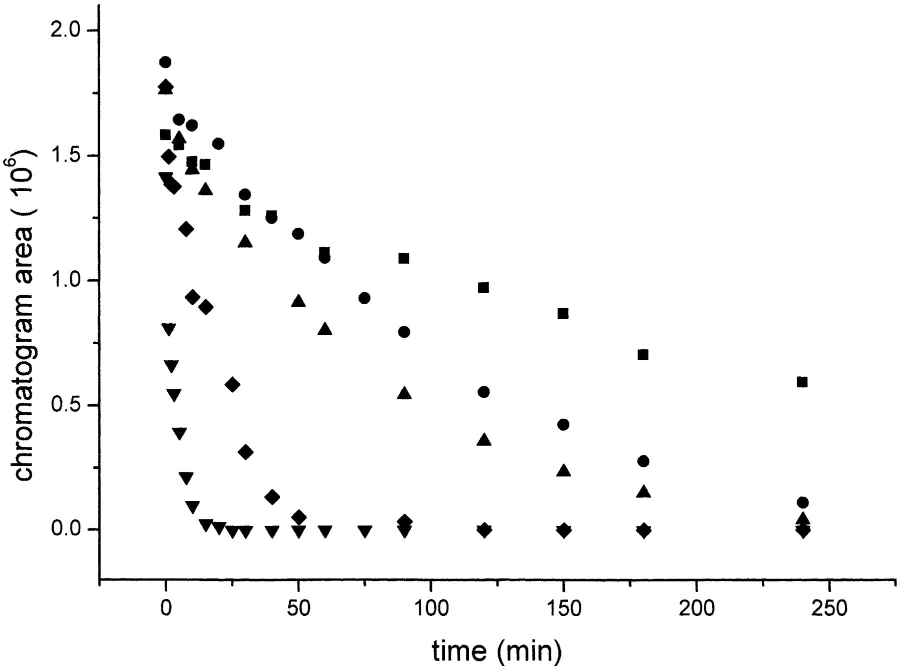

Fig. 2. Disappearance of imazaquin under some experimental conditions: (■) artificial photolysis; (●) solar photolysis; (▲) photolysis with 1×10^{-2} mol l^{-1} H_2O_2; (▼); TiO_2 photocatalysis with solar irradiation; (◆) TiO_2 photocatalysis by irradiation with a 125 W Hg lamp without a bulb.

50.0×10^{-6} mol l^{-1} imazaquin before irradiation. Different amounts of TiO_2 were used in the range 2.0–12.0 g l^{-1}. Fig. 3 shows that the adsorption on the TiO_2 surface was rapidly enhanced in the first 10 min, and then more slowly until reaching a maximum with 1 h sonication, that is, a decrease of 9.2% in the chromatogram area of the imazaquin peak. After this time, the adsorption decreased gradually up to 2 h. This behavior suggests that the adsorption rate was much faster at the beginning because the number of available sites was much greater. With the adsorption of the substrate molecules on the TiO_2 surface, the rate was reduced until adsorption–desorption equilibrium was established. The smaller areas obtained at 90 min and 2 h indicate that the desorption rate was greater than the adsorption rate.

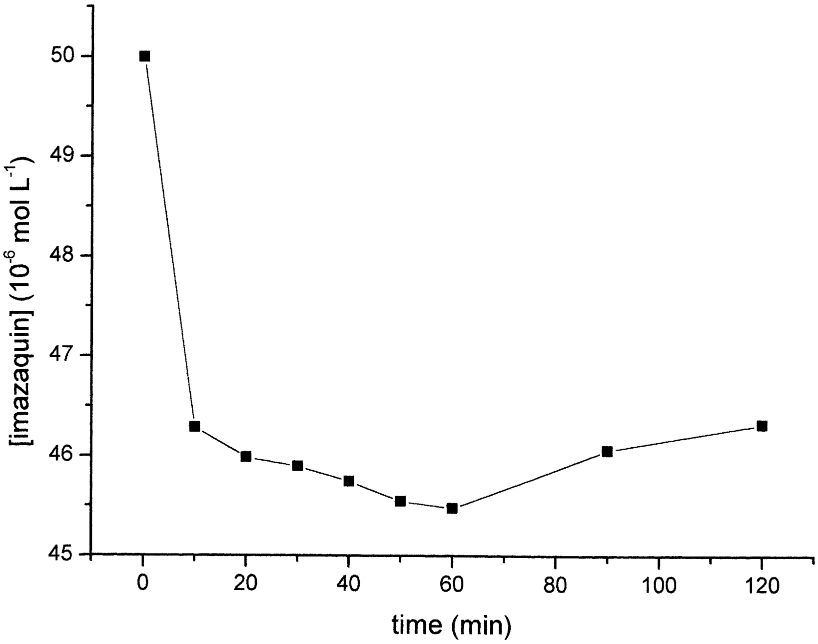

Fig. 3. Imazaquin molecule adsorption (50.0×10^{-6} mol l^{-1}) onto the TiO_2 particle (2.0 g l^{-1}) as a function of the sonication time of the suspension (50 ml).

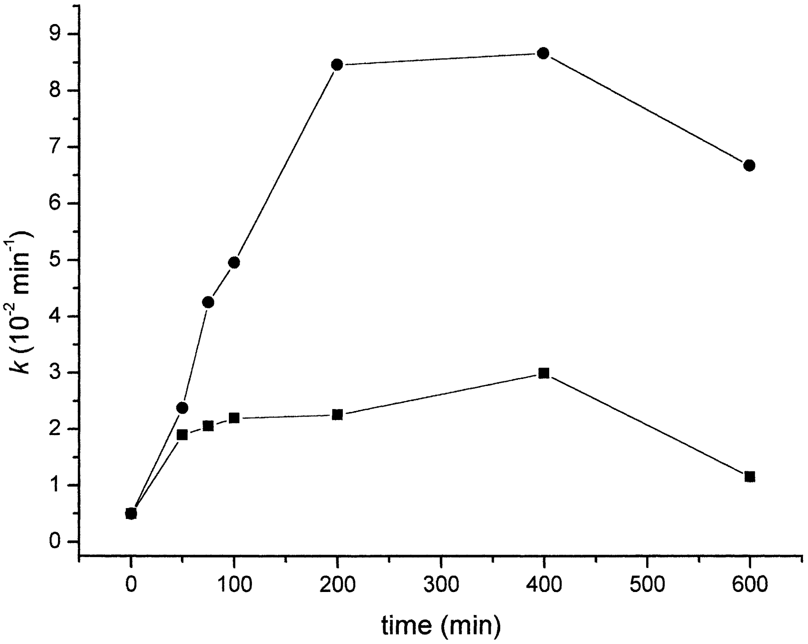

Fig. 4. Effect of TiO_2 amount on the degradation rate constant of 50.0×10^{-6} mol l^{-1} imazaquin at (■) 20 min and (●) 1 h sonication.

3.3. Effect of TiO_2 amount

Two series of experiments were carried out varying the TiO_2 amount from 2.0 to 12.0 g l^{-1} with 20 min and 1 h sonication, respectively (Fig. 4). According to Table 1, the longer the sonication time as a function of TiO_2 amount the higher the degradation rate constant and ammonium and nitrate ion formation (Fig. 4). However, we did not observe the same quantity of TiO_2 for the most efficient degradation and mineralization. Thus, the fastest degradation occurred when 8.0 g l^{-1} TiO_2 was used, whereas the total concentration of mineralized ions was higher for 2.0 g l^{-1} TiO_2 both after 1 h and after 20 min of sonication. In the former case, the rate increased rapidly with increasing catalyst concentration up to 4.0 g l^{-1} and more slowly when the concentration was increased from 4.0 to 8.0 g l^{-1}, and decreased at 12.0 g l^{-1}. The rate constants for irradiation with 20 min sonication presented the same trend with very low rates, as shown in Table 1. This behavior reveals that imazaquin adsorption on the sites of the TiO_2 surface is faster with increasing catalyst concentration, until reaching saturation at 12.0 g l^{-1}. This means that up to 8.0 g l^{-1} the available sites promptly absorb the bandgap energy responsible for the beginning of the redox reaction, suggesting that imazaquin is immediately fragmented. The higher concentrations of ammonium and nitrate ions obtained after 4 h irradiation indicate that NO_3^- oxidation and NH_4^+ reduction do not occur concomitantly to photocatalytic degradation, since the total degradation of imazaquin takes place within 90 min.

3.4. Effect of initial imazaquin concentration

The effect of initial imazaquin concentration was investigated over the range of 5.0×10^{-6} to 100.0×10^{-6} mol l^{-1}. The rate constants obtained in a suspension containing 2.0 g l^{-1} of TiO_2 decreased significantly with the increase

Table 1
Effect of sonication time and TiO_2 concentration on the degradation rate constant, and mineralized ion concentration after 4 h irradiation[a]

[TiO_2] (g l^{-1})	20 min			1 h		
	k (10^{-2} min^{-1})	[NH_4^+] (10^{-6} mol l^{-1})	[NO_3^-] (10^{-6} mol l^{-1})	k (10^{-2} min^{-1})	[NH_4^+] (10^{-6} mol l^{-1})	[NO_3^-] (10^{-6} mol l^{-1})
1.0	1.90	11.46	11.42	2.38	22.91	10.50
1.5	2.18	20.94	14.41	4.25	28.54	12.17
2.0	2.20	18.79	17.71	4.96	26.68	19.20
4.0	2.26	7.47	10.89	8.47	23.56	12.02
8.0	2.99	23.09	7.68	8.67	3.27	8.77
12.0	1.16	18.03	5.54	6.67	2.63	12.68

[a] The experiments were not carried out under these conditions.

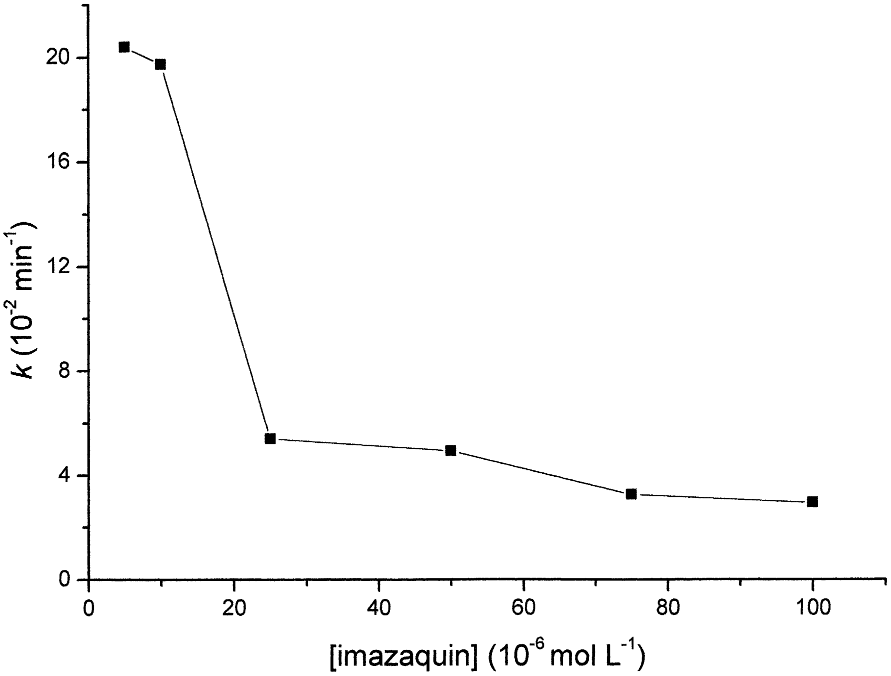

Fig. 5. Degradation rate constant as a function of initial imazaquin concentration in aqueous TiO_2 suspension ($2.0\,g\,l^{-1}$).

in initial concentration, as shown in Fig. 5. A much faster degradation rate at lower imazaquin concentrations may be justified by the fact that the high number of available TiO_2 molecules is able to adsorb most of the molecules in suspension. On the other hand, the process is inverted at higher substrate concentrations, since a large number of substrate molecules compete for the adsorption sites with some intermediates such as carboxylic acids, aldehydes, and aromatics [24]. As a consequence, there is a decrease in the rate constant because the number of available active sites is diminished for redox reaction [25,26]. Although higher concentrations of ammonium ($31.7 \times 10^{-6}\,mol\,l^{-1}$) and nitrate ($35.0 \times 10^{-6}\,mol\,l^{-1}$) ions were obtained for $25.0 \times 10^{-6}\,mol\,l^{-1}$, the formation of both occurred at random, complicating the interpretation. All the other irradiation procedures were carried out using $50.0 \times 10^{-6}\,mol\,l^{-1}$ imazaquin. At this concentration, the rate constant showed a proportional increase up to about 30 min irradiation and remained constant within the experimental error after about 90 min, characterizing a change in the reaction order.

3.5. *Effect of pH*

In this study, the initial pH was maintained at 3.0, 7.0, or 11.0 in a suspension of $2.0\,g\,l^{-1}$ TiO_2 and $50.0 \times 10^{-6}\,mol\,l^{-1}$ imazaquin. During irradiation, the pH varied within the range 3–3.6, 7–6.7, and 11–11.1. When irradiation was performed with no pH control, that is, at the initial natural pH of 4.7, the variation was more noticeable (±1.0). Table 2 shows that degradation occurred more rapidly at pH 3.0.

Different charge densities may be generated in the imazaquin molecule depending on the type of interaction with the titanium dioxide surface, accelerating or retarding the degradation. In the present study, the degradation rate decreased with the increase in pH from 3 to 11. The imazaquin pK_a of 5.11 at 25 °C was calculated from the Henderson–Hasselbach equation [27]. The pH of zero point of charge (pH_{zpc}) of TiO_2 (P-25) is equal to 6.3 [28]. This means that the TiO_2 surface is positively charged when the pH is lower than this value, as shown in the equilibrium among the species on the TiO_2 surface [6]:

$$Ti^{IV}-OH_2{}^{+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} Ti^{IV}-OH \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} Ti^{IV}-O^{-}$$

Then, at pH 3.0 ($<pK_a$), interaction between $TiOH_2{}^{+}$ and imazaquin would occur through one or more atoms with higher negative charge densities, defined by Mülliken [29] calculated with the PC Spartan-Pro geometry optimization program by AM1 method, and presented in Fig. 6. The adsorption to the positive charges on the TiO_2 surface occurs

Table 2
Rate constant and ammonium ion concentration at different pH values produced in the final period of 4 h irradiation[a]

pH	k ($10^{-2}\,min^{-1}$)	$t_{1/2}$ (min)	r	$[NH_4{}^{+}]$ ($10^{-6}\,mol\,l^{-1}$)
Natural	4.94	10.70	0.9965	26.68
3.0	5.22	13.27	0.9951	29.68
7.0	4.36	15.89	0.9819	23.63
11.0	3.61	19.20	0.9674	19.54

[a] $50.0 \times 10^{-6}\,mol\,l^{-1}$ imazaquin in $2.0\,g\,l^{-1}$ TiO_2.

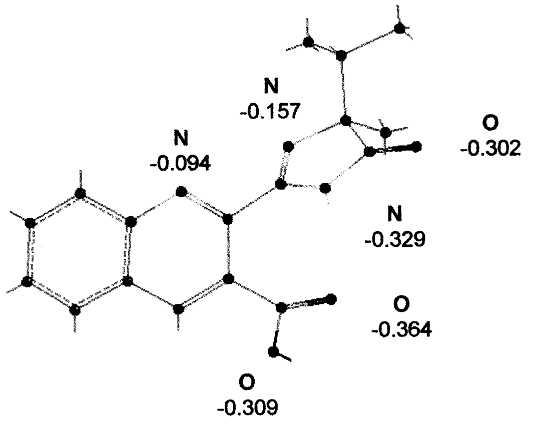

Fig. 6. Charge densities on some atoms in neutral imazaquin.

in the region with higher charge densities produced by the lone pairs, localized on the oxygen atoms of the carboxylic (−0.309 and −0.364), on the carbonyl (−0.302) and on the position-1 nitrogen of the imidazole (−0.329) groups. So, the contribution of partial charges localized on the position-3 nitrogen of the imidazole (−0.157) and quinoline (−0.094) groups would be smaller on the degradation rate.

Therefore, at pH 7 ($>\mathrm{pH}_{\mathrm{cz}}$) TiOH and TiO^- species are present on the TiO_2 surface, indicating that the herbicide suffers dissociation at pH 7.0, yielding the carboxylate ion. This hinders the interaction and consequently, the imazaquin adsorption on the TiO_2 surface. At pH 11, repulsion is much more marked if we consider that both species are negatively charged, thus preventing interaction and delaying degradation. This may be verified by the charge densities calculated for ionized imazaquin on the nitrogen of the imidazole (−0.190 and −0.331) and quinoline (−0.125) groups, as well as on the oxygens of the carboxyl (−0.568 and −0.518) and carbonyl (−0.341) groups shown in Fig. 7, which are more negative compared to those of pH 3.0. Photocatalytic oxidation, which follows a similar behavior, was carried out using substrates such as *o*-methylbenzoic acid [30], trichlopyr [2], and polychlorinated biphenyls [31].

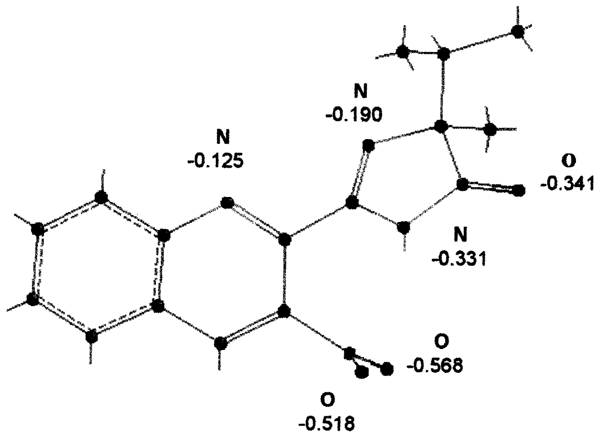

Fig. 7. Charge densities on some atoms in ionized imazaquin.

Table 3
Effect of hydrogen peroxide concentration on the imazaquin degradation rate constant in the presence or absence of TiO_2 (the experiments were not carried out under these conditions)

$[TiO_2]$ ($\mathrm{g\,l^{-1}}$)	$[H_2O_2]$ ($10^{-2}\,\mathrm{mol\,l^{-1}}$)	k ($10^{-2}\,\mathrm{min^{-1}}$)	r
–	–	0.503	0.9922
–	1.0	1.44	0.9964
2.0	–	4.94	0.9965
2.0	0.010	7.42	0.9915
2.0	0.10	8.54	0.9899
2.0	1.0	4.27	0.9843
2.0	5.0	2.71	0.9568

3.6. Effect of H_2O_2 addition

The results of irradiation of suspensions formed by $50.0\times 10^{-6}\,\mathrm{mol\,l^{-1}}$ imazaquin and TiO_2 $2.0\,\mathrm{g\,l^{-1}}$ at different hydrogen peroxide concentrations are presented in Table 3. When irradiation was applied only in the presence of H_2O_2, the herbicide did not degrade satisfactorily, whereas in the presence of the semiconductor the rate increased significantly. On the other hand, the mixture of TiO_2 and 1.0×10^{-4} and $1.0\times10^{-3}\,\mathrm{mol\,l^{-1}}$ hydrogen peroxide increased by 5- and 6-fold, respectively, the degradation rate with respect to H_2O_2, as opposed to a 1.5- and 1.7-fold increase in degradation in the presence of TiO_2 alone. The rate increase with the addition of H_2O_2 at concentrations lower than $1.0\times10^{-3}\,\mathrm{mol\,l^{-1}}$ may be attributed to the enhancement of the initial concentration of hydroxyl radicals [32,33] produced by direct photolysis of H_2O_2 (1) and by reaction with peroxyl ion, $O_2^{\bullet-}$ (2). In addition, H_2O_2 can capture one electron of the conduction band and produce the hydroxyl radical, hindering the process of electron–hole recombination and increasing the rate of the photocatalytic process (3), as shown in Scheme 1 [34].

In the presence of 1.0×10^{-2} and $5.0\times10^{-2}\,\mathrm{mol\,l^{-1}}$ hydrogen peroxide, it may be suggested that the hydroperoxyl radical ($HO_2^{\bullet}$) produced by the reaction between H_2O_2 and the $OH^{\bullet}$ radical (4), as well as the neutral species generated between two radicals, $HO_2^{\bullet}$ and ${}^{\bullet}OH$ (5), as presented in Scheme 2 [35,36] will contribute to the decrease in degradation rate. Similar behaviors were obtained for some

$$H_2O_2 + h\nu \rightarrow 2\,{}^{\bullet}OH \qquad (1)$$

$$H_2O_2 + O_2^{-\bullet} \rightarrow OH^- + {}^{\bullet}OH + O_2 \qquad (2)$$

$$(H_2O_2)_{ads} + e^- \rightarrow OH^- + {}^{\bullet}OH \qquad (3)$$

Scheme 1. Formation of hydroxyl radicals from H_2O_2.

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \qquad (4)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \qquad (5)$$

Scheme 2. Consumption of hydroxyl radicals in excess.

contaminants such as organic phosphorus pesticides [37], trichloroethylene [38] and 4-chlorobenzoic acid [39].

3.7. Effect of radiation source

The suspension of 2.0 g l^{-1} TiO_2 in 50.0 × 10^{-6} mol l^{-1} imazaquin was submitted to the artificial and solar radiation sources in order to determine the extent of light absorption by titanium dioxide. When the mercury lamp powers were changed from 125 to 250 W, without bulbs in both cases, there was an increase of 16%, that is, from 4.94 × 10^{-2} to 5.74 × 10^{-2} min^{-1}. The mineralization of ammonium and nitrate ions also suffered a small variation in concentration from NH_4^+ 23.8 × 10^{-6} mol l^{-1} and NO_3^- 12.8 × 10^{-6} mol l^{-1} for the 125 W lamp to 25.1 × 10^{-6} mol l^{-1} and 7.3 × 10^{-6} mol l^{-1} for 250 W, respectively. This is attributed to the UV radiation intensity used to determine the amount of photons absorbed by the catalyst. Previous investigations have shown that the relationship between degradation rate and intensity would be of half order, that is, directly proportional to the square root of the intensity. This dependence of the reaction rate may arise from enhanced bandgap recombination at higher light intensities, where the surface-bound hydroxy radical would be the principal hole trap and the primary initiator of oxidation of electron-donating substrates when the intensity is increased by about 25 × 10^{-3} W cm^{-2} [40].

The effect of solar irradiation was investigated by controlling the sonication effect and the thermal degradation. After 1 h in an ultrasonic bath, the imazaquin concentration decreased by about 9.2%. On the other hand, there was an increase of approximately 10 °C over 4 h of sun exposure with the reactor covered with three layers of aluminum foil, and a decrease of about 10% in imazaquin concentration. Imazaquin proved to be highly sensitive to sunlight since the relationship between the rate constants ($k_{solar}/k_{art.}$) was 2.18 in the absence of TiO_2 and was enhanced to 5.61 in the presence of TiO_2 in the final 4 h of irradiation. Solar radiation has been used in the photocatalytic degradation of several organic substances such as dyes [41,42], phenols [16] and others.

3.8. Effect of temperature

The effect of temperature was studied in the range 20–40 °C with temperatures kept constant (±0.3 °C). The rate constants increased with increasing temperature, as shown in Table 4. By plotting the natural logarithm of the rate constant as a function of reciprocal absolute temperature, a linear behavior was obtained ($r = 0.9881$) with a deviation at 40 °C. This may indicate that there was a decrease in the adsorption of imazaquin molecules on the TiO_2 surface at this temperature. The activation energy (E_a) was relatively low and was estimated at 24.8 kJ mol^{-1}. The degradation rate constants between a closed reactor at 30 °C (2.29 × 10^{-2} min^{-1}) and at room temperature with a variation from 28 to 30 °C (2.07 × 10^{-2} min^{-1}) are compatible, since in the latter case the rate constant is smaller than at a temperature fixed at 30 °C. When the irradiation was conducted in three reactors without external water circulation, indicated in Table 4 as opened, the resultant rate constant was of 4.94 × 10^{-2} min^{-1} for a variation of 27–33 °C. The highest degradation rate was obtained when the samples were collected from an open reactor, and this may be attributed to the air oxygen entering the reactor, in addition to a wider range of temperature variation. The oxygen would be promptly dissolved in water and adsorbed on the TiO_2 surface in order to be reduced by the conduction band electron, producing the peroxyl radical, $O_2^{\bullet -}$ (6). It is usually accepted that, in addition to the hydroxyl radical, the peroxyl radical is a primary oxidant species in the oxidation cycles of the photocatalytic degradation, as shown in Scheme 3. The peroxyl ion may also interact with water molecules to give continuity to the cycle (7) [17].

Table 4
Effect of temperature on the degradation rate constant with closed and opened reactors[a]

Reactor	Temperature (°C)	k (10^{-2} min^{-1})	r
Closed	20	1.60	0.9957
Closed	25	1.85	0.9886
Closed	30	2.29	0.9952
Closed	35	2.79	0.9876
Closed	40	2.94	0.9945
Closed	No control	2.07	0.9939
Opened	30	3.03	0.9931
Opened	No control	4.94	0.9965

[a] 50.0 × 10^{-6} mol l^{-1} imazaquin in 2.0 g l^{-1} TiO_2.

$$O_2 + e_{bc}^- \rightarrow O_2^{\bullet -} \quad (6)$$

$$2\,O_2^{\bullet -} + H_2O \rightarrow HO_2^- + O_2 + OH^- \quad (7)$$

Scheme 3. Oxygen cycle in the reaction medium.

4. Conclusion

Imazaquin was totally degraded in an aqueous TiO_2 suspension after 1 h sonication in the dark following a pseudo-first-order kinetic behavior, even though with a variation of ±3.0 °C. The addition of H_2O_2 in the range 1.0 × 10^{-4} to 1.0 × 10^{-3} mol l^{-1} to the suspension increased the rate constant, but at higher concentrations there was a decrease. The most favorable pH for this degradation was pH 3. The degradation rate and mineralized ion concentrations under solar irradiation were higher in comparison with artificial irradiation. The use of powerful radiation sources is not necessary since the rate constants are not directly proportional to the increase in lamp power. The temperature variation in the range 20–40 °C showed that the rate constants follow the Arrhenius equation with relatively low activation energy.

Acknowledgements

Research supported by CAPES. JCG was the recipient of a CAPES fellowship. We thank Dr. Wagner José Barreto and Dr. Maria Cristina Solci for valuable suggestions, and Ana Paula S.F. Farias for technical assistance.

References

[1] H. Hidaka, K. Nohara, J. Zhao, K. Takashima, E. Pelizzetti, N. Serpone, New J. Chem. 18 (1994) 541.
[2] I. Poulios, M. Kositzi, A. Kouras, J. Photochem. Photobiol. A 115 (1998) 175.
[3] G.A. Peñuela, D. Barceló, J. AOAC Int. 83 (2000) 53.
[4] P. Qu, J. Zhao, T. Shen, H. Hidaka, J. Mol. Catal. A 129 (1998) 257.
[5] C. Bauer, P. Jacques, A. Kalt, J. Photochem. Photobiol. A 140 (2001) 87.
[6] Y. Wang, C.-S. Hong, F. Fang, Environ. Eng. Sci. 16 (1999) 433.
[7] Q. Huang, C.-S. Hong, Chemosphere 41 (2000) 871.
[8] S. Malato, J. Blanco, C. Richter, B. Milow, M.I. Maldonado, Water Sci. Technol. 40 (1999) 123.
[9] S. Malato, J. Blanco, A. Vidal, C. Richter, Appl. Catal. B 37 (2002) 1.
[10] V. Augugliaro, J.B. Gálvez, J.C. Vázquez, E.G. López, V. Loddo, M.J.L. Muñoz, S.M. Rodriguez, G. Marci, L. Palmisano, M. Schiavello, J.S. Ruiz, Catal. Today 54 (1999) 245.
[11] M.T. El-Morsi, W.R. Budakowski, A.S. Abd-El-Aziz, K. Friesen, J. Environ. Sci. Technol. 34 (2000) 1018.
[12] E. Vulliet, C. Emmelin, J.-M. Chovelon, C. Guillard, J.-M. Herrmann, Appl. Catal. B 38 (2002) 127.
[13] D. Dumitriu, A.R. Bally, C. Ballif, P. Hones, P.E. Schmid, R. Sanjinés, F. Lévy, V.I. Pârvulescu, Appl. Catal. B 25 (2000) 83.
[14] A. Mills, J. Wang, J. Photochem. Photobiol. A 118 (1998) 53.
[15] A.D. Modestov, O. Lev, J. Photochem. Photobiol. A 112 (1998) 261.
[16] K. Tennakone, C.T.K. Tilakaratne, I.R.M. Kottegoda, J. Photochem. Photobiol. A 87 (1995) 177.
[17] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[18] J. Arántegui, J. Prado, E. Chamarro, S. Esplugas, J. Photochem. Photobiol. A 88 (1995) 65.
[19] J.B. Heredia, J. Torregrosa, J.R. Dominguez, J.A. Peres, Chemosphere 42 (2001) 351.
[20] M.V. Shankar, B. Neppolian, S. Sakthivel, Indian J. Eng. Mater. 8 (2001) 104.
[21] B. Neppolian, S. Sakthivel, B. Arabindoo, J. Environ. Sci. Heal. A 36 (2001) 203.
[22] D.A. Potter, M.C. Buxton, C.T. Redmond, C.T. Patterson, A. Powell, J. Econ. Entomol. 83 (1990) 2362.
[23] C.J. Patton, S.R. Crouch, Anal. Chem. 49 (1997) 464.
[24] D.F. Ollis, E. Pelizzeti, N. Serpone, Heterogeneous photocatalysis in the environment: application to water purification, in: N. Serpone, E. Pelizzeti (Eds.), Photocatalysis: Fundamentals and Applications, Wiley, New York, 1989, pp. 603–637.
[25] C.M. So, M.Y. Cheng, J.C. Yu, P.K. Wong, Chemosphere 46 (2002) 905.
[26] N. San, A. Hatipoglu, G. Koçtürk, Z. Çinar, J. Photochem. Photobiol. A 146 (2002) 189.
[27] P. Atkins, Physical Chemistry, 7th ed., Oxford University Press, Oxford, 2002, pp. 242, 879 and 961.
[28] Y. Ku, R. Leu, K-C. Lee, Water Res. 30 (1996) 2569.
[29] B.J. Deepmeier, A.J. Driessen, W.J. Hehre, P.E. Klunzinger, L. Lou, I. Yu, PC Spartan Pro Software, Wavefunction Inc., Irvine, 1998.
[30] K.-H. Wang, Y.-H. Hsieh, C.-H. Wu, C.-Y. Chang, Chemosphere 40 (2000) 389.
[31] I.-W. Huang, C.-S. Hong, B. Bush, Chemosphere 32 (1996) 1869.
[32] T. Hisanaga, K. Harada, K. Tanaka, J. Photochem. Photobiol. A 54 (1990) 113.
[33] K.-H. Wang, Y.-H. Hsieh, M.-Y. Chou, C.-Y. Chang, Appl. Catal. B 21 (1999) 1.
[34] M. Anheden, D.Y. Goswami, G. Svedberg, J. Solar Energy Eng. 118 (1996) 2.
[35] V. Augugliaro, E. Davi, L. Palmisano, M. Schiavello, A. Selafani, Appl. Catal. 65 (1990) 101.
[36] M.W. Peterson, J.A. Turner, J. Nozik, J. Phys. Chem. 95 (1991) 221.
[37] Z. Mengyue, C. Shifu, T. Yaowu, J. Chem. Technol. Biotechnol. 64 (1995) 339.
[38] J.E. Pacheco, M.R. Prairie, J. Yellowhorse, J. Solar Energy Eng. 115 (1993) 123.
[39] D.D. Dionysiou, M.T. Suidan, E. Bekou, I. Baudin, J.-M. Laîne, Appl. Catal. B 26 (2000) 153.
[40] J.-M. Herrmann, Catal. Today 53 (1999) 115.
[41] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Chemosphere 46 (2002) 1173.
[42] W.S. Kuo, P.H. Ho, Chemosphere 45 (2001) 77.