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Evaluation of the main active species involved in the TiO₂ photocatalytic degradation of ametryn herbicide and its intermediates generated

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Abstract

The herbicide ametryn is persistent, bio-accumulates in different ecosystems and causes a negative impact on the environment with emphasis on water compartments. In this study, we investigated the effectiveness of photocatalysis using TiO₂ suspended as catalyst on the removal of ametryn. The evaluation of photocatalytic activity under simulated sunlight was discussed as evidence by numerous controlled trials and several operational parameters such as ametryn concentration, total organic carbon, chemical oxygen demand, specific UV absorbance, biochemical oxygen demand, toxicity and formed intermediates. Moreover, the

roles of reactive species involved in the degradation of ametryn was examined by using different specific scavengers. Ametryn removed by photocatalysis using 0.4 g L^{-1} of TiO_2 was 100% within 60 min, while only 30% was achieved by photolysis at the same time. Biodegradability index improved from 0.3 (raw solution) up to 0.8. The acute toxicity measured by the inhibition percentage of bioluminescence from *Vibrio fischeri* indicates that the photocatalytic treatment promotes 97% of toxicity reduction. The scavenger study shows different percentages of inhibition in ametryn degradation, which allowed to conclude that HO^\bullet , valence-band holes and $\text{O}_2^{\bullet-}$ could intervene in the degradation of ametryn, with predominance of HO^\bullet . Thirty-eight intermediates were identified from the photocatalytic degradation of ametryn. The comparison of the generation of those intermediates with and without the addition of scavengers showed that the different by-products are generated depending on the predominance of the active species. For example, the presence of azide resulted in intermediates formed by condensation reactions. Based on the identified intermediates, reaction pathways of ametryn were defined and a degradation mechanism was proposed, including HO^\bullet radicals, $\text{O}_2^{\bullet-}$, holes, and $^1\text{O}_2$.

Keywords: Biodegradability; Acute toxicity; kinetics; Scavengers; Reaction mechanism.

1. Introduction

Pesticides are one of the main classes of toxic compounds, often classified according to their target organism (i.e. herbicides, fungicides, rodenticides and pediculicides), that are deliberately available for use in the control of pests and vectors of diseases [1,2]. Consequently, the extensive and inefficient use of pesticides for agricultural and nonagricultural practices results in several negative influences ranging from ecological pollution to damage of biodiversity [3,4]. Dispersion of pesticides residues in the environment land cause disastrous

contamination of ecosystems, especially, surface- and ground-water bodies and soil [4]. Thus, these compounds are considered emerging contaminants by the scientific and legislative communities [2].

These contaminants are frequently found in the environment, especially in water compartments, in concentrations that range from ng L^{-1} to $\mu\text{g L}^{-1}$ [5]. Although their concentration is low, the consequences of their exposition are unknown in the long term and are pseudo-persistent in the environment due to their continuous discharge. However, in many cases pesticide concentrations in the environment can be very high, for example, in wastewaters can reach levels up to 500 mg L^{-1} [6].

Triazine herbicides with the advantage of high efficiency for the control of broadleaf and grassy weeds are one of the most widely used groups of herbicides all over the world [7] in many fields such as agriculture, industry and urban area [8]. For example, they are present in the 10 most widely used pesticide formulations in Europe [9]. Chemically, triazine herbicides are characterized by a structure of a hetero-cyclic ring containing three unsaturated nitrogen atoms and are classified as asymmetrical triazines (triazinones, triazidinones) and symmetrical or 1,3,5-triazines (commonly called s-triazines) [10,11].

As triazines are very stable compounds, they accumulate in environmental compartments for a long time and because of their physicochemical properties such as: (i) relatively high water solubility (185 mg L^{-1} , $20 \text{ }^\circ\text{C}$ [11]); (ii) low sorption coefficient ($316 \sim 445 \text{ cm}^3 \text{ g}^{-1}$ [12]); (iii) high polarity ($\log K_{ow} \text{ } 2.7\text{-}3.1$ [11]); or (iv) long half-life time ($70\text{-}250$ days, varying with type of soil and weather conditions [13]). Among triazines, especial emphasis can be made on ametryn ($\text{C}_9\text{H}_{17}\text{N}_5\text{S}$, 2-ethylamino-4-isopropylamino-6-methylthio-s-triazine). Due to its physicochemical properties, ametryn is susceptible to leaching from the soils to natural and even drinking water. In addition, these compounds can undergo slow degradation to water-soluble by-products [10].

Ametryn is known as an endocrine disruptor, aquatic ecosystem disruptor, and can cause various health effects to humans, such as nausea, vomiting, diarrhea, muscle weakness, salivation and cancer [14,15]. Besides, it creates irritation to the skin, eyes and respiratory tract. It is also toxic to terrestrial and aquatic animals [15]. Also, ametryn is known to induce oxidative stress, cellular and DNA damage and cell death [16]. These factors point out that this herbicide represents a risk to the environment and the human health.

Residues of ametryn are sources of contamination of water and soils. As example, the content of ametryn was detected at $1.56 \pm 0.04 \mu\text{g L}^{-1}$ in groundwater samples in Assis city, located in the State of São Paulo (Brazil) [17]. 3.4 mg/L of ametryn were found in the agricultural runoff water in Veerapur village, Belgaum district, Karnataka state, India [18]. Ametryn was found at a concentration of $45 \mu\text{g L}^{-1}$ in water samples from a river near the city of Colima, Mexico [19]. In reservoir water samples located in Shandong City - China, ametryn was detected with concentrations of 3.95–8.48 ng L^{-1} [20]. Ametryn residues were found in activated sludge samples at concentrations of $1.07 \pm 0.005 \text{mg L}^{-1}$, from wastewater treatment plants in KwaZulu-Natal Pietermaritzburg, South Africa [21]. Ametryn has been detected at levels up to 2–9 $\mu\text{g L}^{-1}$ in water samples of the Jiménez River watershed, a tributary of the Parismina River in the Caribbean Coast of Costa Rica [22]. These examples demonstrate that ametryn residues are introduced into several environmental compartments around the world. Once ametryn is present in water compartments, it would be extremely difficult to be treated. A potential strategy for eliminating emerging contaminants from aqueous solutions involves Advanced oxidation processes (AOPs) [23-26]. Among POAs, heterogeneous photocatalysis can be considered an interesting option [27-30].

The heterogeneous photocatalysis is defined as a photochemical process in which the semiconducting species is irradiated with light of sufficient energy (or of a certain wavelength corresponding to the band gap) for the promotion of valence band electrons to the conduction

band. Consequently, the reduction and oxidation sites generated are capable of producing different active species, as such hydroxyl (HO^\bullet), superoxide ($\text{O}_2^{\bullet-}$) and perhydroxyl (HO_2^\bullet) radicals, singlet oxygen ($^1\text{O}_2$), H_2O_2 , and holes (h_{BV}^+) [31-33], that are the main oxidants responsible for the decomposition reactions of organic compounds.

Among a wide spectrum of semiconductors, TiO_2 is an attractive approach to water purification, mainly due to its excellent performance as photocatalyst in UV irradiation, low cost, and long-term stability of the material. In addition, it has other important advantages, such as low toxicity, found commercially and synthesized by various methods, possibility of activation sunlight, insolubility in water, highly resistant to most chemicals and photocorrosion, the ability to photogenerate highly oxidizing holes [34,35].

The most common commercial TiO_2 is Evonik AEROXIDE® TiO_2 P-25 (denoted as P25). This oxide is comprised of individual anatase and rutile nanoparticles, together with around 15% of rutile formed heterojunction structure with anatase phase [36]. Its main advantage is the numerous oxygen vacancies, which assists the absorption of solar/visible light and the separation of e^-/h^+ pairs [37]. Thus, an increase in the active species implies cost reduction, as it is not necessary to use UV radiation. In this context, photocatalytic treatments using sunlight or UVA, highlighting xenon lamps here, are of great interest for economic reasons.

Although photocatalytic processes are well described in the literature, the contribution of the role of reactive oxygen species (ROS) and holes is still controversial and depends of the some factors such as substrate structure, nature of the photocatalyst and source of irradiation [38,39].

In the literature it is possible to find several works focused on understanding the roles of ROS in the entire degradation system using selected chemical scavenger. However, few studies aim to understand the role of active species in the generation of intermediates and

degradation reaction pathways to highlight the role of the ROS involved in the complete photocatalytic degradation process. Ma et al. [40] investigated the roles of ROS involved in the whole degradation of pentachlorophenol and main toxic intermediates and elucidate the degradation mechanisms by TiO₂ under UV light illumination. The results showed that the generation of intermediates depends on the type of active species involved, and the degradation mechanism of pentachlorophenol included HO•, O₂^{•-}, and H₂O₂. Ismail et al. [41] compared the evolution of intermediates generated in degradation of sulfaclozine on TiO₂ suspensions under UV light with and without the addition of methanol as scavengers. Xu et al. [42] evaluated the photodegradation mechanisms of monomethylarsonic acid and dimethylarsinic acid with nanocrystalline titanium dioxide under UV irradiation in the presence of radical scavengers, including superoxide dimutase, sodium bicarbonate, tert-butanol, and sodium azide. From the results obtained about the effect of scavengers on photodegradation and literature data, the authors proposed pathways of photodegradation reactions involving HO• and O₂^{•-} radicals. Jedsukontorn et al. [43] proposed pathways of glycerol conversion and product distribution over the commercial TiO₂ and the black TiO₂ photocatalyst via the dominate ROS. The results indicated that surface hydroxyl radicals (h⁺/HO•_s), bulk hydroxyl radicals (HO•_b), ¹O₂ and O₂^{•-} were the important ROS for glycerol conversion. In a previous work [44] we examined the contribution of the main active species to the photocatalytic degradation of metoprolol using TiO₂ doped with 5% B (w/w) as the photocatalyst, and the relationship between the intermediates formed during the photocatalytic degradation and active species. Based on our results it was possible to prove that there is change in the reactions of the degradation process of metoprolol when it changes the role of any active species generated on the surface of the catalyst.

The intervention of ROS leading to the initial photoreaction process is not the same in all studies since the oxidation can proceed through different mechanisms. In this context, it is

utmost importance to identify the main active species and determine their roles in the formation of intermediates in order to further develop and understand the mechanisms underlying the reactivity of photocatalysts for environmental remediation [45].

In this work, attention has been focused to elucidate the photocatalytic mechanism for the removal of ametryn by TiO₂ catalysts under simulated solar light. To achieve these objectives, studies were conducted to identify the main active species formed in the process using selected chemical scavengers that are specific for HO•, O₂^{•-}, ¹O₂ and holes. In addition, a detailed study of the influence of each active species on the generation of degradation products and degradation pathways has been performed, in which the reaction intermediates were detected by means of exact mass measurements performed by liquid chromatography coupled to quadrupole-time of-flight mass spectrometry (LC-ESI-QTOF-MS/MS). Besides the objective of mechanistic details of the photodegradation, considering the need for more effective investigations for the degradation of ametryn using TiO₂, this paper deals in the optimization of the P25 mediated photocatalytic degradation of ametryn. In this way, a systematic investigation was done on the effect of different operational variables such as: (a) the impact of catalyst dose; (b) the evaluation of kinetic aspects of the process (photolysis, photocatalysis); (c) the evolution of some lumped parameters as TOC, COD, BOD, SUVA and the toxicity using Microtox® test; (d) the determination of the second-order rate constant of reaction between ametryn and HO• radicals, and (e) the identification of the reaction intermediates without scavengers.

Although some studies of ametryn degradation by photocatalysis have been reported [46-51], none of them investigated the role of reactive species involved in the degradation process and their role in the degradation pathways.

2. Materials and methods

2.1. Chemicals

All chemicals used in the experiments were of analytical grade. Solutions of 10 mg L^{-1} of ametryn (CAS number: 834-12-8, purity 99.5%, $\text{C}_9\text{H}_{17}\text{N}_5\text{S}$, MW $227.33 \text{ g mol}^{-1}$, Sigma–Aldrich Chemical Co) were prepared using deionized water. The photocatalyst used (TiO_2 P25) was from Evonik Industries AG (Germany). Formic acid (85%), *tert*-butyl alcohol (99.7%), sodium azide (>99.5%) and *p*-benzoquinone (>99%) were supplied by Probus S.A. (Spain), Panreac (Spain), Sigma–Aldrich Chemical Co and Merck (Germany), respectively. Acetonitrile was purchased from Fischer Chemical and orthophosphoric acid (85%) from Panreac Quimica.

2.2. Photocatalytic experiments

The installation used in the photocatalysis experiments consists of a solar simulator (Solarbox, Co.fo.me.gra, 220 V, 50 Hz, see Fig. 1) equipped with a 1000 W xenon lamp (Xe-OP, Phillips) on the top and an optical filter (cut-off <280 nm) positioned just below the lamp. In this apparatus, the tubular photoreactor (Duran glass material, 24 cm length, 2.11 cm diameter, 0.078 L illuminated volume) was horizontally placed at the bottom of the solarbox on the axis of a parabolic mirror made of reflective aluminum. The photon flux arriving at the photoreactor was measured by *o*-nitrobenzaldehyde (*o*-NB) actinometry [52], being $9.4 \mu\text{Einstein s}^{-1}$ (290–400 nm). Ametryn solution (prepared at the concentration of 10 mg L^{-1} , natural pH of the solution around 5.7) was introduced in a jacketed reservoir tank (total volume 1L). Then, the amount of catalyst under study was added and different scavengers when needed. In this tank, the solution was magnetically stirred and maintained at constant

temperature of 25 °C with a thermostatic bath (Haake K10). The solution to be treated was continuously pumped into the photoreactor by peristaltic pump (Ecoline VC280 II, Ismatec) from the reservoir tank with a flow rate of 0.65 L min⁻¹. After recirculation of the solution, the lamp was activated and began experiments lasting 120 minutes. In order to remove the catalyst, before the analysis, samples were filtered with a polyethersulfone membrane filter of 0.45 μm. The experiments were conducted in duplicate to ensure reproducibility and mean values are reported.

Insert Fig. 1

2.3. Effect of radical inhibitors

The role and contribution of HO[•], O₂^{•-}, h⁺ and ¹O₂, during the TiO₂ photocatalytic process, was investigated by adding well-known radical trapping reagents (scavengers) such as *tert*-butyl alcohol (*t*-BuOH, 60 ml L⁻¹), *p*-benzoquinone (*p*-BQ, 0.001 g L⁻¹ corresponding to a molar relation of 1:10 for *p*-BQ:ametryn), formic acid (AF, 0.82 mL L⁻¹) and sodium azide (NaN₃, 0.77 mg L⁻¹), respectively, in 10 mg L⁻¹ ametryn solutions containing 0.4 g L⁻¹ of catalyst. The concentrations of scavengers used were based on previous research [44,52].

2.4. Analytical Instruments

The monitoring of the decrease in concentration of ametryn was carried out by high-performance liquid chromatography (HPLC) from Agilent 1200 Infinity Series using a SEA18 (5μm 15×0.46 cm from Teknokroma) and a Waters 996 photodiode array detector using the Empower Pro software 2002 Water Co. The mobile phase consisted of 78:22 (v/v) mixture of

water (pH 3 adjusted by H₃PO₄) and acetonitrile, injected with a flow rate of 0.80 mL min⁻¹ and detected at its maximum UV absorbance of 223 nm. In these parameters, the peak associated with ametryn appeared at 3.43 min, showing a limit of detection (LOD) = 0.018 mg L⁻¹ and a limit of quantification (LOQ) = 0.055 mg L⁻¹.

To calculate the kinetic constant of the ametryn reaction by photocatalysis, simultaneous degradation experiments involving ametryn and 2,4-D (2,4-dichlorophenoxyacetic acid) were performed. The concentration decay of the samples was monitored by HPLC from Agilent 1200 Infinity Series under the same conditions that were previously employed for monitoring the degradation of ametryn. 2,4-D was quantified at $\lambda=234$ nm. The calibration curve data for 2,4-D were as follows: area (mAU) = 0.08923 + 126.7361 [2,4-D mg L⁻¹]; R = 0.9998; SD = 1.01146; LQD = 0.0263 mg L⁻¹ and LOQ = 0.0798 mg L⁻¹.

Total organic carbon (TOC) determination was done using a Shimadzu TOC-V CNS instrument. The COD was determined following the colorimetric method 5220D of Standard Methods for Examination of Water and Wastewater [53]. The colour of the sample was measured in terms of the absorbance at 420 nm using a spectrophotometer (Hach Lange DR 2500) after digestion, employing 2 h of extreme catalytic oxidation conditions at 150 °C. The specific UV absorbance (SUVA_{254nm}) values were calculated dividing the absorbance of a sample at 254 nm by its COD value in the predetermined time (SUVA = (UV₂₅₄/COD) \times 100).

The biological oxygen demand (BOD_{5,20}) was determined with the protocol of Standard Methods 5210D [53] by respirometric process using OxiTop equipment during 5 days, under constant stirring and controlled temperature at 20 °C. The acute ecotoxicity of the samples were measured by the Microtox® tests using a Model 500 Analyzer (Azur Environment, Workingham, England), which determines the inhibition of *Vibrio fischeri* bioluminescence at 15 min of incubation. The toxicity was measured as the percentage of inhibition with respect to the light emitted after 15 min exposure. The analyzed data were expressed Results obtained

were expressed as toxicity units (equitox), $TU = [1/EC_{50}] \times 100$, where EC_{50} is the concentration which causes 50% of the light emission reduction.

To identify the by-products, samples collected from degradation experiments were analyzed by using an HPLC system (Agilent Series 1100, Agilent Technologies) connected to LC/MSD TOF (Agilent Technologies) mass spectrometer equipped with an electrospray ionization (ESI) interface operating in the positive ionization mode. The parameters used in the spectrometer were as follows: capillary 4000 V; nebulizer 15 psig; drying gas 7 L min^{-1} ; gas temperature $325 \text{ }^{\circ}\text{C}$; fragmentator 175 V; and HPLC conditions were the same as previously used to monitor degradation of ametryn. Spectra were acquired over the m/z 60–1200 range.

In order to remove the catalyst, before the analysis, all the samples were filtered with a polyethersulfone membrane filter ($0.45 \mu\text{m}$, Chemlab).

3. Results and discussion

3.1. Effect of TiO_2 concentration on Ametryn Degradation

Three different catalyst loads were assessed (0.05 , 0.2 and $0.4 \text{ g L}^{-1} \text{ TiO}_2$) to choose the optimum catalyst concentration for further investigate the role of active species in the mechanisms of the photocatalytic process.

Fig. 2 show the effect of TiO_2 concentration on ametryn degradation and mineralization, and both parameters improve when titania concentration increases. It can be seen that only direct photolysis was insufficient to degrade ametryn, only around 30% of the herbicide was removed in 30 minutes of irradiation, not observing increased rate of degradation until the end of the experiment. Moreover, mineralization reached was insignificant, obtaining 6% after 120 minutes of irradiation. Among the concentrations of catalyst tested, using 0.4 g L^{-1} of TiO_2

leads to the best herbicide removal (100% removal after 60 min of irradiation) and mineralization (>20% after 120 min of irradiation).

Previous studies carried out in our research group with the same experimental installations [54] reported that, working with 0.5 g L⁻¹ of TiO₂, catalyst sedimentation at the bottom of the reactor was observed, therefore concentrations greater than 0.4 g L⁻¹ were not considered for the experiments. The TiO₂ settling in the reactor could increase radiation scattering, decreasing the reaction rate and masking the results of the experiments.

Degradation data were fitted to pseudo-first order kinetics and the values obtained for the apparent rate coefficient (k_{app}) were calculated from the slopes of the regression curves representing $-\ln(C/C_0)$ vs time. It was clearly appreciated that kinetic constant decreases when TiO₂ concentration decreases, being k values $7.7 \times 10^{-2} \text{ min}^{-1}$ ($R = 0.997$), $5.7 \times 10^{-2} \text{ min}^{-1}$ ($R = 0.978$) and $5.3 \times 10^{-2} \text{ min}^{-1}$ ($R = 0.978$), for 0.4, 0.2 and 0.05 g L⁻¹ of TiO₂, respectively. On the other hand, in the absence of the catalyst, the obtained value of k_{app} was $1.2 \times 10^{-2} \text{ min}^{-1}$ ($R = 0.995$), roughly 6.4 times lower than for the experiments performed with 0.4 g L⁻¹ of TiO₂.

Insert Fig. 2

3.2. Evolution of oxidation, aromaticity, toxicity and biodegradability assessment of intermediates

The removal of COD was evaluated during the degradation time and the results are shown in Fig. 3A. The COD reduction found after 120 minutes of irradiation was around 60%. The COD indicates the amount of organic matter in water sample, providing straightforward correlation with C and O atoms in the molecular structure [55,56]. When the results are expressed as a correlation COD vs. time usually provides the S-shape curve [55]. When an

inflection point is observed in this curve, it can be said that aliphatic compounds begin to prevail over the aromatic compounds in the reaction mixture [55]. As can be seen from Fig. 3A, such inflection point was not observed during the experiment performed, indicating a considerable fraction of aromatics, resulting from the formation of intermediates derived from the s-triazine ring of the ametryn molecule.

Aromaticity, represented by SUVA, which indicates the correlation with aromatic organic matter content [57], was determined. These results are also presented in Fig. 3A (blue line in the graph). It is possible to observe an increase of the aromaticity with the increase of the degradation time, reaching a maximum value in 30 minutes of experiment. After 60 minutes there is a decrease in SUVA value, however at the end of the experiment, the value is still higher than the initial one. This indicates that the aromatic intermediates generated in the process were not completely degraded, which is in accordance with the low mineralization obtained (see Fig. 2).

Summarizing, the COD curve and the SUVA results show the presence of aromatic compounds in the system along all the process. These results are in agreement with hydroxylated intermediates proposed for the degradation of ametryn by photocatalysis (see section 3.5.1.).

The biodegradability and toxicity of pesticides are important parameters when considering advanced treatment combined with conventional biological treatment as a strategy to reduce overall operation costs. Pesticides are generally non-readily biodegradable and have high toxicity [58].

The biodegradability index of ametryn solution before and after treatment was calculated as the ratio of $BOD_{5,20}$ to COD. The treated solution was considered biodegradable when this ratio was in the range of 0.40–0.80 [59]. Fig. 3B shows the effect of photocatalytic treatment on biodegradability index ($BOD_{5,20}/COD$ ratio) improvement. The biodegradability

of the initial solution of ametryn was low (0.3), as seen in Fig. 3B. During the treatment period, the BOD_{5,20}/COD ratio steadily increases up to nearly 0.8 after 120 min of irradiation, suggesting that the hydroxylated intermediates formed are much more biodegradable.

Acute toxicity evolution before and after photocatalytic experiment, calculated by the light emission inhibition of *Vibrio fischeri*, is also shown in Fig. 3B. The initial equitox value of the untreated ametryn solution was nearly 8.6 and after the treatment was 0.25, that is, a reduction of around 97% of the toxicity was obtained.

These results are in accordance with the increased biodegradability achieved through this treatment, possibly due to the lower toxicity of the hydroxylated intermediates formed during the treatment.

Insert Fig. 3

3.3. Identification of the main reactive species involved in the photocatalytic degradation of ametryn

As previously reported, photocatalytic reactions involve the generation of various ROS. We utilized four selective radical scavengers to assess the extent of ametryn degradation provoked by HO[•], O₂^{•-}, ¹O₂ and h_{BV}⁺. The scavengers and their reactions with free radicals are summarized in Table 1.

The *t*-BuOH was reported to be a good scavenger of free HO[•] radical [44,45,60]. The ρ-BQ is used to evaluate the contribution of O₂^{•-} radical [38,44]. However, ρ-BQ has also a great capacity to trap electrons at the surface of TiO₂ to form hydroquinone (HQ) [39,60]. The decrease of the amount of electrons reduces the generation of O₂^{•-} and may then inhibit the rate of degradation due to the attack of this active specie [61].

FA could significantly suppressed the h_{BV}^+ and HO^\bullet radicals (free and adsorbed) in TiO_2 photocatalyst [39,44,62]. Sodium azide (NaN_3) was able to scavenger the singlet oxygen produced by the interaction of $O_2^{\bullet-}$ radical and photo generated h_{BV}^+ [63,64]. Additionally, azide ions are also scavengers for HO^\bullet radicals [42], as demonstrated by the mechanism in Table 1.

The effect of these scavengers on the ametryn photodegradation rate is shown in Fig. 4A and B. Table 1 also includes the inhibitory effect of each scavenger expressed as the percentage of decrease of the initial reaction rate, as well as the percentage of contribution of each active species during the photocatalytic degradation of ametryn.

In ρ -BQ presence after 120 min of irradiation, there is only 3% inhibition on the elimination of the herbicide compared to the experiment in the absence of scavengers, which could suggest the non-participation of $O_2^{\bullet-}$ in the process. On the other hand, the k_{ap} constants (see Fig. 4B) in the presence of ρ -BQ decreases to 0.0520 min^{-1} . This means a reduction by about 1.5 times compared to the value of the constant obtained in the absence of scavenger, indicating $O_2^{\bullet-}$ plays a minor role in the degradation process.

As there was inhibition of only 3% of the degradation of ametryn with addition of ρ -BQ, the perhydroxyl radicals (HO_2^\bullet) may participate along with the radicals $O_2^{\bullet-}$ during the photocatalytic process. This occurs because these species are present in equilibrium ($HO_2^\bullet \rightleftharpoons O_2^{\bullet-}$) and this equilibrium depends on the pH of the medium [65]. Since the pKa value of the equilibrium is 4.7, the $O_2^{\bullet-}$ becomes the predominant species in solution at pH 6 [65]. As the experiments were carried out with pH below 6 (around 5.7) the equilibrium can be displaced to the formation of the HO_2^\bullet radicals, explaining the low inhibition rate in the presence of BQ.

In the presence of *t*-BuOH, the efficiency of ametryn degradation reduces from 100% to 18% after 120 min of experiment (*i.e.*, 82% inhibition in the rate of degradation was observed). Consequently, a great inhibitory effect was found in the ametryn kinetic profile (see

Fig. 4B), with a constant rate of 0.0065 min^{-1} . This suggests that free HO^\bullet radicals were mainly implicated in ametryn degradation with TiO_2 P25.

When FA ion was used as a diagnostic tool for suppressing the hole and HO^\bullet (free and adsorbed), the photocatalytic degradation of ametryn was largely inhibited (only 12% removal of ametryn was obtained after 120 min), as shown in Fig. 4A. Consequently, the rate constant decreased to 0.0035 min^{-1} (see Fig. 4B), which was only 4.5% of that in the absence of FA. Since FA is used to evaluate the participation of both species, the greater the inhibition of the reaction by means of the FA in comparison to the inhibition by *t*-BuOH, the greater the direct participation of the h_{BV}^+ in the photodegradation of ametryn. These results indicated that 88% of the degradation rate of ametryn was originated from both the HO^\bullet radicals and photoholes. Thus the contribution percentage of photoholes in the degradation rate was deduced as 6% by subtracting the percentage of HO^\bullet radicals from the total percentage.

Azide, a scavenger for HO^\bullet and $^1\text{O}_2$, also significantly reduced the degradation rate of ametryn (Fig. 4A). When it was added, the rate of ametryn removal was 39% after 120 min of irradiation, *i.e.*, leading to 61% ametryn degradation inhibition with a constant rate of 0.0142 min^{-1} . However, it is verified that this inhibition is smaller than that obtained by adding *t*-BuOH. If $^1\text{O}_2$ contributes significantly to the photodegradation process, inhibition by sodium azide is expected to be greater than *t*-BuOH which only affects HO^\bullet radicals [62,66]. The $^1\text{O}_2$ does not seem therefore to play a meaningful effect on the degradation of ametryn.

Therefore, it can be concluded that the HO^\bullet free radicals are the predominant active species responsible for the major degradation of ametryn using TiO_2 P25 as catalyst, followed by direct oxidation via hole (h_{BV}^+), and to a lesser extent by the contribution of $\text{O}_2^{\bullet-}$ anions.

Table 1 shows that values below 100% are found (91%) by summation of the contribution percentages of each active species evaluated. This difference can be due to the amount of non-captured radicals such as other reactive oxygen species (ROS). However, the

total contribution of these ROS not analyzed was only 9%. Therefore, it was possible to estimate with confidence the participation of the main active species in the ametryn degradation.

Insert Fig. 4

Insert Table 1

3.4. Estimation of the second-order kinetic constant between ametryn and the photo-generated HO• radicals by competition method

As the HO• radicals were the active species that played the most significant role in the photocatalytic degradation of ametryn (more than 80% removal was conducted by free HO• radicals), the next step was to determine the rate constants for the reaction between the herbicide and these radicals.

To calculate the constant considering only HO• radicals, the competitive kinetic model was used. For the application of this model, experiments were performed with the mixture of the compound in study and a reference compound, whose rate constant for the reaction with HO• radicals is previously known, which in this case was the 2,4-D ($k_{HO\bullet} = 5.5 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ [70]).

This procedure is based on the assuming that the reaction between the HO• radical and the organic compound (R) follows an overall second order kinetics: first order in relation to the concentration of organic substance and first order in relation to the concentration of HO• radicals [41]. Then, the rate of disappearance of the organic compound, R, can be expressed by the following Eq. (1):

$$\frac{d[R]}{dt} = -k_{HO^{\bullet},R}[HO^{\bullet}][R] \quad (1)$$

Where $k_{HO^{\bullet},R}$ is the second order kinetic constant for the reaction between R and HO^{\bullet} . In this context, solutions containing both ametryn and 2,4-D with a concentration of 0.04 mmol L⁻¹ were submitted to photocatalytic degradation and their concentrations were followed with the time.

The decay curve of the concentration of each compound in the mixture over time is shown in Fig. 5A. This model is a way of solving the problems encountered to measure the reaction rate of HO^{\bullet} radicals, due to the limitations of analytical techniques since reactions are very fast [71]. The model has been used successfully by several authors, such as, Dantas et al. 2008 [72], de Oliveira et al. [73], Zeghioud et al. [74], Ismail et al. [41], da Silva [75].

The following equations can describe the disappearance rate of both ametryn and 2,4-D:

$$\frac{d[2,4 - D]}{dt} = -k_{HO^{\bullet},2,4-D}[HO^{\bullet}][2,4D] \quad (2)$$

$$\frac{d[Ametryn]}{dt} = -k_{HO^{\bullet},Ametryn}[HO^{\bullet}][Ametryn] \quad (3)$$

Dividing Eq. (3) by Eq. (4) and integrating, Eq. (5) is obtained:

$$\ln \frac{[2,4 - D]}{[2,4 - D]_0} = -\frac{k_{HO^{\bullet},2,4-D}}{k_{HO^{\bullet},Ametryn}} \ln \frac{[Ametryn]}{[Ametryn]_0} \quad (5)$$

According to Eq. (5), by plotting $\ln([2,4\text{-D}]/[2,4\text{-D}]_0)$ against $\ln([A\text{metryn}]/[A\text{metryn}]_0)$, as shown in Fig. 5B, a straight line ($R = 0.9890$) was obtained, whose slope is the ratio of rate constants. As can be observed, points lie very satisfactorily around straight lines, confirming the goodness of the model used. In this way the ratio $k_{\text{HO}\cdot 2,4\text{-D}}/k_{\text{HO}\cdot \text{Ametryn}}$ was found to be 12.0. Hence, the calculated value of $k_{\text{HO}\cdot \text{Ametryn}}$ was $4.57 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. $\text{HO}\cdot$ quickly reacts with most pesticides through electron transfer with second-order rate constants varying between 10^7 and $10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ [76,77]. Therefore, the value found experimentally is in the range of most reactions of $\text{HO}\cdot$ with pesticides confirming that these radicals are the main reactive species involved in the photocatalytic degradation of ametryn with TiO_2 suspensions.

Insert Fig. 5

3.5. Degradation mechanism of ametryn: Relationship between the active species and the intermediates generated

For the identification and structural elucidation of intermediates generated during the photocatalytic treatment, samples collected at various treatment stages (10 min, 30 min and a final sample mixture at 120 min) were analyzed by LC-TOF-MS in positive ionization. The experiments were performed with 10 mg L^{-1} ametryn and $0.4 \text{ g L}^{-1} \text{ TiO}_2$ in the absence and presence of the different scavengers studied.

Under the adopted conditions, a total number of thirty-eight intermediate products have been identified (with or without scavengers) based on LC-MS-TOF analysis. Table S1 (Supplementary material) summarizes the abbreviations used for intermediates, with their

analytical information including observed exact masses of protonated ions, retention time and empirical formula obtained by the equipment software used (LC/MSD TOF ESI-TOF).

Fig. S1 (Supplementary Material) reports a mass spectrum model with the formed intermediates at m/z 159, m/z 175, m/z 186, m/z 200 and m/z 210, corresponding to ametryn solutions irradiated with TiO_2 particles in the absence of scavengers.

In this section, a discussion was first conducted addressing the intermediates generated in the photocatalytic process without scavengers. Subsequently, the generation of intermediates was evaluated with the addition of different scavengers. All these data allowed us to propose a mechanism for ametryn degradation shown in Fig. 9.

3.5.1. Identification of by-products structures during photocatalytic reaction without addition of scavengers

Fig. 6 presents a scheme with fourteen intermediate products that were identified in the TiO_2 process with m/z 159, m/z 175, m/z 186, m/z 200, m/z 219, m/z 236, m/z 238, m/z 240, m/z 242, m/z 244, m/z 250, m/z 254, m/z 264 and m/z 278. The formed intermediates with m/z 186, m/z 200, m/z 244 are common by-products of ametryn oxidation, as identified in our previous study [73] and also by other researchers. Chen et al. [78] found in his study degradation products for ametryn with the same m/z 186 and m/z 200. The intermediate with m/z 200 was also proposed by Gozzi et al. [79] for the degradation of ametryn by solar photoelectro-Fenton, as well as a metabolite generated from biodegradation of the herbicide by entomopathogenic fungal cosmopolite *Metarhizium brunneum* ARSEF 2107 [10]. The intermediate with $m/z = 244$ was also identified by Lopes et al. [80] and Mascolo et al. [81] in the degradation of ametryn by means of sodium hypochlorite and chlorine dioxide

disinfectants. Liu et al. [82] also proposed this intermediate in the heterogeneous reaction of ametryn particles with NO_3 radicals.

In our previous study of ametryn degradation by homogeneous oxidative processes [73], we identified the intermediate with m/z 240 and proposed the same structure as presented in this study. On the other hand, to the best of our knowledge, no intermediates with m/z 159, m/z 175, m/z 219, m/z 236, m/z 254, m/z 264 and m/z 278 have been identified so far.

With the exception of intermediates with m/z 186 and m/z 200, all other by-products generated in the photocatalytic process are hydroxylated compounds, derived from sustained HO^\bullet radicals attacks on sulfur in the R-S-CH_3 bond and/or the aliphatic part of the ametryn molecule.

The hydroxylation of the group (R-S-CH_3) led to the formation of sulphoxides (R-SO-CH_3) with $m/z = 244$, m/z 242 and m/z 240. Successive attacks by HO^\bullet on aliphatic carbon chains of these intermediates resulted in hydroxylated compounds of lower molecular weight with m/z 219, m/z 175 and m/z 159 owing to the breakdown of the aliphatic part of the sulphoxides.

Sulphones ($\text{R-SO}_2\text{-CH}_3$) with m/z 236, m/z 250, m/z 264 and m/z 278 were detected as intermediates, resulting from the addition of an oxygen atom to the sulfur atom of intermediate with m/z 244, and subsequent attacks by HO^\bullet on aliphatic carbon chain, forming carboxylic acids and alcohols in the aliphatic part.

The attack of the HO^\bullet radical on the generated sulfone (intermediate with m/z 250) led to the formation of intermediates with the sulphonic acid group ($\text{R-S(=O)}_2\text{-OH}$). In this way, the inedited by-products, with mass peaks at m/z 238 and m/z 254, were proposed on basis of the formation of sulphonic acid group. The degradation by-product m/z 200 could come from the deethylation of ametryn molecule. Additionally, the by-product m/z 200 underwent further demethylation to produce the intermediate with m/z 186.

Insert Fig. 6

3.5.2. Evolution of by-products generated in ametryn degradation in the presence of scavengers

3.5.2.1. Effect of $O_2^{\bullet-}$ and e_{BC}^- scavengers

During photocatalytic degradation of ametryn in the presence of p -BQ, a total of fifteen intermediates were identified with m/z 144, m/z 158, m/z 164, m/z 182, m/z 186, m/z 198, m/z 200, m/z 214, m/z 240, m/z 242, m/z 243, m/z 244, m/z 250, m/z 264, and m/z 266, indicating that although inhibition of $O_2^{\bullet-}$ radicals generation occurs, there is a predominance of HO^{\bullet} radicals. Comparing the intermediates generated in this process with the experiment performed with the catalyst alone and/or several experiments with other active species, it appears that the intermediates with m/z 158, m/z 164, m/z 182, m/z 198, m/z 214, m/z 243 and m/z 266 were generated only in the presence of p -BQ (see Fig. 7). In this process the main paths involved in the generation of intermediaries can be summarized in the sequential attack of HO^{\bullet} radicals on the sulfur atom of the methylthio group in the ametryn molecule; by breakdown of the aliphatic part and by abstracting hydrogen from the aliphatic carbon chain, leading to the formation of double and triple bonds.

Intermediate identified with m/z 158 is a common by-product of ametryn degradation, as proposed by de Oliveira et al. [73], Chen et al. [78] and Liu et al. [82]. The intermediates with m/z 182, m/z 198 and m/z 266 were also identified in our previous study [73]. It is noteworthy that the intermediates with m/z 164, m/z 214 and m/z 243 were not found in the literature for other ametryn degradation studies.

3.5.2.2. Effect of HO• scavengers

As discussed above, the addition of *t*-BuOH dramatically reduces the degradation rate of the ametryn by conventional TiO₂ photocatalysis, indicating that HO• mediated oxidation processes are the predominant pathways leading to degradation under xenon lamp irradiation. Analysis by LC–MS-TOF allowed the identification of thirteen intermediates during ametryn photocatalytic degradation with the addition of the alcohol as shown in Table S1 in the Supplementary Material and Fig. 7. Specifically, in this case the generated by-products presented mass peaks at *m/z* 116, *m/z* 132, *m/z* 144, *m/z* 156, *m/z* 174, *m/z* 186, *m/z* 200, *m/z* 216, *m/z* 236, *m/z* 240, *m/z* 242, *m/z* 250 and *m/z* 262. The presence of these intermediates, generated with little or no participation of HO• radicals, also demonstrates that the degradation of ametryn is driven by the participation of other active species such as O₂^{•-} radicals and direct oxidation via holes.

The intermediates formed in this case are markedly different. Comparing with intermediates reported only in the presence of catalyst or with the addition of other sequestering agents, 6 specific different intermediates were identified in the presence of *t*-BuOH. These products exhibiting [M+H]⁺ ions at *m/z* 116, *m/z* 132, *m/z* 156, *m/z* 174, *m/z* 216 and *m/z* 262 and their proposed molecular structures are presented in Fig. 7. With the exception of the intermediate with *m/z* 216 that was identified in our previous study [73], these other intermediates have not been identified so far. This finding suggests that O₂^{•-} and holes are also involved in the degradation process, however their role is less important.

Ring opening might occur via subsequent addition of HO₂[•] radical/O₂^{•-} anion [44,83,84]. The identified by-products, with mass peaks at *m/z* 116 and *m/z* 132, are characterized by the opening *s*-triazine ring.

The attack of O_2^{\bullet} radicals on the sulfur atom of the methylthio group followed by the breakdown of C-N single bonds between the s-triazine ring and isopropyl groups of the ametryn molecule, generated the sulphoxides with m/z 174 and m/z 216. It was also verified the generation of a hydroxy sulphone with m/z 263, as the result of the O_2^{\bullet} radical attacks on the sulfur atom and via hydroxylation by O_2^{\bullet} in the ethylamine part. The abstraction of hydrogen corresponding to methylthio group by reactions involving O_2^{\bullet} radicals and/or holes formed the intermediate with m/z 156.

Insert Fig. 7

3.5.2.3. Effect of holes and HO^{\bullet} scavengers

When FA was added to the reaction system, only eight intermediates with m/z 127, m/z 186, m/z 240, m/z 242, m/z 244, m/z 246, m/z 250 and m/z 260 were identified by LC-TOF-MS analysis in positive mode (see Table S1). Since HO^{\bullet} radicals and h_{BV}^+ do not participate (or their participation is significantly decreased) in the degradation of ametryn (see section 3.3), only the reaction with O_2^{\bullet} radicals and 1O_2 is favored in this system.

The intermediates with m/z 240, m/z 242, m/z 244 and m/z 250 can be generated by the addition reaction of O_2^{\bullet} radicals on the sulfur atom and/or alkyl chain and by oxidation of alkyl chain. On the other hand, m/z 186 and 127 are formed via the oxidation of the alkyl substituent with the stepwise decomposition of methyl, ethyl and isopropyl groups. From these intermediates generated, the by-product with m/z 127, m/z 246 and m/z 260 were formed only in the presence of FA (see Fig. 7) and to the best of our knowledge was not found in the literature in studies on ametryn degradation.

Similarly, the intermediate with m/z 260 was also identified in our previous study [73]. However, we here propose a different structure for this intermediate, based on the formation from oxidation of ametryn by $^1\text{O}_2$, which could attack the electron-rich groups by electron transport in an ene reaction [85-87]. A mechanism has been proposed for the formation of intermediates with m/z 246 and m/z 260, based on an ene reaction with singlet oxygen via the electron richer Nisopropyl group (see Fig. 8) [87,88]. These results suggest that $^1\text{O}_2$ initially may have participated in the degradation process, although from the results shown in Table 1, no percentage contribution of ametryn degradation was attributed to $^1\text{O}_2$, because the predominance of HO^\bullet radicals can mask the process.

Insert Fig. 8

3.5.2.4. Effect of $^1\text{O}_2$ and HO^\bullet scavengers

A total of nine intermediates were detected for the degradation of ametryn in experiments performed with the addition of azide. Table S1 shows that, in the presence of azide, they appear intermediates generated in the presence of other active species (with m/z 250 and m/z 254), but new seven intermediates were also generated (with m/z 105, m/z 146, m/z 165, m/z 187, m/z 351, m/z 411 and m/z 433, Fig. 7) that were not detected in the other cases.

As azide scavenges both, HO^\bullet radicals and $^1\text{O}_2$, the intermediates generated may result from the attack of O_2^\bullet radicals and direct oxidation via holes. However, it has also to take into account the possible intermediates produced by activity of azidyl radical (N_3^\bullet), which are highly oxidative species [89], and/or by the extra amount of O_2^\bullet generated during the $^1\text{O}_2$ scavenging process (see table 1).

The intermediates with m/z 105, m/z 146 and m/z 165 are resulting from cleavage s-triazine ring, possibly via addition of O_2^{\bullet} radicals. The intermediate with $m/z = 105$ was also identified in our previous study [73], on the other hand, to the best of our knowledge, the intermediates with m/z 146, m/z 165, m/z 187, m/z 351, m/z 411 and m/z 433 were not found in the literature.

Products resulting from dimerization can be generated by condensation reactions. Three intermediates identified with m/z 351, m/z 411 and m/z 433 are dimeric species.

3.5.3. Comparison of the same by-products generated with and without addition of the different scavengers.

Fig. 7, besides showing the molecular structures of the intermediates generated in the presence of each scavengers, also shows a comparison of common by-products that were formed in more than one or several investigated processes.

The sulphone at m/z 250 was detected in all cases investigated (with different scavenger and non-scavenger systems). The intermediates with m/z 186, m/z 240 and m/z 242 were not only identified in the experiment performed with azide. These by-products are considered to be the main products of photocatalytic degradation of ametryn and can be generated by the attack of the different ROS.

Other typical by-products of ametryn degradation already identified by other researchers and also identified in this study (see Fig. 7) were the intermediates with m/z 200 and m/z 244.

The sulphones with m/z 236 and m/z 264 were both detected in the absence of scavengers, and in the presence of p -BQ and t -BuOH respectively. From these observations, it

can be assumed that the sulphone with m/z 236 was generated by $O_2^{\bullet-}$ radicals attack, in contrast to sulphone with m/z 264 which was generated via HO^{\bullet} radicals.

The intermediate at m/z 254 with the sulphonic acid group was generated in the experiment performed in absence of scavengers and in the experiment with azide. The sulphoxide of low molecular weight at m/z 144 was identified for the experiment performed in the presence of ρ -BQ and t -BuOH. Thus, the formation of these by-products may involve HO^{\bullet} or $O_2^{\bullet-}$ radicals.

Simulated solar radiation-induced TiO_2 photocatalysis involves the formation of different active species responsible for the formation of by-products resulting from degradation of ametryn. Therefore, the reaction pathway of the ametryn photocatalytic degradation catalyzed via commercial TiO_2 with main contributed ROS can be proposed in the scheme shown in Fig. 9.

Insert Fig. 9

4. Conclusion

The most remarkable conclusions drawn for the present study can be summarized as follows:

- The photocatalysis using TiO_2 P25 as catalyst is proved to be efficient technique for the degradation of ametryn herbicide in aqueous solutions under simulated solar radiation. Using 0.4 g L^{-1} of catalyst, a complete ametryn degradation was reached after 60 min of experiment.
- Photocatalytic oxidation of ametryn significantly increased the biodegradability by a factor of around 2.7, making the final solution biodegradable. The toxicity assessment with *Vibrio*

fischeri revealed that the degradation process has eliminated virtually all toxicity of the ametryn and no toxic intermediates were formed at the end of the treatment.

- Experimental evidence obtained with radicals and hole scavengers indicates that the HO• free radicals have a preponderant participation in the oxidation of ametryn with a high second order rate constant ($4.57 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$), followed by direct hole ametryn oxidation. Also, a slight contribution in the oxidation can be attributed to O₂^{•-} anions species.
- The assessment of the roles of active species in the generation of intermediates has been systematically studied. From the by-products formed, it can be observed that the HO• radicals primarily leads to the formation of sulphones, sulphoxides and sulphonic acid, produced by the sequential attack of HO• radicals on the sulfur atom on the methylthio group. Meanwhile, O₂^{•-} can attack ametryn to form the open-s-triazine ring products, besides forming sulphoxides and hydroxy sulphones resulting from the attack of O₂^{•-} radicals on the sulfur atom. The oxidation of ametryn by ¹O₂ leads to the formation of N-hydroperoxy specie and cyclohydroperoxy hemiaminal intermediate arising from the participation in an ene reaction with ¹O₂ via the electron richer Nisopropyl group. Finally, the direct attack by positive holes can lead to compounds resulting from dimerization products by condensation reactions. These results offered an insight into the degradation mechanism of ametryn involving several active species, which can serve as a way to block the formation of possible toxic intermediates through regulating the active species type during the ametryn degradation.

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Figure captions

Fig. 1. Scheme of the solar simulator and experimental device.

Fig. 2. Effect of the TiO₂ concentration on ametryn degradation and mineralization in solar simulator device. Initial ametryn concentration 10 mg L⁻¹, initial pH_{free} ≈ 5.7.

Fig. 3. (A) Oxidation (COD) and SUVA, (B) Biodegradability (BOD_{5,20}/COD) and Equitox for ametryn promoted by TiO₂ photocatalysis. [Ametryn]₀ = 10 mg L⁻¹, initial pH_{free} ≈ 5.7, [TiO₂] = 0.4 g L⁻¹.

Fig. 4. Effect of different scavengers on ametryn removal efficiency (A) and pseudo-first-order rate constants (B) using 0.4 g L⁻¹ of TiO₂ catalysts under Xenon lamp at pH_{free} ≈ 5.7. Ametryn]₀ = 10 mg L⁻¹; [p-BQ] = 0.001 g L⁻¹; [AF] = 0.82 mL L⁻¹; [NaN₃] = 0.77 mg L⁻¹; [t-BuOH] = 60 ml L⁻¹.

Fig. 5. (A) Simultaneous degradation of ametryn and 2,4-D by photocatalysis, both at 0.04 mmol L⁻¹, [TiO₂] = 0.4 g L⁻¹, 25 °C, pH = 4.4 ± 0.2. (B) Neperian logarithms of the normalized concentrations of 2,4-D and ametryn for determination of second-order rate constant for the reaction between ametryn and HO• radicals.

Fig. 6. Molecular structures of intermediates formed upon demethylation, deethylation and hydroxylation processes, proposed for the degradation of ametryn during photocatalytic treatment using TiO₂ P25 as catalyst.

Fig. 7. Scheme showing the possible ROS involved in the generation of by-products resulting from the photocatalytic degradation of ametryn observed by LC/MS using commercial TiO₂ in the presence of specific scavengers.

Fig. 8. Proposed mechanisms for the formation of by-products at m/z 246 and m/z 260 resulting from photodegradation of ametryn by commercial TiO₂ catalyst in aqueous solution with addition of FA.

Fig. 9. Mechanisms postulated showing the proposed pathways for the photocatalytic degradation of ametryn by commercial TiO₂ catalyst via the dominate ROS involved in the process.

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