Photodegradation of the herbicide azimsulfuron using nanocrystalline titania films as photocatalyst and low intensity Black Light radiation or simulated solar radiation as excitation source

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ABSTRACT

Aqueous solutions of the herbicide azimsulfuron have been treated by a photocatalytic process employing titania nanocrystalline films as photocatalyst. Results showed that solutions of this herbicide at maximum possible concentration can be photodegraded in a time of a few hours by using low intensity UVA radiation comparable with that of the UVA of solar noon. Similar results have also been obtained with simulated solar radiation. Thus heterogeneous photocatalysis can be employed for the treatment of waters polluted by this herbicide.

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1. Introduction

Herbicides constitute a major pollution source for both underground and surface waters. The population increase and the increase of demand for agricultural products, not only for food but also for other uses, like the recently rapidly developing energy applications, is expected to make herbicide pollution increase in the near and far future. The awareness on the related environmental issues has attracted large attention in the Scientific World and has induced large-scale scientific research efforts. Among the various methods developed for the treatment of herbicide (and pesticide) polluted water, advanced oxidation processes (AOPs) are recognized as the most viable approach for the degradation of such persistent hazardous substances [1–3]. AOPs include several different processes. All are characterized by a common feature, that is, they all aim at the production of the highly reactive OH• radicals. The oxidative potential of OH• is 2.8 eV [1] and can non-selectively attack any organic substance. Among the various AOPs, heterogeneous photocatalysis using TiO_2 photocatalyst is the most popular and the most extensively studied process. Heterogeneous

photocatalysis is associated with the possibility of employing solar radiation to carry out the process. However, TiO_2 does not absorb Visible light while only a small portion of solar radiation on the surface of the Earth belongs to the UVA part of spectrum (320–400 nm), where TiO_2 absorbs. The popularity of TiO_2 aroused from the following simple facts. TiO_2 is a stable and non-toxic material, at least, no toxic effects have been so far detected. It is easy to produce in nanocrystalline form, i.e. with large active surface area, both on an industrial or a laboratory scale. It is well known and used for a long time, since it is a whitening additive for paints. It is among the most abundant materials in the Earth's crust. Titanium itself is among the ten most abundant elements, it is strong, light and corrosion resistant and imparts its properties to its compounds. Finally, TiO_2 is a very efficient photocatalyst and for this reason, even by only absorbing in the UVA part of the solar spectrum it is still very interesting for cost-effective photocatalytic applications.

Heterogeneous photocatalysis using a light-absorbing semiconductor photocatalyst is an AOP in the sense that OH• radicals are also in this case the main pollutant-degrading chemical species. Indeed, when a semiconductor is excited, an electron–hole pair is created. Positive holes interact with OH^- groups attracted on the photocatalyst surface producing OH• radicals. In addition, electrons are scavenged by O_2, when present, and produce superoxide O_2• and hydroperoxide HO_2• radicals, which are also very reactive chemical species [4]. In the case of nanocrystalline TiO_2 semiconductor, which has a very large absorption cross-section in the UVA, if it is

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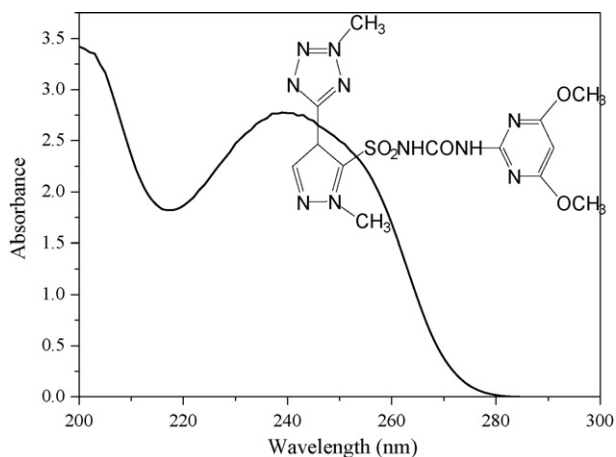
Fig. 1. Absorption spectrum of AZS (concentration 60 mg l⁻¹). The chemical structure of AZS is given in the insert.

Fig. 2. Schematic representation of the reactor used in this work.

properly dispersed it can be very efficient for pollutant photodegradation, even by exploiting only the UV part of the solar radiation. The UVA intensity of the solar radiation varies in a range of a few mW/cm² [5,6]. This radiation flow can be easily obtained with commercial low-cost Black Light tubes. In addition then to solar light, low-cost installations may be used for artificial UVA radiation to carry out photodegradation. Indeed, in the present work we present such a low-cost home-made reactor employing low intensity Black Light tubes to carry out photodegradation of a herbicide, namely, azimsulfuron (AZS). The chemical structure of AZS is shown in Fig. 1.

AZS belongs to the class of sulfonylurea herbicides, which have a broad spectrum of weed control, have low application rate and low animal toxicity [7,8]. Some of this class of herbicides have been previously studied by photocatalysis [5]. Very few reports have been published on AZS itself [8]. Thus in this work, AZS photodegradation is studied by TiO₂ heterogeneous photocatalysis. Many of these herbicides are directly photodegradable (photolyzed), however, the ensuing products are of unknown toxicity and may be even more toxic than the original substance itself [8]. TiO₂ photocatalysis leads to complete mineralization. For this reason, studies of the efficiency of these processes are helpful to structure a protocol for the control and the management of these environmentally hazardous materials.

2. Experimental

2.1. Materials

Azimsulfuron (99.3% purity) was donated by DuPont de Nemours, France. All the rest of reagents were obtained from Aldrich. Millipore water was used in all experiments.

2.2. Description of the reactor

The cylindrical reactor schematically shown in Fig. 2 was used in all experiments. Air was pumped through the gas inlet using a small pump to ensure continuous oxygen supply to the reaction solution while simultaneously agitating it. In some cases, experiments were carried out by relying on the oxygen dissolved in the reaction solution after saturating it with air. In cases where experiments were carried out in the absence of oxygen, the solution was deoxygenated by nitrogen flow. In these last two particular cases the gas inlet and outlet did not communicate with the environment. Four Black Light fluorescent tubes, each of 4 W nominal power, were placed around the reactor. The whole construction was covered with a cylindri-
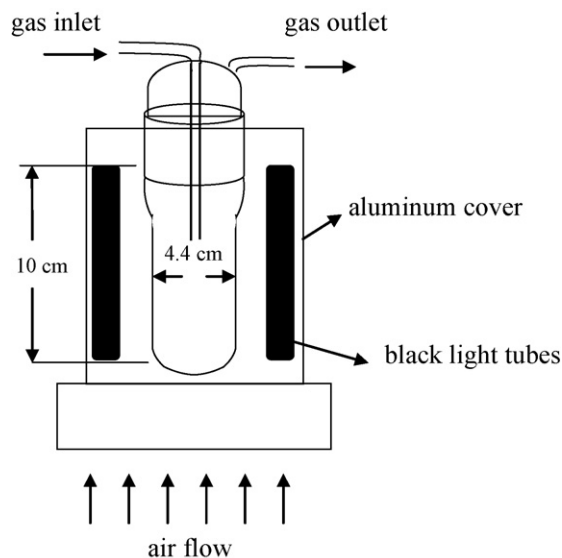
cal aluminum reflector. Air flown from below using a ventilator assured cooling of the reactor. The catalyst was in the form of four glass rings, covered on both sides with nanocrystalline TiO₂ film. Film deposition is described below. The glass rings were of 38 mm of diameter and 15 mm height, stacked and coaxially placed inside the reactor. Thus the total geometrical surface of the photocatalyst film was approximately $2 \times 71.6 = 143$ cm². The intensity of radiation reaching the surface of the film on the side facing lamps was measured with an Oriel Radiant Power Meter and found equal to 0.79 mW/cm². This value is comparable with the above-mentioned solar UVA intensity.

2.3. Deposition of nanocrystalline titania films

Titania films were deposited by following the previously reported procedure [9–11]. Briefly, for a 25-ml sol, 3.6 g of the non-ionic surfactant Triton X-100 [polyoxyethylene-10-isooctylphenyl ether] was mixed with 20 ml of ethanol, followed by addition of 1.6 ml of glacial acetic acid and 1.8 ml of titanium isopropoxide under vigorous stirring. Self-organization of the surfactant in this original sol creates organized assemblies that act as templates defining nanoparticle size. The surfactant is burned out during calcination. After a few minutes stirring, the glass rings described above, which were previously thoroughly washed, sonicated in ethanol and dried in a N₂ stream, were dipped in the above sol and withdrawn slowly by hand. After leaving the film to dry in air for a few minutes, it was calcined in an oven. The temperature was raised at a heating rate of 20 °C/min to 550 °C and left at that temperature for about 10 min. When the titania-covered rings were taken out of the oven, they were transparent and optically uniform. The above procedure was repeated several times in order to reach the quantity of catalyst necessary for the purposes of the present work. The final mass of titania on the four glass rings was 80 mg (20 mg on each glass ring).

2.4. Photodegradation procedure

The reactor was filled with 100 ml water in which 6 mg AZS were dissolved. Standard solutions were employed in all experiments. AZS is not adsorbed on titania films, however, about an hour of equilibrium was allowed before illumination. The concentration

of AZS in solution was monitored by absorption spectrophotometry at 240 nm using quartz cuvettes (an absorption spectrum of AZS is shown in Fig. 1). In order to assure linear relationship between absorbance and concentration, preliminary measurements have been made. The linear relationship was established in the range 0–60 mg l^{-1}. Thus the presently chosen concentration, i.e. 60 mg l^{-1}, was the maximum concentration of the established linear concentration vs. absorbance range. It was found that this concentration is also close to the solubility limit of AZS in water. A 3-ml aliquot was collected for performing absorption spectrophotometry and it was poured back into the reactor after measurement. The first concentration measurement was done in the dark. It was then verified that the herbicide was not adsorbed on the titania film. Finally, the products of photodegradation have been monitored by LC–MS-MS analysis (see below) while the evolution of CO_2 was monitored by using an apparatus working in a closed air circuit and based on an IR detector.

2.5. Apparatus and methods

Absorption measurements were made with a Cary 1E spectrophotometer and CO_2 evolution was monitored using an Anagas CD95 instrument based on an IR detector. LC–MS-MS analysis was carried out on a Varian 1200L mass spectrometer equipped with electrospray ionization interface (ESI). The ion trap was connected to a Varian 1200 LC system consisting of two individual pumps, a membrane degasser, an autosampler with temperature control and a thermostatic column control. The chromatographic separation was performed on a reversed phase Varian Polaris C-18 column (150 mm × 2.1 mm, 5 μm particle size) at 30 °C. The concentration of AZS at each degradation stage was calculated by using an external calibration curve from LC–MS-MS measurements of AZS at five different concentrations. Stock solution was prepared by diluting the appropriate amount of the analytical standard with water/methanol (70/30) at concentration 60 ppm. In order to determine the degradation products formed during AZS photocatalysis, ESI ionization in both negative- and positive- ion modes were investigated. The results indicated that the ESI source at positive-ion mode with collision energy at 30 V was most appropriate for the analysis of the degradation products.

3. Results and discussion

3.1. Characteristics of the photocatalyst

The films made by the sol–gel procedure described in the Experimental section were similar to those reported in previ-
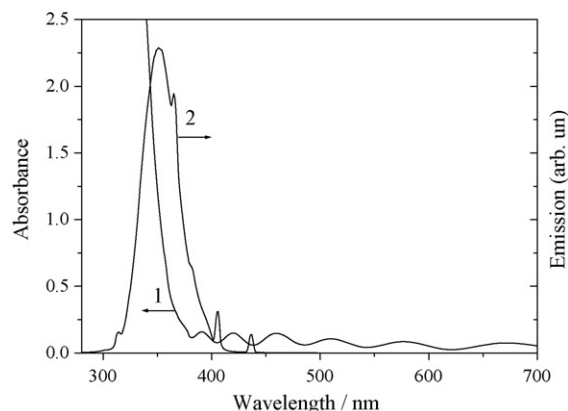

Fig. 3. Absorption spectrum of a typical nanocrystalline titania film (1) and emission profile of a Black Light tube (2). The periodic ripples in the absorption of Titania at >375 nm are due to interference fringes.

ous publications [9–11]. They consist of anatase nanocrystals of about 15 nm average size. Size polydispersity is limited and the active surface area is around 110 m^2/g, as measured by nitrogen adsorption–desorption using the BET model. These films have been proven to be very efficient in photodegradation experiments [9,10], dye-sensitized solar cells [10] and photocatalytic H_2 production [11]. The absorption spectrum of a similar film deposited on a glass slide is shown in Fig. 3. Fig. 3 also shows the emission profile of the Black Light tube employed in the present work as excitation source. It is obvious that the proposed combination provides band-gap excitation of titania and thus secures optimized excitation conditions without internal energy losses.

3.2. Photodegradation studies of AZS

Fig. 4A presents photodegradation data of AZS under the conditions described in Section 2. In the absence of catalyst, the rest of the conditions kept the same, no photolysis of the herbicide was detected. Even though, it is known that this type of herbicides are vulnerable to photolysis [8], apparently, the mismatch of the spectral distribution of the excitation source with the absorption spectrum of AZS plus the low intensity of incident radiation did not produce any detectable photolysis. In the presence of titania, all herbicide was photodegraded in a time of several hours. Since the intensity of UVA presently employed is comparable or lower than the solar UVA, as explained above, it is obviously viable to employ solar radiation for photodegrading AZS through titania heterogeneous photocatalysis. Indeed, photodegradation was also
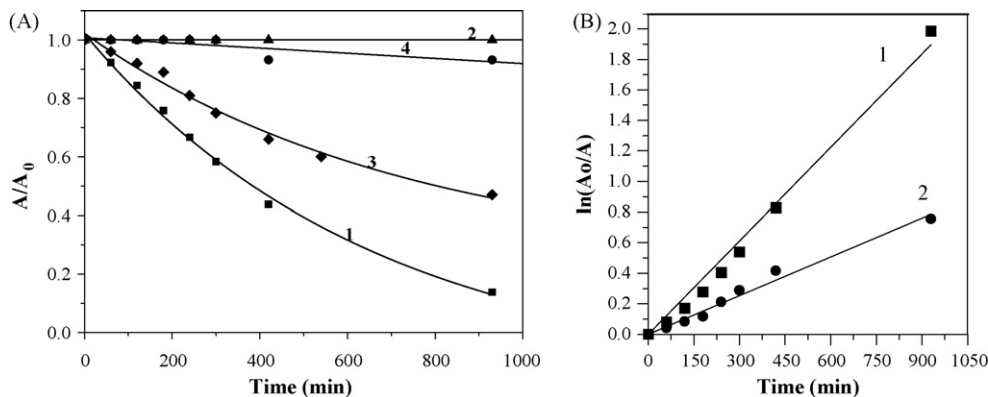

Fig. 4. Photodegradation curves (A) and analysis by Eq. (1) (B): Phodegradation by using Black Light radiation (A1); Black Light illumination in the absence of photocatalyst (A2); photodegradation by using simulated solar light (A3); photodegradation in the absence of oxygen (A4); analysis of curve A2 (B1); analysis of curve A3 (B2).

carried out by using radiation from a Xenon lamp. The radiation entered into a metallic cavity where the intensity was controlled to be approximately 1 sun (100 mW cm^{-2}). The same as above reactor was introduced into the cavity. The photodegradation curve obtained in that case is given by curve #3 of Fig. 4A. Photodegradation in both cases followed pseudo-first-order kinetics [12,13] as seen by the straight line plots of Fig. 4B, which obey the following equation:

$$\ln\left(\frac{A_0}{A}\right) = K_{app}t \tag{1}$$

The corresponding pseudo-first-order rate constant was 0.0021 min^{-1} in the case of Black Light excitation (line #1 of Fig. 4B) and 0.0008 min^{-1} in the case of simulated solar excitation (line #2 of Fig. 4B). Photodegradation was practically impossible in the absence of oxygen, as can be seen by the data of curve #4 of Fig. 4A. By taking into account the fact mentioned above that no AZS was detectably adsorbed on the titania films, it is possible that photodegradation is carried out in the liquid phase and it is also possible that superoxide O$_2^\bullet$ and hydroperoxide HO$_2^\bullet$ species, which are only formed in the presence of oxygen, play a major role. The possibility that photodegradation may be carried out in the liquid phase may explain why it is relatively slow. Indeed, organic substances, which are strongly adsorbed on titania are more rapidly photodegraded (cf. Refs. [9,10]) and this is true for photodegradation being carried out both in air and in solution. As a matter of fact, positively charged dyes, which are strongly adsorbed on titania at neutral or basic pH, are much more rapidly photodegraded by using the same reactor and catalyst configuration as in the present case [14]. During photodegradation, the produced CO$_2$ continuously increased reaching a plateau after several hours, as can be seen in Fig. 5. Increasing of CO$_2$ is expected since it was continuously and additively measured in a closed air circuit connecting gas inlet and outlet of the reactor with the monitoring device. Before making this connection, the reaction solution was saturated with oxygen by blowing air. The plateau was reached at about the same time when photodegradation was completed, as seen by curve #2 of Fig. 4A. These results indicate that photodegradation of AZS was accompanied by continuous production of CO$_2$.
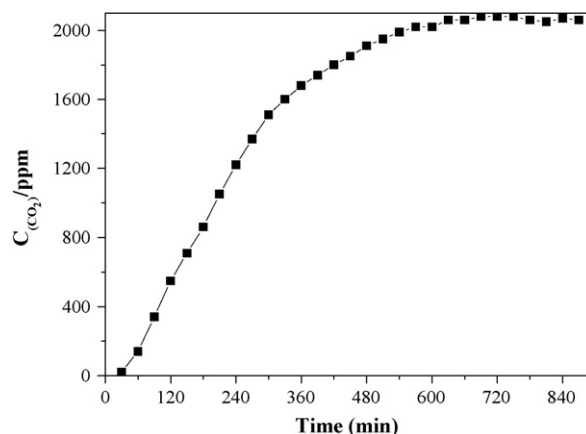

Fig. 5. CO$_2$ evolution during photodegradation of AZS by Black-Light irradiation.

Finally, it must be underlined that the above photocatalyst can be easily recuperated, since it is deposited on the above glass rings and be employed in several experiments with small loss of efficiency. Indeed, we have used the same photocatalyst for three subsequent photodegradation procedures with identical fresh AZS solutions and we got only small variation of the photodegradation rate constants, i.e. K_{app} = 0.0021 min^{-1} (first time); 0.0019 min^{-1} (second time); 0.0018 min^{-1} (third time).

3.3. Photodegradation byproducts

Byproducts of photodegradation were studied by LC–MS-MS. Two major ions were detected in all photodegradation stages one with *m/z*: 199 and the other with *m/z*: 244. These two fragments exactly correspond to the amino-dimethoxypyrimidine moiety (right-side fragment in Fig. 6) and 1-methyl-4-(2-methyl-2*H*-tetrazole-5-yl)-1*H*-pyrazole-5-sulfonamide moiety (left-side fragment in Fig. 6), respectively, which AZS consists of. The amino-dimethoxypyrimidine-containing ion yielded a major fragment ion at *m/z*: 74.5, which could correspond to the break down of the carbon link between the two nitrogen atoms leading to the forma-
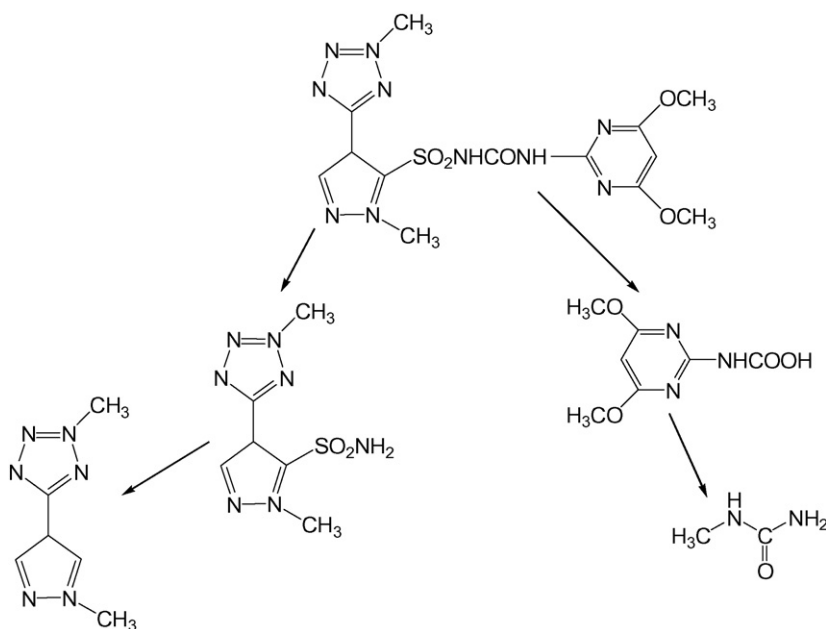

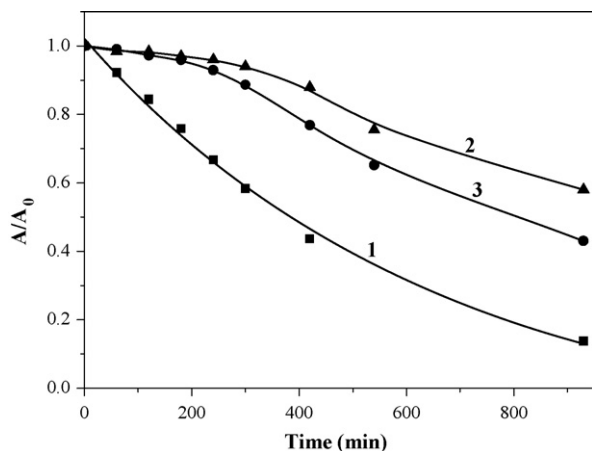**Fig. 6.** Photodegradation pathways for AZS.

Fig. 7. Photodegradation of AZS at various pH values: 4.7 (natural pH) (1); 2.8 (2); 9.9 (3).

tion of methylaminocarboxylic acid $CH_3NHCOOH$. Ion 244 yielded a major further fragment ion at m/z: 83.3, which could correspond to the sulfonamide SO_2NH_2-group. We thus believe that the above results define the first steps of the first steps of the photodegradation route presented in Fig. 6. Such a scheme is in accordance with the results of Ref. [8].

3.4. Effect of pH

Finally, photodegradation of AZS was studied by black-light irradiation at various pH values. The results are presented in Fig. 7. pH values were modified by adding either H_2SO_4 or NaOH, both at a concentration of 0.1 mol l^{-1}. The fastest photodegradation was obtained at natural pH (4.7), while photodegradation was much slower at basic pH and even slower at acidic pH. This behavior was similar to that of the photodegradation of another herbicide, Imazapyr, reported in Ref. [4], which also possesses chargeable chemical groups like AZS. In analogy then to Imazapyr [4], it is highly probable that at low pH, AZS is positively charged, and at high pH, it is negatively charged. However, as it is well known, the surface of titania is also charged with the same charge at the same pH [4]. Therefore, at low or high pH, there is a repulsion that separates the catalyst surface from the target molecule and makes it more difficult for the reactive radical species, which are generated on the surface of the catalyst, to reach the target. Hence the lower photodegradation rates in those cases.

4. Conclusions

The herbicide AZS can be effectively photodegraded by employing titania nanocrystalline films as photocatalyst and low intensity

Black Light tubes as illumination source or (simulated) solar radiation. The installation was very simple. The catalyst was deposited by the sol–gel method on glass rings. It could be thus easily recuperated and repeatedly used in subsequent photodegradation procedures. The pH of the aqueous solution of AZS affected photodegradation rate. The fastest rate was obtained in the case of natural pH of the solution.

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