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Factors influencing the photocatalytic degradation of sulfonylurea herbicides by TiO_2 aqueous suspension

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Abstract

The photocatalytic degradations of six sulfonylurea herbicides have been investigated in aqueous solutions containing TiO_2 suspensions as photocatalyst, in order to assess influence of various parameters, such as adsorption, initial concentration and photon flux on the photocatalytic process. Results show that adsorption is an important parameter controlling the apparent kinetic order of the degradation (either one in the case of associative adsorption or a half in the case of dissociative adsorption). In respect to the Langmuir–Hinshelwood model, the photocatalytic reaction is favoured by a high concentration. A higher efficiency is observed under the lower photon fluxes, the limiting factor being the electron–hole pair recombinations.

Keywords: Sulfonylurea degradation; Herbicides; Photocatalytic degradation; TiO_2; Quantum efficiency

1. Introduction

Heterogeneous photocatalysis is an efficient technique to destroy organic pollutants in water [1–7]. This technique is based upon the use of UV-irradiated semiconductors (generally titania under the form of anatase). When TiO_2 is irradiated with photons whose energy is equal to or greater than its band gap energy ($E_G = 3.2\,eV$) i.e. with $\lambda < 390\,nm$, electron–hole pairs are created. In aqueous system, holes react with H_2O or OH^- adsorbed at the surface of the semiconductor to produce $OH^\bullet$ radicals which are the most oxidising species in this process. On the other hand, electrons are trapped at surface sites and removed by reactions with adsorbed molecular O_2 to form superoxide anion radical $O_2^{\bullet -}$ (or $HO_2^\bullet$ at lower pH).

Sulfonylureas (*Sus*) belong to a relatively new class of herbicides structure which is characterised by three moieties (see Fig. 1): an aryl group, a sulfonylurea bridge and a s-triazine group.

Recent articles [8,9] have shown that *Sus* are easily destroyed using TiO_2 as photocatalyst in aqueous suspension. The degradation pathway involves several steps: hydroxylations, aromatic ring opening, mineralisation and cleavage of the sulfonylurea bridge to form cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine) as the only organic final product, refractory to photocatalytic degradation.

The objective of this work was to study the influence, on the photocatalytic degradation of *Sus* herbicides, of various parameters such as the initial concentration, the previous adsorption in the dark, the light flux and the molecular structure. For this purpose, six different *Sus* has selected.

2. Material and methods

2.1. Materials and reagents

Cinosulfuron (CiS) [1-(4,6-dimethoxy-1,3,5-triazin-2-yl)-3-[(2-methoxyethoxy)-phenyl]urea] (98% purity), triasulfuron (TrS) [2-(6-methoxy-4-methyl-1,3,5-triazin-2-yl)-1-[2-(2-chloroethoxy)phenylsulfonyl]urea] (99% purity), prosulfuron (PrS) [1-(4-methoxy-6-methyl-1,3,5-triazine)-3-[2-(3,3,3-trifluoropropyl)-phenylsulfonyl]urea] (98.1% purity) and metsulfuron-methyl (MeS) 2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)benzoic acid (99.4% purity) were purchased from Riedel-de Haën. Chlorimuron-ethyl (Chi) 2-(4-chloro-6-methoxypyrimidin-2-ylcarbamoylsulfamoyl) benzoic acid (98% purity) and chlorsulfuron (ChS) 1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (99% purity) were purchased from Chem Service.

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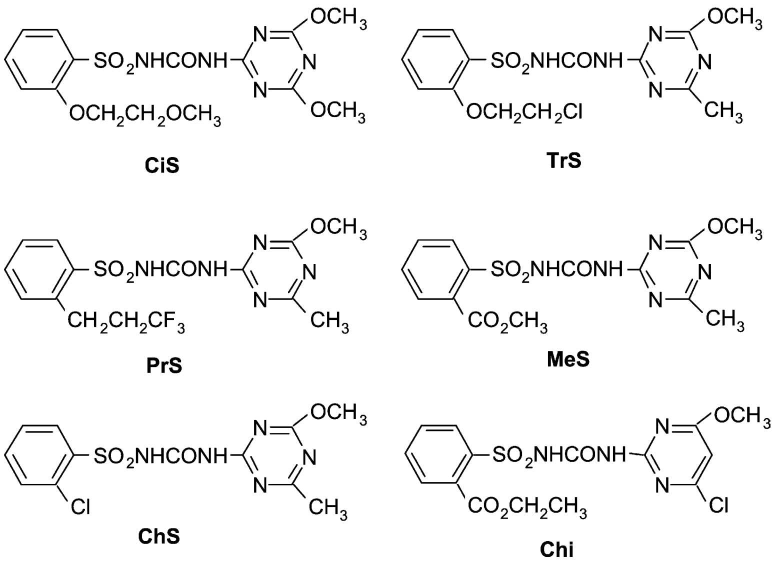

Fig. 1. Molecular structures of the six sulfonylureas studied.

Other reagents were at least of analytical grade. Herbicide solutions were prepared with water from a Millipore Waters Milli-Q water purification system. The photocatalyst was TiO_2 Degussa P-25, mainly anatase, with a specific area of 50 $m^2\,g^{-1}$ corresponding to a particle size of ca. 30 nm.

2.2. *Irradiation experiments*

The irradiation experiments were carried out with a HPK 125 W Philips mercury medium pressure UV lamp, in a Pyrex cylindrical flask opened to air with an optical window of 11 cm^2 area. The initial solution volume was 20 ml. The irradiation light spectrum was cut-off below 340 nm using a Corning 0–52 filter in order to work in a pure photocatalytic regime with the elimination of short wavelengths able to induce side photochemical reactions. In these conditions, the lamp spectrum had a maximum emission at 365 nm. The light intensity could be reduced by including metallic calibrated grids between the lamp and the reactor. This corresponds to a non-wavelength-dependent beam attenuator. The radiant flux was measured using a radiometer United Detector Technology Inc., Model 21A power meter. It has been found that the number of photons potentially absorbable by TiO_2 in the irradiation cell could vary from 0.4×10^{16} to 1.26×10^{17} photons s^{-1}. For all experiences, the suspensions were magnetically stirred. The concentration of TiO_2 was set at 2.5 $g\,l^{-1}$. This concentration corresponds to the maximum amount of TiO_2 in which all the particles are totally illuminated [6].

2.3. *Samples preparation*

During the irradiation, aqueous suspensions were collected (250 μl) and filtered, at regular intervals, through a 0.45 nylon filter (Millipore) to remove TiO_2 particles.

Table 1
Isocratic elution conditions for the six sulfonylureas

Sulfonylurea	Mobile phase (v/v)	λ-detection (nm)	Retention time (min)
CiS	40% (A) + 60% (B)	220	6.8
TrS	45% (A) + 55% (B)	220	5.6
PrS	60% (A) + 40% (B)	220	1.9
MeS	50% (A) + 50% (B)	225	4.4
ChS	50% (A) + 50% (B)	225	5.6
Chi	65% (A) + 35% (B)	235	4.4

For HPLC diode array detector (DAD) analyses, samples were injected directly.

2.4. *Analytical determinations*

The HPLC DAD analyses were performed with a Shimadzu VP series HPLC. The column was a Hypersil BDS C_{18}, 5 μm, 125 mm × 4 mm; the flow rate was 1 ml min^{-1}; the injection volume was 20 μl, the mobile phase was methanol (A) and water (B) the pH of which was set up at 2.80 using H_3PO_4. Isocratic elution conditions are collected in Table 1.

3. Results and discussion

3.1. *Preliminary adsorption in the dark*

A series of experiments were carried out in the dark to study the isotherm adsorption of the various *Sus* on TiO_2 surface. The pesticide solutions were magnetically stirred in the dark for 90 min with samples collected regularly. For each *Sus*, the adsorption equilibrium was rapidly attained (in 15 min). Fig. 2 shows that the quantity adsorbed (Q_{ads})

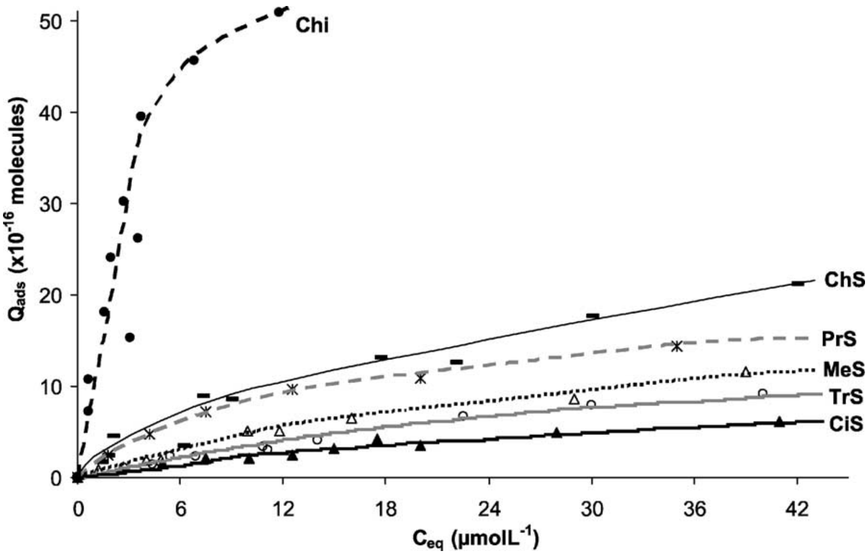

Fig. 2. Langmuir adsorption isotherms of CiS, TrS, PrS, MeS, ChS and Chi on TiO_2: quantities adsorbed as a function of equilibrium concentrations.

increases with concentration at the adsorption equilibrium (C_{eq}). This behaviour looks like the classical Langmuir adsorption model, followed by numerous compounds in aqueous suspension according to:

$$\theta = \frac{Q_{ads}}{Q_{max}} = \frac{K_{ads}C_{eq}}{1 + K_{ads}C_{eq}} \quad (1)$$

where θ is the TiO_2 surface coverage, Q_{ads} the adsorbed quantity, Q_{max} the maximal adsorbable quantity, C_{eq} the concentration of the compound at the adsorption equilibrium and K_{ads} the Langmuir adsorption constant (specific of the pair compound/catalyst).

The linear transformation of (1) can be expressed by the function $1/Q_{ads} = f(1/C_{eq})$

$$\frac{1}{Q_{ads}} = \frac{1}{Q_{max}} + \frac{1}{Q_{max}K_{ads}C_{eq}} \quad (2)$$

The six linear transforms are given in Fig. 3. The ordinate at the origin is equal to the reciprocal of Q_{max}, whereas K_{ads} can be calculated from the slope α ($=1/Q_{max}K_{ads}$).

In Table 2, adsorption parameters (K_{ads} and Q_{max}) for the six herbicides are reported, as well as the maximal coverage of TiO_2 determined by taking into account the maximum number of adsorption sites estimated to be equal to 5 nm^{-2} [10,11]. It appears that the adsorption coverages are small for the six *Sus* and substantially vary from a herbicide to another. In particular, Chi exhibits the higher adsorption constant and adsorbed quantity.

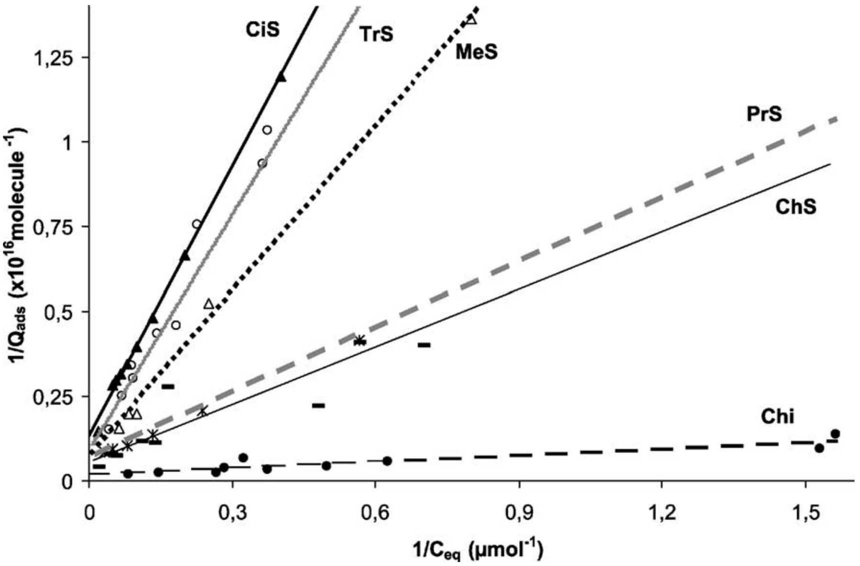

Fig. 3. Transformation of Langmuir isotherm: reciprocal of the quantity adsorbed as a function of the reciprocal of equilibrium concentration.

Table 2
Adsorption characteristics of the six sulfonylureas: linear regression coefficient (r^2) of Langmuir linear expression, Langmuir constant (K_{ads}), maximal adsorbable quantity (Q_{max}) and maximal coverage of TiO_2 adsorption sites (θ_{max})

	r^2	K_{ads} ($l\,mol^{-1}$)	Q_{max} (μmol)	Q_{max} (molecules nm^{-2})	θ_{max} (%)
CiS	0.974	4.93×10^4	6.3	0.03	0.61
TrS	0.969	7.49×10^4	8.0	0.04	0.77
PrS	0.932	8.96×10^4	14.6	0.07	1.41
MeS	0.963	2.89×10^4	11.4	0.06	1.10
ChS	0.849	5.81×10^4	21.9	0.1	2.11
Chi	0.922	1.81×10^5	68.5	0.33	6.6

3.2. Photocatalytic degradation of Sus

For the subsequent experiments, the herbicide solutions were magnetically stirred in the dark during 30 min before irradiating the reactor to make sure that adsorption equilibrium was reached. In the absence of TiO_2, no herbicide conversions were obtained, indicating that the system was working in a pure photocatalytic regime. During photocatalytic degradation, intermediates are formed and may interfere in the determination of kinetics because of competitive adsorption and degradation. Therefore, calculations were done for conversions smaller than 15%. During this interval time, intermediates effects could be considered as negligible.

3.2.1. Degradation kinetic order

Even if some authors consider that the Langmuir–Hinshelwood model is not sufficient to describe and explain the whole photocatalytic process, this model is widely used because it enables one to correlate the degradation rate to the instantaneous concentration according to the expression:

$$r = k_{LH}\theta = k_{LH}\frac{(K_{LH}C_0)^{\alpha}}{1+(K_{LH}C_0)^{\alpha}} \qquad (3)$$

where r is the initial rate of photocatalytic degradation, k_{LH} the true rate constant, C_0 the initial concentration (after adsorption step), K_{LH} the Langmuir–Hinshelwood adsorption constant and α the kinetic order with respect to herbicide.

At low concentrations, $(K_{LH}C_0)^{\alpha}$ can be neglected with respect to 1 and one gets the simplified expression:

$$r = k_{LH}\theta = k_{LH}(K_{LH}C_0)^{\alpha}$$

Generally, photocatalytic degradation of organic compounds follows a first-order kinetic law. In our case, we observed that the first-order rate constant did not remain constant when varying the initial sulfonylurea concentration, even if the linear form of kinetics was good. In order to determinate the kinetic order of the photocatalytic reaction, a series of kinetic experiments have been made under a constant photonic flux (2.35×10^{16} photons s^{-1}) but with different initial concentrations of each herbicides. The photocatalytic degradation rate r of the herbicide can be expressed as a function of the concentration at the adsorption equilibrium according to:

$$r = \frac{-dC}{dt} = k_{ap}C_{eq}^{\alpha} \qquad (4)$$

with k_{ap} as the apparent rate constant.

The log–log plot of $r = f(C_{eq})$ gives a straight line ($\log r = \log k_{ap} + \alpha \log C_{eq}$) of which slope is equals to the kinetic order. Fig. 4 shows the log–log diagrams obtained with two different behaviours:

- For CiS, the slope is equal to unity ($\alpha = 1$). The reaction followed an apparent first-order kinetic law, according to the equation: $-dC/dt = k_{ap}C_{eq}$.

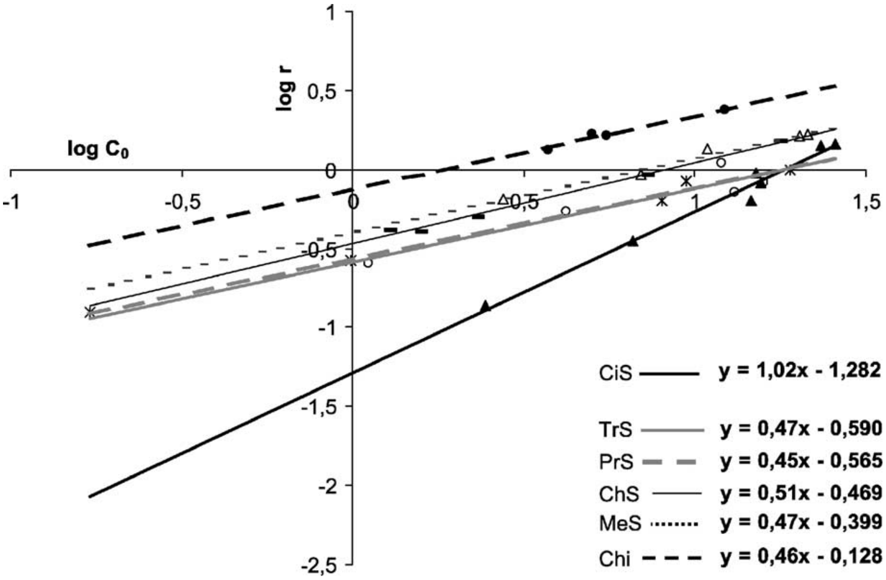

Fig. 4. log–log of the initial rate of photocatalytic degradation of *Sus* as a function of the initial concentration.

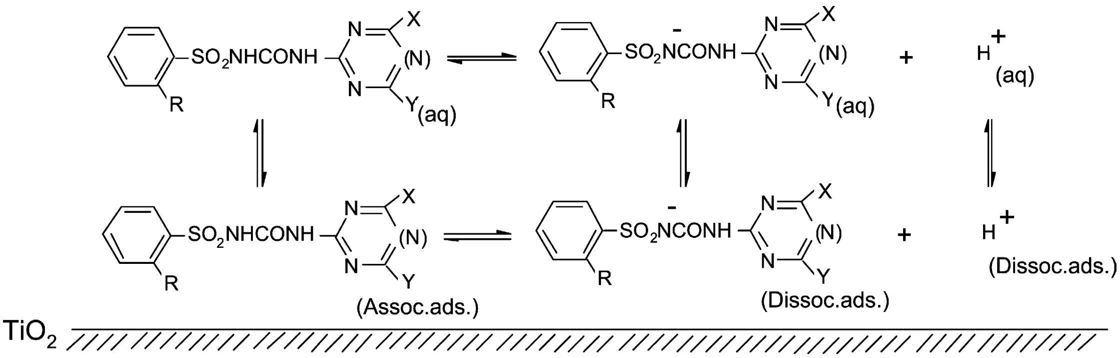

Fig. 5. Associative or dissociative adsorption of sulfonylurea molecules on TiO_2.

- For other herbicides, the slopes $\alpha = 1/2$. The reactions followed a half-order kinetics, according to the equation: $-\mathrm{d}C/\mathrm{d}t = k_{\mathrm{ap}}\sqrt{C_{\mathrm{eq}}}$.

An apparent first-order kinetics suggests a catalytic reaction with an associative adsorption of the reactant, whereas half-order kinetics suggests a dissociative adsorption [12–14]. Sulfonylureas are weak acids whose pH are comprised between 3.3 and 3.7 [15]. As the pH of the irradiated solutions is 4.2 ± 0.1, the protonated and deprotonated forms are present in solution. Therefore, sulfonylurea adsorption could involve two adsorption sites as represented by Fig. 5.

The two adsorption types (associative and dissociative) can coexist on TiO_2 surface. In the dark, adsorption is mainly associative. The half-order kinetics found for five over six sulfonylureas indicates that these molecules preferentially react under illuminated titania in the dissociated state.

CiS does not follow a half-order kinetic law, suggesting that the molecule is adsorbed in the neutral form. Initially, we have thought that this behaviour was linked to the pK_a values. But for example the pK_a of CiS and TrS are nearly the same (4.72 and 4.64, respectively) so the pK_a could not be the single parameter to explain the difference between CiS and other herbicides. On the other hand, the negative charge is differently delocalised across the sulfonylurea molecules. For CiS the delocalisation is extended on the benzenic and s-triazinic rings, the sulfonylurea bridge, the two s-triazinic methoxy subsitutents and the oxygen from $O–CH_2CH_2OCH_3$. In other molecules, negative charge delocalisation is less expanded. So the highly delocalised charge in the CiS molecule could be less disposable to establish a dissociative adsorption. Consequently CiS is adsorbed under an associative form and is degraded with a first-order kinetic law.

3.2.2. Langmuir–Hinshelwood constants

The linear form of Eq. (3) becomes:

$$\frac{1}{r} = \frac{1}{k_{\mathrm{LH}}} + \frac{1}{k_{\mathrm{LH}} K_{\mathrm{LH}} C_{\mathrm{eq}}} \quad \text{for CiS} \tag{5}$$

$$\frac{1}{r} = \frac{1}{k_{\mathrm{LH}}} + \frac{1}{k_{\mathrm{LH}} (K_{\mathrm{LH}} C_{\mathrm{eq}})^{1/2}} \quad \text{for the five others} \tag{6}$$

In Fig. 6, we have presented the linear forms of Langmuir–Hinshelwood model for the six herbicides. The linear plots confirm the Langmuir–Hinshelwood relationship and indicate that adsorption represents the initial step in the photocatalytic process. The slope gives K_{LH} values which are presented in Table 3.

In the preceding section (see Table 2), we have found adsorption constants very different from K_{LH} values. These differences can seem surprising for a Langmuir–Hinshelwood model because if K_{LH} truly reflected the adsorption affinity of herbicides for TiO_2 surface, K_{ads} and K_{LH} should be identical. There have been several studies reporting that K_{LH} could be substantially larger than K_{ads}: 280 times for metobromuron [16], 13 times for benzylic alcohol [17], 220 times for 4-chlorophenol [18]. Various suggestions have been formulated: (i) a photoadsorption would happen [19]; (ii) the reaction would take place not only at the surface but also in the bulk solution [20,21]; (iii) the number of adsorption sites would not be enough numerous to initiate the reaction [22]; or (iv) UV-illuminations would change electronic properties of the TiO_2 surface [23]. A recent study [17] has put in evidence the influence of the light intensity on the variability of K_{LH}. The results show that irradiation modifies adsorptive sites, and the consequence is that K_{LH} measured under irradiation is different from K_{ads} measured in the dark.

In our case, K_{ads} is larger than K_{LH} (see Table 3). The explanation could be a desorption of the herbicide when the semiconductor is irradiated. Indeed, we have observed in several experiments an increase of the herbicide concentration during the first seconds of illumination, as presented in

Table 3
Langmuir–Hinshelwood adsorption constant (K_{LH}) and kinetic constants (k_{LH})

	CiS	TrS	PrS	MeS	ChS	Chi
k_{LH} (μmol l^{-1} min^{-1})	20.8	15.7	3	17	70.4	55.9
K_{LH} (l mol^{-1})	2680	256	10840	565	24	168

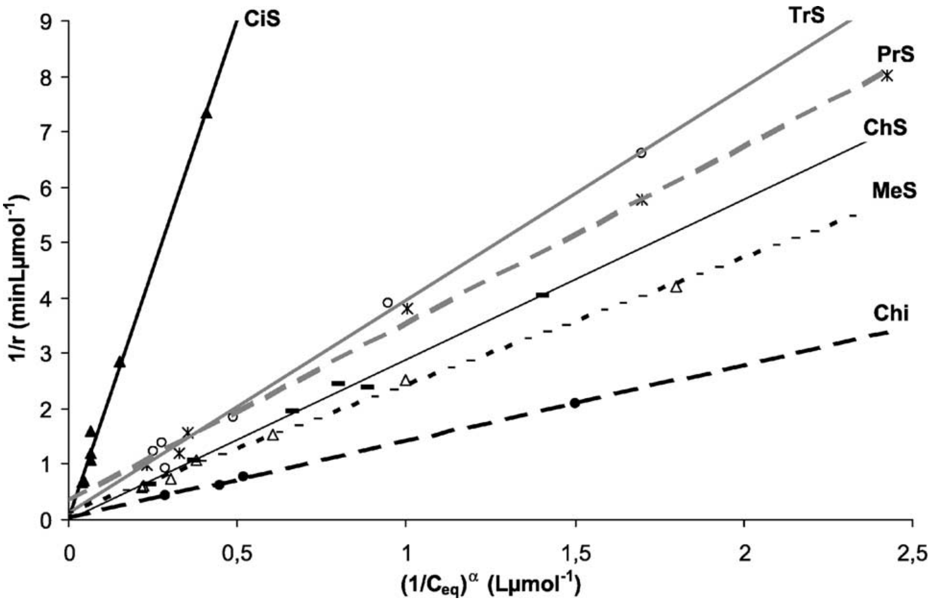

Fig. 6. Linearisation of Langmuir–Hinshelwood isotherm: reciprocal of the initial rate as a function of the reciprocal of the initial concentration.

Fig. 7. Therefore, K_{LH} cannot be considered as a constant reflecting the adsorption/desorption equilibrium during reaction. The desorption could be explained by a thermodesorption, i.e. induced by an increase of surface temperature due to (i) electron–hole recombinations; (ii) the first oxidative transformation reactions whose enthalpies are very negative. Meanwhile a photodesorption phenomena should not be excluded.

3.2.3. Influence of the light flux

Experiments have been made using different radiant fluxes and corresponding to efficient photon fluxes varying from 0.4×10^{16} to 1.26×10^{17} photons s^{-1} (from 1.3 to 39.8 mW cm^{-2}).

We have represented in Fig. 8 the influence of the photonic flux (ϕ) on the initial degradation rate. The curves obtained can be divided into two parts:

- For low fluxes ($\phi \leq 4.2 \times 10^{16}$ photons s^{-1}), the reaction rate is proportional to ϕ. It means that the process works in a good photocatalytic regime: the incident photons are efficiently converted into active species that act in the degradation mechanism.
- For higher fluxes, the rate varies as the square root of the radiant flux at least until 40 mW cm^{-2} (the maximum radiant flux used in this study). This indicates that the process is still photocatalytic but that the electron–hole recombinations become predominant. This has been demonstrated in [6,7]. This indicates that part of light absorption and of electron–hole pairs are lost because of recombination.

These linear or square root features have been observed by many research groups [24–26]. In some cases, a zero-order between the rate and the flux was reported for very high fluxes [27].

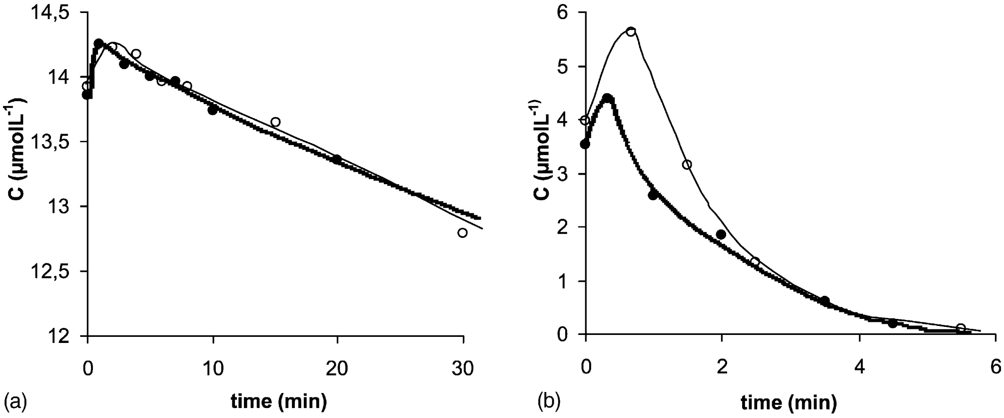

Fig. 7. Evidence for *Sus* (photo)-desorption during the first few minutes of their photocatalytic degradation. Desorption examples: (a) MeS 3.83×10^{15} photons s^{-1} and (b) PrS 1.32×10^{15} photons s^{-1}.

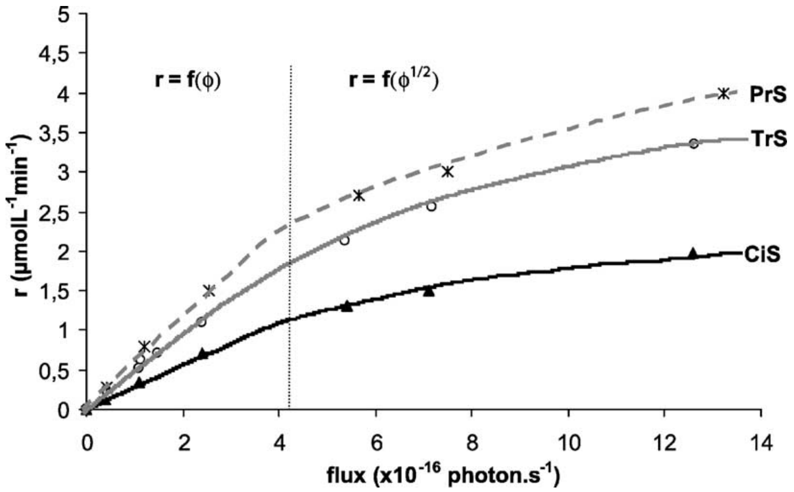

Fig. 8. Influence of the efficient photon flux on the initial rate of photocatalytic degradation of *Sus* (equilibrium concentration: 12 µmol l^{-1}).

3.2.4. Quantum efficiency

The quantum efficiency (φ) is defined as the ratio of the number of transformed molecules per second to the number of photons potentially absorbable by TiO_2 per second. In order to determine φ, several parameters were taken into account: the spectral distribution and the nominal power of the lamp as provided by the manufacturer, the transmission of the optical filter, the total incident radiant flux and the absorption of TiO_2 at each emission wavelength of the lamp (365, 403 and 435 nm). The knowledge of φ allows an estimation of the relative degradability of different products, in the same experimental conditions (T, mass catalyst, C_{eq}, ...).

Fig. 9 shows the influence of the radiant flux on the quantum efficiency of four *Sus*. It appears that φ is more important for the lowest fluxes. For high fluxes, in spite of the increase of the reaction rate with light intensity, two phenomena are limitant: (i) the electron–hole pairs recombination, and (ii) the desorption that increases with flux. Thus, the quantum efficiency decreases with increase in flux.

The quantum efficiency values obtained are in the same range as that of other pollutants photodegraded with nearly the same radiant flux: φ ranging between 0.6 and 1.3% for chlorobenzoic isomers [28], $\varphi = 0.86\%$ for carbetamide [29]. These values can seem low, but because of the light scattering by the TiO_2 particles, they are under-estimated and can be considered as a lower limit of true quantum efficiency. In addition, since the quantum efficiency φ is proportional to the reaction rate which is proportional to the concentration (order 1) or to its square root (order 1/2), this clearly indicates that φ cannot reach high values in the treatment of diluted solutions of traces pesticides.

3.3. Relations between physico-chemical sulfonylurea properties and photodegradation

Within the sulfonylurea herbicide family, it could be interesting to correlate the photocatalytic degradability of a compound with its physico-chemical properties.

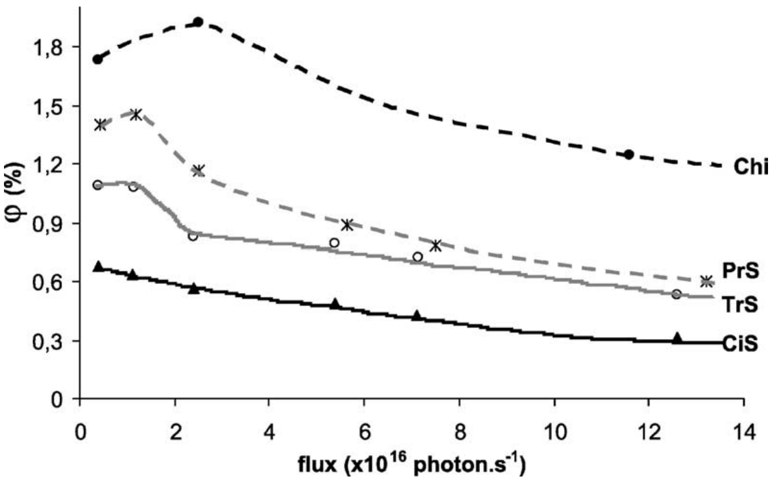

Fig. 9. Influence of flux on quantum efficiency of *Sus* (equilibrium concentration: 12 µmol l^{-1}).

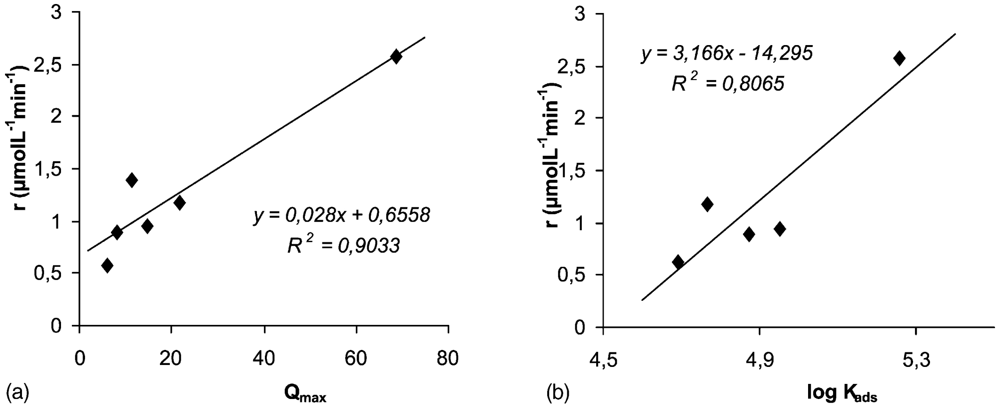

Fig. 10. Relation between sulfonylurea rate disappearance and (a) maximal adsorbable quantity $Q_{\max}$ and (b) adsorption constant K_{ads}.

Considering the preceding results, we know that sulfonylurea photodegradation is directly related to adsorption onto the photocatalyst. Sulfonylurea adsorption could be represented either by the $Q_{\max}$ value or by the adsorption constant K_{ads}. Fig. 10 represents the relation between the degradation rate and these two parameters. In each case, the correlation coefficients of the linear relation was quite satisfactory. The photocatalytic degradability of sulfonylurea herbicides is directly related to their adsorption capacity in the dark. On the other hand, we found that sulfonylurea adsorption or degradation are not related with their $\mathrm{p}K_{\mathrm{a}}$ values.

Generally, organic compounds adsorption is linked to their water solubility and to their octanol–water partition coefficient K_{ow}. Unfortunately, the values of solubilities of most sulfonylureas used in this study were not found in the literature at the pH 4.2 used here.

So we studied only the K_{ow} coefficient, which reflects hydrophobicity of a compound. Values of K_{ow} were found in the literature for three sulfonylurea herbicides (TrS, PrS and Chi) at the adequate pH value [15]. Therefore, we used experimental method recommended by OECD [30] to determine K_{ow} in the three other cases (CiS, MeS and ChS). This method consists in determining the chromatographic capacity factor k'_{w} with a 100% water mobile phase composition. Sulfonylureas were too much hydrophobic to be eluted in a reasonable time under these elution conditions and with our C_{18} column. So we determined the k' values for different concentrations of organic modifier in the eluent in order to extrapolate the results to 100% water. These experiments were brought with the six herbicides. In order to correlate the k'_{w} thus calculated with the corresponding K_{ow}, we used the three K_{ow} disposable values (TrS, PrS and Chi) as calibration compound, as described in [31].

Then we consider the relationship between $\log K_{\text{ow}}$ and (i) the adsorption constant K_{ads} and (ii) the initial rate of disappearance (flux 2.51×10^{16} photons s^{-1}). We found the following linear relationships:

$$\log K_{\text{ads}} = 0.397 \log K_{\text{ow}} + 4.294 \qquad (R^2 = 0.86)$$

$$r = 1.191 \log K_{\text{ow}} - 0.517 \qquad (R^2 = 0.90)$$

This result is interesting because it could make possible to envisage which would be the adsorption capacity and the photocatalytic rate of disappearance of a sulfonylurea molecule, without it being necessary to carry out experiments.

Sometimes, it is possible to correlate pollutants degradability to the Hammett constants [32,33]. In our case, the Hammett coefficients could not be used because the *ortho* substitutents are not defined for them (*ortho* effect).

4. Conclusions

The photocatalytic degradation of six sulfonylurea herbicides in aqueous solution was studied using TiO_2 as the semiconductor catalyst. It appears that adsorption is an essential factor in the degradability of these herbicides. Depending on the kinetic order of the reaction with respect to sulfonylurea concentration, adsorption was found either associative (i.e. non-dissociative) for CiS or dissociative for the other five sulfonylureas. In the latter case, dissociative adsorption was ascribed to a proton separation from the molecule. A two regime law has been found for the reaction rate as a function of the radiant flux. At moderate light fluxes (i.e. $\phi \leq 13.3\,\mathrm{mW\,cm^{-2}}$ corresponding to an efficient photonic flux $\varphi \leq 4.2 \times 10^{16}$ photons s^{-1}), the rate is proportional to ϕ giving an optimum quantum efficiency. For higher values, the electron–hole recombination becomes predominant decreasing the quantum efficiency although the reaction rate still increases. This indicates that for each system including the nature of the pollutant, the mass of catalyst, the irradiation lamp and the design of the photoreactor, the optimum radiant flux has to be clearly defined to work with the optimum quantum efficiency.

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