



ORIGINAL ARTICLE

Photodegradation of imazethapyr herbicide by using slurry and supported TiO₂: Efficiency comparison



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Abstract Kinetic photodegradation of imazethapyr, a herbicide from imidazolinone class of pesticides, has been investigated in aqueous solution using slurry titanium dioxide (TiO₂) and supported on Ahlstrom paper (flexible photocatalytic support). Two types of TiO₂ e.g., Millennium PC500 (100% anatase) and Degussa P25 (80% anatase, 20% rutile) were used. Experiments were investigated to evaluate the effect of the adsorption, initial concentrations of the pesticide as well as catalyst doses on the photocatalytic degradation of imazethapyr. Kinetic parameters were experimentally determined and a half-order kinetic was observed. Regarding Langmuir–Hinshelwood model, the kinetic of the imazethapyr degradation was more efficient at higher pesticide concentrations and catalyst doses. Accordingly, Degussa P25 shows higher photocatalytic activity in regard to PC500 Millennium.

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1. Introduction

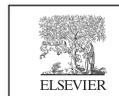
Generally, the photodegradation studies involving titanium dioxide as photocatalyst has been extensively investigated as an alternative physical–chemical process for decontamination of water pollution. Thus, the use of UV energy and TiO₂ as

semiconductor either in suspension or immobilized on a thin layer can completely degrade or mineralize organic pollutants (Kinkennon et al., 1995; Djebbar and Sehili, 1998; Guillard et al., 2003a,b; Garcia and Takashima, 2003; El Madani et al., 2006; Harir et al., 2008). In regard to the advantages of supported catalysts, slurry systems are till nowadays more efficient (Macounova et al., 2003). Several works were established to increase the efficiency of photochemical catalysts e.g., coated titanium oxide on sol–gel process (Pozzo et al., 1997), coated titanium dioxide on glass and non-woven paper using synthetic fibers and sol–gel methods (Guillard et al., 2002), colloidal solutions of Q-TiO₂ particles by hydrolysis of titanium tetrachloride (Macounova et al., 2003), microfibrillar TiO₂ supported by metal–organic chemical

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(Sarantopoulos et al., 2009) and TiO₂-SiO₂ mixed oxide supported MoO₃ (Kemdeoa et al., 2010).

The pesticide selected here is imazethapyr [5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid] which belongs to imidazolinone class of pesticides (Grichar and Sestak, 2000; Hidayat and Presto, 2001). Imazethapyr acts as an inhibitor for plant growth systems and is not interacting with animals. It has been reported that imazethapyr is not adsorbing strongly to soils (Mangels and Shaner, 1991; El Madani et al., 2003) and sufficiently soluble to reach and contaminate the aquifers.

The aim of this work is to study the kinetic photochemical behaviour of imazethapyr by using both PC500 and P25 titanium dioxide as photocatalysts. The efficiency of PC500 coated on Ahlstrom paper and under slurry form was compared. In parallel, the effect of TiO₂ doses under slurry form was studied to enhance the imazethapyr photodegradation.

2. Experimental

2.1. Chemicals

Imazethapyr (Fig. 1), purity 99.9%, was purchased from Riedel-de-Haen, Germany. All other reagents used were analytical grade. The catalysts used were Millennium PC500 Titania (mainly anatase, surface area 340 m² g⁻¹ and mean crystallite size of 5–10 nm) and Degussa P25 Titania (anatase/rutile (80/20), v/v; surface area 50 m² g⁻¹ and a mean crystallite size 30 nm). Titania PC500 was coated on non woven cellulose paper with commercial name of NW10 (12 g m⁻²) using an inorganic binder SiO₂ (12 g m⁻²). Purified water with Milli-Q water system was wholly used in all experiments.

2.2. Irradiation experiments

The irradiation experiments were carried out using two kinds of photoreactors as described in Goutailler et al. (2001). The photoreactors were placed in front of a magnetic stirring plate and on an HPK 125W Philips lamp, at a fixed distance of 3 cm. To eliminate the short wavelengths, a 0–52 filter was used to cut-off irradiation light below 340 nm. The lamp spectrum had a maximum light emission at 365 nm. A radio-meter Biollach Scientific model CX-365 was used in all experiments to measure the light flux (in mW/cm²).

2.3. Samples preparation

A stock solution of imazethapyr (0.34 × 10⁻³ M) was prepared in pure water. For photodegradation studies, TiO₂ was added to 20 ml of the solution to reach appropriate suspension

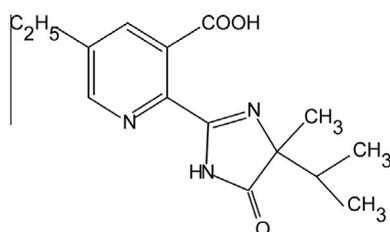


Figure 1 Chemical structure of imazethapyr.

concentration of the catalyst prior to the experimental treatment. The mixture was stirred in darkness for 30 min before starting the irradiation. During the adsorption and the photodegradation experiments of imazethapyr, aliquots of the aqueous suspensions were collected at regular times and were filtered using 0.45 nylon filters (Millipore) to take out TiO₂ constituent part. Parallely, no obvious degradation of imazethapyr was observed in darkness at room temperature (pH 5) within 48 h indicating that no hydrolytic process is occurring during the photodegradation experiments.

2.4. High-performance liquid chromatography

HPLC-UV analyses were performed using Varian Prostar equipped with a UV detector, and a Column Hypersyl BDS C18 (125 mm × 4 mm, particle size 5 μm) was used. In all chromatographic analyses, isocratic elution was applied. The mobile phase was a mixture of water (pH 2.8; H₃PO₄) and methanol (65/35; v/v); the flow rate, injection volume, retention time and wavelength were 1 mL/min, 50 μL, 9.4 min and 255 nm, respectively.

3. Results and discussion

3.1. Preliminary study of imazethapyr adsorption into TiO₂

To investigate the adsorption kinetics and the isotherm adsorption of imazethapyr on TiO₂-PC500 surface, a series of experiments were performed in darkness. A pesticide solution of 20 ml (69 μmol/L) with 12 mg of PC500 was magnetically stirred in darkness for 60 min to study the kinetic behavior of the pesticide. A regular volume of samples was collected at different time intervals, filtered and analyzed by HPLC. The results show that the adsorption equilibrium is rapidly reached after 20 min of stirring. Thus, to investigate the adsorption isotherm, 20 mL of the herbicide solutions (14.5, 30.3, 69.2 μmol/L) and 12 mg of PC500 were magnetically stirred in darkness for 30 min and the results fitted to Langmuir adsorption model Eq. (1).

$$\frac{1}{Y} = \frac{1}{nK_{ads}C_{eq}} + \frac{1}{n} \quad (1)$$

where Y is the amount of imazethapyr adsorbed by 1 g of TiO₂, C_{eq} is the concentration of imazethapyr present in solution when the equilibrium of adsorption is reached and K_{ads} is the Langmuir adsorption constant. In parallel, the linear form of the Eq. (1) is presented in Eq. (2).

$$Y = n \cdot K_{ads}C_{eq}/(1 + K_{ads}C_{eq}) \quad (2)$$

The linear fit of Langmuir equation applied to the adsorption of imazethapyr by PC500 Millennium is shown in (Fig. 2a). The calculated values of the adsorption parameters K_{ads} and n are presented in Table 1.

3.2. Degradation kinetic order

Generally, the photodegradation of organic compounds follows a first-order kinetic (Pichat et al., 1981; Mathew and Khan, 1996; Herrmann and Guillard, 2000; Gerecke et al., 2001; Macounova et al., 2001; Higarashi and Jardim, 2002; Vulliet et al., 2003; Farran and Ruiz, 2004). Thus, to determine

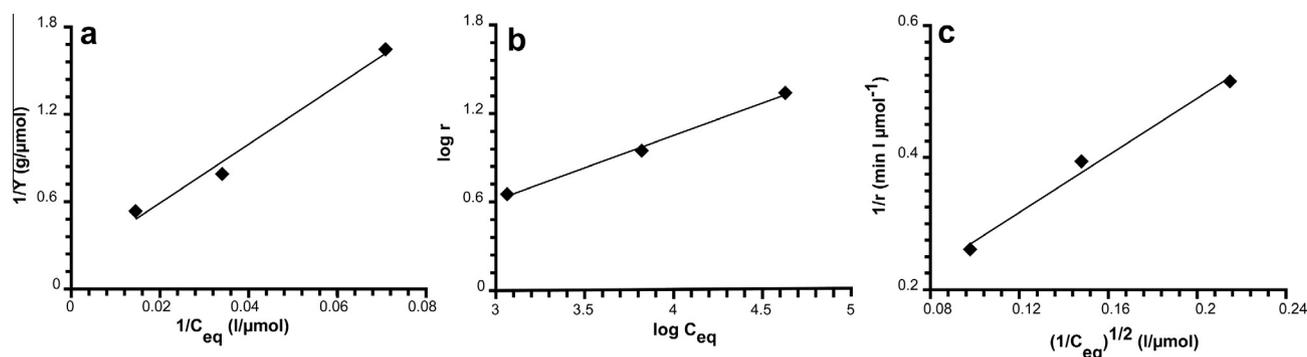


Figure 2 (a) Linear transformation of Langmuir isotherm relative to the adsorption of imazethapyr by PC500-TiO₂, (b) the initial rate of photocatalytic degradation of imazethapyr as a function of its initial concentration by PC500 (its corresponding logarithmic plot $y = 0.4385 - 0.7032x$; $r^2 = 0.9941$) and (c) linearization of Langmuir–Hinshelwood isotherm: reciprocal of the initial rate as a function of the reciprocal of the initial concentration of imazethapyr.

Table 1 Adsorption parameters of imazethapyr to PC500.

$K_{\text{ads}} (\times 10^{-3} \text{ l}/\mu\text{mol})$	$n (\mu\text{mol}/\text{g})$	R^2
9.164	5.40	0.9881

the kinetic order of the imazethapyr photodegradation, the rate constant of degradation was calculated as a function of the imazethapyr concentration at the adsorption equilibrium according to the Eq. (3). Where k_{ap} is the apparent rate constant and r was calculated as $r = \Delta C/\Delta t$ for each catalyst.

$$r = -\frac{dC}{dt} = K_{\text{ap}} C_{\text{eq}}^n \quad (3)$$

The $\log r = \log k_{\text{ap}} + n \log C_{\text{eq}}$ plot gives a straight line of which slope is equal to the kinetic order. The slope obtained for imazethapyr is near 1/2 (Fig. 2b). The reaction followed a half-order kinetic according to the equation $-[dC/dt] = k_{\text{ap}} \sqrt{C_{\text{eq}}}$ indicating a dissociative adsorption (Parra et al., 2001; Marinas et al., 2001). Such a result could be explained by the fact that imazethapyr is a weak acid with a $\text{p}K_{\text{a}}$ value of 3.8 corresponding to the carboxylic acid. Hence, at pH 5, imazethapyr is present in the solution under protonated and deprotonated forms explaining the associative and dissociative adsorptions behavior that might coexist on TiO₂ surface. In darkness, the adsorption is essentially associative but is preferentially dissociative under illuminated titanium. The same tendency was observed for diuron and sulfonylurea herbicides (El Madani et al., 2006; Marinas et al., 2001).

3.3. Langmuir–Hinshelwood constants

In spite of the fact that some authors consider that the Langmuir–Hinshelwood model is not sufficient process, this model is widely used because it enables one to correlate the degradation rate to the instantaneous concentration according to the Eq. (4).

$$r = k(K_{\text{LH}} C_{\text{eq}})^n / (1 + (K_{\text{LH}} C_{\text{eq}})^n) \quad (4)$$

where r is the initial rate of photocatalytic degradation, k is the true rate constant, K_{LH} is the Langmuir–Hinshelwood adsorption constant, C_{eq} is the initial concentration after the adsorption and n is the kinetic order. The linear form of the Eq. (4) is presented in Eq. (5).

$$1/r = 1/k + 1/k(K_{\text{LH}} C_{\text{eq}})^n \quad (5)$$

In parallel, Fig 2c presents the linear forms of Langmuir–Hinshelwood model for imazethapyr in the presence of PC500. The calculated constants k and K were $17.153 \times 10^{-2} \mu\text{mol L}^{-1} \text{ min}^{-1}$ and $K_{\text{LH}} = 7.31 \times 10^{-4} \text{ L}/\mu\text{mol}$, respectively. Hence, the calculated values of K_{LH} ($7.31 \times 10^{-4} \text{ L}/\mu\text{mol}$) and K_{ads} ($1.164 \times 10^{-3} \text{ L}/\mu\text{mol}$) were slightly different. This difference can be neglected in comparison with previous studies where this difference was found much more important (Marinas et al., 2001; Yu et al., 2003). The difference obtained in this study can be attributed to the inexactitude of Langmuir and Langmuir–Hinshelwood alignments. Thus, the adsorption affinity of imazethapyr on the surface of PC500 can be reflected by the parameter K_{LH} .

3.4. Influence of PC500 support on the kinetic of imazethapyr degradation

It is well known that the easiest way to remove slurry TiO₂ from the solutions is either by filtration and/or by centrifugation as well as sedimentation, and this is depending on its mobility, size of particles and its colloidal stability (El Madani et al., 2006; Guillard et al., 2002). However, to avoid this inconvenience, many works have been focused on coating titanium by using several supports e.g., stainless steel, quartz, Pyrex, Fiberglass, glass, fabric, monoliths and paper (El Madani et al., 2006; Guillard et al., 2002; Grichar and Sestak, 2000; Goutailler et al., 2001; Lichtin et al., 1994; Sauer and Ollis, 1996; Goswami et al., 1997; Shifu et al., 1998; Herrmann et al., 2002; Larson et al., 1995). In this work, the decomposition of imazethapyr ($69 \mu\text{mol}/\text{l.20 ml}$) in the presence of PC500 (12 mg) incorporated onto support of paper with NW10 was investigated and the results were compared to those obtained with the same catalyst (PC500, 12 mg) in its slurry form. The results are shown in Fig. 3. It is clear that the catalyst PC500 is more efficient when used in its slurry form than supported on NW10 paper [$r(\text{PC500-Powder})/r(\text{PC500-NW10}) = 2.3$] (Fig. 3). The time necessary to degrade $69 \mu\text{mol}/\text{l}$ of imazethapyr is two times more important when the catalyst is supported. This result can be attributed to the presence of the binder molecules (SiO₂), which may probably prevent the adsorption of imazethapyr on the TiO₂ surface.

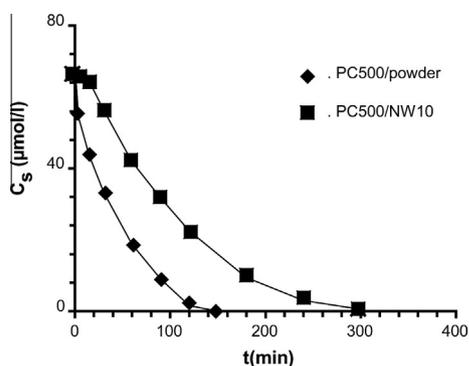


Figure 3 Comparison of the imazethapyr kinetic of degradation between PC500 in slurry and PC500 supported on NW10 paper.

3.5. Influence of TiO_2 amount on the kinetic of imazethapyr degradation

It has been previously confirmed that the optimum concentration of TiO_2 (the minimum photocatalyst concentration enabling to reach the highest rate) depends on the origin of the TiO_2 used. Therefore, an extra experiment was performed to find the optimum concentration of the catalyst millennium PC500 necessary to absorb all the photons emitted from the HPK lamp. A concentration of imazethapyr ($69 \mu\text{mol/L}$) was irradiated in aqueous solution in the presence of 6, 12 and 20 mg of PC500, respectively. Samples of imazethapyr were collected over 120 min and the results are shown in Fig. 4a. Thus, the corresponding rates constant as well as the half-life

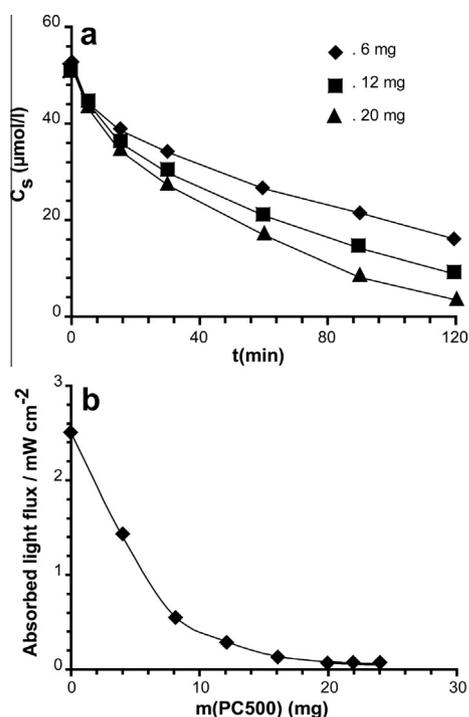


Figure 4 (a) Effect of UV irradiation on imazethapyr degradation ($69 \mu\text{mol/L}$ of imazethapyr; 6, 12 and 20 mg of PC500; pH 5 and ambient temperature) and (b) absorption of light by different amount of PC500 catalyst.

Table 2 Rate constant of imazethapyr degradation. Conditions: $69 \mu\text{mol/L}$ of imazethapyr; 6, 12 and 20 mg of PC500; pH 5 and ambient temperature (see Fig. 4a).

Amount of PC500 (mg)	k_{obs} (min^{-1})	$t_{1/2}$ (min)	R^2
6	0.0091	76.15	0.9797
12	0.0140	49.50	0.9933
20	0.0214	32.40	0.9891

times of imazethapyr degradation are presented in Table 2. It is clear that the efficiency of PC500 to decompose imazethapyr is increased by increasing the doses from 6 to 20 mg. To explain this fact, the light flux versus PC500 doses was calculated in aqueous solution and the results are shown in Fig. 4b. Fig. 4b shows that more than 24 mg (1.2 g/L) are required to reach the highest rate of light absorption. By correlating the results from Fig. 4a and b we sum up that as the more the photons absorbed (up to 24 mg); the more is the photocatalytic efficiency. Similar behavior was reported in the presence of Degussa P25 (Ishiki et al., 2005).

3.6. Influence of the TiO_2 nature on imazethapyr degradation

Two types of TiO_2 e.g., P25 Degussa and PC500 Millennium were chosen to compare their photocatalytic efficiency. An aqueous solution of imazethapyr ($85.8 \mu\text{mol/L}$) was irradiated in the presence of 12 mg of TiO_2 -P25 and TiO_2 -PC500, respectively. Irradiated samples of imazethapyr solutions were collected over 150 min. Fig 5a and Table 3 shows the obtained results. It is clear that imazethapyr is degraded more efficiently

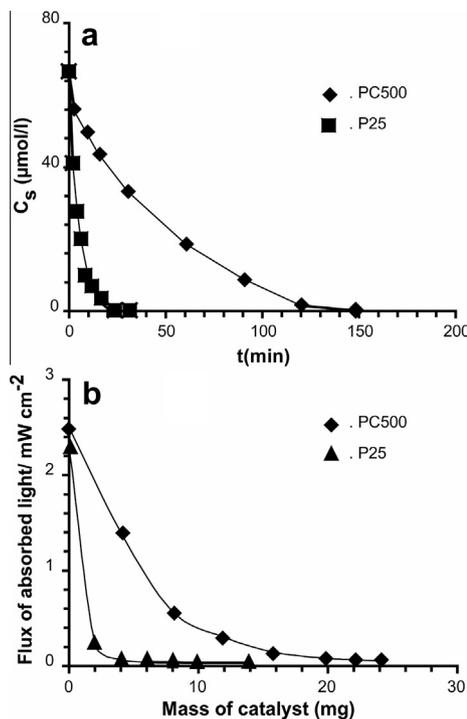


Figure 5 (a) Effect of TiO_2 nature (P25 or PC500) on the kinetic of imazethapyr degradation ($85.8 \mu\text{mol/L}$ of imazethapyr, P25 = 12 mg; pH 5 and ambient temperature) and (b) absorption light comparison from the catalysts P25 and PC500.

Table 3 Rate constant of imazethapyr degradation. Conditions: 85.8 μmol/L of imazethapyr, m(photo-catalysts) = 12 mg; pH 5 and ambient temperature (see Fig. 5a).

Type of photocatalyst	k_{obs} (min ⁻¹)	$t_{1/2}$ (min)	R^2
P25	0.0273	25.38	0.9838
PC500	0.0329	21.06	0.9824

in the presence of P25 in comparison to PC500. By using P25, imazethapyr was fully degraded in less than 25 min of irradiation time, whereas 150 min was crucial for PC500. However, to better understand this fact, additional experiments were performed and the flux of light absorbed from each catalyst as a function of their weight was calculated. The results are shown in Fig. 5b. Below 25 mg of catalyst doses, P25 absorb more efficiently the photons than PC500. Such efficiency of P25 in comparison with PC500 could be explained by the presence of around 20% of rutile for which the band gap is 3.0 eV (the band gap of anatase is 3.2 eV) meaning that its absorbance is higher.

4. Conclusion

The photocatalytic degradation of imazethapyr was investigated using slurry and supported TiO₂ as a semiconductor photocatalysts. The results obtained are as follow:

- Adsorption is considered a crucial factor for the photocatalytic degradation of imazethapyr.
- The kinetic order of imazethapyr degradation followed a half order indicating a dissociative adsorption of the pesticide on the catalyst surface.
- The efficiency of the supported PC500 catalyst was lower than that observed in its slurry form. This effect could be due to the presence of silica binder in PC500 catalyst with respect to the slurry one.
- The influence of TiO₂-PC500 doses on the photocatalytic degradation of imazethapyr shows an increase of the degradation rates by increasing TiO₂-PC500 doses which could be explained by the quantity of the absorbed photons by TiO₂.

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