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Photocatalytic degradation of imazapyr in water: Comparison of activities of different supported and unsupported TiO_2-based catalysts

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Abstract

Photocatalytic oxidation in aqueous phase of imazapyr, a systemic herbicide characterized by its high persistence and mobility in soils, has been investigated using two different titania photocatalysts: commercial Degussa P-25 and industrial Millennium PC-500. Despite potentially better textural and crystalline properties of PC-500, its photocatalytic activity is smaller than that of P-25 for that reaction. A less efficiency of PC-500 powders absorbing the irradiated photons, as well as a low substrate adsorption capacity, has been attributed as the main responsible for such behaviour. Variables such as concentration of imazapyr, amount of catalyst and the physical state of TiO_2 (as a powder or deposited on an Ahlstrom paper) have been studied to elucidate their influence on the efficiency of the photocatalyzed degradation of imazapyr. It has been determined that both adsorption capacities of the catalyst and the reaction rates are strongly affected by the above mentioned parameters. They are even able to modify both the mechanism and kinetic order of the process, by affecting the interfacial substrate–TiO_2 interactions.

Keywords: TiO_2; Kinetic; Mechanism; Imazapyr

1. Introduction

The development of new photocatalytic systems for the detoxification of both polluted waters and air requires deep studies to elucidate all the variables influencing the efficiency of the process. It is known that the viability of each catalytic environmental technology depends on parameters such as the type of the catalyst, the flow and composition of the stream to be treated and the kinetics of the reactions involved. This last parameter is necessary to determine the final dimensions of the purification plant. Consequently, the investigations on photocatalysis at laboratory scale are to be focused on (i) the preparation and characterization of highly efficient catalysts and (ii) the kinetics and the reaction mechanism of the degradation of simple pollutants preliminarily to that of more complex mixtures of contaminants.

Nowadays, because of its high photoactivity, non-toxicity, photocorrosion resistance and other physical and chemical properties, TiO_2 is the most promising photocatalyst, especially the commercial titania Degussa P-25. One of the limitations for the use of titania-based materials available until now is that the difficult recoverability of the catalyst, when used in the form of slurries, remains unsolved. Several industries have developed new titania materials with different structural and textural properties [1,2] but definitive solutions have not been yet achieved. A large variety of supporting materials have been tried as carriers of TiO_2 to facilitate its recovery and reutilization [3]. Among the most usual supports are glass [4], stainless steel [5], paper [6], zeolites [7] and mesoporous silicas [8]. Otherwise, more work has to be made to understand and extrapolate the role of the many variables influencing the efficiency and applicability of photocatalytic processes.

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Concerning the aqueous pollutants, pesticides constitute one of the most widespread type of contaminants of waters and soils. Imazapyr [9] is a broad-spectrum herbicide belonging to the family of imidazolinones, which has the capacity to kill indiscriminately almost all the plants which come into contact with it, even at concentrations below the detection limits of analytical equipments. Moreover, imazapyr is a persistent herbicide, which has a half-life varying from 21 days to 49 months in field studies, with a high mobility in soils. Therefore, it is likely suspected to contaminate groundwater. Attempts to eliminate imazapyr present in drinking water by treatment with ozone have been demonstrated to be unsuccessful since half of the initial compound remains in water after the process. Photocatalysis emerges as the most suitable alternative for the management of streams affected by this pollutant, since its ability to totally destroy most of stable compounds has been established. Nevertheless, previous to the real application of this technology, detailed information on the kinetic and mechanistic aspects of the photocatalytic oxidation of imazapyr is required. Up to now, most of the studies already performed have been focused on the direct photolytic decomposition of imazapyr [10–13]. Very few data has been obtained on the photocatalytic route [11].

In the present work, we report the results obtained from the study of the photocatalytic degradation of imazapyr in water using TiO_2 as photocatalyst. A kinetic characterization about reaction of the disappearance of imazapyr has been done. The activity of two titania photocatalysts with different textural properties has been compared: commercial Degussa P-25 (anatase/rutile = 80/20, $S_{BET} = 50\ m^2\ g^{-1}$) and industrial Millennium PC-500 (anatase, $S_{BET} > 250\ m^2\ g^{-1}$) [14]. Both catalysts were also tested as deposited on flexible photoinert supports (Ahlstrom non-woven papers) [6], these materials coming from an industrial attempt to enhance their recoverability after use.

2. Experimental section

2.1. Chemicals and photocatalysts

Imazapyr (PESTANAL) was purchased by Sigma-Aldrich, with a purity of 99.9%. The chemical structure of this herbicide is shown in Fig. 1.

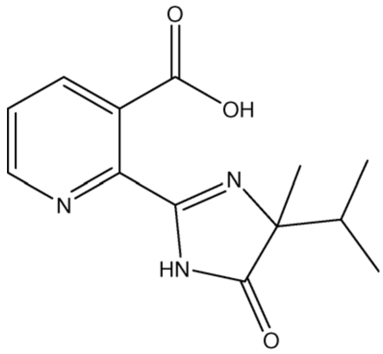

Fig. 1. Chemical structure of imazapyr.

The investigated photocatalysts were commercial Degussa P-25 and industrial Millennium PC-500 (by Millennium Inorganic Chemicals), both in powdered and supported forms (the latter provided by AHLSTROM Research & Services). For the supported catalysts, flexible Ahlstrom non-woven papers were used as the substrates where the TiO_2 powders were attached by a binder based on a suspension of colloidal SiO_2 with a loading of titania ranging from 11.8 to 12 g m^{-2} (EP1069950B1 European Patent). These photocatalytic systems were cut in disc shapes of 10 cm^2 area to cover the surface of the optical window of the photoreactor. Thus, the titania loadings into the reaction volumes were of 11.8–12 mg/20 ml (see below).

2.2. Photocatalytic reactors

The reaction system (Fig. 2(a)) consisted on a batch Pyrex cylindrical reactor (100 cm^3) opened to air. Inside the reactor, a 20 ml aqueous solution of imazapyr was put into contact with a certain amount of the photocatalyst, under stirring. The directly irradiated side of the reactor was the bottom window suprasil disk, 3.75 cm diameter. The reactor for supported TiO_2 catalysts (Fig. 2(b)) was made with the same materials and had the same optical window, but was adapted to hold the papers 1 cm far from the bottom window, this free space being occupied by the imazapyr solution. A high pressure Hg lamp was used as the light source, with the wavelengths shorter than 340 nm being cut off by a Corning 0-52 UV-filter and the IR beams eliminated by a water circulating cell. The distance from the bottom of the reactor to the lamp was 3 cm, giving a mean radiant flux of 4.9 mW cm^{-2} for a wavelength of 365 nm. All reactions were carried out at ambient temperature.

Control reactions were carried out in order to verify that neither hydrolysis under darkness conditions nor photolysis of imazapyr was produced under the experimental conditions used.

2.3. Reaction procedure

In a typical reaction, 20 ml of a solution of imazapyr (pH 4.3 for 20 mg l^{-1} in distilled water) was introduced into the reactor where a certain amount of the catalyst had been previously added. Immediately afterwards, the system was totally covered to avoid direct exposure with sunlight and the stirring was started and maintained during 30 min to ensure that equilibrium of imazapyr adsorption onto titania particles had been reached. Then, the reactor was uncovered allowing the light coming from the lamp to irradiate the whole reaction volume. Thirty minutes before the illumination of the reactor, the lamp was switched on in order to stabilize the light flux. No more than six samples with a maximum volume of 0.5 ml were taken from each reaction

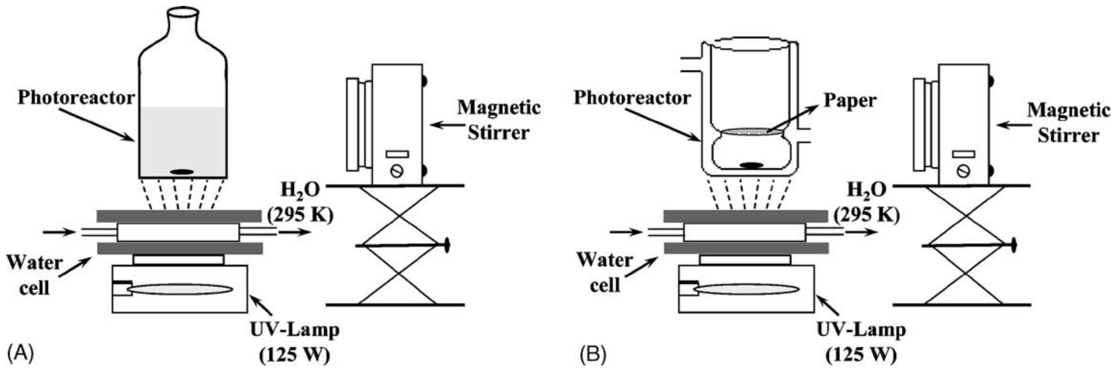

Fig. 2. Scheme of the two photoreaction installations.

just to avoid drastic reductions of the volume. When more than six samples were needed, the same reactions were replicated, previous verification that the reproducibility of the results was good enough.

2.4. Analytical methods

The evolution of imazapyr concentration with time was determined by HPLC, the samples being previously filtered with 0.45 μm nylon filters (Millipore). The column was a Hypersyl BDS C_{18}, 5 μm, 125 mm × 4 mm. The flow rate was 1.0 ml min^{-1}. The mobile phase was methanol (80%) and water (20%), whose pH was adjusted to 2.80 by means of H_3PO_4.

The light flux coming from the lamp was measured using a radiometer CX-365, which was calibrated for absorption quantification at the wavelength of 365 nm (calibration number, 99-534). Quantifications of the percentage of light penetrating the photoreactor and being retained by the catalysts were carried out by measuring the light flux coming out from the photoreactor, always at the same distance. Blank measurements were performed in order to discount water and installation interferences. Although the value does not correspond to the real absorption of light by the sample but it includes the fraction of light dispersed by titania particle reflections, sufficiently comparable results were attained.

3. Results and discussion

3.1. Influence of photocatalyst concentration

The mass of catalyst used in the photoreactor has to be properly selected since it plays an important role on the global efficiency of the reaction. It has been determined that the initial reaction rate of a photocatalytic reaction is directly proportional to the titania concentration [15]. This behaviour is a consequence of an increase in the number of illuminated particle surfaces, which produce a larger amount of reactive electron–hole pairs (e^-–h^+). Nevertheless, there is a limit for the mass of catalyst to be introduced into the reactor, corresponding to the total absorption of the photons coming from the light source. Higher amounts of titania result in a lower efficiency of the reaction since screening effects begin to be predominant. Assuming that the optimal amount of the photocatalyst depends on the reaction conditions, this value has to be determined for each experimental configuration.

Fig. 3 shows the absorption of light as a function of catalyst concentration for two different titania materials: Degussa P-25 and PC-500. It is clear that P-25 is much more efficient capturing the photons emitted from the same lamp. Thus, while 0.2 g l^{-1} could be considered as the optimum concentration of Degussa P-25, this parameter is situated at 1 g l^{-1} for Millennium PC-500. The optimum amount of Degussa P-25 agrees well with that reported by other authors [6]. On the contrary, for PC-500 the optimum amount measured in our experiments is around twice the value reported before [6]. A possible explanation resides in the fact that Degussa P-25 disperses in water much more easily than Millennium PC-500, probably due to different particle sizes between both materials. In effect, with the photocatalytic reactor employed and under stirring conditions, difficulties in suspending PC-500 were found. Moreover, rapid deposition of that powder onto the bottom of the reactor was observed just after stopping the magnetic stirring.

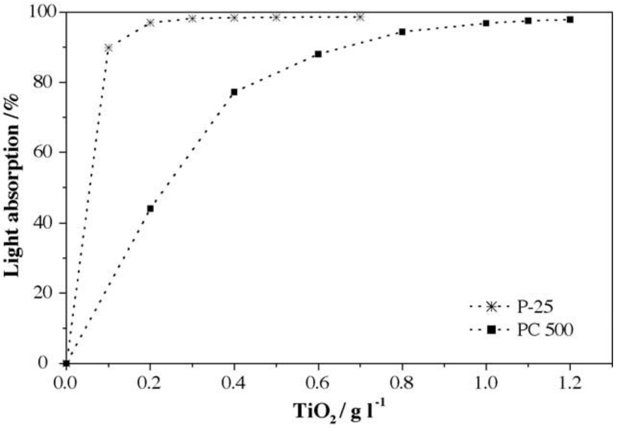

Fig. 3. Variation of light absorption efficiency of both Degussa P-25 and Millennium PC-500 as a function of their concentration in water.

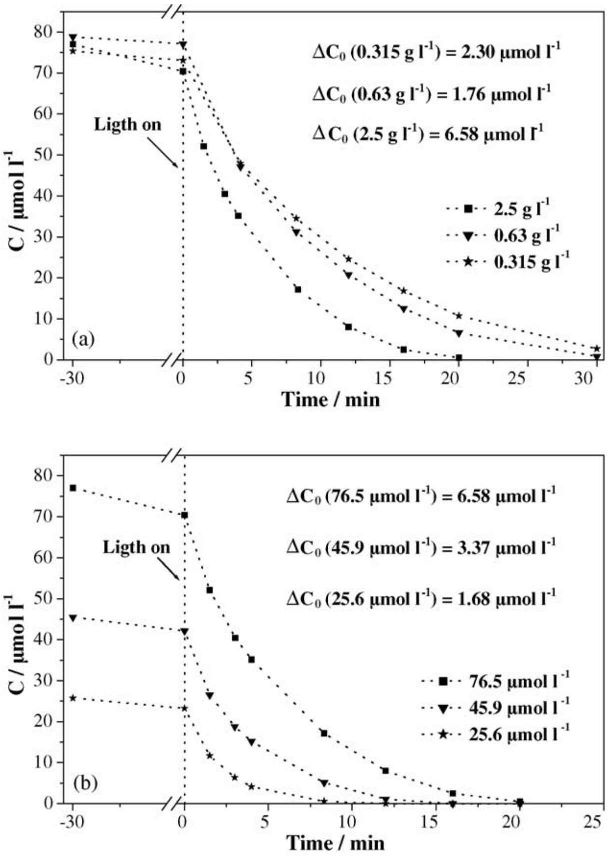

Fig. 4. Evolution of imazapyr concentration as a function of time for (a) different P-25 titania amounts and (b) different initial concentrations of imazapyr. ΔC_0 is the variation of the concentration of the initial solution after the equilibrium adsorption step.

The evolution of concentration of imazapyr with irradiation time, when different amounts of P-25 were used as photocatalyst, is represented in Fig. 4(a). The initial concentrations of the herbicide before and after darkness adsorption stage have been also plotted (time range of −30 to 0 min). It can be observed a slower degradation of imazapyr when the mass of catalyst is decreased from 2.5 to 0.63 g l^{-1} while the disappearance rate is similar between 0.63 and 0.315 g l^{-1}. However, the time required to totally remove imazapyr from the solution varies from 20 to 30 min, which is significantly less than the degradation time of imazapyr by photolysis. Actually, no degradation of imazapyr occurs without TiO_2 during this time in our UV light conditions. Moreover, the half-life time for 25 ppm of imazapyr in distilled water has been found as 1.85 days, when a 24 h daily simulated sunlight exposure is considered [10].

Given that the light uptake is maxima for the three catalyst amounts, this variable does not seem to influence the observed results. On the other hand, the adsorption of imazapyr is higher when the largest mass of P-25 is used, and it is almost the same for the two lowest concentrations. This higher adsorption capacity, which implies a higher proportion of molecules of the substrate contacting with the active sites, could be assumed as the main feature responsible for the faster degradation rate of imazapyr.

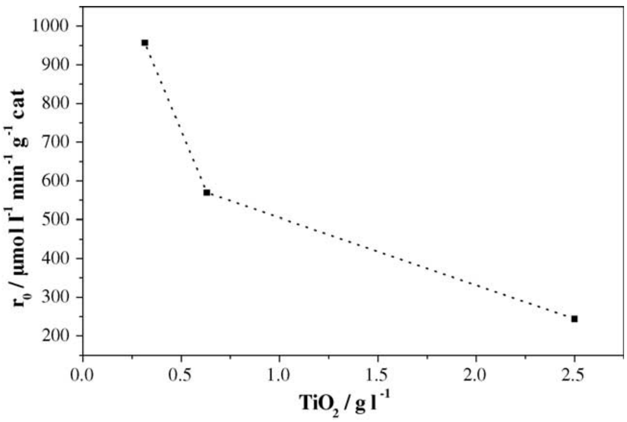

Fig. 5. Variation of the initial reaction rate as a function of the concentration of P-25.

Fig. 5 shows the initial specific reaction rates (r_0), *specific* meaning per mass unit of catalyst. The initial specific reaction rate displays a clear diminution as the mass of Degussa P-25 is increased. This behaviour is more pronounced for the variation of the catalyst amount from 0.315 to 0.63 g l^{-1}. Since the maximum absorption of light is already achieved with the lowest mass of Degussa P-25, an overload of the catalyst for the upper concentrations is occurring. In this situation, screening effects of the irradiation due to an excess of TiO_2 becomes dominant. Thus, an important fraction of titania particles are not reached by the photons emitted by the lamp, leading to a reduction of the photocatalytic efficiency.

3.2. Influence of concentration of imazapyr

Three initial concentrations of imazapyr were used to evaluate the influence of the amount of the herbicide on the efficiency of the reaction with Degussa P-25: 76.5, 45.9 and 25.6 µmol l^{-1} (20, 12 and 6.7 mg l^{-1}, respectively). For this series of experiments the catalyst loading was kept constant at 2.5 g l^{-1}. Fig. 4(b) illustrates the values of imazapyr concentration measured before and after the adsorption step under darkness conditions, as well as the progression of the disappearance of the herbicide when the reactor was illuminated. As the initial concentration of imazapyr decreases, the time required to reach its total disappearance decreases too. Thus, while 20 min are necessary to totally eliminate an initial amount of imazapyr of 76.5 µmol l^{-1}, this time is reduced to 16 and 12 min when 45.9 and 25.6 µmol l^{-1} of the herbicide, respectively, are initially present in the solution. This behaviour is expected since the ratio imazapyr molecules/active sites of TiO_2 is lower leading to a faster overall disappearance of the compound.

The adsorption equilibrium of imazapyr onto the titania surface has been calculated assuming the Freundlich isotherm as following (Eq. (1)):

$$n_{\text{ADS}} = f(C) = KC^n \tag{1}$$

where n_{ADS} represents the number of molecules of imazapyr adsorbed per mass unit of titania, and C the corresponding equilibrium concentration of imazapyr in solution (μmol l^{-1}). Eq. (2) shows the result obtained from the linearization of the equation written above, when it was applied to the data derived from the three investigated concentrations of imazapyr, once the equilibrium of adsorption had been established:

$$\ln(n_{\text{ADS}}) = 1.2447 \ln(C) - 3.1851, \qquad R^2 = 0.9993 \tag{2}$$

It can be observed that the data fit well with a straight line, with a slope (n) close to 1, this parameter being an indicator of the capacity for imazapyr adsorption. In this sense, it has been reported that values of n ranging from 1 to 10 represent favourable sorption conditions [16]. The adsorption equilibrium constant calculated from the linear regression is 0.0414 l $\text{g(TiO}_2)^{-1}$. Thus, the interfacial adsorption stage between the entities of imazapyr and the titania particles could play an important role on the global efficiency of the photocatalytic process, as typically occurs in heterogeneous catalytic processes.

The experimental reaction data fit well with a potential kinetic model ($-\text{ra} = kC^n$) with a kinetic order $n = 1$ respect to imazapyr concentration. The three reactions exhibited an apparent rate constant decreasing as the initial herbicide concentration increases. Thus, calculated kinetic constants were 0.4449, 0.2560 and 0.1773 min^{-1} for 25.6, 45.9 and 76.5 μmol l^{-1}, respectively. This dependence of the value of k on the concentration of imazapyr can be explained by assuming that they are surface limited reactions with a diluted contaminant as the substrate. In this situation, competition between imazapyr and either its intermediates or by-products for the titania active sites may also occur [17]. Therefore, a first order kinetic for the reaction is not reliable, but it is a Langmuir–Hinshelwood-type behaviour, which presumably, is dominating the kinetics of this photocatalytic system.

In line with interfacial catalytic processes, Langmuir–Hinshelwood models (Eq. (3)) were tested to accomplish simultaneous adjustment of the three reaction data. The best resultant fit corresponded to the kinetic equation shown below (Eq. (4)), providing a mean error, relative to concentrations of imazapyr, of ±13% due to excessively high degradation rates:

$$-r_{\text{IMAZAPYR}} = \frac{K' C^n_{\text{IMAZAPYR}}}{1 + KC_{\text{IMAZAPYR}}} \tag{3}$$

$$-r_{\text{IMAZAPYR}} = \frac{0.8569 C_{\text{IMAZAPYR}}}{1 + 0.0867 C_{\text{IMAZAPYR}}} \tag{4}$$

As degradation of imazapyr was very fast under the reaction conditions employed in this section, particularly for the lowest concentrations of imazapyr, experimental errors associated to the calculation of the initial reaction rates may be important. To minimize this error, the comparison between reaction rates of the three experiments was realized by calculating that parameter at different times of irradiation, the corresponding graphs being simultaneously represented in Fig. 6(a). It is clear that degradation rate is higher when larger amounts of imazapyr are initially dissolved into the water. This fact denotes, again, that the kinetics of the reaction is dependent on the concentration of the herbicide, as typically occurs with heterogeneous catalyzed reactions using diluted solutions. Under these conditions, the larger concentration of imazapyr, the more the number of active sites of titania are occupied by such molecules which are photooxidized leading to a faster global reaction rate.

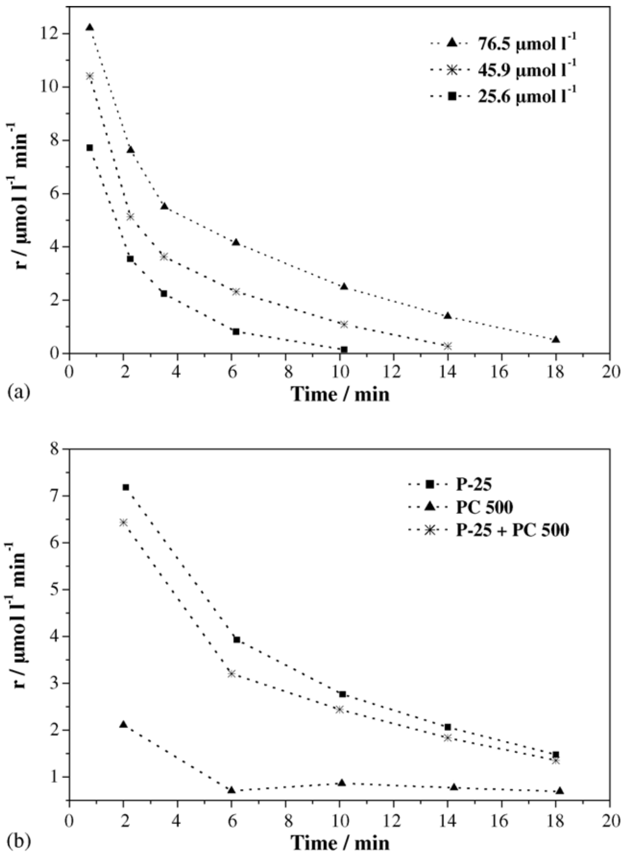

Fig. 6. Reaction rates as a function of time for (a) different initial concentrations of imazapyr and (b) different TiO_2 powders.

3.3. Comparison between different TiO_2 powders

In this section two commercial titania powders were examined: Degussa P-25 and Millennium PC-500. Degussa P-25 is characterized by a medium surface area (50 $\text{m}^2\ \text{g}^{-1}$) with a crystal size of 30 nm, its allotropic composition being of 80% anatase and 20% rutile. On the contrary, Millennium PC-500 is a porous powder which exhibits a larger specific surface area (>250 $\text{m}^2\ \text{g}^{-1}$) with a mean pore diameter of 6 nm and the structure made of smaller and pure anatase crystallites (5–10 nm).

Table 1
Photocatalytic parameters corresponding to the three powdered titania catalysts

Catalyst	C_{Titania} (g l^{-1})	Φ_{ADS}[a] (%)	ΔC_0[b] (μmol l^{-1})	X_{IMA} (%)	n	K'	$K \times 10^3$	Mean error (±% C_{IMA})
P-25	0.630	98.5	1.76	99	1	0.142	6.07	4.45
PC-500	0.630	89.0	1.88	45	1	0.0225	0.185	4.44
P-25 + PC-500	0.315 + 0.315	98.2	1.76	95	1	0.102	2.82	4.64

[a] Percentage of light, irradiated from the lamp, absorbed by the reaction volume.

[b] Variation of initial concentration of imazapyr after adsorption equilibrium step.

Table 1 contains the results derived from the study of the photocatalytic degradation of 76.5 μmol l^{-1} of imazapyr after 30 min of illumination. Catalyst concentrations were 0.63 g l^{-1}, the composition varying as follows: (a) 100% Degussa P-25; (b) 100% PC-500; (c) 50% P-25 + 50% PC-500. Despite the higher surface area of Millennium PC-500, the activity of this catalyst was clearly lower than that of P-25 for the same TiO_2 loading into the reactor. Thus, after 30 min of reaction, Degussa P-25 reached nearly the total conversion of imazapyr, only small traces of the herbicide being detected by HPLC. By contrast, Millennium PC-500 exhibited a conversion of 45%. This smaller efficiency of Millennium PC-500 was previously observed by Guillard et al. [14] when the same catalysts were tested in laboratory experiments for the photocatalytic degradation of dyes.

According to the characteristics of photocatalytic processes, several factors may be influencing these results, as described below. First, suspension and homogenization of the PC-500 powder was difficult, as previously commented. In addition, for PC-500 under the reaction conditions used in this research, not the total light flux absorption capacity is reached, but 89% of the photons coming from the lamp are captured by the TiO_2 particles (Fig. 3). This means that the reaction rate is not independent of the catalyst amount, as it would be desirable for investigations related to the activity comparison between different photocatalytic systems. On the contrary, Degussa P-25 shows a total absorption of light for the same concentration. Then, the maximum efficiency of the reaction provided by this variable is reached.

Other parameters affecting the reaction rate are related to the chemical and crystalline properties of the catalyst. In this sense, it is well known that anatase phase usually offers the higher activities in the photocatalytic reactions, while rutile commonly gives either very low or no activity [18,19]. Assuming this information, PC-500, which is composed by pure anatase crystallites, should be the most efficient catalyst of the two investigated powders. Nevertheless, other factors [15,20] such as crystal size, existence of structural defects into the crystalline framework, compositional impurities and chemical properties of the titania surface (polarity and hydroxylation grade) play an important role on the recombination rate of the redox pairs (e^-–h^+), as well as on the adsorption ability of the herbicide molecules to be degraded. For example, the adsorption of imazapyr is smaller on PC-500 than on P-25. This fact is not clearly evidenced for the concentrations of the catalysts employed in this section but it was verified when 2.5 g l^{-1} of TiO_2 was put into contact with 76.5 μmol l^{-1} of imazapyr solution. Under these last conditions Degussa P-25 retained 6.58 μmol l^{-1} of imazapyr after the equilibrium adsorption stage, while Millennium fixed onto its surface only 2.83 μmol l^{-1}. The different synthesis routes of both materials probably have led to a less hydrophilic surface in the case of Millennium PC-500, justifying the adsorption and photocatalytic results above described.

Surprisingly, when 0.63 g l^{-1} of a mixture of PC-500 and Degussa P-25 with a ratio 1:1 was used as the catalyst composition, imazapyr disappeared practically at the same rate as for the reaction carried out with pure P-25. Therefore, no synergy effect was observed when mixing both catalysts, which would have combined the good photocatalytic properties of Degussa P-25 and the high surface area of Millennium PC-500. On the other hand, an intermediate activity between the two pure catalysts previously tested was not achieved either. As it was demonstrated in Fig. 3, even with 0.315 g l^{-1} of Degussa P-25 almost the whole photons irradiated by the lamp were absorbed by the titania suspension. In this situation, Degussa P-25 seems to have a predominant effect on the kinetic behaviour of the reaction, PC-500 not affecting in a significant way.

Fig. 6(b) illustrates the variation of reaction rate as the illumination time advances, for the three catalytic compositions evaluated in this section. According with the results above discussed, PC-500 gives always the lowest degradation rate, whereas the mixture of both powders leads to reaction rates very close to that of pure P-25. The three photocatalytic systems agree well with kinetics of Langmuir–Hinshelwood type (Eq. (3)). The values of the parameters (n, K' and K) are registered in Table 1, as well as the fit error associated to the herbicide concentration. It can be seem that the adsorption constant for Degussa P-25 ($K = 0.00607$) presents an important contribution on the global kinetic behaviour, which marks imazapyr adsorption onto titania surface as an influencing step. Nevertheless, the adsorption coefficient is almost negligible for the reaction catalyzed by PC-500 ($K = 0.000185$). In this case, the kinetic model could be approximated to a first order potential model with a rather low kinetic constant equivalent to K'. The photochemical degradation of imazapyr in aqueous solution, presents a first order kinetic constant [10,12] owing to interfacial processes are not implicated. A presumed less hydrophilic nature, together with the lower adsorption capacity on the titania surface of PC-500 might be, then, responsible of its different behaviour. Concerning the powder containing the mixture P-25 + PC-500, although both constants (K' and K) are smaller than that obtained for pure Degussa P-25, they are closer to that catalyst than to Millennium PC-500, this fact in consonance with the observed degradation rates. Taking into account that concentrations of powdered Degussa P-25 of 0.63 and 0.315 g l^{-1} led to practically the same disappearance rates of imazapyr, it is deduced, that the effect of Millennium PC-500 on the global kinetics of the reaction is hardly perceptible, being Degussa P-25 the dominating catalyst.

3.4. Comparison between supported and powdered TiO_2 materials

In this work two different titania materials, incorporated in a flexible Ahlstrom paper support (commercial name of NW10), were tested. Both catalysts Degussa P-25 and Millennium PC-500 were supported. The concentrations of the TiO_2 particles present on the papers were 11.8 and 12 g m^{-2}, respectively. In addition, another paper loaded with a 50/50 mixture of both catalysts was studied. Each supported material was compared to the corresponding powder with the same concentration in the reaction volume. In all cases, the initial imazapyr solution contained a concentration of 76.5 μmol l^{-1} of such herbicide. No leaching of the catalysts was detected for any of the three supported systems.

Whatever the TiO_2 composition used, the deposition of the catalysts leads to a drastic decrease of the activity for the degradation of imazapyr. For example, while in 30 min near the whole molecules of imazapyr were degraded with both P-25 and P-25 + PC-500 powder mixture (see Table 1), only 11.5 and 13.9 μmol l^{-1} of imazapyr were oxidized with the corresponding supported catalysts. For pure PC-500, after 30 min of reaction, the variation was from 33.1 to 2.64 μmol l^{-1} of eliminated imazapyr for the powdered and supported forms, respectively. To explain this important decrease of the efficiency when TiO_2 is supported, it could be suggested that both the contact with the compounds to be degraded, the absorption of light and generation of reactive electron–hole pairs are restricted. However, these hypotheses do not agree with the results obtained in the degradation of 4-chlorophenol and formetanate, which are degradated with comparable efficiencies in the presence of TiO_2 used as powder or supported [6]. As previously suggested by Guillard et al. [6], this behaviour could be explained by a electrostatic repulsion between imazapyr, negatively charged in our working conditions, and the silica binder. Moreover, the type of photoreactor could also contribute to explain this decrease of efficiency. Actually, in the same publication [6] a solar photoreactor was used, its operating conditions based on the multi-step cascade falling-film principle, which ensured enough turbulence to avoid mass transfer limitations. On the contrary, and despite the roughness of the paper, which favours a turbulent regime next to its surface, the characteristics of the batch reactor used in the present work may not be adequate to assure good mass transfer.

On the other hand, it is important to remark that no adsorption of imazapyr was detected for any supported titania materials, whereas the powder seems to adsorb a small amount of herbicide. The pH of the initial solution, when operating with the powders, was equal to 4.3. This value corresponds to the natural pH of imazapyr solution in distilled water. The pH increased to 5.1–5.7 when paper-supported titania was used. The rise of pH is attributed to the presence of the silica binders into the papers. Since the isoelectric point of silanol groups is pzc = 2, the matrix into which the TiO_2 particles are inserted is negatively charged. Imazapyr has three pK_a's (1.9, 3.6 and 11.2), corresponding to the formation of three different ionic species. The increase of pH from 4.3 to 5.7 leads to a higher contribution of imazapyr molecules with their carboxylic group negatively charged. Thus, electrostatic repulsions between the supported catalyst and the herbicide become more predominant, inhibiting the attraction and the adsorption of imazapyr onto the surface of TiO_2. This fact might be another reason justifying the behaviour we observed, since adsorption of the substrate onto the surface of the catalysts represents a crucial step on the photocatalytic efficiency of the process. Similar behaviour has been observed in the study of dyes removal in water employing the same catalysts [6,14]. In this case, the smaller photocatalytic activity of supported TiO_2 was attributed to the electrostatic repulsions between the anionic dyes and the silica binders which were negatively charged due to their pzc = 2, approximately.

Taking into account these results, the reaction times were enlarged up to 4 h, the results of final conversion and kinetic parameters being presented in Table 2. Then, after 4 h of irradiation the conversions of imazapyr were 82, 89 and 21.4% for supported P-25, P-25 + PC-500 and PC-500, respectively.

The reaction carried out with paper containing Degussa P-25 was conducted in accordance with a Langmuir–Hinshelwood kinetic model of order $n = 1$ with respect to the molecules of imazapyr. The resulted L–H parameters are included in Table 2, together with the average error of the theoretical concentration of imazapyr provided by such adjustment. It is remarkable that adsorption constant

Table 2
Photocatalytic parameters corresponding to the three supported titania catalysts

Catalyst	$C_{Titania}$ (g l^{-1})	pH_0	X_{IMA} (%)	n	K'	K	Mean error (±% C_{IMA})
P-25 paper	0.630	5.7	82.0	1	0.00799	0.00359	3.39
PC-500 paper	0.630	5.1	21.4	0	0.0679	–	0.59
P-25+PC-500 paper	0.315 + 0.315	5.3	89.0	1	0.0138	0.0159	0.62

(K = 0.00359) is around half of that reported for the equivalent mass of catalyst in the powdered form (K = 0.00607). On the other hand, paper supporting PC-500 showed an extremely high K value which leads to a simplification of L–H equation to a potential kinetic model of order n = 0. This result denotes a more complex situation that it is attributed to the adsorption difficulties of such TiO_2 phase. Finally, the system P-25 + PC-500/paper fits with a Langmuir–Hinshelwood equation, with both constants (K' and K) higher than that obtained for pure P-25. Just as it occurred with the powders, the degradation rate seems to be controlled by the presence of Degussa P-25, the contribution of PC-500 phase being almost not appreciable.

Reaction rates of Degussa P-25 and Millennium PC-500 were calculated from the corresponding kinetic equations assuming a 50% degradation of imazapyr. The values so obtained were 0.274 and 0.0679 μmol l^{-1} min^{-1} for supported P-25 and PC-500, respectively, while the same concentrations of both TiO_2 powders provided reaction rates of 4.44 and 0.825 μmol l^{-1} min^{-1}, respectively. The ratio of the degradation rates between Degussa P-25 and PC-500 were 5.42 and 4.03 for unsupported and supported TiO_2 systems, respectively, indicating a stronger inhibition for the former photocatalyst as a consequence of its deposition into the substrate.

4. Conclusions

The higher specific surface area of Millennium PC-500, together with its composition of pure anatase nanocrystallites, was expected to overcome the adsorption and interfacial processes limitations occurring with Degussa P-25. Consequently, this would lead to higher photocatalytic efficiency when comparing their activities for the photocatalytic oxidation of imazapyr in water. Nevertheless, absorption of light by Millennium PC-500 is less efficient, which is even five times lower than for P-25. On the other hand, maybe due to the synthesis procedure, the particle surfaces of Millennium PC-500 seems to be less hydrophilic, this fact causing a reduction of the adsorption capacity for the molecules of imazapyr. This fact causes the reaction mechanisms to be different for the two catalysts: while both kinetic and adsorption constants of a typical Langmuir–Hinshelwood model are relevant for Degussa P-25, the last parameter is negligible in the case of PC-500, the kinetic model being simplified to a first order potential kinetics. In addition, no synergic effects are observed when mixtures of both catalysts are used, the kinetic behaviour being mainly that of Degussa P-25.

Supporting the powders on a flexible photo-inert Ahlstrom non-woven paper makes recovery of the catalysts after use much easier, no leaching of the titania particles being observed. However, the partial charge of the support induced by the presence of silica binder and the ionic charge of imazapyr in our pH conditions, led to electrostatic repulsions, which decrease the photocatalytic efficiency of supported TiO_2 samples. Moreover, the use of static reactor could also be suggested as participating to this lower efficiency of supported TiO_2 due to mass transfer problems. More investigations have to be performed in order to better understand the impact of ionic state of photocatalyst and reactor (static or dynamic).

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