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Comparison of various titania samples of industrial origin in the solar photocatalytic detoxification of water containing 4-chlorophenol

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Abstract

The degradation of 4-chlorophenol (4-CP) was used as a model reaction to investigate the photocatalytic properties of different industrial TiO_2 catalysts and to compare their efficiencies in the treatment of contaminated waters. Parallel experiments have been performed using either artificial UV-light in a batch photoreactor in laboratory experiments or solar energy in the flow reactor of the pilot plant at Plataforma Solar de Almeria (PSA) in Spain. Depending on the kinetic criteria chosen for comparison ((i) initial rate of pollutant disappearance; (ii) amounts of intermediate products present in solution at a given time; (iii) time necessary to obtain total mineralization), different classifications of photocatalyst activities were observed. Among various physical characteristics such as particle size, structure or active site density, which may intervene on the photocatalytic activity, the influence of the surface area appeared of prime importance. For lower surface area catalysts, there is a decrease in the readsorption rate of intermediate products and consequently in the overall photodegradation rate. By contrast, for higher surface area catalysts, it was observed a lower final rate of total organic carbon (TOC) disappearance because of a very low coverage in pollutant which favors electron–hole recombination.

The comparison of the kinetic results for decontaminating water at PSA and in laboratory experiments indicated the same kinetic order (apparent first order) for 4-CP disappearance and the same apparent quantum yield. However, fewer intermediate products and a faster TOC disappearance were observed in the solar pilot reactor at PSA, which, in addition, worked with a smaller optimum concentration of suspended titania. This was ascribed to the design of the photoreactor. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Water detoxification; TiO_2; Titania; Pesticides; Solar application; 4-chlorophenol

1. Introduction

Heterogeneous photocatalysis has recently emerged as an efficient method for purifying water and air [1–5] in most of the cases encountered. More than 1700 references have been recently collected on this discipline [6]. Up to now, titania under the shape of anatase has always been found as the best photocatalyst.

Several attempts has been performed to increase its photoefficiency either by noble metal deposition or by ion doping. In photocatalytic reactions of organic pollutant degradation, which are essentially total oxidation reactions, such modifications did not enhance the photocatalytic activity of titania and were rather detri-

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mental. For ion doping, either of the p-type obtained by dissolving in the lattice of titania heterocations of valency lower that of Ti^{+4} (Al^{+3}, Cr^{+3}, Ga^{+3}) or of the n-type obtained by dissolving heterocations of valency higher than +4 (Nb^{+5}, Ta^{+5}, Sb^{+5}) the inhibiting effect was ascribed to an increase in the electron–hole recombination rate [7]. Actually, p-type doping agents create acceptor centers which trap photo-electrons and then, once negatively charged, attract holes, thus behaving as recombination centers [8]. On the opposite, n-type doping agents create donor centers. By increasing the concentration of conduction electrons in the solid, they also favor the electron–hole recombination, which is detrimental for the photoefficiency [8]. Noble metal deposits help the electron–hole pair separation by attracting the photo-electrons because of a favorable difference between their Fermi level and that of titania. However, once negatively charged, metal particles, especially for highly loaded samples (%M > 5%), attract holes and subsequently recombine them with electrons [7]. Up to now, unmodified titania was always selected as the optimal photocatalysts ever found.

The photocatalytic pilot plant of the Plataforma Solar de Almeria (PSA) is a unique settlement in Europe [9]. Removal of several organic pollutants have been successfully tested at PSA: phenol [10], 2,4-dichlorophenol [11], pentachlorophenol [12,13], atrazine [14], dichloracetic acid [15] and other commercial pesticides [16–19]. In the last study, it was checked that the kinetic results obtained with microphotoreactors at the laboratory scale could be extrapolated to pilot photoreactors with a capacity of several hundreds of liters, using a circulating suspension of titania. It was also attempted to study the variations of photo-efficiencies with solar high fluxes and to detect any influence of possible thermal effects induced by solar light. The main objective was, however, to perform tests on the disappearance rate of a chosen organic pollutant and on the formation of intermediates or by-products which may arise before the total mineralization expected.

In the present study, we have tested the photoactivities of various titania samples of different industrial origins and used under identical conditions to study the influence of their structural and textural characteristics on their solar efficiencies. 4-chlorophenol (4-CP) which has been the topic of many recent investigations [20] and therein, has been chosen as model molecules for this study.

2. Experimental

2.1. Photoreactors and light sources

Two photoreactors have been used for this study. The compound parabolic collector (CPC) pilot photoreactor was selected for solar experiments because it has the advantage of using both direct and diffuse UV-light [11,17]. The configuration of CPC solar reactor at PSA consists of six modules connected in series. These modules of a total reflective surface of $9\,m^2$ are mounted on a fixed platform inclined at 37° corresponding to the latitude of Almeria. A more detailed description of this recirculating reactor have been previously described [18]. The overall photonic flux entering the CPC was 1.26×10^{-3} Einstein s^{-1} (1 Einstein = 1 mol of photons) for a global solar radiant flux of $46\,W\,m^{-2}$. The wavelength range is $\lambda > 290$ nm and corresponds to the solar spectrum [22]. This value was calculated by multiplying the flux by the irradiated surface area of the collector ($9\,m^2$). For a global UV-radiant flux of $46\,W\,m^{-2}$, corresponding to an average value around noon at PSA in June, the photonic flux was equal to 1.4×10^{-4} Einstein $m^{-2}\,s^{-1}$ [22].

For parallel laboratory experiments, a pyrex batch reactor of 90 ml equipped with an optical window of $12\,cm^2$ section area was employed. The solid was maintained in suspension by magnetic stirring. A cut-off filter at 340 nm was used to avoid photolysis and mimic solar irradiation. The heating of the solution was eliminated by the use of a water-circulating cuvette. The irradiation was provided by a Philips HPK 125 W mercury lamp. In this case the overall photonic flux potentially absorbable by TiO_2 was 2.7×10^{-7} Einstein s^{-1}.

2.2. Reactants

4-chlorophenol (99% purity) was purchased from Aldrich and used as received. Four industrial photocatalysts whose characteristics are given in Table 1 were used. The water used in all solar experiments was obtained by distillation in the PSA solar desali-

Table 1
Physical characteristics of the TiO_2 samples

Sample	Supplier	Surface area ($m^2\,g^{-1}$)	Structure
P-25	Degussa	50	80% anatase, 20% rutile
HombikatUV 100	Sachtleben Chemie	250	Anatase (very pure)
TiLCOM HC 120	Tioxide	120	Anatase
TiONA PC 10	Millennium Inorganic Chemicals	9	Anatase

nation Plant. Its conductivity was below 10 μS and its total organic carbon (TOC) content was lower than $0.5\,mg\,l^{-1}$. The ultra-pure water used in laboratory experiments was provided by a Milli-Q Plus Millipore system.

2.3. Procedure and analysis

In PSA experiments, a volume of 247 l of a 4-chlorophenol solution ($0.16\,mmol\,l^{-1}$) was circulated at a flow rate of $3.5\,m^3\,h^{-1}$. It contains a suspension of TiO_2 at a concentration of $0.2\,g\,l^{-1}$ corresponding to the optimal amount determined for the Degussa P-25 sample. The circulated suspension was maintained in the dark for 1 h to reach the adsorption equilibrium of the pollutant. Time zero corresponded to the beginning of UV-irradiation and samples were collected at regular intervals at the CPC exit.

In laboratory experiments, 20 ml of 4-CP solution ($0.16\,mmol\,l^{-1}$) was magnetically stirred with $2.5\,g\,l^{-1}$ of TiO_2 in the dark for 60 min before irradiation in order to reach the equilibrium adsorption, similarly to solar experiments.

In all cases, the concentrations of pollutants and of their main degradation intermediates were determined using HPLC equipped with a UV-detector (set at 220 nm). In laboratory experiment a ODS-2 column of 250 mm long and 4.6 mm diameter was employed, whereas a RP-18 column of 150 mm long and 3.9 mm diameter was used in PSA experiment. The eluent was a methanol/water mixture (60%/40%) whose pH was adjusted at 3.

The overall TOC content of both dissolved and adsorbed organic molecules, was measured directly in the slurries by using a Heraus–Foss electric TOC-2001 apparatus. TOC was measured by IR after photochemical oxidation in presence of sodium persulfate, the inorganic carbon being removed by a previous acidification and O_2 purging. When CO_2 evolution is mentioned in PSA experiments CO_2 values are calculated from TOC, whereas in laboratory experiments, CO_2 was directly determined by GC (using a Intersmat IGC 120 MB chromatograph, equipped with a Porapak Q column, 3 m long and 6.3 mm i.d. at a temperature of 363 K).

3. Results

3.1. Comparison of the photocatalytic activities of various industrial TiO_2 photocatalysts in 4-chlorophenol degradation

3.1.1. Kinetics of disappearance of 4-chlorophenol

To compare the photocatalytic activities of different catalysts, the radiant flux has to be carefully taken into account, since it can strongly vary from one day to another, depending on the presence of clouds, as can be seen in Fig. 1(a–d). In these figures are represented the records of the global UV-fluxes as a function of local time for the different experiments on the disappearance of 4-chlorophenol in the presence of Degussa P-25, TiONA PC 10 (a Millennium Inorganic Chemicals sample from the range TiONA PC), Hombikat UV 100 and TiLCOM HC120 (a sample of Tioxide) catalysts, respectively.

On each curve, the local times corresponding (i) to the beginning of degradation and (ii) to the total disappearance of 4-CP are indicated by arrows. In the case of P-25 and TiLCOM HC 120 catalysts a quasi-linear initial increase of the global flux was observed, whereas for Hombikat UV 100 and TiONA PC 10 photocatalysts a low global flux was observed with steep variations due to short sunny periods during the cloudy days when the corresponding experiments were performed.

To compare the different activities, the disappearance of 4-CP is represented as a function of the expo-

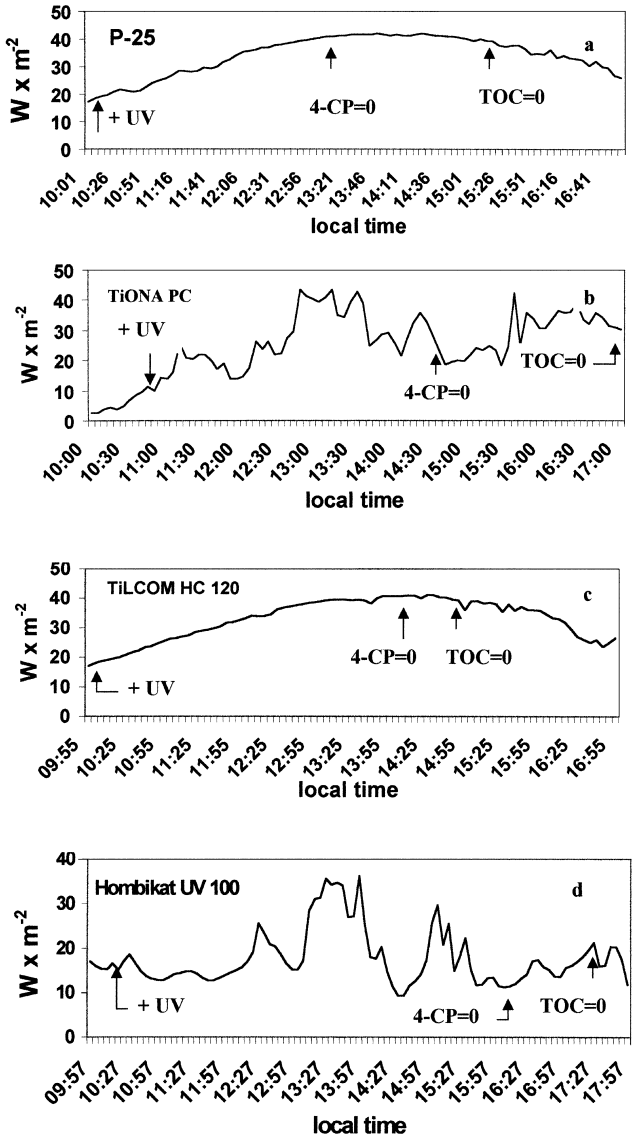


Fig. 1. Records of the global UV flux as a function of local time for the disappearance of 4-chlorophenol in the presence of P-25 (3 June 1997), TiONA PC 10 (4 June 1997), TiLCOM HC 120 (11 June 1997) and Hombikat UV100 (10 June 1997) catalysts.

sure (Fig. 2). Solar exposure is defined as the product of the residence time(t_R) by the corresponding instantaneous global flux. These values were calculated by considering small increments of Δt_R and the mean solar global flux measured during this period of time. The solar exposure at time t corresponds to the area below the curve $\Phi = f(tr)$. Thence, we get rid of the temporal variations of solar flux in cloudy days.

The dimensions in SI units actually correspond to $J\,m^{-2}$ but we conserved the units in $min\,W\,m^{-2}$ in conformity with the term exposure, first used in surface science (expressed in Langmuir or Torr) and then in catalysis (molecular exposure expressed in mol s [23]).

The activity pattern based on the rate of disappearance of the initial compound under solar exposure was:

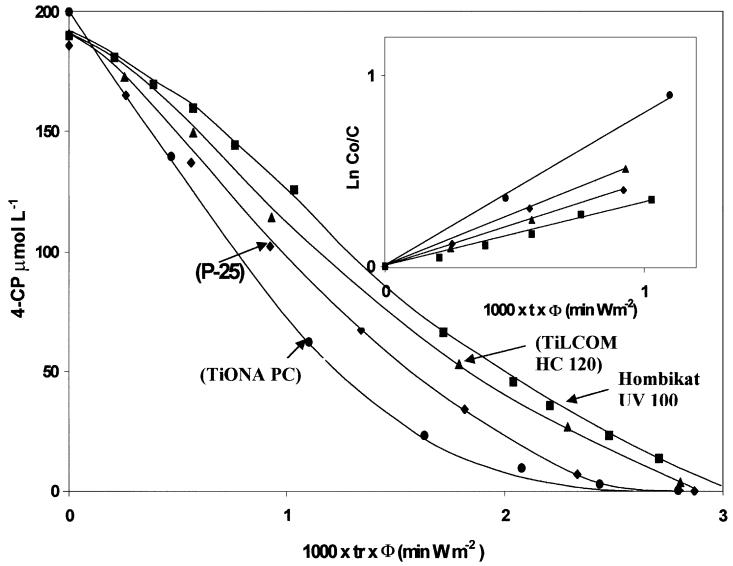


Fig. 2. Disappearance of 4-CP as a function of solar exposure in presence of P-25, TiONA PC 10, TiLCOM HC 120 and Hombikat UV 100 catalysts. The insert shows the linear transformation $\ln C_o/C = f(t_R \times \Phi)$. The exposure could also be expressed in $J\,m^{-2}$.

Table 2
Pseudo-first order rate constants of TiONA PC 10, P-25, TiLCOM HC 120 and Hombikat UV 100 photocatalysts

Catalyst	TiONA PC 10	P-25	Tioxide TiLCOM HC 120	Hombikat UV 100
$k \times 10^4$ ($min^{-1}\,W^{-1}\,m^2$)	7.5	5.5	4.0	3.5

$$\text{TiONA PC 10} > \text{P-25} > \text{TiLCOM HC 120} \geq \text{Hombikat UV 100}$$

The TiONA PC 10 photocatalyst has an activity about twice higher than Hombikat UV 100 and TiLCOM HC 120 and 1.4 times higher than that of P-25 which is the reference photocatalyst (Table 2).

All these catalysts have mainly the anatase structure. They essentially differ by their surface areas, their crystallite and particle sizes and their chemical of surface. It seems that the shorter the surface area, the more important the initial 4-CP photodegradation. At high surface area, no difference of photoactivity is observed between Hombikat UV 100 and TiLCOM HC 120 catalysts. This activity pattern is unexpected because if the nature of active site is the same for all catalysts, the biggest surface areas should be able to adsorb more organic compounds and therefore be more active [24]. Actually, the adsorption is more important for TiLCOM HC 120 than for Degussa P-25 and TiONA PC 10 catalysts (Table 3). About the same amount of 4-CP is adsorbed on both Hombikat UV 100 and TiLCOM HC 120 catalysts.

So, either the active sites are different and the sites of TiONA PC 10 catalyst would be about 1.4 times more active than those of Degussa P-25 and twice higher than those of Hombikat UV 100 and TiLCOM HC 120 catalysts, or a competition between the degradation of intermediate products and of the initial reactant occurs as discussed further.

Table 3
Surface coverage for TiONA PC 10, P-25, TiLCOM HC 120 and Hombikat UV 100 catalysts

Catalyst	Surface coverage (molecules per nm^2)
TiONA PC 10	1.8 ± 0.3
P-25	1.8 ± 0.3
TiLCOM HC 120	1.0 ± 0.3
Hombikat UV 100	0.5 ± 0.3

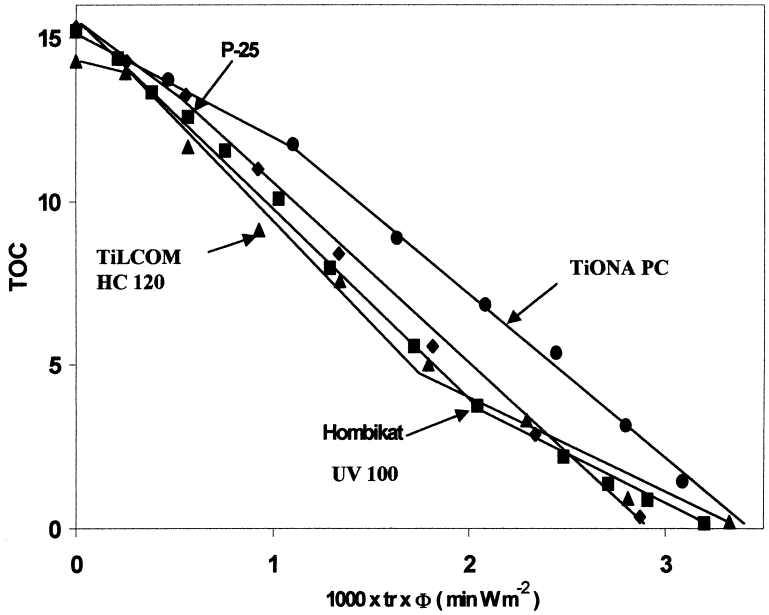


Fig. 3. Evolution of TOC as a function of solar exposure in presence of P-25, TiONA PC 10, Hombikat UV 100 and TiLCOM HC 120 catalysts. The exposure could also be expressed in $J\,m^{-2}$.

3.1.2. Kinetics of total mineralization

Fig. 3 shows the variations of TOC as a function of solar exposure. The times corresponding to the total mineralization have been indicated by arrows on Fig. 1(a–d). Several domains with different slopes were determined for each catalyst and the temporal comparison of activities became difficult. It can be observed that TiONA PC has the lowest initial activity in TOC disappearance. Between 20 and 70% conversions, the slopes of the linear section of the curves are approximately the same for the four catalysts.

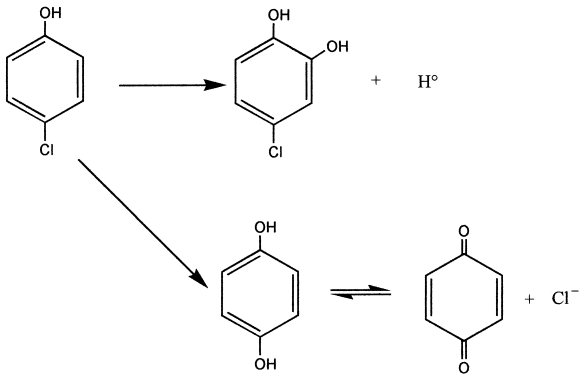
The activities of Hombikat UV 100 and TiLCOM HC 120 catalysts decrease at an exposure of ca. $2 \times 10^3\,min\,W\,m^{-2}$.

If one compares the solar exposures required for a total disappearance of TOC, the following activity pattern can be obtained:

$$\text{P-25} > \text{Hombikat UV 100} \approx \text{TiLCOM HC 120} > \text{TiONA PC 10}$$

3.1.3. Nature and evolution of intermediate products

Three intermediate products were detected in the solution: Hydroquinone (HQ), benzoquinone (BQ) and 4-chlorocatechol (4-CCT). The scheme of degradation is described below:



HQ and BQ were obtained with the four catalysts. However, 4-CCT was detected only with TiONA PC 10 and Degussa P-25 catalysts. This phenomenon does not correspond to a difference in the reaction mechanism which would vary with the nature of the photocatalyst. It must rather be ascribed to the difference in the total surface exposed. 4-CCT has an important adsorption constant ($1.5 \times 10^5\,l\,mol^{-1}$), whereas that of hydroquinone is negligible [25]. TiLCOM HC 120

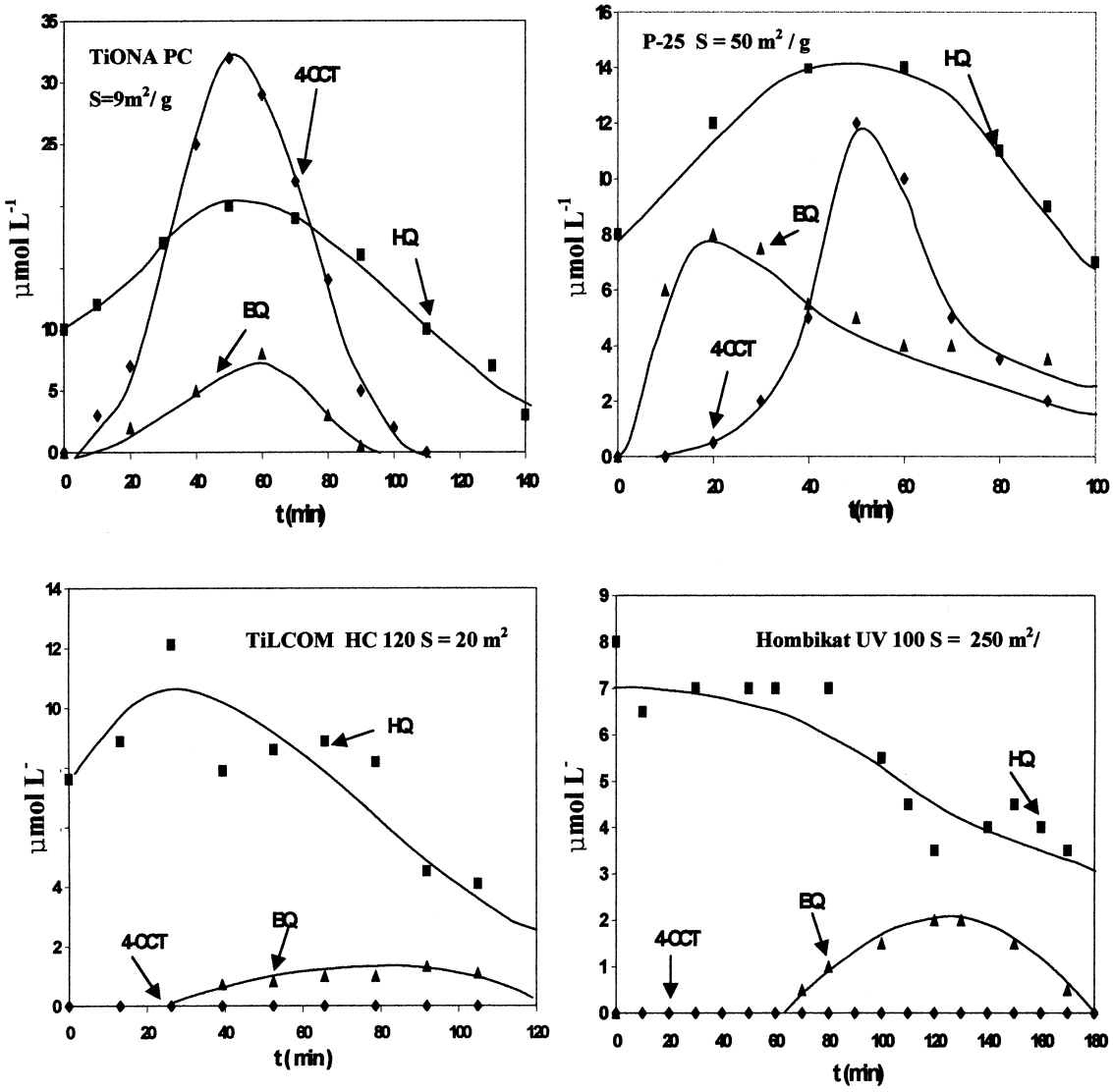


Fig. 4. Evolution of intermediate products (4-CCT: diamond, HQ: square, BQ: triangle) present in the solution with P-25, TiONA PC 10, Hombikat UV 100 and TiLCOM HC 120 catalysts in the degradation of 4-CP.

and Hombikat UV 100 catalysts have an important surface area and they probably totally readsorb all the 4-CCT produced as soon as it is evolved in the solution. By contrast, because of their lower total surface exposed, Degussa P-25 and TiONA PC 10 photocatalysts cannot adsorb all the 4-CCT produced despite its high adsorbtion contant. This is why it can be detected with a maximum occurring at $t_R = 50$ min (Fig. 4).

3.2. Comparison between solar and artificial irradiation in presence of TiO_2 P-25 catalyst

3.2.1. Kinetics of 4-CP disappearance: quantum yields

The kinetics of 4-CP disappearance determined previously in laboratory by D'Oliveira et al. [21] under artificial UV-light ($\lambda > 340$ nm) is of an apparent first

Table 4
Rate constants of 4-chlorophenol disappearance for TiONA PC 10 and P-25 catalysts in PSA and in laboratory experiments

Catalysts	k (PSA) $\times 10^4$ min^{-1} W^{-1} m^{-2}	k (laboratory) $\times 10^2$ min^{-1}
TiONA PC 10	7.5	6
P-25	5.5	4
$k_{\text{TiONAPC10}}/k_{\text{P-25}}$	1.3	1.4

order. In the presence of solar light the 4-CP disappearance as a function of the residence time seems to be of the zero order (Fig. 5a). However, the solar flux was not constant during the run, and varied between 16 and 40 W m^{-2}. If one uses the exposure to take into account the variation of the solar light flux, an apparent first order kinetics is obtained. Therefore, whatever be the irradiation source, the same apparent kinetic order is observed.

The time necessary for 4-CP total disappearance is approximately the same in laboratory experiments with artificial light as that obtained at the Plataforma Solar. However, it is difficult to compare directly the rate constants because UV-spectra are different. The only possibility to compare their rates of disappearance is to determine the apparent quantum yield which is the number of molecules degraded per time unit and per absorbable photons reaching the surface during the same time. In the case of solar light, the apparent quantum yield determined would correspond to a lower limit of the true one, since all the incident solar photons are taken into account and not only those absorbable by titania.

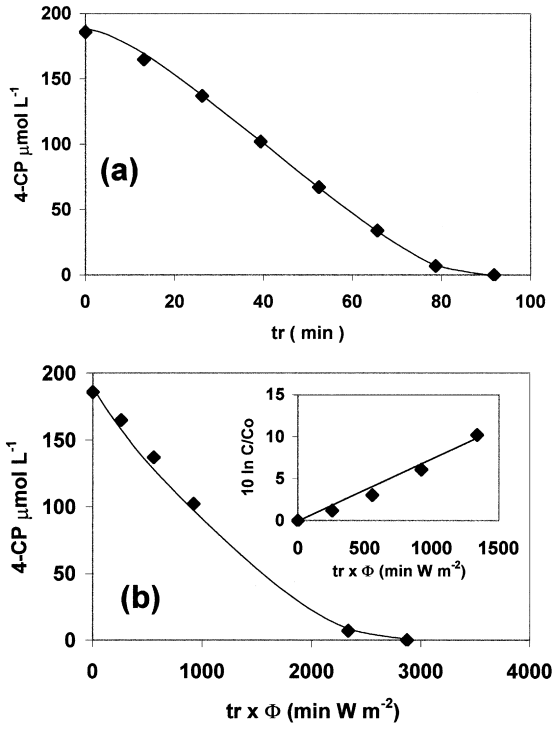


Fig. 5. Disappearance of 4-CP by solar irradiation of P-25 catalyst as function of irradiation time (a) and as a function of solar exposure. First order linear transform $\ln C_o/C = f(t_r \times \Phi)$ in the insert (b). The exposure could also be expressed in J m^{-2}.

The global photonic flux calculated in [22] is equal to 1.4×10^{-4} Einstein m^{-2} s^{-1} for a global UV-light flux of 46 W m^{-2}. The apparent quantum yield was found equal to 1.3% for both experiments.

The rate constants for TiONA PC 10 and Degussa P-25 TiO_2 catalysts remain in the same ratios (Table 4), although the irradiation sources, the amounts of TiO_2 as well as the reactor design are quite different.

3.2.2. Kinetics of TOC and of intermediate product disappearance

An important time difference is observed in both experiments to reach a total TOC disappearance (Fig. 6). At PSA, only 1.5 h are required, whereas more than 5 h are necessary in laboratory experiments. However, this difference is probably due to the reactor design and not to the nature of the irradiation source. Actually, for the same number of photons received, the conversion obtained at the end of one pass at the exit of the irradiated part of the recirculation photoreactor is higher than that obtained in a batch photoreactor of the same size. Therefore, the suspension recycled at the end of one pass is strongly depleted in pollutant and in its main intermediate degradation products. The reservoir connected to the reactor is thus fed with an already relatively cleaned suspension, which explains that fewer intermediates are detected in this type of reactor.

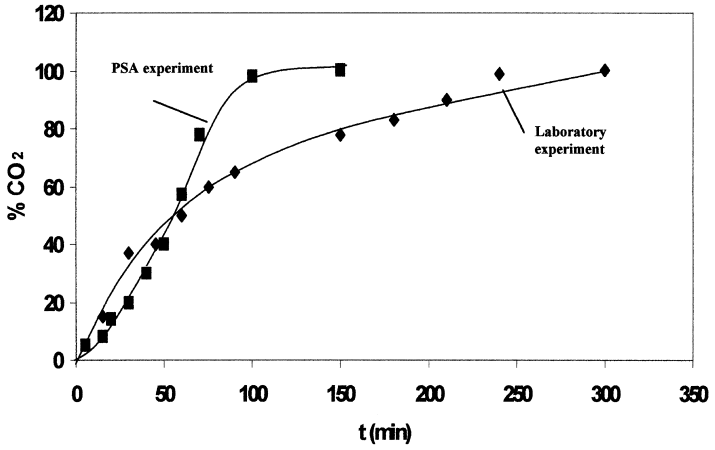


Fig. 6. Mineralization of 4-CP in presence of P-25 in laboratory experiment (artificial light) and at PSA (solar light).

The smaller total amount of identified aromatic intermediate products detected in the solution in PSA is in agreement with this hypothesis (Fig. 7a and b)). However, as previously observed, the concentration in TiO_2 also plays a role in the quantity of aromatic intermediate products detected. In the case of solar degradation the amount of TiO_2 used is 12 times smaller. This could explain the presence of 4-CCT obtained in that case. In addition, the reactor design plays a more important role than the amount of TiO_2 on the total amount of intermediate products temporarily released in the solution.

4. Discussion

The photocatalytic activities can be estimated with two kinetic parameters: (i) the rate of the initial pollutant disappearance and (ii) the rate of TOC disappearance.

The activity pattern for 4-CP disappearance was:

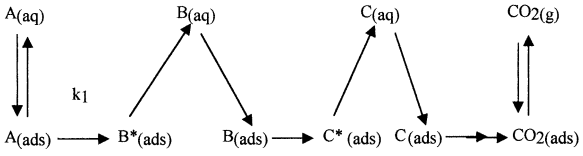
$$\underset{(1)}{\text{TiONA PC 10}} > \underset{(0.73)}{\text{P-25}} > \underset{(0.46)}{\text{TiLCOM HC 120}} \approx \underset{(0.53)}{\text{Hombikat UV 100}}$$

The numbers indicated below correspond to the relative activities, unity being given to TiONA PC 10 catalyst.

Although TiO_2-TiONA PC 10 has the smallest BET surface area, it is the most active in 4-CP disappearance. This means that, once attained the adsorption equilibrium in the dark, it is the most efficient in absorbing a given global UV-flux, in creating electron–hole pairs, in separating them to let electron be trapped by chemisorbed oxygen as O_2^- species and holes create $OH^\bullet$ radicals, according to:

$$OH^- + p^+ \rightarrow OH^\bullet$$

If one considers the rate of TOC disappearance, the classification is different. The kinetic curves of TOC disappearance, plotted as a function of the energetic exposure, have a sigma shape more complex to analyze. If one considers that the temporal variations of TOC are the opposite of that of CO_2 evolved, the curves $TOC = f(t_R \times \Phi)$ correspond to typical ascending sigma-shaped curves relative to CO_2, which have been discussed in [18]. CO_2, as a final product, results from a rake mechanism initially proposed in [26] and modified in the case of photocatalysis [23].



Because of the many intermediate products detected, the long process of photodegradation requires a large number of adsorption sites, not only for the initial pollutant but also for all its fragments. It can therefore be easily conceived that the higher the spe-

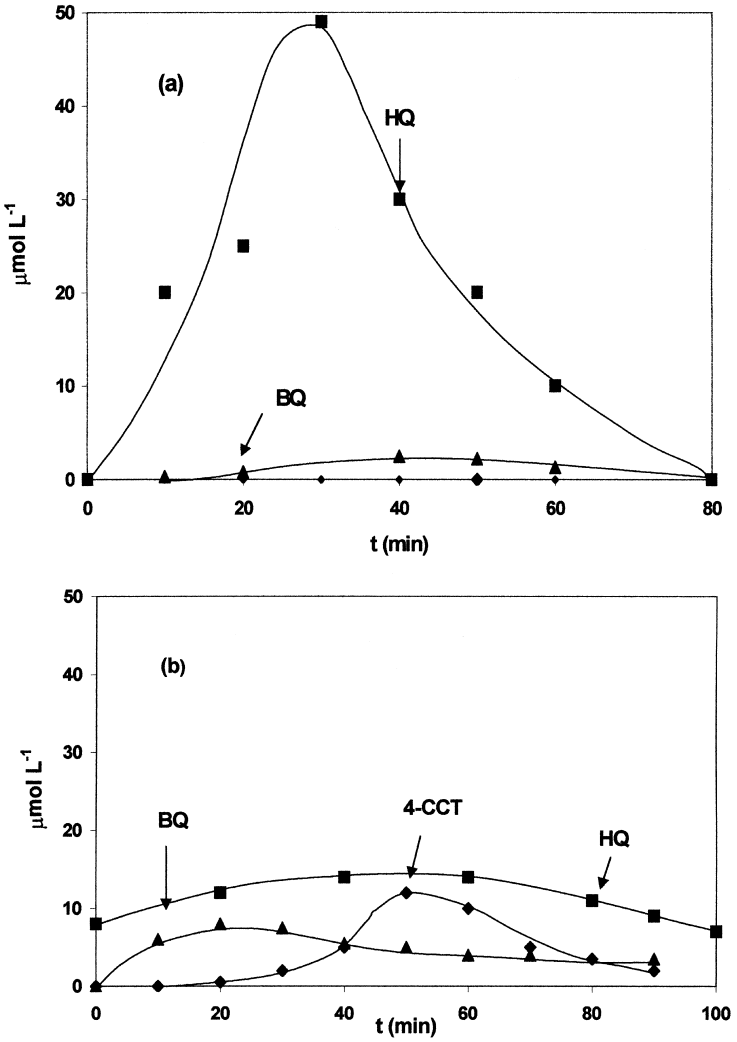


Fig. 7. Evolution of intermediates of 4-CP degradation in laboratory (a) and in PSA (b) experiments.

cific area, the higher the efficiency in destroying all the sequential intermediate products. CO_2 is more rapidly formed with the highest surface area catalysts.

From Fig. 3, it can be seen that during the time necessary to convert ca. 70% of TOC, the conversion pattern was the following:

$$\underset{(120\,m^2/g)}{\text{TiLCOM HC 120}} \geq \underset{(250\,m^2/g)}{\text{Hombikat UV 100}} \geq \underset{(50\,m^2/g)}{\text{Degussa P-25}} > \underset{(9\,m^2/g)}{\text{TiONA PC 10}}$$

This pattern follows the order of the specific areas, except for TiLCOM HC 120 which appears slightly more active than Hombikat UV 100 whose specific area is twice higher. This observation could be explained by a 'quantum size effect' ([27,28] and references therein). When the particles become too small, there is a 'blue shift' with an increase of the band gap energy, detrimental to the near UV-photon absorption, and an increase of the electron–hole recombination. Too high specific area is not beneficial for an optimum efficiency and this explains why TiLCOM HC 120 is slightly more active than Hombikat UV 100, despite its lower surface area.

The decrease in activity observed for Hombikat UV 100 and TiLCOM HC 120 catalysts after the disap-

pearance of 70% of TOC is probably due to a low superficial density of pollutant (in molecule per nm^2). Therefore, the probability of e^-/h^+ recombination becomes higher than that of the reaction of these species with the reactants.

An ultimate comparison could be done by comparing the final times necessary for a complete disappearance of TOC. One gets

$$\text{Degussa P-25} > \text{Hombikat UV 100} \approx \text{TiLCOM HC 120} > \text{TiONA PC 10}$$

This confirms that Degussa P-25 despite of its 'moderate' specific area ($50\,m^2\,g^{-1}$) remains a very efficient photocatalyst.

5. Conclusion

The TiONA PC 10 catalyst presents a higher activity for 4-CP disappearance than the other industrial catayst (Degussa P-25, TiLCOM HC 120 or Hombikat UV 100). However, because of its smaller surface area, the rate of readsorption of the intermediate products released in the solution is lower, thus decreasing the subsequent total mineralization. In the future, it will be attempted to synthesize a TiONA PC solid as efficient in reducing the TOC as in degrading 4-CP.

In a complex reaction, the catalytic activity has to be examined at least with two parameters, such as the initial rate of disappearance of the pollutant and the total conversion into CO_2. The physical characteristics of each solid intervene in the kinetics. Besides a good UV-light absorption, an optimum efficiency would be obtained with a surface area combining a large adsorption and a limited electron–hole recombination.

The comparison between experiments obtained either in a solar pilot reactor or in a microreactor working with artificial UV-light gives the same first order kinetic law for the pollutant disappearance, and a comparable quantum yield. Moreover, the activity pattern for the different catalysts tested was the same. However, a more efficient TOC disappearance and the presence of fewer intermediates in solution despite of a smaller concentration of TiO_2 were observed in the solar reactor. This phenomenon is probably due to the reactor design.

In the solar reactor, the total organic carbon disappearance was reached within less than half an hour. If we consider that about 9 h of solar irradiation are available per day, 1500 l of a solution contaminating $25\,mg\,l^{-1}$ of organic compound could be treated daily.

Acknowledgements

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