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Relationship between TiO_2 particle size and reactor diameter in solar photoreactors efficiency

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Abstract

The optimal experimental conditions for photocatalysis are determined for a cylindrical non-concentrating photoreactor using a TiO_2 catalyst suspension using technical grade Imidacloprid (50 mg/l) as a model compound, two different particle sizes (obtained by several preparation protocols) of the same TiO_2 (Degussa P25) and three concentrations (50, 200 and 500 mg/l) to test the optimal TiO_2 concentration. Three inner diameters of reactor were also tested for the best dimension for each catalyst concentration. These experiments have demonstrated that the optimum conditions tested were 2.55 cm inner diameter, 200 mg TiO_2/l and 300 nm mean particle size. At the same time, the influence of the relationships between the three parameters studied (catalyst concentration, particle size and reactor diameter) is discussed.

Keywords: Solar photocatalysis; Imidacloprid; Titanium dioxide; Colloidal suspension; Photoreactor efficiency

1. Introduction

In the last few years, research on new methods for advanced wastewater treatment has progressed from processes involving only phase transfer of a contaminant to its complete destruction. The latest possibility of applying heterogeneous photocatalysis, the removal of organics from water, is being investigated all over the world [1].

Particulate suspensions of TiO_2 irradiated with natural solar light catalyses the oxidation of organic contaminants. Developments in the field of the chemical treatment of water have made several oxidative degradation procedures available for the elimination of pesticides. One of the more promising methods is the use of TiO_2/ultraviolet solar radiation [2–4]. Previous work [5–11] has shown that suspensions of titanium dioxide particles in an aqueous medium are more efficient than the same catalyst fixed to a film. In two similar reactors, the catalyst area is clearly higher in the first case than in the e second. This paper focuses on the influence of the catalyst particle diameter, using commercial TiO_2 (Degussa P25) suspended in water, on the decomposition of an insecticide. The chosen insecticide is Imidacloprid. Imidacloprid is a new systemic insecticide of the chloronicotinyl group, used in soil, seeds and foliage for the control of sucking insects. It is most commonly used for rice, cereal, maize, potatoes, and other vegetables. The chemical works by interfering with transmission of stimuli in the insect's nervous system by causing blockage in a type of neuronal pathway that is more abundant in insects than in warm-blooded animals.

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Photocatalytic efficiency in this type of process can be measured directly by obtaining the quantum yield or its efficiency in producing a given oxidizable product [12–15]. The quantum yield is defined as the ratio between the total number of molecules oxidised and the total amount of photons absorbed. It is determined by the competition between reactions in which electrons and holes participate and their recombination. The electrons reduce electron acceptors, and the holes created oxidise electron donors. Electron reactions with oxidised products and those of holes with the reduced products might also be considered in the quantum yield. Evaluating all those processes for a spherical catalyst particle (R = radius), Gerischer [13,14] obtained several quantum yield (ϕ) expressions that take into account the superficial recombination of pairs ($\phi \propto R^{-1/2}$), inner recombination ($\phi \propto R^{-1}$ or $\phi \propto R^{-2}$) and reverse reactions ($\phi \propto R^{-1/2}$). All these situations have been studied theoretically as a function of particle radius and the very complex expressions obtained are of interest in that in all cases, the quantum yield increases with decrease in radius. As the radius is highly related to mean particle size in colloidal suspensions, this work evaluates (among other aspects) the effect of particle size on the rate of degradation of an organic compound.

In photocatalytic reactors, the number of photons adsorbed is difficult to assess experimentally because of reflection, scattering, transmission and absorption by suspended particulates, so that using quantum yield is very often impossible [15]. Since, as in catalyst suspensions, the quantum yield depends strongly on the catalyst concentration, initial substrate concentration, nature of the catalyst particle, the reactor design and/or geometry, the light intensity, the temperature, the pH and the chemistry of the substrate [15], an attempt was made to keep almost all these variables constant. The photocatalytic reactions were carried out with natural, non-concentrated, solar UV light. Although this factor can not be kept steady, the experiments were carried out under perfectly sunny conditions at the same time of year and a corrective equation (Eq. (1)) was used. The same initial concentration of substrate was always used so that any influence of its concentration could be discarded. The same commercial TiO_2 powder was employed in all the experiments. Since the geometry of the reactor is also a determinant factor in the reaction efficiency [15], a cylindrical reactor in which only the diameter varies was used, because cylindrical reactors are the most commonly used in solar energy devices and chemical reactors and they facilitate circulation of the fluid [16]. Although the temperature was not fixed, all the experiments were performed at ambient temperature (25–30°C), at the same time of day and year. The initial pH was always the same in the experiments and its evolution during degradation is almost parallel in all the tests. Thus experimental variables are reduced to catalyst concentration, reactor diameter and particle size.

This work is therefore intended to contribute to finding the optimal conditions of TiO_2 particle concentration for each reactor diameter, or the optimal reactor diameter for each concentration of particles, by diminishing the number of experimental variables.

2. Experimental section

2.1. Photoreactors

Each reactor is a Pyrex glass cylinder. The three reactors (dimensions shown in Table 1), located outdoors in the sun, but avoiding shadows between them, were in vertical position perfectly aligned east–west and facing south. The illuminated area is the cross-section of the tubes (see Table 1) since no reflector is used.

At the beginning of the experiments, the water, TiO_2 powder and pesticide were mixed to constant concentration. When the experiments evaluated the effect of particle size, mixing was by ultrasonic bath for 10 min. A black cover was employed during the preparation protocol to avoid light entering the reactors. Afterwards, the cover was removed and the samples were collected at predetermined times. The liquid suspension was stirred throughout the experiment to ensure the homogeneity of the suspensions. All the experiments were carried out in pairs for reproducibility of results.

2.2. Materials and reagents

The chemical structure of the pesticide selected (Imidacloprid) is given in Fig. 1. The IUPAC name of this pesticide is 1-(6-chloro-3-pyridylmethyl)-*N*-nitroimi-

Table 1
Geometrical characteristics of the cylindrical reactors employed in the experiments

	Inner diameter (cm)	Volume (*L*)	Area of cross section (cm^2)	Height (cm)
Reactor 1	2.55	0.5	249.6	98
Reactor 2	7.60	0.5	83.6	11
Reactor 3	15.00	3.0	255	17

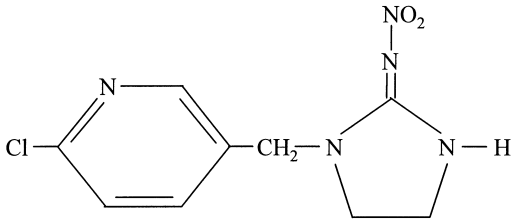

Fig. 1. Chemical structure of Imidacloprid.

dazolidin-2-ylideneamine. The oral dose of technical-grade Imidacloprid that resulted in mortality to half of the test animals (LD50) is 450 mg/kg body weight in rats and 131 mg/kg in mice [17].

This insecticide is highly soluble in water (0.51 g/l at 20°C) with a stability of >30 days between pH 5 and 11. The experimental technical-grade Imidacloprid (97.9%) was supplied by Bayer AG (Leverkusen, Germany). Imidacloprid analytical standard (99.7%) was purchased from Dr. Ehrenstorfer (Augsburg, Germany). It was used as a model compound because it is a complex molecule containing several chemical structures. Its photocatalytical degradation with solar illumination has been studied previously by Agüera et al. [18]. In these experiments, 50 mg/l of Imidacloprid was always used.

The photocatalyst, Degussa P25 titanium dioxide (Frankfurt, Germany) was used as received (surface area 50–55 $m^2\,g^{-1}$). Transmission electron microscopy (TEM) measurements have shown irregularity shaped particles and photon correlation spectroscopy (PCS) revealed high polydispersity [19]. Three catalyst concentrations have been employed: 50, 200 and 500 mg/l. Analytical grade HCl was employed. Water having a conductivity of $<10\,mS\,cm^{-1}$ and organic carbon of $<0.5\,mg\,l^{-1}$ obtained from the PSA Desalination Plant (a multi-effect evaporation system using solar energy) was used in all the experiments.

2.3. Hydrodynamic size

The titanium dioxide employed in the photocatalytic experiments is disposed as a colloidal suspension. The great difference between considering the TiO_2 from dry powder and TiO_2 particles suspended in an aqueous medium is the mean size of the particles. Although TEM measurements have shown P25 to have 30–40-nm particles, PCS measurements give information about the particle size in colloidal state, which is of interest in this system. Therefore, the hydrodynamic size could be defined as the particle diameter measured in liquid suspension from the diffusion coefficient of the particle by the photon correlation spectro- scopy technique. Besides, due to the high polydispersity of the samples, we have defined 'mean particle size' as the average of the hydrodynamic size obtained in different PCS measurements. The irregular shape of particles could explain the different particle sizes obtained by TEM and PCS. Obviously, the mean particle size obtained by PCS does not correspond with surface area (50–55 $m^2\,g^{-1}$) because this is obtained with dry samples and PCS with liquid suspensions. The polydispersity can be observed in the inset of Fig. 2. Mean particle size of the titanium dioxide in suspension in the presence of Imidacloprid was measured with a Zetamaster-S (Malvern Instruments). TiO_2 was dispersed following two different protocols: sonicating for 10 min [19] and maintaining constant agitation during PCS measurements, in the case of *sonicated samples*; and stirring all the time in the case of *agitated samples*. The samples were prepared with 50 mg/l of Imidacloprid at several concentrations of TiO_2 (50, 200 and 500 mg/l) at the different pHs expected during the degradation experiments. The particle mean-size measurements remained constant for 53 h. The mean particle size obtained during the assays (at different pHs) are plotted in Fig. 2, where the error bars are obtained from the statisti-

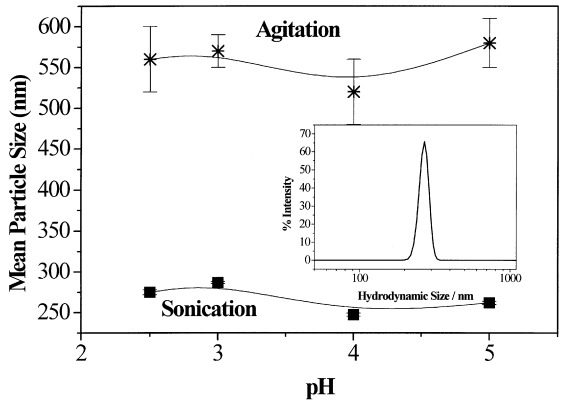

Fig. 2. Mean particle size of TiO_2 particles in colloidal suspension as a function of pH. Agitation (*) and sonication (■). The inset figure shows the hydrodynamic size distribution of TiO_2 particles in colloidal suspension. Sonicated sample at pH∼5.

cal dispersion of all the average measurements. These measurements were repeated several times during the degradation experiments to confirm particles size stability. The pH evolution during Imidacloprid degradation experiments was always very similar: from pH 5 (initial) to pH around 2.5 at the end.

2.4. Analytical determinations

Imidacloprid mineralization was followed by total organic carbon (TOC) analysis. The TOC determinations were carried out using direct injection of the samples into an Heraeus-Foss Electric TOC-2001 (Hanau, Germany, UV-peroxydisulphate method, EPA 415.1). Imidacloprid concentration was determined after 1 : 1 dilution with acetonitryle and filtration (0.45 μm) of aqueous TiO_2 slurries by HPLC-UV (Hewlett-Packard, series 1050) with a C-18 column (Merck, LiChroCART RP-18, 5 μm, 4 × 125 mm). The chromatographic conditions were 75%/25% water pH 3/acetonitrile at 1 ml/min at 270 nm. With this method the concentration of Imidacloprid may be quantified with total confidence to 0.5 mg/l (quantification limit, LOQ) and its presence may be detected in concentrations of over 0.04 mg/l (limit of detection, LOD). The accuracy of the measurements is ensured by calibration with Imidacloprid (standard analytical grade, Riedel).

2.5. Evaluation of solar radiation

Solar ultraviolet radiation (UV) is a highly important parameter for the correct treatment of data obtained from solar photocatalytic experiments. A global-UV radiometer (KIPP&ZONEN, model CUV3) with typical sensitivity of $264\,mV\,W^{-1}\,m^2$, placed on a horizontal platform, provides data in terms of UV solar energy power incident per unit area ($W\,m^{-2}$). The amount of energy collected by the reactor (per unit of area) from the start up of the experiment until each sample is collected may be found by

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n\,\overline{UV}_{G,N}$$
$$\Delta t_n = t_n - t_{n-1} \quad (1)$$

where t_n is the experimental Δt_n time of each sample, $\overline{UV}_{G,n}$ is the average during Dtn and Q_{UV},n is the accumulated energy (per unit of area, $kJ\,m^{-2}$) incident on the reactor for each sample taken during the experiment. Consequently, when Q_{UV} is used, the reaction rate in the initial stage of the photoreaction ($r_{Q,0}$) is expressed in terms of $mg\,l^{-1}\,m^2\,kJ^{-1}$. However, sometimes it is necessary to explain the results in terms of illumination time instead of Q_{UV}. For this purpose it may be assumed that the average solar UV on a perfectly sunny day is about $25\,W\,m^{-2}$. Under these conditions $1\,kJ\,m^{-2}$ is equivalent to 40 s illumination time.

3. Results

3.1. Particle sizing

The oxide/electrolyte interface has an electrical surface charge, which strongly depends on the pH of the medium. The electrokinetically mobilised charge is a determining parameter in the colloidal stability of the oxide particle suspensions. This involves the study of particle sizing depending on the pH; if the pH is equal to the point of zero charge (PZC) the particles aggregate and ensembles are larger [19]. The hydrodynamic particle-size measurements are presented in Fig. 2. These measurements ensure that modifying preparation of samples has varied the catalyst particle area exposed to the photocatalytic process. Particle

size in samples prepared with the sonication protocol is smaller than particles dispersed by agitation regardless of pH. The surface area in the sonicated suspensions is clearly at least four times higher that the others. Better efficiency may be expected in experiments performed with the suspensions dispersed with ultrasound.

3.2. Imidacloprid degradation

A Langmuir–Hinshelwood kinetics (L–H) model is commonly used for quantitative descriptions of the gas-solid reactions between two adsorbed reactants that take place on the interface of the two systems. It has also been efficient as a standard quantitative description of liquid–solid reactions [20,21]. Extrapolation of the L–H model for liquid–solid reactions requires some modification for a TiO_2 solid surface in aqueous suspension, since hydroxyl groups and water molecules cover it. Rigorous analysis of the kinetics [22,23] in the photocatalytic oxidation of organic compounds by irradiated semiconductors distinguishes four possible situations: (i) the reaction takes place between two adsorbed substances; (ii) the reaction occurs between a radical in the solution and the adsorbed substrate; (iii) the reaction takes place between the radical linked to the surface and the substrate in the solution; and (iv) the reaction occurs with both species in solution. In all cases, the expression of the equation rate is similar to the L–H model. But with kinetic studies only, it is not possible to find out whether the process takes place on a surface or in a solution [24,25].

Therefore, for the standard L–H data treatment, it is assumed that the reaction occurs on the surface, which is also the assumption most widely accepted as possible. Under these conditions, two extreme situations [26] are defined to illustrate the adsorption on the catalyst surface: (I) Imidacloprid and water compete for the active sites of the catalyst and (II) the reactant and the solvent are adsorbed on the surface without competing for the same active catalyst sites. It should be emphasised that Imidacloprid photodecomposes giving rise to intermediates [18], which could also be adsorbed, competitively on the surface of the catalyst. The concentration of these intermediates varies throughout the reaction up to their mineralization. The reaction rate may thus take the following form [21]:

$$r = -\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{k_r K C}{1 + KC + \sum_{i=1}^{n} K_i C_i}, \quad (i = 1, n) \tag{2}$$

where i is the number of intermediates formed during degradation (the solvent is also included in the summation), k_r is the reaction rate constant, K is the reactant (Imidacloprid) adsorption constant, C is the Imidacloprid concentration and C_i is the intermediate concentration at any time. Without considering the concentrations of the intermediates, Eq. (3) can be obtained:

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{k_r K C}{1 + KC} \tag{3}$$

By integrating Eq. (3), the next expression is obtained:

$$\ln\left(\frac{C_0}{C}\right) + K k_r (C_0 - C) = K k_r t \tag{4}$$

If the initial Imidacloprid concentration is very small, Eq. (4) can be approximated to the following form:

$$\ln\left(\frac{C_0}{C}\right) = K k_r t \tag{5}$$

Obviously, as explained in the Section 2.5, Q_{UV} can substitute time (t). In that case, the proportionality constant is redefined as k_{ap}:

$$\ln\left(\frac{C_0}{C}\right) = k_{\mathrm{ap}} Q_{\mathrm{UV}} \tag{6}$$

So if $\ln(C_0/C)$ is plotted versus Q_{UV}, the slope is the apparent reaction rate constant k_{ap}. Furthermore, during the initial stages of degradation, the initial rate is defined by Eq. (7):

$$r_{Q,0} = \left(\frac{\Delta C}{\Delta Q_{\mathrm{UV}}}\right) \tag{7}$$

Eq. (7) means that the initial rate of photodegradation has been calculated as the slope of Imidacloprid concentrations plotted versus accumulated UV energy (Q_{UV}) with the points of initial linear fit. The degradation experiments can be evaluated by comparing the values obtained for $r_{Q,0}$ and/or for k_{ap}. Obviously, the good linear fit of the experiment to Eq. (6) indicates that all the experiments may be compared using k_{ap}.

The results of a degradation experiment carried out in Reactor 1 with two catalyst conditions at a concentration of 200 mg/l: small particles (sonicated samples)

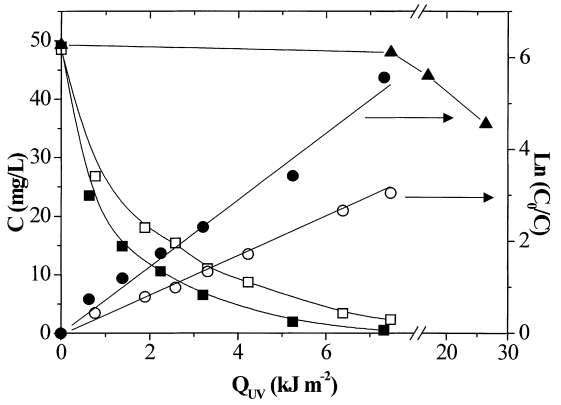

Fig. 3. Disappearance of Imidacloprid (Reactor 2) versus accumulated UV energy. [TiO_2] = 200 mg/l, pH_0 = 4, sonicated (■,●) and stirred (□,○) samples in. Imidacloprid photolysis (without TiO_2) versus accumulated UV energy (▲). ln(C_0/C) as a function of the accumulated UV solar energy is indicated in right axis (circles).

and large particles (stirred samples), are presented in Fig. 3. This figure shows the relevance of considering the logarithmic slope instead of the initial rate of degradation ($r_{Q,0}$) of the experiment. The slight differences from the comparison of $r_{Q,0}$ observed are more evident when k_{ap} is used. Nevertheless, the initial rate is not a negligible parameter and the results will be explained here by studying the behaviour of both values. Disappearance of Imidacloprid during photolysis was tested in a very long experiment (Fig. 3) in which it may be concluded that disappearance of Imidacloprid during photocatalytic degradation is due only to solar UV/TiO_2 photocatalysis.

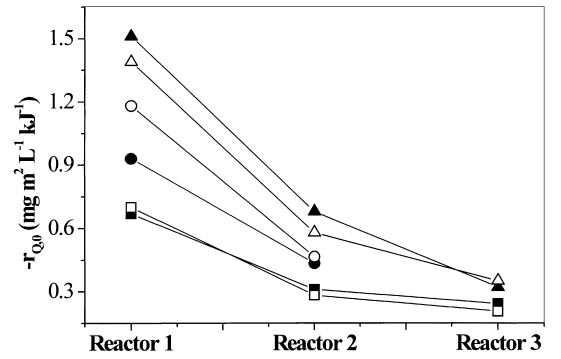

Fig. 4. Initial degradation rate ($r_{Q,0}$) as a function of the reactor diameter for different concentrations of TiO_2: 50 mg/l (sonication ■, agitation □), 200 mg/l (sonication ▲, agitation △) and 500 mg/l (sonication ●, agitation ○).

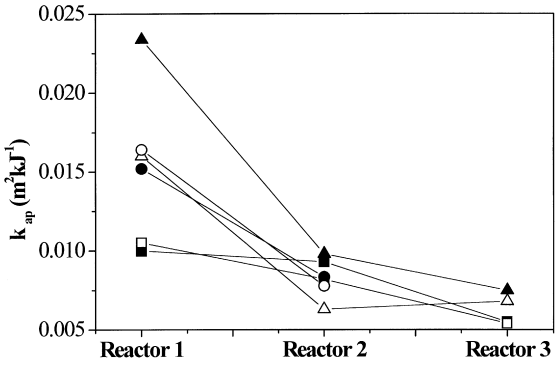

Fig. 5. First order kinetic constant (k_{ap}) as a function of the reactor diameter for the same experiments described in Fig. 4.

Fig. 4 shows the initial rates calculated as Eq. (7) indicates. The resulting modification of the particle surface during the experiment (agitation or sonication of samples) and variations in particle concentration (50, 200 and 500 mg/l of TiO_2) are studied in each reactor under several experimental conditions. Fig. 5 shows the same experiments, but using k_{ap} as crucial parameter. It may be observed that the effect of the experimental conditions in the initial stages and in total degradation is very similar.

4. Discussion

4.1. Effect of particle size

Fig. 3 shows a general tendency of the sonicated samples to a higher reaction rate, which agrees with the arguments of Gerischer et al. [13]. In this case, it is not possible to talk about particle radius, because TiO_2 powder is irregularly shaped, and when it is dispersed in an aqueous medium the 'particles' (300–600 nm sized) are clusters of primary particles (20–40 nm sized), not spherical or monodisperse. Hydrodynamic size only gives an idea of the order of magnitude of the particle diameter under the actual experimental conditions. However, particle radius can be associated with this particle size by Gerischer's comment [13].

If all the experiments carried out in all the reactors with each catalyst concentration and with small and more widely dispersed particles were compared to each other, some differences in effectiveness would

be noted in the degradation rate. As mentioned before, the initial rate ($r_{Q,0}$) is not a suitable parameter for this kind of comparison, because the different behaviour of the suspended particles is manifested throughout the period of the experiment. Therefore, the differences observed for $r_{Q,0}$ are amplified using k_{ap}. This effect may be analysed in Fig. 5, which clearly shows that small particles yield higher efficiencies than larger particles in Reactors 1, 2 and 3 with $[TiO_2] = 200$ mg/l and very similar efficiencies in the rest of the assays. Particle size affects some particular cases more than others do. As will be seen later, particle size, reactor diameter and particle concentration are correlated in the same way since they determine the behaviour of light passing through colloidal suspensions.

4.2. Effect of reactor diameter

In order to examine the problem from the point of view of reactor dimension, the effects of the different reactors (each with the same geometry) are compared in Figs. 4 and 5, where it may be observed that Reactor 1 is the best in all cases, especially for 200 mg/l of TiO_2. For a given catalyst concentration, Reactor 1 always yields the fastest reaction. Reactors 2 and 3 have similar reaction rates, although Reactor 3 is the worst in all cases.

4.3. Effect of TiO_2 concentration

Figs. 4 and 5 indicate that for the three reactors, when ultrasound is used for dispersing the samples, the best concentration is 200 mg/l. The experiment performed with 50 mg/l in Reactor 1 is very slow because of the loss of photons due to the small diameter of the reactor. In Reactors 2 and 3, for a 50-mg/l catalyst concentration, the long path length attenuates the loss of photons, so $r_{Q,0}$ and k_{ap} are similar in those reactors at that concentration. When catalyst concentration is 500 mg/l, the loss of photons has an inverse effect, as light absorption and extinction due to the length of path in the reactor produces loss of UV energy.

4.4. Relationship between particle size, reactor diameter and TiO_2 concentration

There are a number of studies in the literature on the influence of catalyst concentration on process efficiency. Although the results are quite different, it may be deduced from all of them that incident radiation on the reactor and length of path inside the reactor are fundamental in determining optimum catalyst concentration:

- If the lamp is inside, but the path length is short (1–2 cm max.), r_{max} is obtained with 1–2 g l^{-1} of TiO_2 [7,24,27–33].
- If the lamp is outside, but the path length is several centimetres long, as in a reactor illuminated by solar radiation, the appropriate catalyst concentration is several hundred milligrams per liter [34–38].

In these extracts, only the reactors used by Ahmed et al. [27] and Pacheco et al. [37] correspond to reactors illuminated by solar UV. In all the cases described above, a 'screening' effect is produced when the TiO_2 concentration is very high. The reaction rate diminishes due to the excessive opacity of the solution, which prevents the catalyst farthest in from being illuminated. According to Ollis [36], 1 g l^{-1} of catalyst reduces transmissivity to zero in a 1-cm inner diameter cylinder. For the reactors studied, it is therefore necessary to find out the optimum catalyst concentration experimentally. That is, the minimum concentration at which the maximum reaction rate is obtained. But it does not seem to be necessary to test concentrations over 1 g l^{-1} [39,40].

Although it is not the object of this work to evaluate this loss of light, this effect is one of the key factors in the interpretation of those results. When the catalyst concentration is very high, after travelling a certain distance on an optical path length, turbidity impedes further penetration of light in the reactor. Obviously, the same reasons that justify the results obtained are qualitative. The percentage of photons absorbed by the suspension and the percentage of photons scattered by the TiO_2 particles is a very complex problem that cannot be solved experimentally [15], but must be estimated.

The optical behaviour of colloidal dispersion of Degussa P25 TiO_2 has been studied by Cabrera et al. [41] who have demonstrated that the scattering coefficient is always more than two thirds of the extinction coefficient at wavelengths between 275 and 405 nm (extinction coefficient = absorption coefficient + scattering coefficient). The solar UV spectrum radiates on a 300 to 400 nm wavelength. Taking light extinction in the UV range estimated by Cabrera

Table 2
Optical path length for extinction of the 99% (Eq. (8)) of the total light intensity (375 nm) inside sonicated samples of TiO_2 Degussa P25 vs. concentration of catalyst

$[TiO_2]$ (mg/l)	L_{99} (cm)
50	4.13
200	1.03
500	0.41

et al. [41] and the catalyst concentration into account, an idea of the order of magnitude of the optical path length penetrated by the UV photons inside the suspension may be obtained. For each wavelength (λ) and optical path length (L), the relationship between absorbance readings (Abs(λ), for that wavelength), catalyst concentration ($[TiO_2]$) and extinction coefficient ($\beta^*(\lambda)$) is given by the following expression:

$$\mathrm{Abs}(\lambda) = \frac{L[\mathrm{TiO_2}]\beta^*(\lambda)}{2.303} = -\ln\left(\frac{I}{I_0}\right) \quad (8)$$

where I_0 is the intensity of incoming light and I the intensity of light from the suspension once it has gone through the reactor.

Let us calculate the particular case of 345 nm of wavelength, for which the extinction coefficient is 51305 $cm^2\ g^{-1}$ for samples prepared with ultrasound [41]. Assuming that 99% of incident radiation is extinguished inside the reactor ($I = 0.01 I_0$), the optical path lengths (L_{99}) corresponding to the catalyst concentrations as presented in Table 2 are obtained. The data from Table 2 partially explain the results obtained in the reactors. The most extreme case is the experiment carried out with a catalyst concentration of 50 mg/l in reactor 1. Note that the reactor diameter (2.55 cm) is smaller than L_{99}. Degradation rate is optimal when particle concentration is 200 mg/l, better than with 500 mg/l. This can be explained with other wavelengths, taking into account the dependence of β on λ at a concentration of 200 mg/l, more UV light passes through the suspension (1.03 cm) that for 500 mg/l (0.41 cm). Reactors 2 and 3 have a very low UV-path-length/diameter ratio, which causes very high loss in effective total volume, because only a small part of it is illuminated. For example, of 200 mg/l of catalyst suspended by sonication in a total volume of 3000 cm^3 in Reactor 3, only 104.5 cm^3 is illuminated and in Reactor 2 only 85.8 cm^3 of 500 cm^3 is illuminated. Similar results are obtained with other wavelengths because $\beta^*(\lambda)$ depends on λ [41]. This qualitative estimation makes it clear that light extinction has a very significant effect on reactor design.

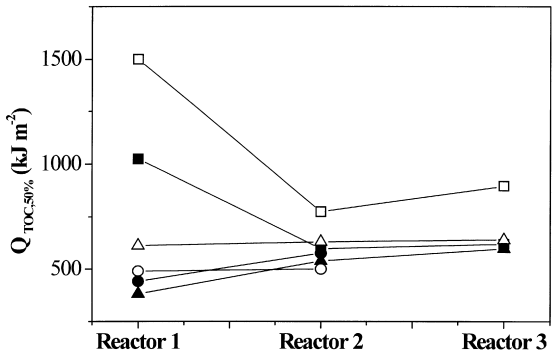

Fig. 6. UV energy per unit of area necessary for disappearance of the 50% of the initial TOC as a function of the reactor diameter, for the same experiments described in Fig. 4

All the above results were estimated for sonicated samples. If two samples with the same catalyst concentration but dispersed with different protocols (ultrasounds and stirring) are compared; sonicated samples are found to be more efficient. Although in stirred samples there are fewer TiO_2 clusters, larger clusters screen light better than small ones. This could explain the lower efficiencies found in systems dispersed by stirring. The best choice for a cylindrical reactor should therefore be the reactor diameter that equals the path length of the UV light for a given set of wavelengths passing through the suspension with a given concentration. Figs. 4 and 5 show that the reaction rate in Reactor 1 is faster than in the other two reactors. In particular, the optimal concentration of TiO_2 corresponds to 200 mg/l when ultrasound is applied to the sample. The lower rate is obtained for a catalyst concentration of 50 mg/l.

4.5. Mineralisation rate

The resulting UV energy per square meter necessary to mineralise 50% of the total organic carbon ($Q_{TOC,50\%}$) in each reactor is shown in Fig. 6. The results obtained are in agreement with Figs. 4 and 5. The disappearance of 50% of the total organic carbon is used since it is a reference common to all the experiments. Faster photoreactions will yield lower

$Q_{TOC,50\%}$. As expected, photocatalytic mineralisation with smaller particles is better at each catalyst concentration than mineralisation obtained for the same concentration with larger particles.

5. Conclusions

The photocatalytic experiments carried out with different particle sizes have demonstrated that efficiencies are better with small particles than with larger particles only when reactor diameter and catalyst concentration are optimised to allow UV photons to penetrate along the entire photoreactor path length, leads to the conclusion that light extinction in colloidal suspensions is a determining parameter for solar photoreactor design.

Particle size (within the range tested) affects reactor efficiency. A 30% increase (200 mg/l at Reactor 1) is obtained by decreasing particle size from 550 nm to 250 nm, although a suspension of small particles provides a 2.2 times larger surface area than suspensions with larger particles. It should also be recalled that small particle sizes cause additional problems for catalyst separation after photocatalytic treatment.

The best inner reactor diameter, for solar photocatalytic applications is in the range of a few centimetres with a few hundred mg of TiO_2/l. The results obtained with Reactor 1 show that an inner reactor diameter of a little over 2.55 cm might produce a similar rate with sonicated and non-sonicated TiO_2 without diminishing the overall efficiency of Reactor 1 (with sonicated TiO_2). The area/volume ratio is also a crucial parameter, and if this ratio is optimised the reactor efficiency would also be increased.

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