Photon Absorption by Aqueous TiO_2 Dispersion Contained in a Stirred Photoreactor

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A major problem in the research area of heterogeneous photocatalysis is the possibility of correctly comparing reactivity results obtained in different laboratories. In the literature concerning heterogeneous photocatalytic reactions the available information concerns the type of reactor and lamp and the features of the radiation hitting the reactor; sometimes the energy of radiation impinging onto the photoreactor is also given.

Childs and Ollis (1980) suggest that the two basic quantities needed for computing reaction rates of heterogeneous photocatalytic systems are the active site concentration of catalyst and the photon absorption rate. As the authors note, evaluating active sites and absorbed photons may be a difficult task. They suggest that, without information about these basic parameters, the photocatalytic reaction rate should be referred to the following experimentally determinable quantities: 1. The total surface area of the catalyst (generally measured with the BET technique), and 2. The rate of photons emitted by the lamp.

Now, while the first quantity indicated by Childs and Ollis (1980) may be directly relevant (probably together with other physical features of the powder, such as pore size distribution), the second quantity may lead to errors. Indeed, the amount of emitted photons is clearly independent of the specific features of the photoreacting system, and therefore it cannot be used in place of the photon absorption rate. This last quantity was never reported in photocatalytic works.

In this note we present a simple experimental method which allows the evaluation of the absorbed photon flow. The method is based on measurements of transmitted photon rates (by means of standard actinometer solutions) for different reactor thicknesses and/or catalyst concentrations. The method was applied to the phenol degradation reaction carried out in a stirred batch photoreactor containing aqueous TiO_2 (anatase) dispersion, directly irradiated by a 1,500 W Xe lamp. This system has been the object of several extensive studies (Okamoto et al., 1985; Al-Ekabi and Serpone, 1988; Augugliaro et al., 1988) by using this information, the present work has been focused mainly on the investigation of the proposed method for the evaluation of the absorbed photons. It must be outlined, however, that the method is suitable for comparison only when it is applied to setups and operative conditions (particle sizes and concentrations) similar to those prevailing in the present investigation.

Experimental Studies

The experimental apparatus, shown in Figure 1a, was composed of two cylindrical vessels (ID = 5.64 cm) of Pyrex glass, vertically positioned one on top of the other; the upper vessel contained the aqueous TiO_2 dispersion, and the lower one the actinometer solution. In a few runs, the arrangement was modified as shown in Figure 1b, i.e., by surrounding the upper vessel with an annulus (1-cm-thick) filled with actinometer solution for a height equal to that of the adjoining dispersion. The external surfaces of the lower vessel and of the annulus were always covered by mirror-polished aluminum sheets. For the arrangement without the annulus (Figure 1a), two alternatives were used: either the cylindrical surface of the upper vessel was covered with a mirror-polished aluminum sheet or it was without any covering.

The whole apparatus was kept in a Solarbox (CO.FO.ME.GRA., Italy) equipped with a 1,500 W Xe lamp, and was directly irradiated only from the circular top surface of the upper vessel. A Pyrex sheet was placed on top of the upper vessel; the distance between this sheet and the lamp was of 15 cm.

Different volumes of dispersion, in the 12.5–125 cm^3 range, with heights in the 0.5–5 cm range were used. The volume of the actinometer solution was always of 25 cm^3 and filled the lower vessel for a height of 1 cm. The dispersion was magnetically stirred at a speed that gave no particle sedimentation and negligible cone formation. For a few runs also, the actinometer solution was magnetically stirred but no difference with experiments carried out (at equal conditions) without stirring was observed.

The dispersion conditions were: temperature = 328 K; pH = 3; initial phenol concentration = 10^{-4} $g \times cm^{-3}$. The TiO_2 concentration varied in the $0.2\text{–}1 \times 10^{-3}$ $g \times cm^{-3}$ range. The ac-

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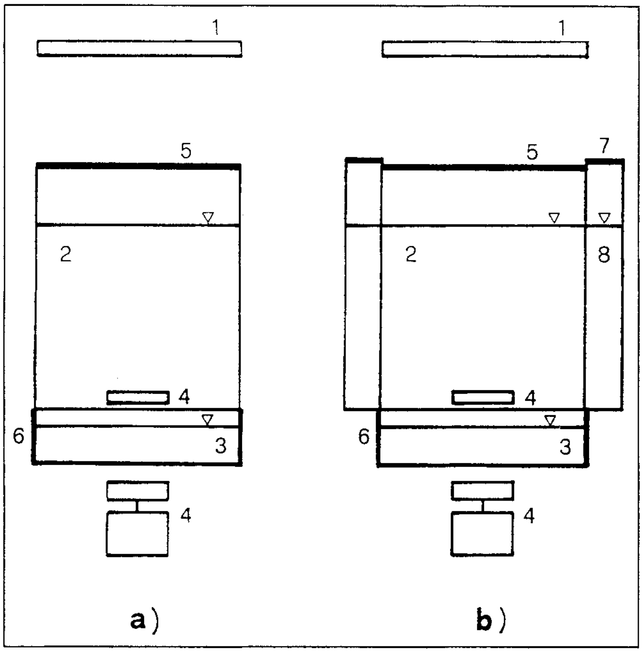


Figure 1. Arrangements of the experimental set up: a) without and b) with an annulus surrounding the upper vessel.

1 = lamp
2 = upper vessel containing reacting dispersion
3 = lower vessel containing actinometer solution
4 = magnetic stirrer
5 = Pyrex sheet
6 = mirror-polished aluminum sheet
7 = black sheet
8 = annulus containing actinometer solution

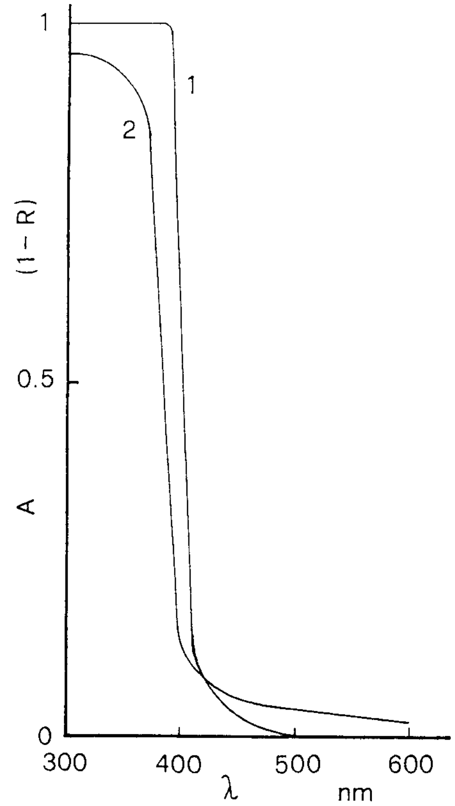


Figure 2. Absorbance spectrum.

1. Actinometer solution as A vs. wavelength, and diffuse reflectance spectrum; 2. TiO_2 (BDH) specimen as $(1-R)$ vs. wavelength

tinometer solution was of the ferric oxalate type and was prepared as described in literature (Murov, 1973); the absorbance spectrum of this solution, for an optical pathlength of 1 cm, is reported in Figure 2. The spectrum was obtained with a Varian DMS 90 spectrophotometer. In the absorption measurements of the irradiated actinometer solution (to be described later) the same instrument was used.

The actinometry runs lasted 2 minutes. For each TiO_2 concentration a few photodegradation runs, carried out with a dispersion volume of 50 cm^3, lasted 1 hour; every 20 minutes during the irradiation a sample of 3 cm^3 was withdrawn for phenol quantitative determination, performed by a standard colorimetric method (Taras et al., 1971). As oxygen is needed for the occurrence of phenol photodegradation (Okamoto et al., 1985; Al-Ekabi and Serpone, 1988; Augugliaro et al., 1988), oxygen was always bubbled for 1 hour into the dispersion before starting the irradiation. All the runs were performed without bubbling of gas, though a flow of oxygen in the Solarbox was maintained. Results of previous experiments showed that, with such a procedure, the reaction kinetics always remains unaffected by the possible oxygen depletion (Augugliaro et al., 1988).

At the very start of the irradiation, i.e., when only phenol degradation takes place (later in the process degradation of intermediate compounds also occurs), the radiant energy forward-scattered by the dispersion was determined by means of the actinometer solution of the lower vessel. The annulus, when present, simultaneously measured the radiant energy scattered by the dispersion through the side wall of the reactor. The actinometer sample was withdrawn after 2 minutes, during which time the fractional conversion of actinometer never exceeded 20%, i.e., below the recommended upper limit (Murov, 1973). The absorbance of the actinometer sample was measured at the wavelength of 510 nm by using a cell with optical pathlength of 1 cm.

Commercial TiO_2 powders and two "home-made" TiO_2 (anatase) specimens were used; one (T3) was prepared from a 15% $TiCl_3$ solution and the other (T4) from a 98% $TiCl_4$ solution (both from Carlo Erba, RPE). Details on the catalyst preparation can be found in Sclafani et al., 1990. Before performing the experiments, the T3 and T4 specimens underwent a thermal treatment at 873 K for 3 h, whereas the commercial ones were tested as received. The powders were crushed and accurately sieved, commercial ones included; the dimensions of the particles were in the 40-500 μm range. The surface area of the powders was determined by the dynamic BET method using a Micromeritics Flowsorb 2300 apparatus and N_2 as adsorbate. The diffuse reflectance spectra of all the TiO_2 specimens showed similar features; in Figure 2 a typical one is reported.

Results

From the actinometry experiments the photon flow, P, was calculated with the following equation (Murov, 1973):

$$P=(AV_2V_3)/(fytlV_1) \tag{1}$$

in which: A was the measured absorption of irradiated acti-

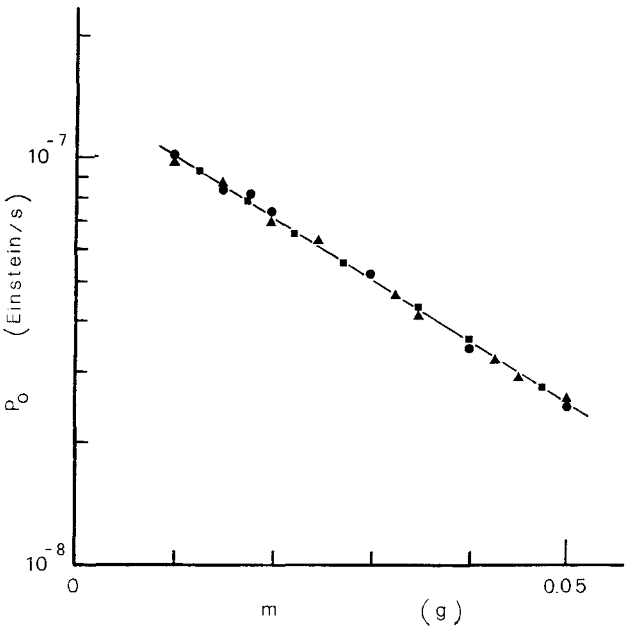


Figure 3. Forward scattered photon flow, P_o, vs. powder mass, m.

The data were obtained with TiO_2 (Merck) powder: ●, unclassified ▲, with particles in the 40-60 μm range and ■, with particles in the 400-500 μm range

nometer solution; V_1 and V_2 the volumes of actinometer solution withdrawn and irradiated, respectively; V_3 the flask volume used for diluting V_1; f the extinction coefficient of ferrous phenanthroline complex at 510 nm (1.11×10^7 $mol^{-1} \times cm^2$); y the quantum yield of ferrous ions production (1.21 mol × $Einstein^{-1}$ in the wavelength range of radiation reaching the solution); t the irradiation time (120 s) and l the cell optical pathlength (1 cm).

The actinometry measurements performed with the annulus surrounding the upper vessel showed that, in the absence of the solid catalyst suspension, no radiation reached the annulus. This indicated that the irradiation of the system occurs "directly," i.e., by means of parallel beams. Also, when the solid suspension was present in the vessel, the rate of photons reaching the actinometer solution of the annulus was two orders of magnitude less than that reaching the lower vessel, or was even below detection. The finding that the lateral light scattering was negligible was further confirmed by the fact that the actinometer measurements performed with the arrangement reported in Figure 1a were insensitive to the presence or absence of the mirror-polished aluminum sheet covering the cylindrical surface of the upper vessel.

Actinometer measurements, carried out with the upper vessel containing phenol aqueous solutions without the catalyst, indicated that the solution behaves as a nonabsorbing medium. Also, preliminary experiments performed at different speeds of stirring showed that the fluid dynamic conditions of the suspension did not affect the reactivity (i.e., the phenol degradation) and actinometry results.

In order to investigate the possible influence of particle size, three series of experiments were performed by using: 1. Unclassified powder, 2. Powder with particle dimensions in the 40-60 μm range, and 3. Powder with particle dimensions in the 400-500 μm range. For each size, various concentrations of the same TiO_2 variety (Merck, surface area of $10.5\ m^2 \times g^{-1}$) were used. For all these runs, the suspension volume was 50 cm^3. The reactivity results showed the expected proportionality to the catalyst mass; they did not show, however, any dependence on the particle size at equal mass of catalyst. Also the actinometry results, reported in the semilogarithmic plot of Figure 3 as rate of photons reaching the actinometer solution, P_o, vs. catalyst mass, m, showed that no difference exists due to particle size.

The actinometry results obtained by using dispersions of commercial TiO_2, T3, and T4 at different volumes and concentrations are reported in the semilogarithmic plot of Figure 4 as P_o vs. the mass of powder in the dispersion, m. It may be noted that for each powder a single line correlates the data independently of the way m was obtained as the product of dispersion volume times the catalyst concentration. Thus, under the conditions of this experiment, the fraction of forward-scattered photons was determined solely by the catalyst mass in the photoreactor.

In agreement with previous work (Okamoto et al., 1985; Al-Ekabi and Serpone, 1988; Augugliaro et al., 1988), a pseudo first-order kinetics with respect to phenol fitted very well the experimental data of phenol photodegradation. The integration of the corresponding rate equation gives the following equation:

$$c = c' \exp(-kt) \tag{2}$$

in which c is the phenol concentration at time t, c' the initial value and k the pseudo first-order rate constant. As mentioned previously (see also Augugliaro et al., 1988), k is proportional to the catalyst concentration. By means of a least-square fitting procedure applied to Eq. 2, the values of k for the various runs were calculated and found to agree with the expected proportionality. In particular, Table 1 reports the values of k obtained for each catalyst at the concentration of $10^{-3}\ g \times cm^{-3}$; Table 1 also reports the values of the surface area of the catalysts.

Discussion of Results

The photocatalyst used in this work is a n-type semiconductor which can absorb radiation with energy not less than its band gap energy: about 3.2 eV for anatase TiO_2, corresponding to a wavelength of about 410 nm. Due to the presence of a Pyrex filter between the lamp and the reacting powder, UV radiation with wavelength less than 300 nm does not reach the dispersion. Therefore the wavelengths of the radiation that can be absorbed range from 300 to 410 nm. This radiation is absorbed only by the catalyst, since the liquid phase behaves as a nonabsorbing medium. The almost complete overlapping of the diffuse $(1-R)$ spectrum of TiO_2 upon the absorbance spectrum of the actinometer solution (both reported in Figure 2) indicates that during the irradiation of the dispersion the actinometer solution is absorbing, and therefore measuring, the same kind of photons that can also be absorbed by the semiconductor.

The macroscopic balance of radiant energy, performed on the dispersion by taking into account only photons with wave-

Table 1. Values of SA, k, K, P', Reflection, and qy for Commercial and Home Prepared TiO_2 Specimens*

Catalyst	SA m^2/g	$k \times 10^4$ s^{-1}	K g^{-1}	$P' \times 10^6$ Einstein/s	P_r/P_i %	qy molec./Einstein
T3	45	1.33	9.7	148	4.5	0.13
T4	26	2.64	43.2	149	53.5	0.22
TiO_2 (Tioxide)	14	2.62	44.9	148	4.5	0.07
TiO_2 (Montedison)	22	1.08	15.1	140	9.7	0.06
TiO_2 (Merck)	10.5	2.25	34.9	142	8.4	0.05
TiO_2 (BDH)	10.5	1.75	86.6	40	74.2	0.24

*The qy values have been calculated for a dispersion with a powder mass of 0.05 g.

SA = surface area

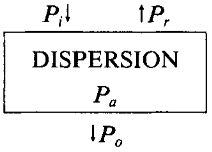
k = kinetic constant

K = effective extinction coefficient

P' = rate of entering photons

qy = quantum yield

length in the 300-410 nm range, may be written in the following way:



$$P_i - P_o = P_a + P_r \text{ [Einstein} \times s^{-1}] \quad (3)$$

in which P_i is the rate of photons impinging onto the upper boundary plane of the dispersion, P_a the rate of photons absorbed by the particles of the dispersion, P_r the rate of photons backward-scattered from the upper boundary plane of the dispersion, and P_o the rate of photons forward-scattered by the dispersion across the bottom boundary plane. In the previous balance the rate of photons scattered by the dispersion in direction perpendicular to that of incident radiation has been neglected in view of the results of the annulus. As the particles of the catalyst have dimensions at least two orders of magnitude greater than the wavelengths of the radiation, it may be excluded from the occurrence of Rayleigh or Mie scattering (Hottel and Sarofim, 1967), and consequently the spectral distribution of P_r and P_o are not different from that of P_i.

In the radiant energy balance expressed by Eq. 3, the terms P_i and P_o were directly measured by actinometry. The value of P_i was obtained by performing experiments without the reacting dispersion. Repeated measurements gave a reproducible value of P_i of 1.55×10^{-7} Einstein × s^{-1}.

The values of P_o, reported in Figure 4 for the various powders, clearly indicate that the rate of forward scattered photons only depends upon the mass of powder present in the photoreactor, for whatever concentration and/or height of the dispersion. An exponential relationship was found to best correlate the data of P_o vs. m:

$$P_o = P' \exp(-Km) \quad (4)$$

where P' and K are adjustable parameters. Since Eq. 4 has the same form of the Lambert-Beer law, K can be defined as the effective extinction coefficient of the dispersed powder. The meaning of P' is trivially that of P_o in the limit $m \rightarrow 0$. By applying a least-square fit to the data, the values of P' and K have been obtained; they are reported in Table 1 for each powder used in this work.

It should be noted that the values of P' are *always* smaller than that of P_i. This result, i.e., the existence of a nonzero reflection term P_r, outlines the main difference between Eq. 4 and the Lambert-Beer law. The l.h.s. of Eq. 3, $(P_i - P_o)$, is the measured quantity which is a function of the powder mass, m (see Eq. 4). On the righthand side of Eq. 3, the rate of photons absorbed by the catalyst, P_a, obviously depends on m and becomes zero for $m = 0$. Thus, the extrapolation to $m = 0$ of experimental data of Figure 4, i.e., the values of P' reported in Table 1, allow one to calculate P_r (at $m = 0$) as the difference $P_i - P'$. The question now arises on whether or not P_r remains the same also for a finite mass of dispersion. The assumption is made here that P_r is independent of m, i.e., that the photons backward-scattered from the upper boundary of the reactor

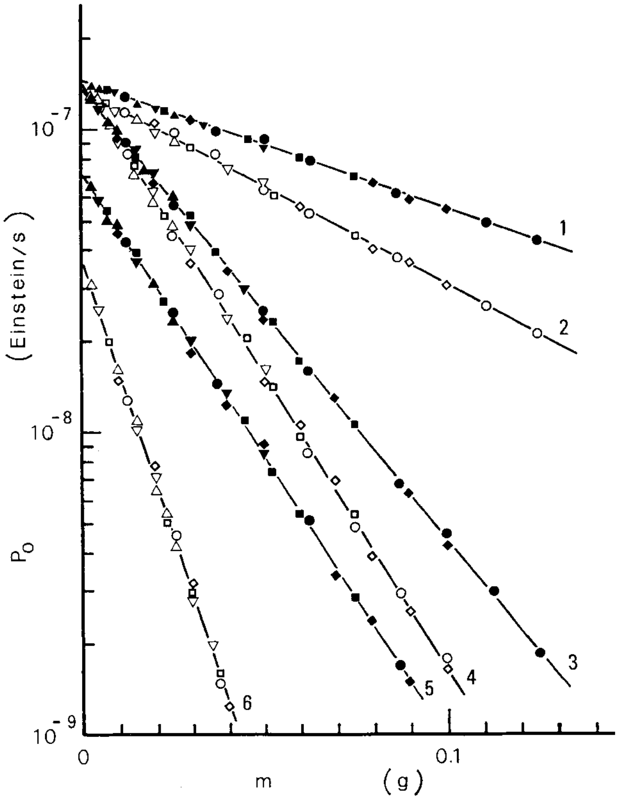


Figure 4. Forward scattered photon flow, P_o, vs. powder mass, m.

For dispersions of $T3$ (line 1), Montedison TiO_2 (line 2), Merck TiO_2 (line 3), Tioxide TiO_2 (line 4), $T4$ (line 5), and BDH TiO_2 (line 6) at powder concentration of: ▲, △, 0.2×10^{-3}; ▼, ▽, 0.4×10^{-3}; ■, □, 0.6×10^{-3}; ◆, ◇, 0.8×10^{-3}; and ●, ○, 1×10^{-3} $g \cdot cm^{-3}$

are those reflected from a top layer of particles, and that the reflection of this top layer is essentially unaffected by variations in dispersion height and concentration. Regarding the latter variable (the concentration) we certainly expect this assumption to break at very low concentrations, much smaller than those used in this work.

The assumption made here is based on the fact that the particles are much larger than the wavelength of the incident radiation, so that the laws of geometrical optics can be applied. For this case it has been shown (Van der Hulst, 1957) that the forward scattering of the incident radiation largely predominates over both the scattering towards the light source and that in the perpendicular direction. The latter feature is indeed confirmed by the results obtained in the annulus.

In conclusion, the backward-reflected photons are given by:

$$P_r = P_i - P'. \tag{5}$$

Thus, the P' values reported in Table 1 have a physical meaning. They represent the rate of photons which are able to penetrate the dispersion. Table 1 also reports the values of the ratio (P_r/P_i), i.e., the fraction of the incident radiation which is backward reflected by the dispersion. It should be noted that, except for the T4 and TiO_2 BDH specimens, the amount of photons reflected by the suspension varies in a narrow range and it never exceeds 10%. Table 1 also reports the values of quantum yield for photoreaction, calculated as the ratio between reacted molecules and absorbed photons. These values are calculated for the first two minutes of irradiation by applying Eq. 2 for determining the number of reacted molecules. It may be noted that the efficiency of the process is relatively high; on an average, in the present case, one out of ten photogenerated pairs is used in the photocatalytic process.

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