Special Communication to the Editor

Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis [1]

Nick Serpone *

Center for Fast Laser Spectroscopy and Laboratory of Pure & Applied Studies in Catalysis, Environment & Materials, Department of Chemistry and Biochemistry, Concordia University, 1455 deMaisonneuve Blvd. West, Montreal, Quebec, H3G 1M8, Canada

Abstract

Quantum yield and *quantum efficiency* (QY) as used in heterogeneous photocatalysis (solid/liquid or solid/gas systems) have too often been used incorrectly to mean *the ratio of the rate of a given event to the rate of incident photons impinging on the (external) reactor walls, typically for broadband radiation*. There is little accord on how to express process efficiency. At times QY is defined, often ill-defined, and more frequently workers fail to describe how it was assessed. This has led to much confusion in the literature, not only because of the different meaning of QY from that in homogeneous photochemis' $\cdot$ /, but also because this method of describing photon efficiency precludes a comparison of results from different laboratories because of the variations in light sources, reactor geometries, and overall experimental conditions. It cannot be overemphasized that the reported QY is an *apparent* quantum yield, indeed a *lower limit* of the true quantum yield. This position paper addresses this issue, and argues that any reference to *quantum yields* or *quantum efficiencies* in a heterogeneous medium is ill-advised unless the actual number of photons absorbed by the light harvester (the photocatalyst) has been determined. The extent of light scattering in a solid/liquid heterogeneous medium is significant. A practical and simple alternative for comparing process efficiencies was recently suggested by defining a relative photonic efficiency ζ_r. A quantum yield can subsequently be determined from ζ_r, as $\Phi = \zeta_r \Phi_{phenol}$, where Φ_{phenol} is the quantum yield for the photocatalyzed oxidative disappearance of phenol (a standard secondary actinometer) using Degussa P-25 TiO_2 as the standard catalyst material. © 1997 Elsevier Science S.A.

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1. The nature of heterogeneous photocatalysis

Heterogeneous photocatalysis describes a process whereby the illumination of a semiconductor particulate (CdS, TiO_2, ZnO, WO_3, etc.) with UV–visible light suitable to its bandgap energy ultimately generates thermalized conduction band electrons (e^-) and valence band holes (h^+) which, subsequent to their separation and other competitive photochemical and photophysical channels, are poised at the particulate/solution interface ready to initiate redox chemistries. The energy level at the bottom of the conduction band reflects the reduction potential of the photo-electrons, whereas the upper-most level of the valence band is a measure of the oxidizing ability of the photo-holes. The flatband potential V_{fb}, which is fixed by the nature of the material and the proton exchange equilibria, determines the energy of the two charge carriers at the interface. Hence reductive and oxidative processes for adsorbed couples with redox potentials more positive and more negative than the V_{fb} of the conduction and valence band, respectively, can be driven by surface-trapped e^- and h^+ carriers. Fig. 1 illustrates a fraction of the complex events taking place in a semiconductor photocatalyst.

Irradiation of the semiconductor particle with suitable energy ($\geq E_g$) generates a bound electron/hole pair (the exciton) which can recombine in competition with dissociation to give a conduction band electron and a valence band hole, which in turn can also recombine and migrate to the surface while scanning several shallow traps (anion vacancies and/or Ti^{4+} for the electrons; oxygen vacancies or other defect sites for the hole). On the surface, both charge carriers scan the surface, visiting several sites to reduce adsorbed electron acceptors (A_{ads}) and oxidize electron donors (D_{ads})

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[1] This position paper is presented to initiate reflection and debate that should ultimately lead to an understanding and ultimately consensus, where possible, on the issues raised here. The reader is therefore invited to submit suggestions or a critique to the author for a final draft report. This author also welcomes others to determine the quantum yield for phenol with the same or some other equivalent approach [see, e.g., Augugliaro et al., *Sol. Energy Mater. Sol. Cells*, 38 (1995) 411].

* Fax: +1 514 848 2868 (department) +1 514 848 3345 (office); e-mail: serpone@vax2.concordia.ca
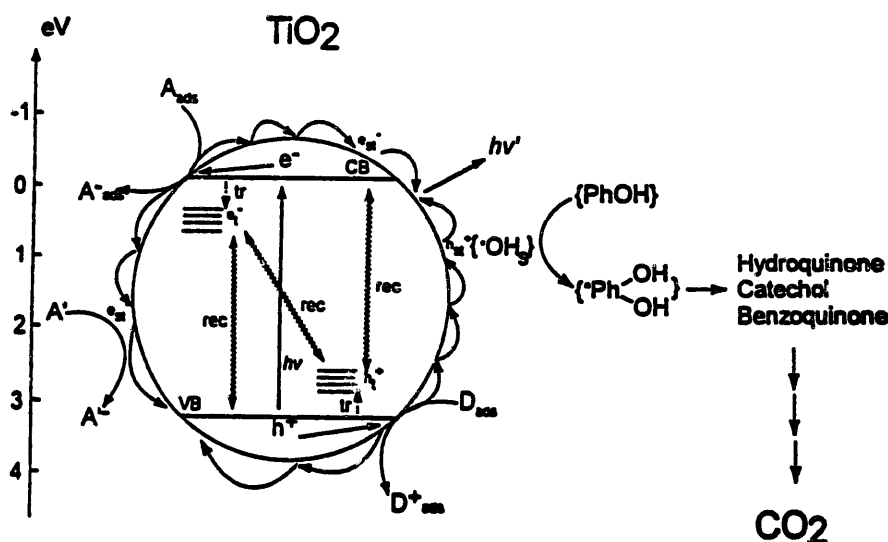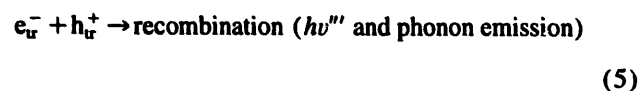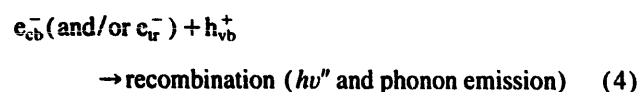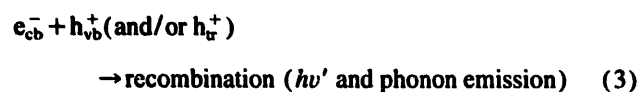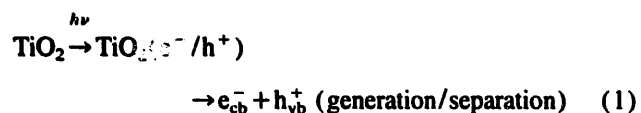
Fig. 1. Sequence of photophysical and photochemical events taking place upon irradiation of a TiO_2 particle with $h\nu$ greater than E_g together with secondary reactions to total mineralization to CO_2.

in competition also with recombination of surface trapped electrons and holes (e_{st}^- and h_{st}^+) to produce light emission and/or phonon emission. In heterogeneous photocatalysis, oxygen is often present as the electron acceptor, whereas OH^- and H_2O are available as electron donors to yield the strongly oxidizing $\cdot OH$ radicals. Trapping of electrons and holes in pristine naked TiO_2 colloids (a few nm in size) takes place in less than 30 ps [1–3]. At concentrations of organic pollutant substrates normally found in the environment (a few tens of mg l^{-1}), the $\cdot OH$ radicals are the primary oxidizing entities to produce, in the case of an aromatic substance, the corresponding $\cdot OH$ adduct (the cyclohexadienyl radical), which ultimately yields a variety of intermediate products on the way to total mineralization to carbon dioxide.

The function of photo-excited semiconductor particulates, then, is to act as pools of electrons and holes; these have been exploited in several multi-electron transfer processes [4]. Taking titania as an example, we obtain

$$TiO_2 \xrightarrow{h\nu} TiO_2(e^- /h^+)$$

$$\rightarrow e_{cb}^- + h_{vb}^+ \quad \text{(generation/separation)} \quad (1)$$

$$e_{cb}^- + h_{vb}^+ \rightarrow e_{tr}^- + h_{tr}^+ \quad \text{(lattice and/or surface trapping)} \quad (2)$$

$$e_{cb}^- + h_{vb}^+(\text{and/or } h_{tr}^+)$$

$$\rightarrow \text{recombination } (h\nu' \text{ and phonon emission)} \quad (3)$$

$$e_{cb}^-(\text{and/or } e_{tr}^-) + h_{vb}^+$$

$$\rightarrow \text{recombination } (h\nu'' \text{ and phonon emission)} \quad (4)$$

$$e_{tr}^- + h_{tr}^+ \rightarrow \text{recombination } (h\nu''' \text{ and phonon emission)}$$

$$(5)$$

$$\equiv Ti - \cdot OH + RH \rightarrow \rightarrow \rightarrow ....\text{photo} - \text{oxidations} \quad (6)$$

where e_{tr}^- is a trapped electron (e.g., as Ti^{3+}) and h_{tr}^+ is a trapped hole denoted as a surface-bound $\cdot OH$ radical, $\equiv Ti$-$\cdot OH$ [3,5].

The utility of heterogeneous photocatalysis (HP) has been examined extensively and is being explored as a potentially viable alternative technology to classical "best" technologies in both environmental detoxification and energy production. This relatively novel technology has had, if not its debut, certainly its development with the many studies in the late 1970s to early 1980s [6] which explored ways to photogenerate clean alternative fuels (e.g. H_2 from water splitting), upon realization that processes carried out with organized assemblies afforded some advantages over homogeneous processes where the energy-wasting back electron transfer is not negligible.

Photocatalysis has witnessed significant advances during the last decade; several research groups, notably those of Gratzel, Ollis, Pelizzetti, Serpone, Pichat, Matthews, Bard, Fox, Bahnemann and Hoffmann, among others, have actively examined the utilization of illuminated semiconductor photocatalysts towards the photo-oxidative mineralization of organic substrates in the environment (pesticides, herbicides, and others). A recent (1992) international symposium, whose theme was "TiO_2 Photocatalyzed Purification of Water and Air", saw no fewer than 200 participants from industry and academia actively engaged in this environmental application—a useful sign of the importance of this seemingly phenomenologically facile technology [7]. Close examination of the field, however, reveals some serious gaps in our understanding of the basics that underlie heterogeneous photocatalysis.

Indeed, some of the issues that have hampered progress in our collective fundamental understanding of heterogeneous photocatalysis are the descriptions of (i) photocatalysis, (ii) turnover numbers, turnover rates and turnover frequencies, and (iii) quantum yields. After much reflection, the term

"photocatalysis" continues to elude acceptance, as attested by the spectrum of specific labels used to describe a variety of mechanistic possibilities for a given process [8,9]. For simplicity, we continue to adopt the view that "photocatalysis" refers simply to a catalyzed process implicating light absorption by the catalyst.

In initiating the debate, we begin by recalling the photochemist's definition of quantum yield symbolized by Φ, and the constraints under which it is measured. It needs to be emphasized that, until such time as the rate of absorption of photons can be assessed adequately for a solid photocatalyst, reference to *quantum yield* (or *quantum efficiency*, often used interchangeably by photochemists) has not been useful in heterogeneous photocatalysis because of the confusion such a term has engendered. It becomes useful only if it has the identical meaning to Φ in homogeneous photochemistry.

2. Practical efficiencies in an industrial environment

In an industrial environment, where the efficiency of a given process is a significant component to determine its economic viability, Bolton et al. [10] have suggested such figures of merit as *"Electrical energy per order"* (EE/O) and *"Electrical energy per unit mass"* (EE/M).

In practical oxidative degradations, as envisaged in water treatment technologies, not only is the simple disappearance of the pollutant relevant; but conversion of total organic carbon (TOC) into inorganic carbon CO_2 is also most important. The pertinent process is the complete mineralization of all organic carbon to insure that the substrate(s) and any intermediate product(s) formed during the degradative process have also been degraded [11]. In some cases, conversion to an innocuous product may be acceptable (e.g., atrazine to cyanuric acid [12]) if the end product is environmentally friendly.

For an industrial environment where an engineering efficiency is more useful, Braun [13] has proposed the usage of *"Energetic efficiency of degradation"* (EED) given as ppm $(mg\ l^{-1})$ of organic carbon in a given solution volume irradiated per kWh of electrical energy used, or the more recent suggestion of using volume-corrected efficiencies (mg C per kWh) [14], as a cross-check of different methods of water treatment. This would presumably include the analytical procedure in any comparison between different processes, different reactors, and different light sources, among others. Just like the EE/O, the EED is useful in an economic analysis of various given processes.

The EE/O, EE/M, EED and other figures of merit, however, do not provide that fundamental parameter in heterogeneous photocatalysis that provides a quantity which would indicate the efficiency of an absorbed photon to induce a certain event. In homogeneous photochemistry we have the quantum yield Φ. We therefore seek to define and experimentally to attain something similar to, or better, identical with in heterogeneous photocatalysis.

3. Quantum yield in homogeneous photochemistry

Knowledge of *quantum yield* (the rate at which molecules undergo a given event per photons *absorbed* per unit time) is central to photochemistry. Photochemists routinely determine quantum yields of reactant disappearance, product formation, light emission, and various other photochemical and photophysical events occurring in some photochemical reaction. Many of these processes have been examined in great detail by several laboratories, and the precision in the quantum yield data is unquestioned [15]. Ferrioxalate {$[Fe(C_2O_4)_3]^{3-}$; UV and visible region to ≈ 500 nm}, Reinecke's salt {$[Cr(NH_3)_2(SCN)_4]^-$; for visible region}, uranyl oxalate {$[UO_2(C_2O_4)2]^{2-}$; for UV region}, and more recently Aberchrome 540 {for the 310–370 nm and 436–546 nm ranges} and others [16] have become secondary standards to measure the photon flow incident on the inner front window of a photolytic cell; these have become known as *chemical actinometers* because the product quantum yield from these substances is rather insensitive to temperature changes, changes in reactant concentration, changes in photon flow, and changes in the wavelength of the absorbed light. Procedures are well established and analysis of products is simple and precise [15].

Utilization of actinometric substances has simplified the determination of the photon flow compared with earlier, more tedious radiometric procedures [16,17]. Placing the actinometer in the same photolysis cell used for the subsequent photochemical study, while maintaining the same optical train, avoids the need to correct for differences between the fraction of incident light *reflected* from the front window of the photolysis cell if different cells are used.

If the photochemical reaction of the actinometer (Ac) is Ac $\rightarrow$ B, and if Ac is the *only* substance which absorbs light at the wavelength of irradiation, the extent of the photon flow absorbed by Ac is given by

$$N_{Ac,\lambda} = N_{o,\lambda}^o (1 - 10^{-A_\lambda^{Ac}})$$

$$(\text{photons s}^{-1} \text{ or einsteins s}^{-1}) \tag{7}$$

where A_λ^{Ac} is the absorbance at wavelength λ. Operationally, $A_\lambda^{Ac} \geq 2$ during the entire irradiation period t to ensure that the light harvester collects $\geq 99\%$ of the photon flow, such that $N_{Ac,\lambda} \approx N_{o,\lambda}^o$, where $N_{o,\lambda}^o$ is the photon flow from the irradiation source. The photon flow incident just within the front window of the photolysis cell, $N_{o,\lambda}^i$, is given by [15,16]

$$N_{o,\lambda}^i = \frac{n_B}{\Phi_B t (1 - 10^{-A_\lambda^{Ac}})} \ (\text{photons s}^{-1}) \tag{8}$$

where n_B is the number of product molecules formed from the irradiated actinometer. Thus, actinometry allows determination of the incident photon rate for a system of *specific geometry* and in a *well defined spectral domain* [16]. Effective stirring of the actinometric solution must be maintained during irradiation, and the photolysis cell must contain no particulate matter that might reflect or scatter light; the latter

would have a detrimental effect on the precision and accuracy of the quantum yield data.

An added complication in measurements of quantum yields under polychromatic irradiation is the required knowledge of the action spectrum in the spectral region of interest (λ_1 to λ_2) to the reaction being examined.

Thus

$$\Phi = \frac{\int_{\lambda_1}^{\lambda_2} \Phi(\lambda)\,d\lambda}{\int_{\lambda_1}^{\lambda_2} d\lambda} \qquad (9)$$

When the action spectrum is unknown, Braun et al. [16] suggest the use of the *quantum efficiency*, η, as *the ratio of the number of molecules of product formed to the total number of photons absorbed in the spectral region used during the reaction period*. Note that $\eta \neq \Phi$ and also note the different meaning that η takes in this context. Detailed procedures for determining quantum yields in homogeneous media are available elsewhere [16–18].

It will be advantageous to use simple methods (procedures) that involve the most basic of instrumentation to define a parameter such that heterogeneous photocatalytic data from various sources can be evaluated and compared.

The above discussion presents nothing significantly new to seasoned photochemists. Unfortunately, the heterogeneous photocatalysis literature also reports *quantum yields* and in other cases *quantum efficiencies*. Not only do these two terms have distinct meaning [16] as noted above, but the terms are used synonymously and have come to refer, incorrectly, to the number of molecules undergoing an event referenced to the total number of photons *incident* on the reactor walls, for some ill-defined reactor geometry and for a large spectral (non-monochromatic) irradiation window. It cannot be emphasized sufficiently in this context that it is the *photons actually absorbed* that induce the photocatalytic process.

What has not been fully appreciated and recognized in measurements of photons absorbed by the semiconductor light harvester is the significant extent of light scattered or reflected by the particulate matter in the dispersion. We must acknowledge that, to varying extents, all molecules are both light absorbers and light scatterers depending on the nature of the medium. It also needs to be emphasized that light-collecting particulates having large refractive indices cannot absorb all the photons impinging on the dispersion. Such significant losses, often of unknown magnitude, preclude any reference to quantum yields in particulate suspensions. Thus there is a need to consider simple alternatives in heterogeneous photocatalysis to express process efficiencies that ultimately can be related to photons absorbed. Any proposed procedure must be simple and compatible with common instrumentation normally available in most (photo)catalysis laboratories.

4. Suggested protocol in heterogeneous photocatalysis

4.1. General discussion

Process efficiencies in an industrial environment described by EE/O [19] and EED [13] are useful in comparing the economics of different industrial strategies; trends in EE/O or the equivalent EE/M inversely reflect the trends in quantum yields. However, they fail to provide a relatively simple method to establish photon efficiencies [20,21].

In heterogeneous photocatalysis, *quantum yield* has come to define the number of molecules converted relative to the total number of photons *incident* on the reactor walls, for an undefined reactor geometry and for polychromatic radiation, rather than the number of *absorbed* quanta at a given wavelength (recall that Φ values are often wavelength dependent) to satisfy the photochemical definition of Φ in homogeneous photochemistry [15,16].

The overall quantum yield $\Phi_{overall}$ expresses the number of molecules N_{mol} undergoing an event (conversion of reactants or formation of products) relative to the number of quanta N_{ph} absorbed by the reactant(s) or by the photocatalyst (Eq. (10)) [15].

$$\Phi_{overall} = \frac{N_{mol}\ (\text{mol s}^{-1})}{N_{ph}\ (\text{einstein s}^{-1})}$$

$$= \frac{\text{rate of reaction}}{\text{rate of absorption of photons}} \qquad (10)$$

Analogous descriptions have been proposed for heterogeneous systems [16,22,23]. No particular difficulties are encountered in homogeneous media. In a heterogeneous system, the relationship in Eq. (10) has been extended, modified and applied in an analogous fashion [24–27]. Because the number of absorbed photons N_{ph} is experimentally difficult to access owing to reflection, scattering (see below), transmission (for transparent colloidal sols) and absorption by the suspended particulates, usage of the term *quantum yield* referenced to *incident* photons in heterogeneous photocatalysis has led to a high degree of confusion. Some suggested methods to determine N_{ph} have appeared [25–28].

An important observation about Eq. (10) is that, as the numerator also expresses the rate of reaction, $\Phi_{overall}$ depends on the reactant concentration. As correctly noted by Braun et al. [16] and re-emphasized recently by Cabrera et al. [28], only for a zero-order reaction is $\Phi_{overall}$ uniquely defined at a given wavelength. In homogeneous photochemistry, the problem is normally overcome by determining Φ at small (less than $\approx 10\%$) conversions of reactants, a point not often respected in heterogeneous photocatalysis, where the focus is complete mineralization (100% transformation) of the substrate, at least in studies of environmental interest that focus on the elimination of organic pollutants in water.

The factor that most markedly complicates measurements of the number (or rate) of absorbed quanta by a semiconductor photocatalyst is the significant extent of light scattered

by the particulate matter in the dispersion. This could reach, according to some accounts, 13–76% of the total incident photon flow [25]. Using the photodegradation of TCE in a TiO_2 slurry, Cabrera et al. [28] confirmed some of these findings, noting that only $\approx 15\%$ (for Aldrich TiO_2) of the radiation measured by homogeneous actinometry inside the reactor was effectively absorbed. They also concluded that radiation flow measurements at the reactor entrance or homogeneous actinometry inside the reactor volume can be very misleading and scattering effects are important.

A metal oxide material such as particulate TiO_2 (anatase and/or rutile) could never absorb all the incident photon flow from a given source, despite recent claims to the contrary [29–31], as the intensity of light scattered, I_{sc}, by the suspension depends, among other things, on the refractive indices of the scattering molecule/particle (n_1) and the surrounding medium (n_0). Consider the diagram below [32]
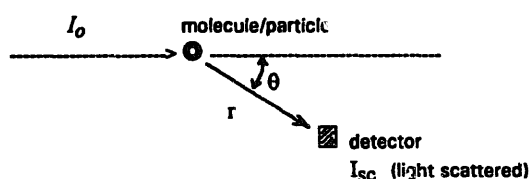
for which

$$\frac{I_{sc}}{I_0} \propto \frac{N_p(n_1/n_0)^4 P(\theta) v^2}{\lambda^4 r^2} \tag{11}$$

Eq. (11) indicates that the fraction of light (I_{sc}/I_0) scattered by a molecule/particle scatterer depends on the number of particles N_p, on the square of the volume v, and hence on the sixth power of the radius, of the particle, on a factor $P(\theta)$ that accounts for the scattering from different parts of the same particle and on the fourth power of the ratio of the refractive indices (n_1/n_0), and depends inversely on the fourth power of the wavelength λ and on the square of the distance r of the detector from the molecule/particle scatterer.

For the materials making up a typical photocatalytic system in heterogeneous photocatalysis, n_0 is 1.33 for H_2O and n_1 is 1.5–1.7 for glass, 3.87 for rutile TiO_2, and ≈ 2.5–3 for anatase TiO_2, all at 365 nm [33,34]. When $n_1 \approx n_0$, the extent of scattered light is negligible, as is commonly noted in the normal spectroscopy of dilute solutions relative to the case when $n_1 > n_0$ for which the light is expected to be highly scattered. In this regard, it is worth noting that,whenever light traverses an optical element, losses of ≈ 5–10% of the light flow always occur, a fact well known to spectroscopists. The percentage of photons absorbable by TiO_2 seems to be around 50–65% in some cases [33,35].

Additional considerations suggest that the photochemically defined *quantum yield* will be difficult to describe experimentally [28], particularly for complex reactor geometries. Consequently, reported quantum yields are but lower limits that have not allowed for scattered light [23]. In defining Eq. (10), we must recognize that semiconductor-assisted photooxidations take place on the solid catalyst (see Fig. 1), and

thus the catalytic properties of the catalyst surface are important, as the course of the reactions depends highly on the characteristics of the surface on light activation. For example, usage of two TiO_2 photocatalysts obtained from different sources, or from different batches from the same source, gives different intermediate products and different distributions of intermediates for experiments carried out under otherwise identical conditions [21]. This calls attention to the necessity of reporting the characteristics of the photocatalyst [23,24,27]. Moreover, a distinction should be made between the light-activated steps (that is, all the steps from the photon absorption event to formation of the ·OH radicals on the particle surface) which are related to the quantum yield, and the ensuing catalytic steps in the photocatalyzed process (including adsorption/desorption events and reaction of the ·OH radicals with the adsorbed substrate and beyond) which depend highly on the surface properties of each photocatalyst.

In heterogeneous photocatalysis, the numerator in Eq. (10) expresses the rate of a catalyzed heterogeneous reaction [2] which is related to the number of catalytically surface active sites [24]; unfortunately, these are also not experimentally measurable [9]. To bypass this difficulty, the number of active sites is often replaced [36] by (i) the surface area of the catalyst, (ii) the mass of the catalyst, or (iii) the number of surface OH^- groups on a photocatalyst such as TiO_2 [25–27]. Regrettably, none of these suggestions describes the actual heterogeneous rate, as measuring the surface area for a somewhat porous catalyst (for example) comprises both the external and internal surfaces [28]; for various reasons the latter may not be useful in some catalytic events. Also, not all the surface sites occupied by OH^- groups are necessarily catalytically active [9], especially because there are different kinds of OH^- groups (two in titania). Also, depending on the reactor geometry, particle aggregation, and stirring, not all the BET catalyst surface (Brunauer–Emmett–Teller measurements in the dry state) is accessible to the substrate being converted.

A simple alternative means of assessing process efficiencies for equal absorption of photons is therefore desirable in heterogeneous photocatalysis.

4.2. Relative photonic efficiencies

One of the objectives of this position paper is a method or protocol to standardize process efficiencies of degradation of various organic substrates for a given set of conditions. The method should circumvent the inherent difficulties encountered in the precise evaluation of the number of quanta absorbed by the photocatalyst (titania), difficulties with utilization of different light sources, different reactor geometries and other unspecified factors by referring all the results to an

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[2] The units that describe a heterogeneous reaction are typically $cm^{-3} s^{-1}$ for both the numerator and the denominator in Eq. (10). However, since the intent is to establish how many moles of reactant (or product) molecules have reacted (or been produced), description of the reaction in homogeneous terms is satisfactory and in no way changes the arguments.

equivalent experiment carried out under identical conditions for a standard process. [3]

The notion of *relative photonic efficiency* (ζ_r) was suggested earlier [9,20], in which the effects of reactor geometry, light source, and photocatalyst properties are fixed in assessing ζ for phenol and for the test molecules [20]. This approach affords comparison of process efficiencies, and avoids the confusion with quantum yields in the literature. Serpone et al. [20] proposed an efficiency term that is foreign to homogeneous photochemistry: *Photonic efficiency* (ζ) describes *the number of reactant molecules transformed or product molecules formed divided by the number of photons, at a given wavelength, incident inside the front window of the cell (flat parallel windows)*.Thus

$$\zeta = \frac{N_{molecules}\ (mol\ s^{-1})\ transformed/produced}{N_{photons}(einstein\ s^{-1})\ incident\ inside\ reactor\ cell}$$

(12)

to avoid unnecessary errors and the need to stipulate reactor geometry and light source, together with the properties (size, surface area, etc. ...) of the photocatalyst material used, the method proposed defined an efficiency that could be used to cross-reference experiments and that would be reactor-independent: the *relative photonic efficiency*, whereby ζ_r is related to an acceptable standard process, a standard photocatalyst material [21], and a standard "secondary actinometer" in photocatalyzed processes.

A preliminary report suggested feasibility [20] using Degussa P-25 TiO_2. The results were encouraging even when broadband AM1 simulated sunlight irradiation from a Solarbox was used. More extensive studies [21,37] have confirmed the usefulness of ζ_r. The initial photoconversion of phenol was chosen as the standard process and Degussa P-25 titania, a material used extensively by several workers, was selected as the standard photocatalyst [21]. The choice of phenol was dictated by the recognition that the molecular structure of phenol is present in many organic pollutants and, like many of these, is degraded essentially by oxidation rather than reduction.

Ultimately, these ζ_r values can be converted into the photochemically defined quantum yield Φ once a quantum yield Φ_{stand} for a given photocatalyst and a given substrate has been determined (see below): whence

$$\Phi = \zeta_r \Phi_{stand}$$

Recent laser work from our laboratory suggests that Φ is likely to be around $\approx 10\%$ for the TiO_2 photocatalyst [3], at least for pristine, electronically pure colloidal samples.

A method to determine photon efficiencies is to relate the initial rate of substrate degradation with the rate of incident

photons reaching inside the front window of the reactor. When the photonic efficiencies ζ for the test substrates and for the standard secondary actinometer (here, phenol) are obtained under identical experimental conditions, there will be no need to measure the photon flow, though it should still be reported when experimentally feasible (certain reactor geometries may preclude such measurements). Thus

$$\zeta_r = \frac{Initial\ rate\ of\ disappearance\ of\ substrate}{Initial\ rate\ of\ disappearance\ of\ phenol}$$

(13)

where both (initial) rates are obtained under exactly identical conditions.

Ideally, ζ_r values should not depend on light intensity and reactor geometry, or on such other parameters as pH, photo-

Table 1

Relative photonic efficiencies ζ_r and quantum yields Φ of the photodegradation of various organic substrates ($\sim 200\ \mu M$) in air-equilibrated aqueous TiO_2 (Degussa P-25; $2\ g\ l^{-1}$; $pH \approx 3$) dispersions

Substrate	Relative photonic efficiency ζ_r^a	Quantum yields[b] $\Phi_x = \zeta_r \Phi_{phenol}$
Phenol[c]	1.0	0.11 ± 0.01
2-Methylphenol	1.2 ± 0.1	0.13 ± 0.01
3-Methylphenol	1.3 ± 0.1	0.14 ± 0.01
4-Methylphenol	1.6 ± 0.1	0.18 ± 0.01
2,3-Dimethylphenol	2.0 ± 0.2	0.22 ± 0.02
2,4-Dimethylphenol	2.7 ± 0.1	0.30 ± 0.01
2,5-Dimethylphenol	2.3 ± 0.1	0.25 ± 0.01
2,6-Dimethylphenol	3.0 ± 0.2	0.33 ± 0.02
3,4-Dimethylphenol	2.5 ± 0.2	0.28 ± 0.02
3,5-Dimethylphenol	1.6 ± 0.2	0.18 ± 0.02
2,3,5-Trimethylphenol	2.8 ± 0.4	0.31 ± 0.04
2-Chlorophenol	1.2 ± 0.1	0.13 ± 0.01
3-Chlorophenol	1.0 ± 0.1	0.11 ± 0.01
4-Chlorophenol	1.2 ± 0.1	0.13 ± 0.01
2,4-Dichlorophenol	1.0 ± 0.1	0.11 ± 0.01

[a] N. Serpone, G. Sauve, R. Koch, H. Tahiri, P. Pichat, P. Piccinini, E. Pelizzetti and H. Hidaka, *J. Photochem. Photobiol. A: Chem.*, 94 (1996) 191.
[b] N. Serpone and J. van de Ven, to be submitted for publication.
[c] Standard substrate.

Table 2

Relative photonic efficiencies ζ_r and quantum yields Φ of the photodegradation of phenol ($\approx 200\ \mu M$) in air-equilibrated aqueous dispersions with various TiO_2 particulates ($2\ g\ l^{-1}$; $pH \approx 3$)

Titania TiO_2	Relative photonic efficiency ζ_r^a	Quantum yields[b] $\Phi_{TiO_2} = \zeta_r\ \Phi_{P-25}$
Degussa P-25[c]	1.0 ± 0.1	0.11 ± 0.01
Baker & Adamson	0.38 ± 0.02	0.042 ± 0.002
Tioxide	1.9 ± 0.1	0.22 ± 0.01
Sargent–Welch	2.1 ± 0.1	0.23 ± 0.01
Fluka AG	2.2 ± 0.2	0.25 ± 0.02
Hombikat UV-100	0.25 ± 0.02	0.028 ± 0.002

[a] N. Serpone, G. Sauve, R. Koch, H. Tahiri, P. Pichat, P. Piccinini, E. Pelizzetti and H. Hidaka, *J. Photochem. Photobiol. A: Chem.*, 94 (1996) 191.
[b] N. Serpone and J. van de Ven, to be submitted for publication.
[c] Standard titania.

[3] It must be remembered that workers who delve into heterogeneous photocatalysis specifically applied to environmental remediation come from various cultures, the least of which is photochemistry. In this light, it is therefore necessary to define a protocol that the vast majority of these workers can utilize with resources not necessarily photochemical in nature.

catalyst concentration, substrate concentration, and temperature.

The efficiencies ζ_r reported elsewhere [21] and in part reproduced here (Tables 1 and 2) refer specifically to substrate disappearance and demonstrate the general applicability of the proposed method. Although the ζ_r presented in Table 1 are given for substituted phenols, the concept of relative photonic efficiencies is by no means restricted to these species; it should be applicable also to other substances with the only constraint that phenol be the standard substrate against which all ζ_r are reported (note that experimental conditions must also be reported for such efficiencies to be useful). The effects of variations in light intensity (13–100%, where 100% is 190 mW cm^{-2}), reactor geometry, pH (3–6), temperature (12–68°C), concentration of organic substrate (40–800 μM), and loading of photocatalyst material TiO$_2$ (0.2–2 g l^{-1}) on the relative photonic efficiencies were examined [21] for three phenolic substrates: 2-methylphenol, 2,4-dimethylphenol, and 4-chlorophenol; see Fig. 2. Additionally, ζ_r values of other organic substrates were determined under certain specified conditions (Table 1).

The effects of the nature and the source of various TiO$_2$ specimens on ζ_r were also explored and are summarized in Table 2. It is interesting to note that the Tioxide, the Sargent–Welch and the Fluka titania specimens are about twice as efficient as the Degussa P-25 specimen in the photooxidation of phenol. In this regard, Riegel and Bolton found by spin-trap EPR studies that the production of 'OH radicals on the P-25 titania sample relative to those generated on an Aldrich anatase sample differs by a factor of ≈ 1.9 [38], rendering the former more efficient towards photo-oxidations by such radicals.

The method that is being proposed [21] does have the advantage of simplicity and affords a means by which other investigators can compare their results with those of others.

In heterogeneous photocatalysis, the focus must be and remains to demonstrate the total mineralization or disposal of a given pollutant substrate, not least of which is the identification of the various intermediate species in their course to the ultimate oxidation product(s). It will be relevant also to assess the photonic efficiencies for these processes and, as noted by Braun and co-workers [11], the mineralization of TOC is of prime significance in any water treatment process. Indeed, a recent study by Serpone et al. [39] demonstrates that, at least for one specific case, the relative efficiency of the disappearance of phenol using two entirely different industrially available titania photocatalysts is identical (perhaps fortuitously) with the relative efficiency for the complete mineralization of phenol into carbon dioxide. For example, the relative photonic efficiency for the (initial) disappearance of phenol for the Hombikat UV-100 titania specimen is $\zeta_r = 0.25 \pm 0.03$ (relative to Degussa P-25 titania as the standard photocatalyst); the corresponding ζ_r for the fundamentally more important TOC degradation process is 0.27 ± 0.03 [39].

4.3. Quantum yields in heterogeneous photocatalysis

Apparent quantum yields or, better, photochemical efficiencies based on the total number of photons incident on the reactor for the disappearance of various organic substrates have been determined at 365 nm for cresols and dimethylphenols [40]; they ranged from 0.0076 to 0.010 and from 0.0060 to 0.015, respectively, and reflect the lower limits of the actual quantum yields {2 g l^{-1} TiO$_2$ and 20 mg l^{-1} of organic}. Analogous efficiencies were reported for phenol (0.006; 100 mM; 1 g l^{-1} TiO$_2$) [41], for 4-chlorophenol (0.015; 8 g l^{-1} TiO$_2$; $\lambda > 320$ nm) [30], for H$_2$ formation (0.01; reduction of water) [42], and for hydrogenolysis of CH$_3$C$\equiv$H (0.0012) [43]. The range in these values seems rather general. By contrast, for the disappearance of 1-propanol and propanal, Lepore and coworkers [29,30] reported that apparent quantum yields converge to unity for the pure substrates, and noted that these yields are true quantum yields and that there is efficient competition between substrate oxidation and electron/hole recombination. At concentrations of about 0.10–0.12 M in 1-propanol, the reported quantum yield was ≈ 0.80. These authors basically suggest that charge carrier recombination has essentially been shut off. Perusal of the events noted in the Jablonsky-type diagram of Scheme 1 would suggest otherwise. It would appear unlikely,
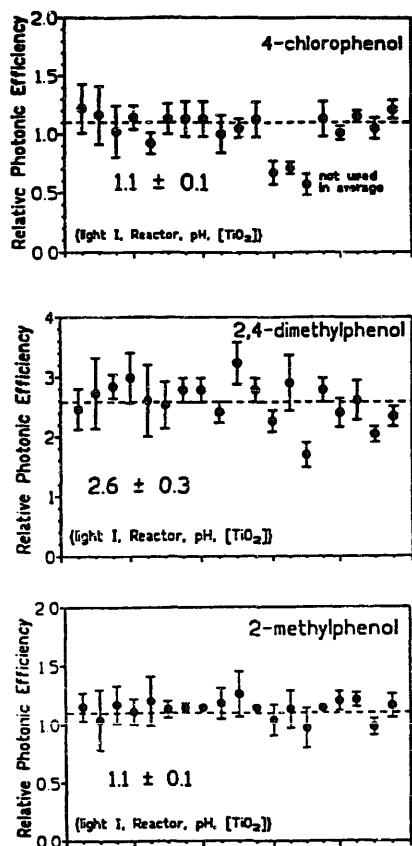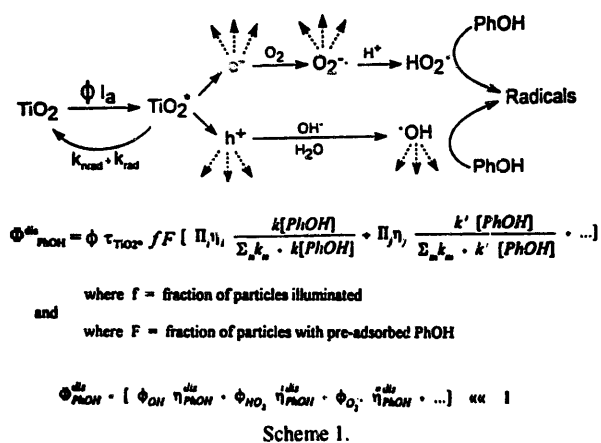

Fig. 2. Relative photonic efficiencies for 4-chlorophenol, 2,4-dimethylphenol and 2-methylphenol showing the values used to calculate averages; includes only the effects of light intensity, reactor geometry, pH and concentration of titania; [substrate]$_i \approx 20$ mg l^{-1}.

Scheme 1.

taking phenol as an example substrate, that even at high phenol concentrations formation of the oxygen-centered radicals (O_2^- ', HO_2^- and 'OH) primary oxidation of phenol by these species would be so efficient (unitary efficiencies) as to totally preclude radiative and nonradiative recombination of the exciton and its dissociated conduction band electrons and valence band holes. We contend that the quantum yield of the primary oxidation of phenol to produce the corresponding cyclohexadienyl radical (or equivalent) and the subsequent intermediate products will probably be far less than unity (Scheme 1).

Quantum yields in heterogeneous media can be described in the same manner as for homogeneous photochemistry if the number of actual absorbed photons or the fraction of light absorbed by the solid photocatalyst can be assessed by some spectroscopic means. Several attempts were noted by Schiavello and coworkers [25–27], by Cabrera et al. [28] and by Valladares and Bolton [44]; the latter workers found a quantum yield of 0.056 for the photobleaching of methylene blue. More recently, Sun and Bolton [35] reported the quantum yield of 'OH radical formation to be 0.040 for an Aldrich TiO$_2$ anatase sample used in the conversion of methanol to formaldehyde.

We have used a modified integrating sphere method, otherwise identical to that of Sun and Bolton [35], to determine the fraction of light absorbed by Degussa P-25 TiO$_2$, which we later used as the standard photocatalyst to determine the quantum yield Φ_{stand} for the oxidative conversion of phenol taken as the standard process and the test molecule, respectively. This quantum yield is subsequently used to convert reported relative photonic efficiencies ζ_r [21] into quantum yields [4] of photooxidation of those organic substrates summarized in Table 1. We now describe some of the details of the procedure.

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[4] The quantum yield data reported in Tables 1 and 2 must be considered preliminary at the stage of development. Work is under way by a different experimentalist (student/post-doc) with a different home built reactor arrangement to attest to the reproducibility of these early measurements and therefore to the validity of the method proposed.

4.3.1. Determination of the fraction of photon flow absorbed by titania P-25

Degussa P-25 titania consists of two crystalline phases, $\approx 80\%$ anatase and $\approx 20\%$ rutile, and also contains some SiO$_2$, some Al$_2$O$_3$, HCl and Fe; it is non-porous with a BET specific surface area of ≈ 55 m^2 g^{-1} and crystallite sizes in the range 25–35 nm [45]. These ≈ 30 nm crystallites aggregate in a regular dispersion; aggregate sizes vary between 50 nm and 200 nm [46,47]. A 250 ml acidified (0.01 M HCl) aqueous suspension of 2 g l^{-1} of P-25 TiO$_2$ was sonicated with an ultrasonic 250 W cell disrupter (Sonics & Materials) at ≈ 50 W for 15 min, subsequent to which the milky dispersion was centrifuged (2000 rpm) in 50 ml portions until a transparent colloidal sol was obtained. This transparent sol was extracted and left to evaporate slowly at ambient temperature. Approximately 250 mg of the TiO$_2$ was recovered and later used to prepare a stock colloidal sol 1 g l^{-1} in titania in 0.01 M HCl aqueous media.

Absorbance measurements were carried out using a 0.20 mm quartz cell on a Shimadzu UV-265 spectrophotometer that was also equipped with a Shimadzu integrating sphere assembly (Fig. 3(a)) which contained BaSO$_4$ as the reflectance substance (Eastman Kodak White Reference Standard; reflectance 98.23% at 365 nm). Fig. 3(b) illustrates the modified method used to assess the fraction of the photon flow, f_λ, actually absorbed by the titania sols (concentration range: 20–100 mg l^{-1}); see ref. [35] for additional details.

With the 0.20 mm cell, unaccountable light scattered is negligible. $A_1 \{ = -\log[(I_0 - 2I_{abs})/I_0] \}$ is the instrument response for a solution with no titania particles, whereas $A_2 \{ = -\log[(I_0 - 2I_{abs} - 2I_{abs}^{sol})/I_0] \}$ is the response for the

(a)

$f_\lambda = I^{sol}_{abs}/I_o = \{10^{-A_1} - 10^{-A_2}\}/2$

$Abs = -\log\{1 - (I^{sol}_{abs}/I_o)\}$
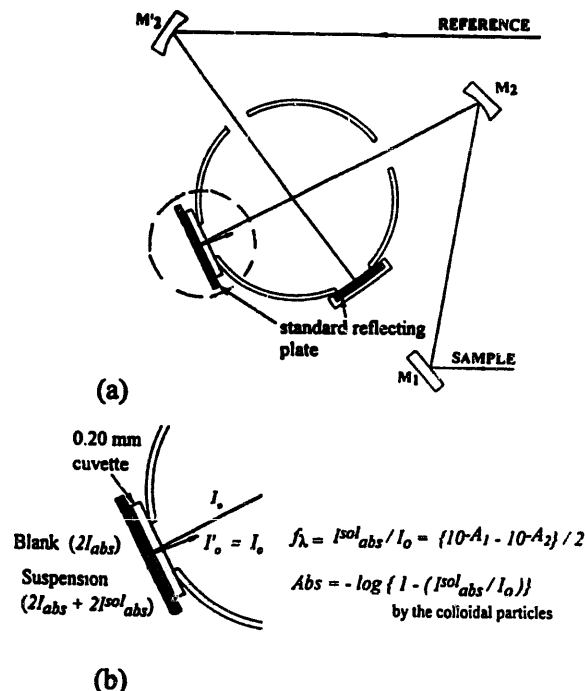by the colloidal particles

(b)

Fig. 3. Modified integrating sphere assembly method to determine the fraction of absorbed light for titania colloidal sols; concentration range 20–100 mg l^{-1}.

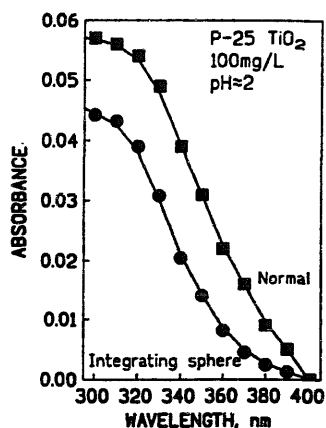Fig. 4. Absorption spectra of a 100 mg l^{-1} Degussa P-25 titania colloidal sol in 0.01 M HCl aqueous media (path length 0.20 mm) using the "normal" absorption spectroscopic method (filled circles) and the integrating sphere method (filled squares).

titania colloidal sol from which the fraction f_λ { = [10$^{-A_1}$ − 10$^{-A_2}$]/2} is evaluated. The absorbance spectrum of the titania particles in the sol can then be calculated from Abs = − log(1 − f_λ). A complete description of this modified method was recently presented by Sun and Bolton [35]. In the configuration of Fig. 3(b), the reflected incident beam I_0' must be nearly identical to I_0; that is, attenuation of the incident beam must be kept at a minimum. The incident photon flow I_0 was determined by Aberchrome 540 actinometry at 365 ± 10 nm by a procedure supplied by Aberchromics Ltd. [18]. The absorbance spectra of the 100 mg l^{-1} titania sample using the integrating sphere assembly (filled circles) and the spectrum of the titania sample recorded using the normal spectroscopic method (filled squares) also employing the 0.20 mm cell are presented in Fig. 4. Note the significant deviation between the two spectra. This deviation reflects the degree to which light is scattered by the particles. At 370 nm about 70% of the "normal" spectrum is accounted for by light scattering, whereas below 300 nm about 20% of the normal spectrum is caused by light scattering; Fig. 5 illustrates this deviation at various wavelengths.

Fig. 6 summarizes the Beer–Lambert behavior of the titania sols at 365 nm for the normal spectra and for the integrating sphere spectra. The fractions of light absorbed at concentrations greater than 0.100 g l^{-1} have been estimated assuming Beer's law to be followed at higher TiO$_2$ loadings.
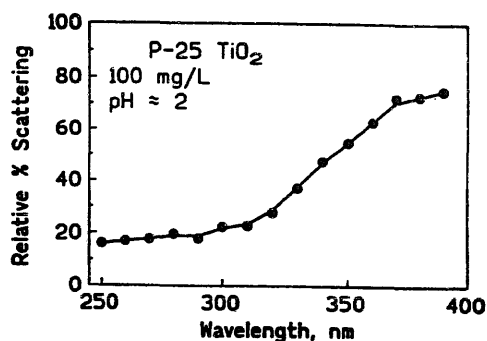

Fig. 5. Relative percent light scattering {as $I_{sc}/(I_{sc} + I_{abs})$} for a 100 mg l^{-1} titania colloidal sol between 250 and 400 nm.
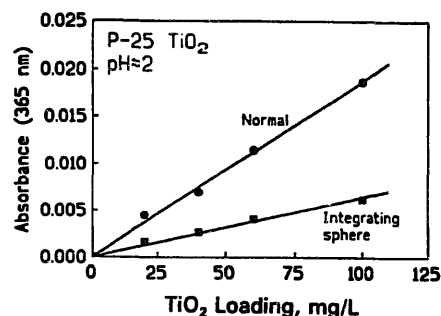

Fig. 6. Absorbance at 365 nm versus titania sol concentration (Beer–Lambert behavior) for spectra taken using the "normal" method and the integrating sphere method.

4.3.2. Determination of quantum yields

Initial rates in the photocatalyzed oxidation of phenol (Aldrich, 99% + redistilled; pH 2.7) were obtained by monitoring the temporal variations in the HPLC chromatograms {Waters 501 HPLC pump; Waters 441 HPLC detector; HP 3396A integrator; Waters Bondapak C-18 reverse phase column} after 365 ± 10 nm (Bausch & Lomb monochromator) irradiation with a 1000 W Hg/Xe lamp (Oriel) and filtration of aliquots through a 0.20 μm Teflon filter. The initial rate data are given in Table 3.

Perusal of the initial rates in Table 3 and the corresponding graphical representation as a function of increasing TiO$_2$ loading (Fig. 7) shows that the rates increase linearly from 0 to 0.50 g l^{-1} loading and then show a negative deviation to very low values at 4.00 g l^{-1}. This is understandable since, as the titania loading increases, the suspension becomes more opaque to light, such that only photons absorbed by titania

Table 3
Spectroscopic parameters and quantum yields for the photocatalyzed oxidative degradation of phenol at ambient temperature and air-equilibrated sols

TiO$_2$ loading/(g l^{-1})	Initial rate ($\times 10^{-8}$ mol min^{-1})	I_a ($\times 10^{-6}$ einstein min^{-1})	f_{365}	Φ_{dis}^{PhOH}
0.10	0.97 ± 0.12	3.035	0.0148	0.215 ± 0.027
0.30	2.54 ± 0.63	3.152	0.0437	0.184 ± 0.046
0.50	4.13 ± 0.51	3.058	0.0718	0.188 ± 0.023
1.00	6.12 ± 0.50	3.058	0.1385	0.144 ± 0.012
2.00	8.84 ± 0.33	2.813	0.2579	0.122 ± 0.005
4.00	1.57 ± 0.53	3.152	0.4492	0.011 ± 0.004

[a]The incident photon flow was measured by Aberchrome actinometry using a procedure supplied by Aberchromics Ltd. of the University of Wales College of Cardiff, Cardiff CF1 3TB, UK.
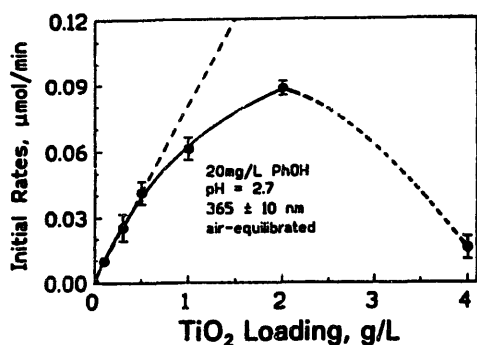
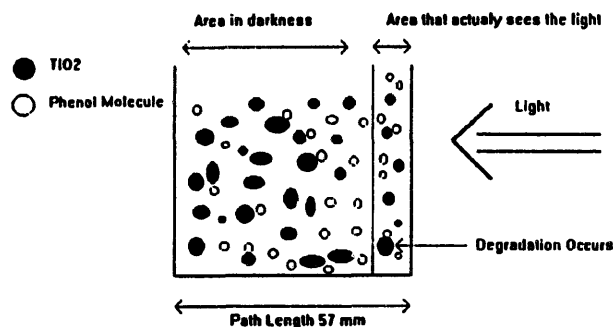Fig. 7. Initial rates versus loading of titania (Degussa P-25).

Fig. 8. Diagram of the reactor cell used in the photocatalyzed oxidative degradation of phenol in determining initial rates of disappearance of phenol and subsequently the preliminary quantum yield data (see Footnote 4).
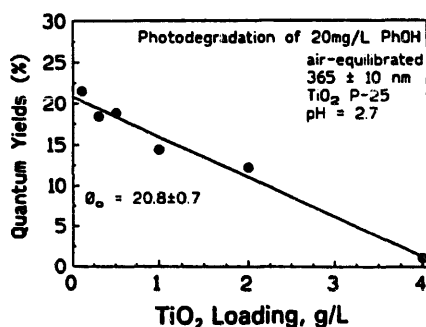

Fig. 9. Dependence of quantum yields on the loading of Degussa P-25 titania colloidal sols.

particles onto which a phenol molecule is pre-adsorbed may be effective in carrying out the redox chemistry. Other incident photons, absorbed or otherwise, are wasted. In essence, the titania particles themselves act as an inner filter (see Fig. 8) despite good stirring of the dispersion during irradiation, a problem also encountered in homogeneous photochemistry.

The parameters used to evaluate the quantum yields for the photocatalyzed oxidative degradation of phenol are summarized in Table 3; the dependence of the quantum yields on the concentration of TiO_2 is portrayed in Fig. 9. At infinite dilution of the colloidal sol the overall quantum yield Φ_0 is 0.21 ± 0.01; at a concentration of 2.00 g l^{-1} of titania, the quantum yield is 0.11 ± 0.01.

Subsequent to determination of the quantum yield for phenol at 2.00 g l^{-1} in titania, the relative photonic efficiencies

reported in Tables 1 and 2 were converted into the corresponding quantum yields (Tables 1 and 2) using $\Phi = \zeta_r \Phi_{phenol}$, where $\Phi_{phenol} = 0.11 \pm 0.01$.

5. Concluding remarks

We have presented above a potentially useful method that correlates the efficiencies of a given process with similar work in other laboratories. The procedure of relative photonic efficiencies is simple and does not require sophisticated instrumentation. Values can be converted into *quantum yields* for the photocatalyzed oxidation of a given substrate (e.g. phenol or other), as the quantum yield for the photo-oxidative degradation of phenol has been determined using an integrating sphere method to determine the extent of light absorbed by the photocatalyst Degussa TiO_2 P-25; Sun and Bolton [35] have reported the value for Aldrich TiO_2. The integrating sphere method is briefly described for determining the fraction of the photon flow absorbed by the titania sample. All the relative photonic efficiencies can subsequently be converted to quantum yields to satisfy the definition of Φ of homogeneous photochemistry.

The quantum yield of formation of $\equiv$Ti-·OH radicals, Φ_{OH}, is 0.040 ± 0.003 [35], consistent with recent findings by Serpone et al. that Φ should be around 0.10 [3] for photocatalyzed oxidations (and reductions) using electronically pure, naked TiO_2 colloids, as $\approx 90\%$ of the photogenerated charge carriers have recombined by 10 ns and therefore are not available for redox chemistry. Another point is worth noting. In our recent work [21] we found different photonic efficiencies for different photocatalyst materials (different batches, different sources, etc.), sometimes by a factor of two or more. Having to use an integrating sphere and an EPR spectrometer each time one wishes to determine the quantum yield of a heterogeneous process for different photocatalysts would indeed be time-consuming, as such experiments are not trivial [35] and the appropriate instrumentation is not always universally available. The relative photonic efficiencies we are advocating in this position paper make sense, as they provide a quick and simple means following which the quantum yield can be obtained as indicated above.

Examination of the quantum yields and relative photonic efficiencies for different photocatalyst materials (Table 2) shows a nine-fold variation between the lowest value (Hombikat UV-100) and the highest (Fluka). Such variations may be due to several factors: (1) differences in the crystalline phase of the titania (anatase versus rutile—the latter is known to be relatively inactive in photodegradations); (2) differences in the sizes and shapes of the particles, thereby affecting the extent of light scattered; (3) differences in the density of OH$^-$ groups on the particle surface and in the number of water molecules hydrating the surface, particularly for particles for which the hydrophilic/hydrophobic properties vary; (4) differences in the number and nature of trap sites both in the lattice and at the surface; and finally (5) the adsorption/

desorption characteristics of each surface, which may vary according to the nature of the photocatalyst material and also the nature of the organic substrate. Such adsorption/desorption variations may also affect the efficiency of the photocathodic reduction of molecular oxygen, which is thought to control the efficiency of the photoanodic process, not to mention the possibility, as suggested by Fox [48], that active sites switch identity with inactive sites during the photocatalytic sequence. Taking all these factors into consideration precludes a definition for a *heterogeneous quantum yield* [defined as a function of a heterogeneous rate in terms of moles of species per unit time per surface area of the catalyst ($mol\ t^{-1}\ cm^{-2}$) divided by the moles of photons absorbed per unit time and unit volume of suspension (einstein t^{-1} cm^{-3})] espoused by Cabrera et al. [28]. The present treatment of quantum yields has therefore assumed a pseudo-homogeneous treatment.

Finally, the congruence between the quantum yield of photo-oxidation of phenol of 0.11 (Table 1) by illuminated Degussa P-25 titania and the value of 0.11 reported by Augugliaro et al. [49], also for the photo-oxidation of phenol, for "home prepared" polycrystalline TiO_2 in the size range 44–250 μm is indeed striking. At this stage of development this striking similarity must be seen as fortuitous and awaiting further verification.

Acknowledgements

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