The P25 TiO2/4-chlorophenol photocatalytic system: Spectral sensitivity or lamp artefact?

Published in:
Journal of Photochemistry and Photobiology A: Chemistry

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

The P25 TiO$_2$/4-chlorophenol Photocatalytic System: Spectral Sensitivity or Lamp Artefact?

Soo-Keun Lee[a], Andrew Mills*[b] and Christoper O'Rourke[b]

a: DGIST, 333, Techno Jungang Daero, Hyeonpung-Myeon, Dalseong-Gun, Daegu, 42988, Korea; b: School of Chemistry & Chemical Engineering, Queen´s University Belfast, Stranmillis Road BT9 5AG, Belfast, United Kingdom.

E-mail addresses: andrew.mills@qub.ac.uk

Abstract

The photocatalysed mineralisation of 4-chlorophenol, 4-CP, by P25 TiO$_2$ is a well-studied photocatalytic system. A previous report (Emeline *et al*, *J. Phys. Chem. B*, 2000, **104**, 11202) reported an action spectrum, i.e. photonic efficiency, η, vs. excitation wavelength, λ(ex), for the P25/4-CP system, that exhibited a series of peaks and troughs which, it was proposed, provided evidence of P25 spectral sensitivity. However, in this re-examination it is shown that the peaks and troughs in the action spectrum occur in the regions of the troughs and peaks in the emission spectrum of the Xe/Hg lamp used by these researchers. The dependencies of η, and quantum yield, ϕ, upon incident light intensity, ρ, in semiconductor-sensitised photocatalytic systems are considered and a rationale provided that suggests the action spectrum reported by Emerline *et al.* is actually due to the variation in ρ in the emission spectrum of the Xe/Hg lamp. In order to test the latter hypothesis, the action spectrum of the same P25/4-CP system is determined, but this time using a Xe lamp; the latter action spectrum has no peaks and troughs and corresponds closely to that of the diffuse reflectance spectrum of the P25 dispersion as expected if there is no spectral sensitivity. This action spectrum, and similar results reported by others for this and other test pollutants, provides strong evidence that the claim of spectral sensitivity for the P25/4-CP system is unjustified, based on the reported action spectrum of Emeline *et al.*, since the latter is due to the spectral variation in irradiance of the Xe/Hg excitation source employed in the original study.

Key words: 4-chlorophenol; spectral sensitivity; titanium dioxide; photocatalysis

Introduction

In a photo-sensitised reaction the ratio of the initial rate of the photoreaction (units: moles (of reactant) s^{-1}), r, to that of the incident intensity, ρ, (units: moles of photons (i.e. einsteins) s^{-1}) of excitation wavelength, $\lambda(ex)$ (units: nm), is the photonic efficiency of the system, η (units: molecules/photon) [1, 2]. In studies of heterogeneous semiconductor photocatalytic systems there is an increasing need to record the action spectrum of the photocatalytic system, i.e. a plot of η vs. irradiance wavelength [3,4], since it can help identify the light-absorbing species, which should be the semiconductor in the case of semiconductor photocatalysis, but can be the test pollutant, especially when using dyes [5,6] or other chemical species that form a charge transfer complex with the semiconductor [7-9], in cases of dye-photosensitisation and photolysis.

One of the most studied semiconductor-sensitised photocatalytic systems is the photo-oxidative mineralisation of 4-chlorophenol (4CP) by dissolved O_2, mediated by TiO_2 [10-23], i.e.

$$\text{4-CP} + O_2 \xrightarrow[\text{UV}]{\text{TiO}_2} \text{oxidation products} \qquad (1)$$
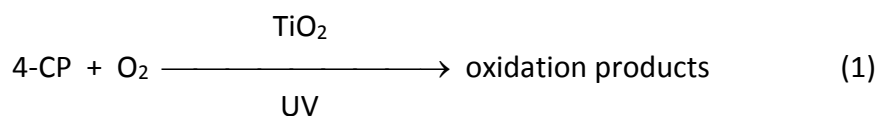
A key feature of 4-CP as a test pollutant is that it does not absorb UVA radiation (320-400 nm), in contrast to TiO_2, with its bandgap of 3.0 (anatase), or 3.2 (rutile) eV, so that, with respect to reaction (1), little or no destruction of 4CP is observed in the absence of TiO_2. The most employed form of TiO_2 for studying reaction (1) is Degussa (now Evonik) P25, referred henceforth as P25, which is an 80:20 mixture of anatase and rutile, with a fundamental particle size of ca. 30 nm, but with a tendency to form aggregated particles up to 1 μm in diameter (average secondary particle size = 473 nm) [24, 25]. In this paper, when any references to eqn(1) is made, it should be assumed that the TiO_2 used is P25, unless stated otherwise.

The kinetics of the P25/4-CP photocatalytic system has been probed extensively and numerous different reaction mechanisms have been proposed to provide a rationale for the observed kinetics [24]. Whatever the actual mechanism, a key **empirical** kinetic feature of reaction (1) is the following dependence of initial rate, r, upon incident (UV) intensity, ρ, for a fixed initial concentration of 4-CP, $[\text{4-CP}]_o$ and excitation wavelength, $\lambda(ex)$ [13,24]:

$$r = k_\theta(\alpha f \rho)^\theta \tag{2}$$

where, k_θ is a proportionality constant (units: moles/s) which depends upon: $[4\text{-CP}]_o$ and the intrinsic activity of the photocatalyst, i.e. the probability that an absorbed ultra-bandgap photon leads to a reaction; α is a proportionality constant of convenience, with a value of unity, but with units: s einstein^{-1}, so that it renders the collection of terms, $\alpha f \rho$, unitless and simplifies the units of k_θ and any subsequent mathematical manipulations of eqn(2); f is the fraction of incident light absorbed and θ is a power term with a value of unity at low ρ, but which tends to 0.5, or zero, at high ρ, depending upon which kinetic model of photocatalysis one adopts [13,24]. For example, in the photocatalysed oxidation of acetic acid [3], by Merck TiO_2, Ohtani and his co-workers suggest a radical chain mechanism mediated by peroxy radicals is responsible for $\theta = 0.5$ over a wide irradiance range (typically ca. 0.1-2 mW cm^{-2}). In contrast, in the photocatalysed oxidation of 4-CP, by P25 TiO_2 reported by Pichat and his co-workers [11], in which $\theta = 0.5$, others suggest that this is due to the dominance of electron-hole recombination at the high irradiances used (2-50 mW cm^{-2}) [24].

The kinetics of photocatalysis depend upon many different variables, including: the nature of the test organic pollutant (4-CP in this work) temperature, pH, wavelength of the UV light, reactor design and materials [24]. As a consequence, it is not possible to identify a general value for ρ, ρ(threshold), for use in eqn (2), much below which r is proportional to ρ, and much above which r is (usually) proportional to $\rho^{1/2}$. In addition, it is clear from many studies of reaction (1), and a feature of most proposed kinetic mechanisms, that ρ(threshold) increases with increasing value of $[4\text{-CP}]_o$. For example, the results of Mills and Wang, using BLB lamps (with λ(max) emission = 365 nm) as the irradiation source in a study of reaction (1), indicate that the irradiance threshold (= ρ(threshold)/irradiation area, σ) is ca. 0.32 mW cm^{-2} at $[4\text{-CP}]_o$ = 0.3 mM which increases to ca. 0.71 mW cm^{-2} at $[4\text{-CP}]_o$ = 1 mM [14]. For simplicity, we shall assume here that at ρ(threshold) the rate may be described equally well by eqn(2), where θ is either 1, or 0.5, since this then reveals a useful relationship between $k_{0.5}$ and k_1, namely $k_{0.5}/k_1$ = $(\alpha f \rho(\text{threshold}))^{0.5}$. Note that ρ(threshold) is a mathematical construct, used here to help identify the regions: (i) $\rho \ll \rho$(threshold), over which rate is proportional to ρ and (ii) $\rho \gg \rho$(threshold), where rate is

proportional to $\rho^{1/2}$; clear examples of this transition have been reported by others [3,26,27] and are a key feature of various kinetic models [25]..

It follows from eqn(2) that, at any excitation wavelength, the measured photonic efficiency, η, will be given by the expression:

$$\eta = k_\theta (\alpha f \rho)^\theta / \rho \qquad (3)$$

And the quantum yield, ϕ, by:

$$\phi = k_\theta (\alpha f \rho)^\theta / f \rho \qquad (4)$$

Similar expressions for the quantum yield of a photocatalytic system have been reported previously [28,29]

It also follows that only **if θ = 1**, will η (now = $k_1 \alpha f$) and ϕ (now = $k_1 \alpha$) be **independent of ρ.** In addition, if the classical band model of semiconductors applies, in which the photogenerated charge carriers are thermalized before reacting, then k_1 would be independent of excitation wavelength and the action spectrum should reflect only the faction of light absorbed by the semiconductor as a function of wavelength, and so help identify the absorbing species [30,31]. In such circumstances the quantum yield will depend only upon k_1 and so will not be dependent upon the excitation wavelength at all. An excellent example of such a case is the action spectrum reported by Ohtani *et al.* for the dehydrogenation of methanol (MeOH) using platinised anatase TiO_2 (from Merck), which revealed that η was largely independent of UV irradiance over the range ca. 0.1 – 10 mW cm^{-2}, using either: 390, 350 or 380 nm light [3]. Thus, in the latter system, even at a high irradiance (ca. 10 mW cm^{-2}) the irradiance threshold is not exceeded and so θ = 1. In contrast, the same researchers reported the action spectrum for the photo-oxidative mineralisation of acetic acid, using the same set-up and photocatalyst as before, which revealed an irradiance threshold < 0.1 mW cm^{-2}, using either: 390, 350 or 380 nm light, and values of η at these three different values of λ(ex) that were proportional to $\rho^{0.5}$ over the low to moderate irradiance range 0.1 to 2 mW cm^{-2} [3]. These findings help highlight the fact that the value of ρ(threshold) depends upon, amongst other things, the nature of the test organic pollutant (4-CP in this work) as well as its concentration, as noted earlier, and cannot be readily predicted, but instead needs to be determined experimentally for each system under study.

In practical terms, the above discussion shows that when running a true action spectrum of a heterogenous semiconductor photocatalytic system, such as reaction (1), it is **<u>essential</u>** that the value of ρ **is < ρ(threshold),** so that $\theta = 1$, **at each wavelength.** It also follows that when $\theta < 1$, the calculated values for η and ϕ will be a function of ρ and tend to decrease with increasing ρ. In a number of studies of reaction (1), [4-CP]$_o$ has been fixed and the rate determined as a function of ρ, so as to yield a value for θ, via eqn (2). Table 1 provides details of some of these studies, including the maximum irradiance used, ρ(max)/σ, and the calculated **average** value of θ over the range 0 - ρ(max), i.e. θ_{av}. It is worth noting that in such studies, in the case of a $\theta_{av} < 1$, then the nearer its value is to 0.5, the more likely it is that the value of θ, in eqn(2), will be 0.5 at ρ(max). A brief inspection of the values of θ_{av} and ρ(max) in table 1, suggests that, in most cases, at the values of [4-CP]$_o$ used, θ **will be ca. 0.5 at a relatively modest UV irradiance, i.e. ca.2-3.5 mW cm^{-2} at 365 nm**.

Table 1: Characteristics of Rate vs ρ studies of reaction (2), with TiO$_2$ = P25

[TiO$_2$] (mg/L)	[4CP]$_o$ (mM)	Light source	ρ(max)/σ (mW/cm^2)	θ_{av}	η (molecules/photon)	Ref
125	0.245	450 W medium pressure Hg lamp	6.4**	0.8	0.012 (360 nm)	10
200	0.155	125 W medium pressure Hg lamp	2-50	0.5	0.009 (> 340 nm)	11
500	1.0	8W BLB lamps	3.3	0.74	0.011	12
300	0.213	1000W Xe/Hg lamp with interference filter	59.8	0.7*	-	13
500	0.3	8W BLB lamps	3.47	0.5*	-	14
300	0.2	1000W Xe/Hg lamp with monochromator	12.3**	1	0.0057	1

*: calculated using data in paper

**: although details of σ are not given in the paper –its value is assumed here to be 1 cm^2.

The spectral sensitivity hypothesis

A notable exception to the kinetics feature described above appears to be the work of Emeline *et al.* [1] on reaction (1), who report $\theta = 1$ for ρ(max) = 12.3 mW at 365 nm, which is taken to be equivalent to an irradiance of ca.12.3 mW cm^2 from this point forward. Note: although details of the irradiation area, σ, are not given, the assumption here that $\sigma = 1$ cm^2 is not altogether unrealistic given the irradiation set up employed and is supported by data from a previous paper from the same authors examining the same photocatalytic system, in which the irradiance at 365 nm is given [13]. To put an irradiance of ca.12.3 mW cm^{-2} into context the solar UV level on a clear summer's day in Melbourne Australia is 5.86 mW cm^{-2}, thus, an irradiance of ca.12.3 mW cm^{-2} is not insignificant [24].
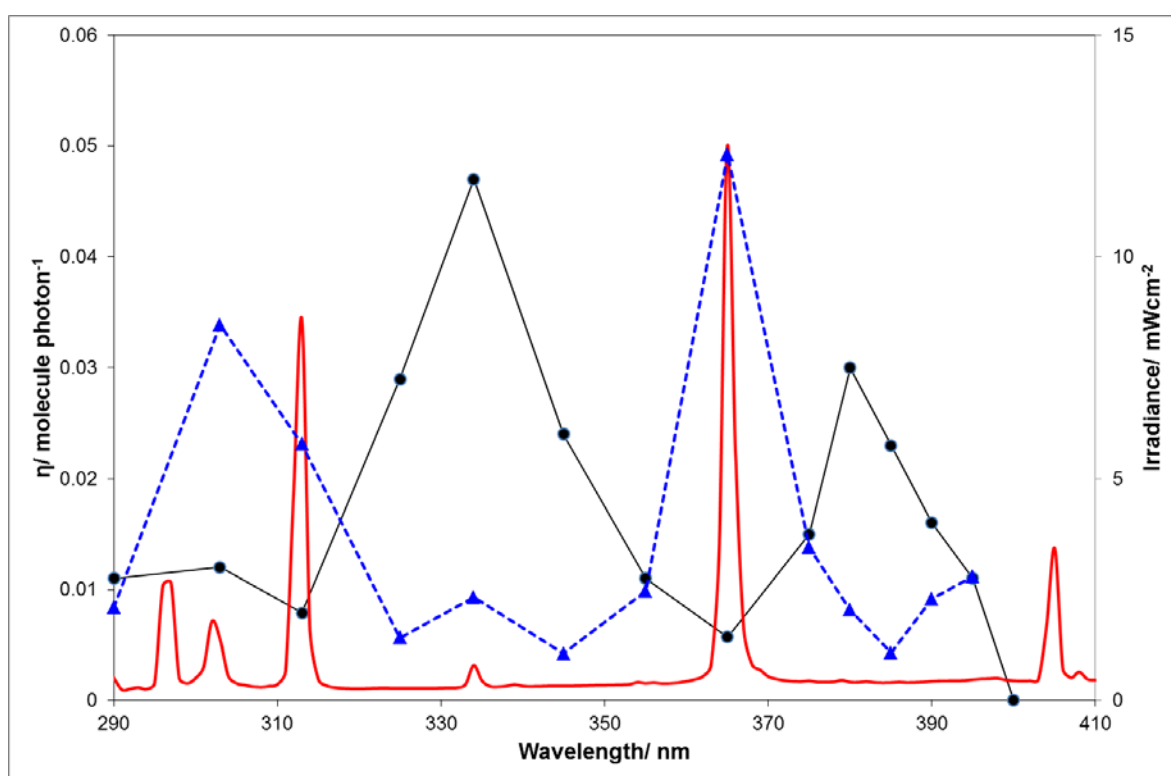

Figure 1: Action spectrum (black line, ● data points) for reaction (1), [P25 TiO$_2$] (300 mg/L), [4-CP]$_o$ (0.2 mM) and pH (pH 3), as reported by Emeline *et al.* [1], generated using the irradiances (assuming $\sigma = 1$ cm^2) illustrated by the blue, broken line and ▲ data points for a 1000W Xe/Hg lamp. A normalised, high definition emission spectrum of a 1000W Xe/Hg lamp is illustrated for comparison purposes (red line).

Emeline *et al.* [1] also found that r was largely independent of [4-CP]$_o$ at ca. 0.2 mM, when [TiO$_2$] = 0.3 g dm^{-3} and pH = 3, which meant that the action spectrum for reaction (1) generated by these researchers under these reaction conditions, illustrated in figure 1 (black

line), was effectively a measure of the combination of the intrinsic activity of the photocatalyst as a function of excitation wavelength, k_1, and the fraction of light absorbed, *f.* However, this η vs λ(ex) action spectrum comprised a series of peaks and troughs (see figure 1, black line) which, the authors claimed, showed that the photocatalysed oxidation of 4-CP by oxygen, photosensitised by P25, i.e. reaction (1) under the conditions described above, is spectrally dependent. This claim was supported by a subsequent plot of the data in the form of: ϕ vs λ(ex), since it showed the same features. As Emeline et al point out, such spectral sensitivity is 'counter to the classical band model of semiconductors and conventional wisdom' [1], in which the photogenerated charge carriers are thermalized before reacting, so as to make spectral sensitivity unlikely. In contrast, these workers propose a spectral sensitivity model, in which the electronic properties and behaviour of the semiconductor are strongly dependent on the co-relation of the electronic states in different valleys, so that excitation at different wavelengths may result in different activities and selectivities [32]. Thus, Emeline *et al.* interpreted the above results in terms of spectral sensitivity exhibited by P25 in reaction (1), not only on the basis of the action spectrum in figure 1, but also because they found, from rate vs ρ studies at 380, 365 and 340 nm, that θ = 1 in all three cases, thereby suggesting that θ = 1 at all the wavelengths employed in their work [1]. The latter is a necessary condition if spectral sensitivity is to be inferred from the spectral variation in the action spectrum illustrated in figure 1.

Reference [1] is just one of many publications of Emeline and his co-workers on spectral sensitivity, in which different light sources, were used to study; (i) the mineralisation of organics (exclusively Xe/Hg lamp) [1,15,33] and (ii) the photostimulated adsorption of gases, such as H_2 and O_2 (Hg (high pressure) [34] or Xe lamp [35-36]). Interestingly, when P25 was used to study the photostimulated adsorption of H_2 [37], its action spectrum, recorded using a Xe lamp, appears relatively featureless compared to that illustrated in figure 1 for the P25/4-CP system.

However, a potential cause for concern that spectral sensitivity might not be the only explanation for the spectral variation in the action spectrum illustrated in figure 1, and the subsequent plot of ϕ vs λ(ex), can be quickly identified by comparing the reported action spectrum (black line, figure 1) and the emission spectrum of the Xe/Hg lamp used in the study, to provide the light of different wavelengths (red line in figure 1). This comparison

reveals that the Xe/Hg lamp has emission peaks that are almost perfectly positioned where the troughs occur in the reported action spectrum and, of course, raises the question: is this feature just co-incidence, or could it be that much, if not all, of the peaks and troughs of the action spectrum in figure 1 are not due to the spectral sensitivity of P25, but rather due to the spikey nature of the emission spectrum of the excitation source, i.e. could the peaks and troughs of the action spectrum in figure 1, which are also found in the plot of ϕ vs λ(ex), be an artefact?

The lamp artefact hypothesis

In recording the action spectrum of any material, ρ should be ideally the same at all excitation wavelengths and obviously this was not the case in the work of Emeline *et al.* [1] who used a Xe/Hg lamp, where the ratio of the highest (365 nm) to lowest (325 nm) irradiance could be as large as ca. 46, when a high resolution emission spectrum of the Xe/Hg lamps is considered, as illustrated in figure 1 (red line). Emeline *et al.* used a monochomator with a spectral resolution of $\pm$ 5 nm (i.e. half (peak) band width (HBW) = 10 nm,) coupled to the 1000W Xe/Hg lamp, in order to select each excitation wavelength band of λ(ex) [1]. As a consequence, such a system yields a broader emission spectrum profile for the Xe/Hg lamp, as illustrated in figure 1 (blue line) [38], although it's worth noting the highest to lowest irradiance ratio is still high, ρ(365)/ρ(325) =9.8, and the peaks and troughs of the emission spectrum still match the troughs and peaks of the reported action spectrum (black line, figure 1).

If the peaks and troughs of the reported action spectrum are due to the troughs and peaks in the Xe/Hg emission spectrum, then this suggests that θ was not actually unity at all the wavelengths used by Emeline *et al.* [1], when they determined the action spectrum illustrated in figure 1. *Obviously, this suggestion cannot be reconciled with the claim of the researchers that θ = 1 at all wavelengths, which they supported in particular with a straight line plot of r vs ρ/ρ_0 for 365 nm* (figure 1 in reference [1]). However, evidence that it is likely that θ **< 1, at 365 nm**, at least, for reaction (1) at the irradiance values used by Emeline *et al.* [1], i.e. ca. 12.3 mW cm^{-2}, is provided by the results reported by other groups [10-14], arising from their studies of reaction (1), see table 1, which indicate, as noted earlier, that

for this reaction, θ is ca. 0.5 at relatively modest UV irradiances, i.e. ca.2-3.5 mW cm^{-2} at 365 nm.

If we assume that in the study of the action spectrum of reaction (1) by Emeline *et al.* [1], that **$\theta < 1$ at some or all wavelengths** then it is useful to explore the effect this would have on the subsequent action spectrum. It is worth noting here that the possible modification of action spectra by non-linear light-intensity dependence has been suggested previously by Ohtani and his co-workers [3,39].

For simplicity, let us consider the case for reaction (1) at an excitation wavelength of 365 nm, where $\theta = 0.5$, as reported by Pichat *et al.* [11] for irradiances as low as 2 mW cm^{-2}! At all irradiance values above the threshold irradiance, η and ϕ will be described by the following expressions:

$$\eta(\theta=0.5) = k_{0.5}(\alpha f)^{0.5}/\rho^{0.5} \tag{5}$$

and

$$\phi(\theta=0.5) = k_{0.5}\alpha^{0.5}/(f\rho)^{0.5} \tag{6}$$

where $\rho > \rho(\text{threshold})$. It follows that the ratios: $\eta(\theta=0.5)/\eta(\theta=1)$ and $\phi(\theta=0.5)/\phi(\theta=1)$, will both $= k_{0.5}/\{k_1(\alpha f\rho)^{0.5}\}$, and since **$k_{0.5}/k_1 = (\alpha f\rho(\text{threshold}))^{0.5}$** (*vide supra*), the following relationships can be derived:

$$\eta(\theta=0.5)/\eta(\theta=1) = \phi(\theta=0.5)/\phi(\theta=1) = \{\rho(\text{threshold})/\rho\}^{0.5} \tag{7}$$

And since $\rho > \rho(\text{threshold})$, then the greater the value of ρ compared to $\rho(\text{threshold})$ the lower the values of η and ϕ.

In fact, for any value of $\theta < 1$, it can be shown that:

$$\eta(\theta < 1)/\eta(\theta=1) = \phi(\theta<1)/\phi(\theta=1) = \{\rho(\text{threshold})/\rho\}^{1-\theta} \tag{8}$$

and, once again, the greater the value of ρ compared to the threshold $\rho(\text{threshold})$ the lower the values of η and ϕ.

From the above discussion it follows that when running the action spectrum of **any photocatalytic reaction**, if $\rho > \rho(\text{threshold})$ at any, or all of the excitation wavelengths employed, then the calculated value of η (or ϕ) at that wavelength will be depressed, so as to create a trough, the depth of which will depend upon how much greater ρ is than

ρ(threshold) at that excitation wavelength. Interestingly, it also follows that if $\rho >$ ρ(threshold) at all excitation wavelengths used to generate the action spectrum, then the action spectrum profile will resemble that of the 'negative' of the excitation source, i.e. it will comprise peaks and troughs where there are troughs and peaks in the emission spectrum of the excitation source, as found in the work of Emeline *et al.*, using a Xe/Hg lamp [1]. The above discussion offers a credible alternative interpretation of the peaks and troughs of the reported action spectrum, η vs λ(ex), illustrated in figure 1 for reaction (1) – and those in the subsequent plot of ϕ vs λ(ex) (figure 3 in reference [1]) – namely, that they are due to the troughs and peaks in the Xe/Hg emission spectrum of the excitation source and not the spectral sensitivity of P25 in reaction (1). However, what is really needed to distinguish between the two hypotheses is a simple test and the results of such a test are described here.

Experimental

Materials

All chemicals were purchased from Aldrich Chemicals in their most pure form and sued as received. The Evonik P25 TiO_2 was a gift from Evonik.

Methods

A Xe KiloArc lamp (*OBB Corp.*), fitted with a monochromator, was used to provide the selected bands, with peaks at λ(ex) (units: nm), of light (HPBW = 10 nm) that were used to irradiate the photocatalyst system under test, i.e. reaction (1), at different wavelengths, spanning the range 290 - 400 nm. In this work the irradiation area, σ, was 1 cm^2.

The rate of reaction (1) was studied as function of excitation wavelength using the Xe lamp/monochromator system described above. The photoreactor comprised a 1 cm quartz cell, containing 3.0 cm^3 of the reaction solution which were stirred continuously. The reaction solution was sampled periodically and analysed using HPLC so as to yield data for the subsequent plot of [4-CP] vs irradiation time decay profiles for each excitation wavelength. These plots were used to provide values for the initial rates of 4-CP removal (i.e. *r*, units: molecules 4-CP removed s^{-1}) at the different λ(ex). In all this work the reaction solution comprised an aqueous dispersion (300 mg dm^{-3}) of P25 TiO_2, in which there was also: 0.001 M HCl and 0.2 mM 4-CP. In this work the 4CP concentration in the reaction

solution product samples was determined using an Agilent 1220 Infinity LC system fitted with a C-18 column. Samples were eluted in a 70:30 v/v ratio of acetonitrile and distilled water, with a flow rate of 1.00 mL min^{-1}.

All light emission spectra were recorded using a high-performance, **calibrated** UV-Vis OL 756 spectroradiometer (Gooch & Housego), equipped with an integrating sphere. The area under the emission spectrum, for each selected excitation wavelength band, λ(ex), generated by the Xe lamp/monochromator system and used to irradiate the reaction solution, was used to determine the total irradiance value, I(λ); units: mW cm^{-2}, for each λ(ex) band, see figure 2. The value of the photonic efficiency at each λ(ex), i.e. η, was then calculated using the following expression:

$$\eta = r/\{\lambda(ex)x1.84x10^{15}xI(\lambda)x\sigma/365\} \tag{9}$$

where σ = 1 cm^2. The diffuse reflectance UV spectra (see figure 2) of the P25 dispersion (0.3 g dm^{-3}) in 0.001 M HCl with 0.2 mM 4-CP, were recorded using a Perkin-Elmer Lambda 35 spectrometer (scan speed 30 nm min^{-1}) equipped with a Labsphere RSA-PE-20 Reflectance accessory.

In Diffuse Reflectance Spectroscopy, DRS, is routinely used to identify where solid materials, absorb, the reflectance, R_∞, is measured as a function of excitation wavelength, λ and then 'one can use either the absorbance (log(1/R_∞) or the Kubelka-Munk, K-M function, i.e. F(R_∞) = (1- R_∞)^2/2 R_∞, as a proxy for the typical absorption spectrum' [40]. Not surprisingly, DRS is routinely used to probe the absorption spectra of semiconductor photocatalysts, [37,39-44] and when combined with an action spectrum can help identify the light-absorbing species [30,31]. In this work the DRS was in the form of absorbance vs λ.

Results

As noted previously, a test is clearly required that will identify which of the two different interpretations of the action spectrum reported by Emeline *et al* [1]., and illustrated in figure 1, (namely: 'spectral sensitivity' versus 'lamp emission artefact') is correct. The most obvious and simplest test is the determination of the action spectrum of the same system as studied by Emeline *et al.*[1], i.e. reaction (1), using the exactly the same reaction conditions,

i.e. [TiO$_2$] (300 mg/L), [4-CP]$_o$ (0.2 mM) and pH (pH 3), except, this time, using a light source that does not have an emission spectrum in the UV with the striking peaks and troughs of a 1000W Xe/Hg lamp (see figure 1); an appropriate alternative light source for this purpose is a 1000 W Xe lamp (see figure 2 – blue line). If spectral sensitivity for the P25/4-CP/reaction (1) system is significant, then the results of such an experiment should reveal an action spectrum that is similar in shape to that illustrated in figure 1, with peaks and troughs in the same wavelength locations. However, if spectral sensitivity is not significant for reaction (1) using P25, then the action spectrum determined using a Xe lamp will have no peaks and troughs, and most likely will resemble that of the diffuse reflectance spectrum (or absorption spectrum) of the P25 dispersion, even if θ is < 1 at some or all wavelengths.
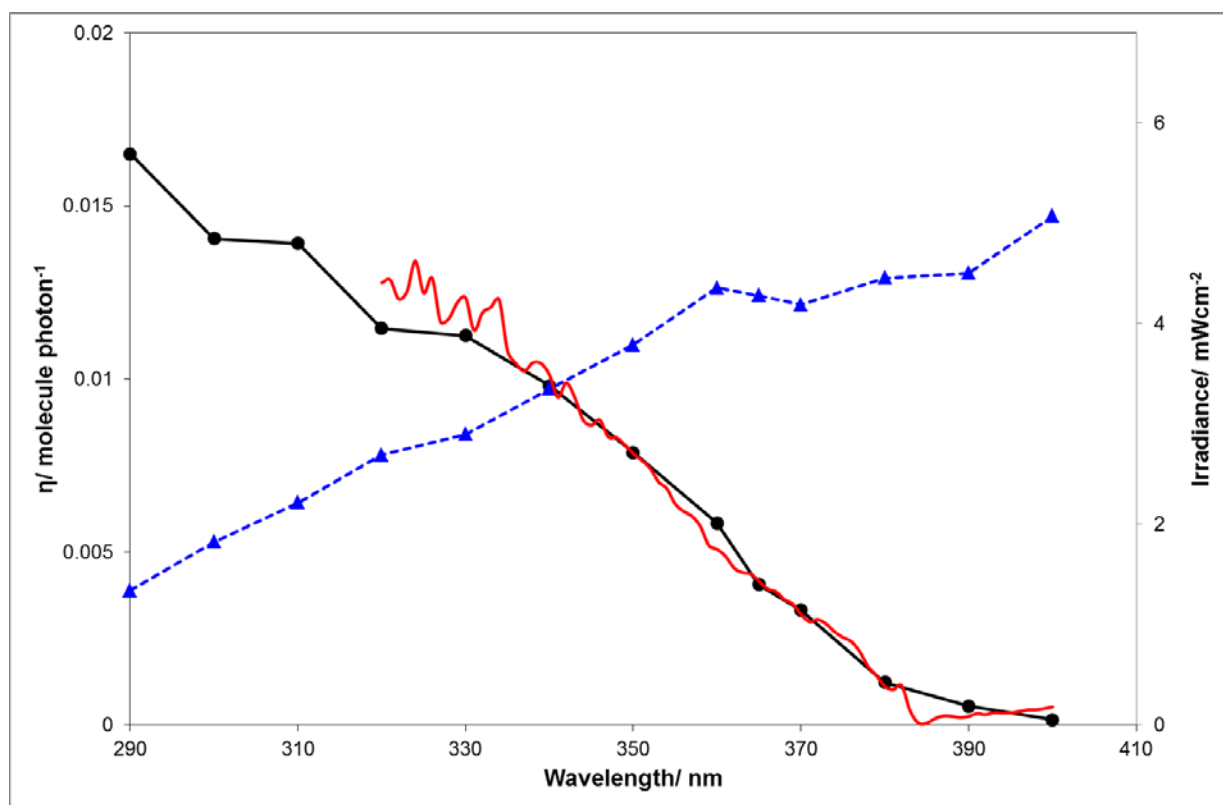

Figure 2: Action spectrum (black line, ● data points) for reaction (1), [P25 TiO$_2$] (300 mg/L), [4-CP]$_o$ (0.2 mM) and pH (pH 3), generated using the irradiances illustrated by the blue, broken line and ▲ data points for a 1000W Xe lamp. The red line corresponds to the diffuse reflectance spectrum i.e. absorbance vs λ, of the reaction solution.

The action spectrum of reaction (1) was thus determined using a Xe lamp (with monochromator) as the excitation source and the results are illustrated in figure 2 (black line). The action spectrum exhibits no evidence of spectral sensitivity, but does show a striking similarity to the diffuse reflectance spectrum absorbance spectrum of the P25 dispersion, also illustrated in figure 2 (red line). The diffuse reflectance absorbance spectrum of the P25 dispersion was found to be the same in the absence and presence of the 4-CP, indicating that the formation of a visible light absorbing charge transfer complex (CTC) was negligible under the experimental conditions employed (i.e. low [4-CP] (0.2 mM), low pH (pH 3) and a moderate level of chloride (1 mM)). Similar results regarding negligible CTC formation between P25 and 4-CP, have been reported by Agrios *et al.*, even though they used a much higher (12.5 x's) level of [4-CP], i.e. 2.5 mM [45]. The lack of any significant TiO_2-4-CP CTC formation under the conditions described here in the study of reaction (1), is supported by the lack of photocatalytic activity at 400 nm reported here (see figure 2) and elsewhere [1] (see also figure 1). Note that a control experiment which shows negligible photoreaction in the absence of TiO2 does not rule out the possibility of the photoabsorption and reaction by surface-adsorbed species [31].

Conclusions

The action spectrum, i.e. η vs. λ(ex) of reaction (1), using: [P25 TiO_2] (300 mg/L), [4-CP]$_o$ (0.2 mM) and pH (pH 3), when determined using a 1000W Xe lamp/monochromator irradiation source does not show any evidence of spectral sensitivity. Instead, the profile is similar to that of its diffuse reflectance spectrum and the action spectra reported by others for P25/4-CP [10] and for anatase/acetic acid [3]. This work shows the importance of using a light source which will deliver similar irradiances over the relevant wavelength range when determining the action spectrum of a photocatalytic system. These findings are consistent with recent suggestions made by Kisch and Bahnemann [46] that all studies should consider carefully the choice of light source, as well as the appropriate model compound, when assessing the activity of newly synthesized and established photocatalysts.

References

[1] A. Emeline, A. Salinaro, N. Serpone, Spectral Dependence and Wavelength Selectivity in Heterogeneous Photocatalysis. I. Experimental Evidence from the Photocatalyzed Transformation of Phenols, J. Phys. Chem. B 104(47) (2000) 11202–11210.

[2] S.E. Braslavsky, A.M. Braun, A.E. Cassano, A.V. Emeline, M.I. Litter, L. Palmisano, V.N. Parmon and N. Serpone, Glossary of terms used in photocatalysis and radiation catalysis (IUPAC Recommendations 2011), Pure Appl. Chem. 83(4) (2011) 931–1014.

[3] T. Torimoto, Y. Aburakawa, Y. Kawahara, S. Ikeda, B. Ohtani, Light intensity dependence of the action spectra of photocatalytic reactions with anatase titanium(IV) oxide, Chem. Phys. Lett. 392(1–3) (2004) 220–224.

[4] T. Torimoto, N. Nakamura, S. Ikeda, B. Ohtani, Discrimination of the active crystalline phases in anatase–rutile mixed titanium(IV) oxide photocatalysts through action spectrum analyses, Phys. Chem. Chem. Phys. 4 (2002) 5910–5914.

[5] M. Rochkind, S. Pasternak and Y. Paz, Using Dyes for Evaluating Photocatalytic Properties: A Critical Review, Molecules, 20 (2015) 88–110.

[6] T. Wu, G. Liu, J. Zhao, H. Hidaka and N. Serpone, Photoassisted Degradation of Dye Pollutants. V. Self-Photosensitized Oxidative Transformation of Rhodamine B under Visible Light Irradiation in Aqueous TiO_2 Dispersions, J. Phys. Chem. B, 102 (1998) 5845–5851.

[7] I. A. Jankovic, Z.V. Saponjic, E.S. Dzunuzovic and J. M. Nedljkovic, New Hybrid Properties of TiO2 Nanoparticles Surface Modified With Catecholate Type Ligands, Nanoscale Res. Lett., 5 (2010) 81–88.

[8] S. Kim and W. Choi, Visible-Light-Induced Photocatalytic Degradation of 4-Chlorophenol and Phenolic Compounds in Aqueous Suspension of Pure Titania: Demonstrating the Existence of a Surface-Complex-Mediated Path, J. Phys. Chem. B, 109 (2005) 5143–5149.

[9] N. Wang, L. Zhu, Y. Huang, Y. She, Y. Yu and H. Tang, Drastically enhanced visible-light photocatalytic degradation of colorless aromatic pollutants over TiO2 via a charge-transfer-complex path: A correlation between chemical structure and degradation rate of the pollutants, J. Catal., 266 (2009) 199–206.

[10] U. Stafford, K.A. Gray, P.V. Kamat, Photocatalytic Degradation of 4-Chlorophenol: The Effects of Varying TiO2 Concentration and Light Wavelength, J. Catal. 167(1) (1997) 25–32.

[11] G. Al-Sayyed, J-C. D'Oliveira, P. Pichat, Semiconductor-sensitized photodegradation of 4-chlorophenol in water, J. Photochem. Photobiol. A 58(1) (1991) 99–114.

[12] A. Mills, S. Morris, Photomineralization of 4-chlorophenol sensitized by titanium dioxide: a study of the initial kinetics of carbon dioxide photogeneration, J. Photochem. Photobiol. A 71(1) (1993) 75–83.

[13] A.V. Emeline, V. Ryabchuk, N. Serpone, Factors affecting the efficiency of a photocatalyzed process in aqueous metal-oxide dispersions: Prospect of distinguishing between two kinetic models, J. Photochem. Photobiol. A 133(1–2) (2000) 89–97.

[14] A. Mills, J. Wang, The Kinetics of Semiconductor Photocatalysis: Light Intensity Effects, Z. Phys. Chem. 213 (1999) 269–278.

[15] A.V. Emeline, N. Serpone, Spectral Selectivity of Photocatalyzed Reactions Occurring in Liquid–Solid Photosystems, J. Phys. Chem. B, 106(47) (2002) 12221–12226.

[16] R.W. Matthews, Purification of water with near—u.v. illuminated suspensions of titanium dioxide, Water Research 24(5) (1990) 653–660.

[17] N. Serpone, Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis, J. Photochem. Photobiol. A 104(1–3) (1997) 1–12.

[18] A. Salinaro, A.V. Emeline, J. Zhao, H. Hidaka, V.K. Ryabchuk, N. Serpone, Terminology, relative photonic efficiencies and quantum yields in heterogeneous photocatalysis. Part II: Experimental determination of quantum yields, Pure Appl. Chem. 71(2) (1999) 321–335.

[19] J. Cunningham, P. Sedlák, Interrelationships between pollutant concentration, extent of adsorption, TiO2-sensitized removal, photon flux and levels of electron or hole trapping additives 1. aqueous monochlorophenol—TiO2(P25) suspensions, J. Photochem. Photobiol. A 77(2–3) (1994) 255–263.

[20] H. Al-Ekabi, N. Serpone, E. Pelizzetti, C. Minero, M.A. Fox, R.B. Draper, Kinetic studies in heterogeneous photocatalysis. 2. Titania-mediated degradation of 4-chlorophenol alone and in a three-component mixture of 4-chlorophenol, 2,4-dichlorophenol, and 2,4,5-trichlorophenol in air-equilibrated aqueous media, Langmuir 5(1) (1989) 250–255.

[21] J. Theurich, M. Lindner, D.W. Bahnemann, Photocatalytic Degradation of 4-Chlorophenol in Aerated Aqueous Titanium Dioxide Suspensions: A Kinetic and Mechanistic Study, Langmuir 12(26) (1996) 6368–6376.

[22] M. Hügüla, I. Bozb, R. Apaka, Photocatalytic decomposition of 4-chlorophenol over oxide catalysts, J. Hazard. Mater. 64(3) (1999) 313–322.

[23] A. Mills, S. Morris, R. Davies, Photomineralisation of 4-chlorophenol sensitised by titanium dioxide: a study of the intermediates, J. Photochem. Photobiol. A 70(2) (1993) 183–191.

[24] A. Mills, C. O'Rourke, K. Moore, Powder semiconductor photocatalysis in aqueous solution: an overview of reaction mechanisms, J. Photochem. Photobiol. A 310 (2015) 66–105 and references therein.

[25] Degussa Technical Bulletin Fine Particles, No. 80, 'Titanium Dioxide p25, Manufacture – properties – Applications, 1998, Degussa AG, Frankfurt.

[26] T.A. Egerton, C.J. King, The Influence of Light Intensity on Photoactivity in TiO_2 Pigmented Systems, J. Oil Col. Chem. Assoc. 62 (1979) 386–391.

[27] K.Y. Okamoto, H. Yanamoto and H. Teneka and A. Itaya, Kinetics of Heterogeneous Photocatalytic Decomposition of Phenol over Anatase TiO_2 Powder, Bull. Chem. Soc. Jpn. 58 (1985) 2023–2028.

[28] A.V. Emeline, V.K. Ryabchuk and N. Serpone, Spectral Dependencies of the Quantum Yield of Photochemical Processes on the Surface of Nano/Micro-Particulates of Wide Band Gap Metal Oxides: I. Theoretical Approach, J. Phys. Chem. B. 103 (1999) 1316–1324.

[29] D. Ollis, 'Photocatalytic treatment of water: irradiance influences, in Photocatalysis and Water Purification, P. Pichat (ed), Wiley-VCH, Weinheim, 2013, Chp. 12.

[30] X. Yan, T. Ohno, K. Nishijima, R. Abe and B. Ohtani, Is methylene blue an appropriate substrate for a photocatalytic activity test? A study with visible-light responsive titania, Chem. Phys. Letts. 429 (2006) 606–610.

[31] B. Ohtani, Hidden but Possibly Fatal Misconceptions in Photocatalysis Studies: A Short Critical Review, Catalysis, 6 (2016) 192–197.

[32] N. Serpone and A.V. Emeline, Modelling Heterogeneous Photocatalysis by Metal-Oxide Nanostructured Semiconductor and Insulator Materials. Factors that Affects the Activity and Selectivity of Photocatalysts. Res. Chem. Intermediat. 31 (2005) 391–432.

[33] A.V. Emeline, X. Zhang, M. Jin, T. Murokami, and A. Fujishima, Spectral Dependences of the Activity and Selectivity of N-doped TiO_2 in Photodegradation of Phenols, J. Photochem. Photobiol. A 207 (2009) 13–19.

[34] A.V. Emeline, E.V. Lobyntseva, V.K. Ryabchuk and N. Serpone, Spectral dependencies of the quantum yield of photochemical processes on the Surface of Wide-Band-Gap Metal Oxides. 2. Gas/Solid System Involving Scandia (Sc_2O_3) Particles, J. Phys. Chem. B, 103 (1999) 1325–1331.

[35] A.V. Emerline, L.G. Smirnova, G.N. Kuzmin, L.L. Basov, L.L. and N. Serpone, Spectral Dependence of Quantum Yields in Gas/Solid Heterogeneous Photosystems. Influence of Anatase/Rutile Content on the Photostimulated Adsorption of Dioxygen and Dihydrogen on Titania, J. Photochem. Photobiol., A 148 (2002) 97–10.

[36] A.V. Emeline, G.N. Kuzmin, and N. Serpone, Quantum Yields and their Wavelength-Dependence in the Photoreduction of O_2 and Photooxidation of H_2 on a Visible-Light-Active N-doped TiO_2 System, Chem. Phys. Lett. 454 (2008) 279–283.

[37] A.V. Emeline, G.N. Kuzmin, D. Purevdorj, V.K. Ryabchuk and N. Serpone, Spectral Dependencies of the Quantum Yield of Photochemical Processes on the Surface of Wide Band Gap Solids. 3. Gas/Solid Systems, J. Phys. Chem. B 104 (2000) 2989–2999.

[38] Private communication A.V. Emeline, 2001.

[39] B. Ohtani, Photocatalysis A to Z—What we know and what we do not know in a scientific sense, J. Photochem. Photobiol. C 11 (2010) 157–178.

[40] J. Torrent, V. Barron, Diffuse Reflectance Spectroscopy. In Methods of Soil Analysis Part 5—Mineralogical Methods, A.L. Ulery, L.R. Drees, Eds.; Soil Science Society of America, Inc., Wisconsin, 2008, ch. 13, 367–385.

[41] B.J. Wood and R.G.J. Strens, Diffuse reflectance spectra and optical properties of some sulphides and related minerals, Mineral. Mag. 43 (1979) 509–518.

[42] W. Zhao, Z. Ai, J. Dai and M. Zhang, Enhanced Photocatalytic Activity for H_2 Evolution under irradiation of UV–Vis Light by Au-modified nitrogen-doped TiO_2, PLoS One 9 (2014) 1–10.

[43] S. Ebraheem and A. El-Saied, Band gap determination from diffuse reflectance measurements of irradiated lead borate glass system doped with TiO_2 by using diffuse reflectance technique, Mat. Sci. Appl. 4 (2013) 324–329.

[44] S. Kim, S-J. Hwang and W. Choi, Visible light active platinum-doped TiO_2 photocatalyst, J. Phys. Chem., 109 (2005) 24260-24267.

[45] A.G. Agrios, K.A. Gray and E. Weitz, Narrow-band irradiation of a homologous series of chlorophenols on TiO_2: charge transfer complex formation and reactivity, Langmuir, 20 (2004) 5911–5917.

[46] H. Kisch and D. Bahnemann, Best Practice in Photocatalysis: Comparing Rates or Apparent Quantum Yields?, J. Phys. Chem. Lett. 6(10) (2015) 1907–1910.