Water Purification by Semiconductor Photocatalysis

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1 Introduction

It has long been recognized[1] that there are many reactions which can be promoted by light-activated solids which are not consumed in the overall reaction; such solids are often referred to as photocatalysts, or photosensitisers, and are invariably semiconductors. Probably the most well-established example of semiconductor photocatalysis is paint chalking,[2] which involves the photodegradation of the organic polymer part of the paint sensitized by the semiconductor pigment, usually TiO_2. Nowadays, this undesirable feature is often largely controlled by coating the pigment with a hydrous layer of an inert oxide, such as silica, alumina, or zirconia.

In recent years, there has been a growing interest in the use of semiconductors as photosensitizers for the complete oxidative mineralization of pollutants by oxygen.[3–6] In semiconductor photocatalysis for water purification the pollutants are usually organic and, therefore, the overall process can be summarized by the following reaction equation:

$$\underset{\text{pollutant}}{\text{organic}} + O_2 \xrightarrow[\textit{ultra}\text{-bandgap light}]{\text{semiconductor}} CO_2 + H_2O + \text{mineral acids} \qquad (1)$$

In contrast to semiconductor photomineralization as a method of water purification, the destructive technologies currently in use in the water industry, such as chlorination and ozonation, all use strong oxidants of a seriously hazardous and, therefore, undesirable nature. The predominant non-destructive technologies currently in use, *i.e.* air-stripping and carbon absorption, are also not without their problems. For example the removal of volatile contaminants by air-stripping, converts a liquid contamination problem into an air pollution problem, and carbon absorption produces a hazardous solid which in turn must be disposed of.

The purification of water by semiconductor photocatalysis is attracting a great deal of interest, not only from research workers but also from water purification companies. This interest arises because (i) the mineral 'effluent' it produces is harmless to the environment, (ii) the process of photomineralization can be turned on or off at the flick of a switch, and (iii) there is a real possibility that it could be readily incorporated into existing UV water purification systems.

2 Semiconductor Photocatalysis

In a solid, the electrons occupy energy bands as a consequence of the extended bonding network. In a semiconductor the highest occupied and lowest unoccupied energy bands are separated by a bandgap, E_{bg}, a region devoid of energy levels. Activation of a semiconductor photocatalyst is achieved through the absorption of a photon of *ultra*-bandgap energy which results in the promotion of an electron, e^-, from the valence band into the conduction band with the concomitant generation of a hole, h^+, in the valence band. For a photocatalyst to be efficient, the different interfacial electron transfer processes, involving e^- and h^+ reacting with adsorbed species must compete effectively with the major deactivation route of electron–hole recombinations.[3–5]

Semiconductor photocatalysis has its origins in the substantial research effort, in the seventies and early eighties, into photoelectrochemical systems and micro-photoelectrochemical systems for solar to chemical energy conversion. The first photoelectrochemical system for splitting water into hydrogen and oxygen was developed by Fujishima and Honda[6] and comprised a TiO_2 semiconductor photoanode coupled up to a Pt cathode and a schematic illustration of this cell is given in Figure 1. After a few years research it was realised[7] that micro-Fujishima–Honda cells, comprising TiO_2 particles with deposits of Pt on them, would also work as photocatalysts for splitting water, as illustrated in Figure 1.

As part of the research effort into solar-to-chemical energy conversion using photoelectrochemical cells some attention was given to the use of platinized TiO_2 powder as a photosensitizer for the production of hydrogen from biomass and water,[8] *i.e.*

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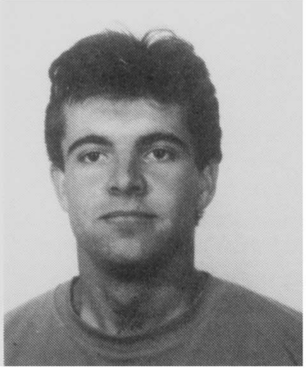
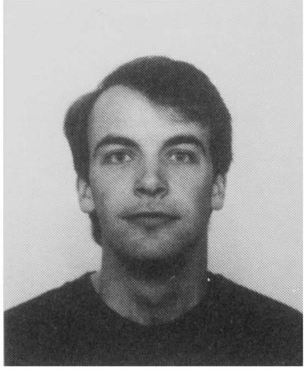


Richard Davies



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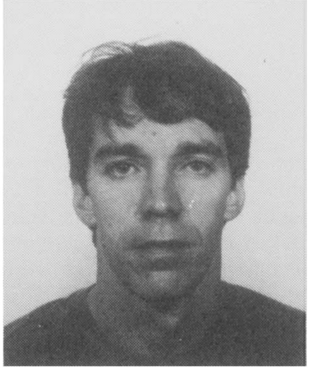

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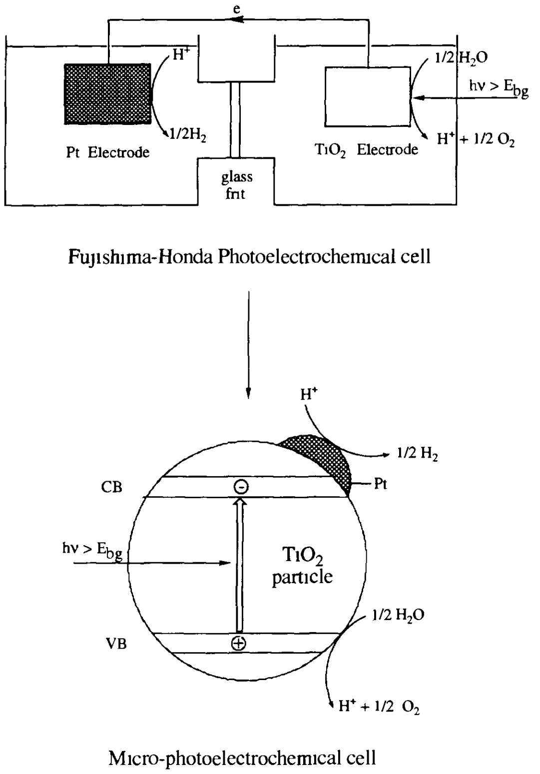


Fujishima-Honda Photoelectrochemical cell

Micro-photoelectrochemical cell

Figure 1 Schematic illustrations of the Fujishima Honda photoelectrochemical cell[6] (top), and a micro version of the cell, for the dissociation of water into H_2 and O_2.

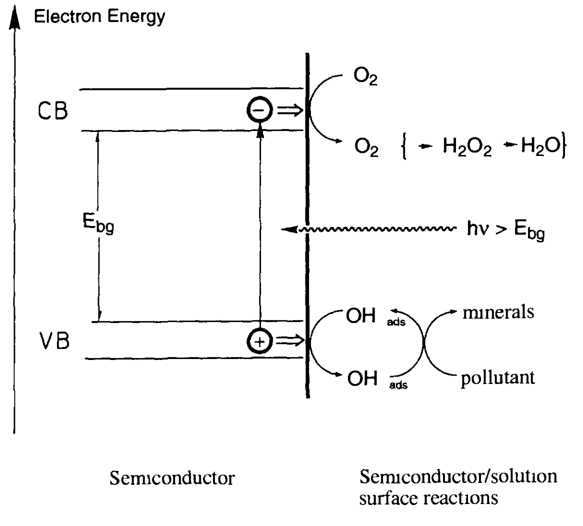


Figure 2 Schematic representation of the band energetic model of the overall process of semiconductor photocatalysis for water purification.

$$\text{biomass} + H_2O \xrightarrow[\textit{ultra}\text{ bandgap light}]{TiO_2/Pt} CO_2 + H_2 \qquad (2)$$

where the biomass was natural products (such as glucose, ethanol, cellulose, *etc.*), food (such as sweet potatoes and fatty oil), grass, clover, wood (including cherry wood), green algae, seaweed, dead animals (e.g. cockroaches), and excrement (including human urine).[8] Of course, for reaction 2 to work, all irradiations had to be carried out in the absence of O_2. It is interesting to note, however, that had the systems been aerated, rather than N_2-purged, then the reaction under study would have been the semiconductor-sensitized photo-oxidative mineralization of the biomass.

The first clearest recognition and implementation of semiconductor photocatalysis as a method of water purification came in 1983 from David Ollis and his co-workers through the publication of two papers[9,10] on the photomineralization of halogenated hydrocarbon contaminants, including trichloroethylene, dichloromethane, chloroform, and carbon tetrachloride, sensitized by TiO_2. (Interestingly, during conventional water chlorination procedures, chloroform is the major halocarbon contaminant formed and is a suspected carcinogen.)

Subsequently, it appeared[11] that reaction 1 might be limited to non-aromatic compounds, however, these fears were quickly eliminated through the work of Matthews,[12] Barbeni *et al.*,[13] and Okamoto *et al.*,[14] who demonstrated that TiO_2 could sensitize the photomineralization of chlorobenzene, chlorophenol, and phenol, respectively. The list of organic pollutants which have been shown to be photomineralized *via* reaction 1 using TiO_2 as the sensitizer is extensive,[15] as indicated by Table 1,[15] and increases daily.

2.1 Semiconductor Photocatalysis for Water Purification: Choice of Semiconductor

There are a lot of different semiconducting materials which are readily available, but only a few are suitable for sensitizing the photomineralization of a wide range of organic pollutants, *i.e.* sensitizing reaction 1. A sensitizer for reaction 1 must be (i) photoactive, (ii) able to utilise visible and/or near UV light, (iii) biologically and chemically inert, (iv) photostable (*i.e.* not liable to photoanodic corrosion for example), and (v) cheap.

In order for a semiconductor to be photochemically active as a sensitizer for reaction 1 the redox potential of the photogenerated valence band hole must be sufficiently positive to generate absorbed $OH^{\bullet}$ radicals, which can subsequently oxidize the organic pollutant, and the redox potential of the photogenerated conductance band electron must be sufficiently negative to be able to reduce absorbed O_2 to superoxide, a schematic representation of the energetics associated with the overall process is given in Figure 2. Figure 3 illustrates band positions for a variety of different semiconductors and the redox potentials for the $H_2O/OH^{\bullet}$ and $O_2/HO_2^{\bullet}$ couple at pH 0. (The relationship between E_{bg}, in units of eV, and the approximate

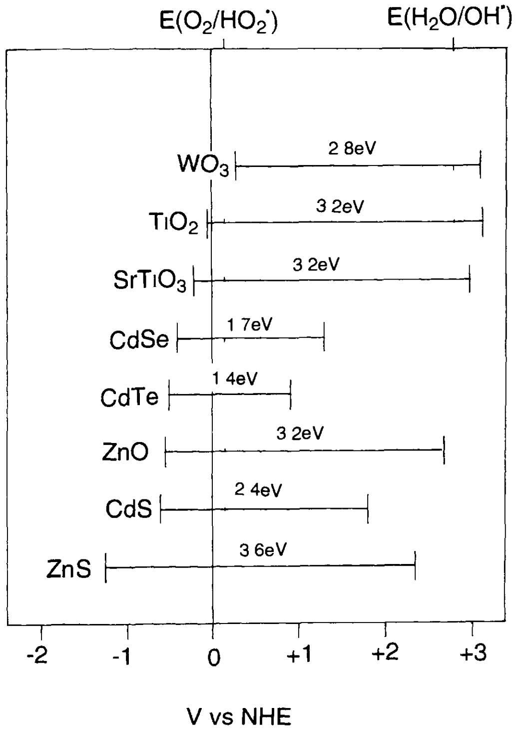


Figure 3 Band positions of common n-type semiconductors used in photocatalysis and the redox potentials of the $H_2O/OH^{\bullet}$ and $O_2/HO_2^{\bullet}$ redox couples at pH 0.

Table 1 Photomineralization of organic pollutants sensitized by TiO_2 Examples of compounds studied[1 5]

Class	Examples
ALKANES	methane, *iso*butane, pentane, *iso*octane, heptane, *n*-dodecane, cyclohexane, methylcyclohexane, 1,4-methylcyclohexane, paraffin
HALOALKANES	mono-, di-, tri-, and tetra-chloromethane, fluorotrichloromethane, 1,1- and 1,2-dichloroethane, 1,1,1,2- and 1,1,2,2-tetrachloroethane, pentachloroethane, 1,1- and 1,2-dibromoethane, tribromoethane, 1,2-dichloropropane, 1-bromododecane, 1,1-difluoro-1,2-dichloroethane, 1,1-difluoro-1,2,2-trichloroethane, 1,1,1-trifluoro-2,2,2-trichloroethane, tributyl tin compounds
ALIPHATIC ALCOHOLS	methanol, ethanol, isopropyl alcohol, cyclobutanol, *n*-propyl alcohol, propan-2-ol, butanol, penta-1,4-diol, 2-elloxyethanol, 2-butoxyethanol, dodecanol, benzyl alcohol, glucose, sucrose
ALIPHATIC CARBOXYLIC ACIDS	formic, ethanoic, dimethylethanoic, mono-, di-, and tri-chloroethanoic, propanoic, butanoic, dodecanoic oxalic
ALKENES	propene, cyclohexene
HALOALKENES	perchlorethene, 1,2-dichloroethene, 1,1,1- and 1,1,2-trichloroethene, tetrachloroethene, mono-, di-, and tetra-fluoroethene, 3,3,3-trifluoropropene, hexafluoropropene
AROMATICS	benzene, naphthalene
HALOAROMATICS	chlorobenzene, bromobenzene, 2-, 3-, and 4-chlorophenol, 2,4- and 3,4-dichlorophenol, 2,4,5- and 2,4,6-trichlorophenol, pentachlorophenol, 2-, 3-, and 4-fluorophenol, 2,4- and 3,4-difluorophenol, 2,4-dinitrophenol, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, 2,3- and 3,4-dichloronitrobenzene 1,2-dichloronitrobenzene
PHENOLS	phenol, hydroquinone, methylhydroquinone, catechol, 4-methyl catechol, 4-nitrocatechol, resorcinol, 2-naphthol, *o*-, *m*-, and *p*-cresol
AROMATIC CARBOXYLIC ACIDS	benzoic, 4-amino benzoic, 3-chloro-4-hydroxybenzoic, phthalic, salicyclic, *m*- and *p*-hydroxybenzoic, 3-chlorohydroxybenzoic
POLYMERS	polyethylene, PVC
SURFACTANTS	SDS, *p*-nonyl phenyl polyoxyethylene ether, polyethylene glycol, *p*-nonyl phenyl ether, sodium dodecyl benzene sulfonate, benzyl dodecyl dimethyl ammonium chloride, *p*-nonyl phenyl poly(oxyethylene)esters, sodium benzene sulfonate, paraxon, malathion, 4-nitrophenyl ethyl phosphinate, 4-nitrophenyl *iso*propyl phosphinate, 1-hydroxy ethane-1,1-diphosphonate, 4-nitrophenyl diethyl phosphate, trimethyl phosphate, trimetyl phosphite, dimethyl ammonium phosphodithionate, tetrabutyl ammonium phosphate
HERBICIDES	methyl viologen, atrazine, simazine, prometon, propetryne, bentazon
PESTICIDES	DDT, parathion, lindane
DYES	methylene blue, rhodamine B, methyl orange, fluorescein, umbelliferone

threshold wavelength of light, λ_{th}, in nm, below which the semiconductor will absorb strongly, i e λ_{th}, is given by the expression $E_{bg} = 1240/\lambda_{th}$)

In many cases, the semiconductor is liable to oxidative decomposition by the photogenerated hole It is generally found that only n-type semiconductor oxides are stable towards photoanodic corrosion, although such oxides usually have bandgaps which are sufficiently large that the semiconductors absorb only UV light CdS is an example of a highly active semiconductor photosensitizer which has the highly desirable feature that it can be activated using visible light (thus, sunlight could be used), but, as is typical for visible light absorbing semiconductors, it is liable to photoanodic corrosion

$$CdS + 2h^+ \rightarrow Cd^{2+} + S\downarrow \qquad (3)$$

and this feature renders it unacceptable as a photocatalyst for water purification

Of all the different semiconductor photocatalysts tested successfully for reaction 1, TiO_2 appears the most active, as illustrated by the results in Figure 4 for reaction 1 where the organic pollutant is pentachlorophenol (PCP)[16] In addition, although TiO_2 is only a UV absorber (E_{bg} = 3 2 eV), it is cheap, insoluble under most conditions, photostable, and non-toxic Indeed, the complete absence of any biological activity associated with this bright white pigment, allows it to be used in a wide range of domestic goods, including sunblocks, vitamin tablets, and chicken roll!

Although there are many different sources of TiO_2, Degussa P25 TiO_2 has effectively become a research standard because it has (i) a reasonably well-defined nature (i e typically a 70 30 anatase rutile mixture, non-porous, BET surface area = 55 ± 15 m^{2} g^{-1}, average particle size 30 nm) and (ii) a substantially higher photocatalytic activity than most other readily available samples of TiO_2

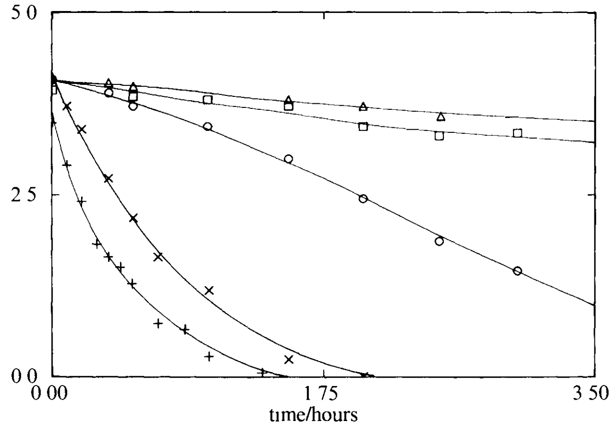


Figure 4 Photodegradation of pentachlorophenol (PCP) sensitized by dispersions of the following semiconductors + TiO_2, × ZnO, ○ CdS, □ WO_3, and △ SnO_2 In each case the solution was air-saturated, and the semiconductor and initial PCP concentrations were 2g cm ^{3} and 45 μmol dm ^{3}, respectively Data from reference 16

2.2 Kinetics of Pollutant Photomineralization Sensitized by TiO_2

In the photomineralization of organic pollutants sensitized by TiO_2, numerous studies[3 5 14] have reported that the initial rate r_i of disappearance of the pollutant S fits a Langmuir–Hinshelwood kinetic scheme, i e

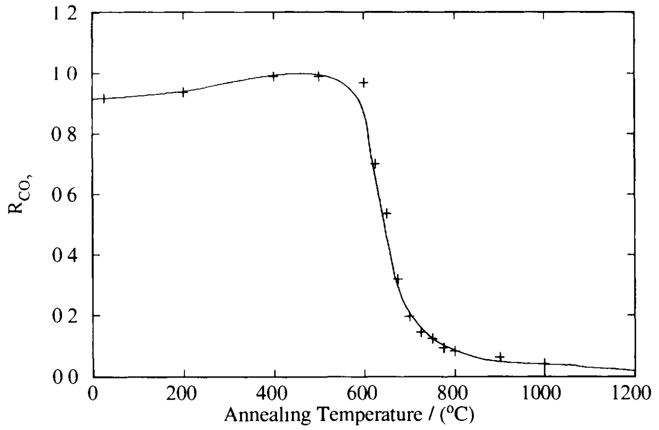


Figure 5 Initial rate of CO_2 generated in the photomineralization of 4-chlorophenol sensitized by TiO_2 *versus* temperature used to anneal the TiO_2 Data from reference 19

$$r_i = \frac{-\,d[S]_i}{dt} = \frac{k(S)K(S)[S]_i}{1 + K(S)[S]_i} \tag{4}$$

where, $[S]_i$ = initial concentration of the pollutant S, and, traditionally, $K(S)$ is taken to represent the Langmuir absorption constant of the species S on the surface of TiO_2, and $k(S)$ is a proportionality constant which provides a measure of the intrinsic reactivity of the photoactivated surface with S It is found that $k(S)$ is proportional to I_a^θ, where I_a is the rate of light absorption and θ is a power term which is equal to $\frac{1}{2}$, or 1, at high, or low, light intensities, respectively It is also found that $k(S)$ is proportional to the fraction of O_2 adsorbed on the TiO_2, i e $f(O_2)$, which is defined as follows

$$f(O_2) = K_{O_2}[O_2]/(1 + K_{O_2}[O_2]) \tag{5}$$

where K_{O_2} is the Langmuir adsorption coefficient for O_2, which appears to be non-competitively absorbed on TiO_2 owing to its exclusive absorption at Ti^{III} sites, hydroxyl radicals and organic substrates are believed to be exclusively absorbed at Ti^{IV}-lattice oxygen sites Thus, a more complete form of equation 4 is given by the following expression

$$r_i = \frac{\gamma K_{O_2}[O_2]I_a^\theta K(S)[S]_i}{(1 + k_{O_2}[O_2](1 + K(S)[S]_i)} \tag{6}$$

where γ is a proportionality constant

Cunningham and his co-workers[17] and others have measured dark Langmuir adsorption isotherms for TiO_2 for a variety of different organic pollutants and found them to be significantly smaller than the values of $K(S)$ obtained from plots $1/r_i$ *versus* $1/[S]_i$ It appears likely that the value of $K(S)$ derived from a kinetic study is not directly equivalent to the Langmuir absorption coefficient for S on TiO_2 Turchi and Ollis[18] have proposed four possible different mechanistic schemes involving $OH^\cdot$ radical attack in TiO_2-sensitized organic photomineralization reactions, all of which yield a rate equation of the form of equation 6 In each scheme the fundamental interpretation of the constant $K(S)$ is different and none are simply equivalent to the dark Langmuir absorption coefficient In the Appendix we describe the two schemes which appear most likely, given the increasing evidence that the $OH^\cdot$ radical is bound to the surface,[4,5] i e Case A adsorbed hydroxyl radical attack on adsorbed S, and Case B adsorbed hydroxyl radical attack on free S In both cases, a final working equation is developed, i e equation A19 in the Appendix, which has an identical form to that of the empirically derived equation 6

Detailed studies of the kinetics of water purification photosensitized by TiO_2 have identified the following important factors

2 2 1 Crystal Phase[19]

Even after choosing TiO_2 as the semiconductor photocatalyst, the choice of which crystalline form is still important The crystalline forms of TiO_2 are anatase, rutile, and brookite, although brookite is not commonly available The result of an initial study on the photomineralization of phenol indicated that rutile TiO_2 is inactive as a catalyst, although it is not clear why this should be, given that the redox potentials of the valence and conductive bands for anatase and rutile TiO_2 are quite similar[19] However, a more rigorous study using the same pollutants showed that TiO_2 was active or inactive according to the initial conditions used to prepare the TiO_2 The popular Degussa P25 TiO_2 used in most photomineralization studies is primarily anatase (70%), but can be converted into rutile TiO_2 by annealing at 800 °C for 5h in air Such treatment reduces the photocatalytic activity of the TiO_2 dramatically, as indicated by the plot of initial rate of CO_2 evolution *versus* annealing temperature for the photomineralization of 4-chlorophenol illustrated in Figure 5[19] However, this behaviour appears to be associated more with the concomitant decrease in specific surface area (from 50 down to 5 $m^2\,g^{-1}$) than the conversion of the TiO_2 from anatase into rutile Thus, the crystal phase of TiO_2 used may not be that important a factor, but the method of its preparation is, especially with regard to its porosity and surface area

2 2 2 TiO_2 Concentration

TiO_2 is often used as a dispersion to sensitize reaction 1, and Figure 6(a) provides an illustration of a typical 'batch' reactor for this work[20] In 'batch' reactors the rate of photomineralization is often found to increase with increasing $[TiO_2]$ and to tend towards a limiting value at high concentrations (typically *ca* 0 5 mg cm^{-3}) In any commercial system it is more likely that the TiO_2 will be fixed and the contaminated water will be flowed over it Such a 'flow' system would eliminate the need for filtration or settling/resuspension of the photocatalyst In the development of a wide range of flow reactors TiO_2 has been (i) incorporated in Nafion film, ceramic film, silica gel, and (ii) attached to glass in the form of tubing, beads, and mesh The tremendous tenacity with which TiO_2 readily adheres to glass makes the production of a glass 'flow' reactor fairly easy, typical glass flow reactors are illustrated in Figure 6(b)[21]

There have been many attempts[3-5] to improve the photocatalytic activity of TiO_2, in particular by depositing small amounts of metal (Pt, Ru, or Cu) on its surface, or extending its

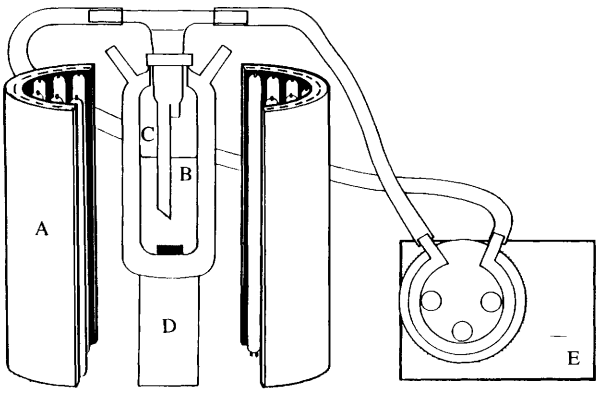
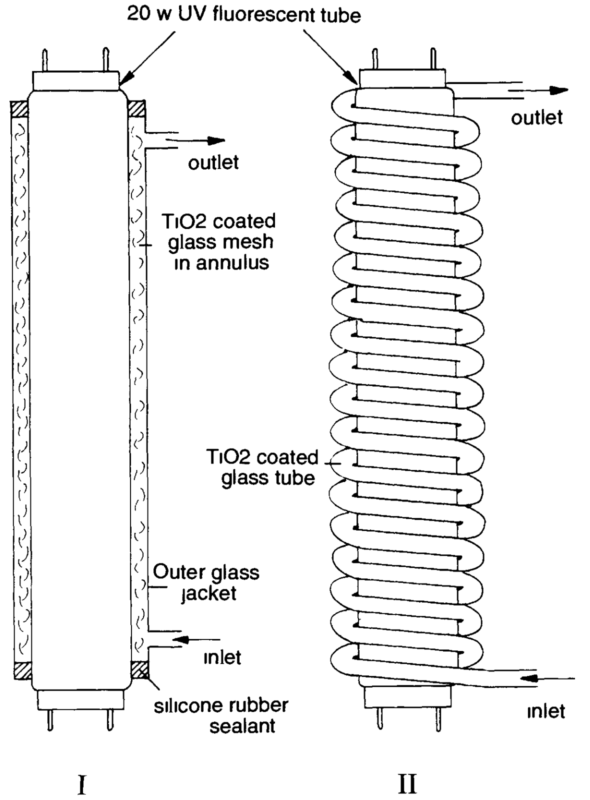


Figure 6 Schematic illustration of the two different types of photoreactor used in the study of water purification by semiconductor photocatalysis, *i e*

(a) a 'batch' photoreactor,[20] comprising two half-cylinders (A), each containing 6 x 8 W Blacklight UVA lamps, which when pushed together form the photoreactor, and a reaction vessel (B) with a top (C) through which O_2 gas is continuously bubbled through the reaction solution by means of a peristaltic pump (E) The reaction solution is usually stirred continuously by means of a magnetic stirrer (D),



(b) two 'flow' reactors,[21] (I) comprising TiO_2-coated glass mesh in the annulus between a UVA lamp and the outer glass wall and (II) comprising a glass tube spiralled around a UVA lamp, with a thin inside coating of TiO_2, over which the polluted water is flowed

wavelength range of photoactivity, by dye sensitization, or doping with transition metal ions (*e.g.* Fe^{III} or Cr^{III}). To date this work has largely been unsuccessful and Degussa P25 TiO_2 remains the best, readily available form of TiO_2 for reaction 1.

2.2.3 Organic Pollutant Concentration

As noted earlier, for most of the organic pollutants tested the kinetics of reaction 1 are described by equation 4, a Langmuir–Hinshelwood-type expression, and this feature is rather nicely illustrated in Figure 7, a plot of rate of oxidation of pollutant to CO_2 *versus* [pollutant], for a variety of different pollutants.[22] It is clear that the kinetics of photomineralization will depend upon the ease with which it can be oxidized by the photogenerated hole and how well it absorbs on the surface of TiO_2.

It is also worth noting that the absorption spectrum of the pollutant can drastically affect the kinetics of photocatalysis. In particular, if the pollutant is a strong UV absorber, then, as its concentration is increased it will eventually begin significantly to screen the TiO_2 from the *ultra*-bandgap light and the kinetics of photomineralization will begin to deviate from equation 4, with the rate decreasing with increasing [pollutant]. Many of the pollutants listed in Table 1 do not absorb significantly in the 300—400nm wavelength region, and the problem of screening (as well as the homogeneous photochemical decomposition of the pollutant) is rendered insignificant through judicious choice of irradiation source (usually black-light bulb, emission λ_{max} = 365nm) and irradiation vessel (usually borosilicate glass which cuts off light below 300nm). The effect of screening on the kinetics of photocatalysis can, however, be readily observed using dyestuffs, such as rhodamine 6G. Screening of the TiO_2 by highly coloured pollutants, or deposits of particulate matter on the surface of TiO_2 for that matter, appears to be a quietly forgotten general major drawback of TiO_2 photocatalysis as a method of water purification.

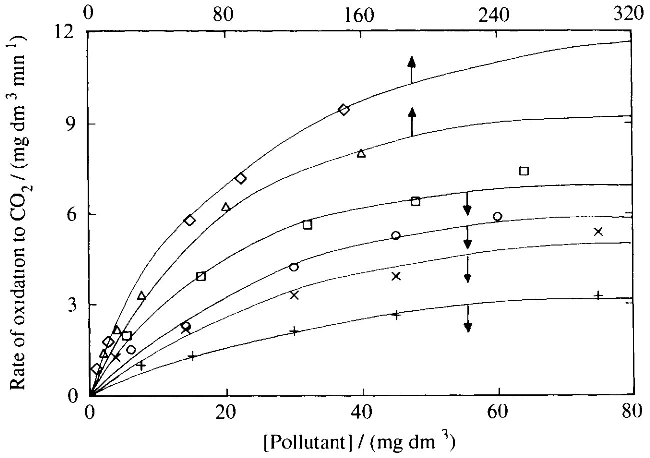


Figure 7 Rates of oxidation to CO_2 *versus* initial pollutant concentration for the following different pollutants (top to bottom) chloroform (◇), methanol (△), 4-chlorophenol (□), phenol (○), acetic acid (×) and propan-2-ol (+). Data from ref. 22, determined using a flow photoreactor (20 W UVA lamp, 40 °C and circulation rate = 300 cm^3 min^{-1})

2.2.4 O_2 Concentration

As you might expect, given the reaction stoichiometry of equation 1, photomineralization will not proceed unless O_2 is present. In most kinetic studies, the observed variation of the rate of photomineralization as a function of $[O_2]$ is described very well by equation 6. Thus, a double reciprocal plot of the data yields a straight line and from the ratio of the intercept to the gradient of the straight line a value of $K(O_2)$ can be obtained. Figure 8 illustrates plots of R_{CO_2} *versus* $\%O_2$ and $1/R_{CO_2}$ *versus* $1/\%O_2$ determined[23] as part of a kinetic study of the photomineralization of 4-chlorophenol by Degussa P25 TiO_2, from this work a value of 0.044 ± 0.005 kPa^{-1} was determined which is a typical for such work. Thus, increasing the O_2 concentration from air-saturated (20% O_2) to O_2-saturated (100% O_2) conditions, will typically only increase the rate by a factor of 1.7.

Oxidants other than O_2, such as H_2O_2, S_2O_8, and Ag^+ ions, have been used with some success but, in terms of a practical approach to water purification, only O_2 and H_2O_2 appear a viable choice of oxidant. Although H_2O_2 does enhance the rate of photomineralization of some organics by TiO_2, with others it

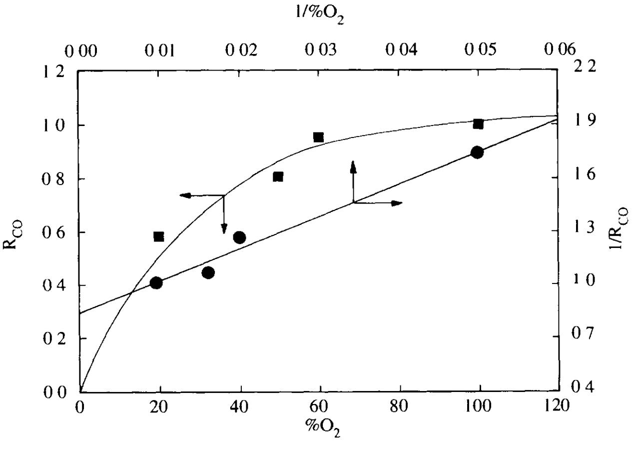


Figure 8 Plots of the initial relative rate of CO_2 generated in the photomineralization of 4-chlorophenol sensitized by TiO_2, *i.e.* R_{CO_2}, *versus* $[O_2]$ and $1/R_{CO_2}$ *versus* $1/[O_2]$. Irradiations were carried out using the batch reactor illustrated in Figure 6(a), with pollutant = 4-chlorophenol (100 cm^3, 10^{-3} mol dm^{-3}), $[TiO_2]$ = 0.5 mg cm^{-3}, pH = 2, T = 30 °C. The results of a least-squares analysis of the data points in the double-reciprocal plot are as follows: gradient = 18.5 ± 2.4 $\%O_2$, intercept = 0.81 ± 0.07, and correlation coefficient = 0.9841. Data from reference 23

has a negative, or no, effect, it has been suggested that H_2O_2 or the hydroperoxy radical may in fact function as a hydroxyl radical scavenger [3 5]

2 2 5 *Light Intensity*

In most kinetic studies of reaction 1, the light intensities used have been such (typically > 6 × 10^{14} *ultra*-band gap photons cm^{-2} $s^{\ 1}$) that the rate has usually been found to be proportional to $I_a^{\frac{1}{2}}$ However, some workers have successfully tested for the theory-predicted transition in dependence of rate from first-order to half-order as the light intensity is increased from low to high levels A notable example of this is the work of Egerton and King,[24] on the photo-oxidation of isopropyl alcohol to acetone (on its way to complete mineralization) by rutile TiO_2 in air-saturated solution, the results of this work are illustrated in Figure 9

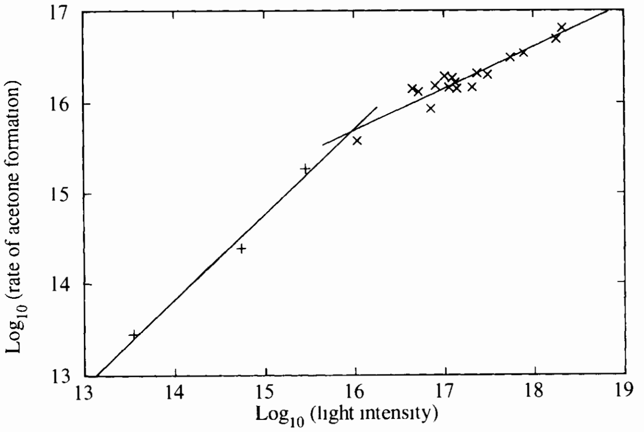


Figure 9 Rate of acetone generation from isopropyl alcohol photosensitized by pure rutile (400 mg in 40 cm^3) *versus* incident light intensity Data from reference 24

2 2 6 *Temperature*

The overall process of semiconductor photocatalysis is not usually found to be very temperature sensitive, thus, reported activation energies generally lie in the range 5—16 kJ mol^{-1}

2 2 7 *pH and Anions*

The pH of the aqueous solution significantly affects TiO_2, including the charge on the particles, the size of the aggregates it forms, and the positions of the conductance and valence bands It is somewhat surprising, therefore, that the rate of photocatalysis is not usually found to be strongly dependent upon pH, typically varying by less than an order of magnitude from pH 2 to pH 12 Higher reaction rates for various TiO_2-sensitized photomineralizations have been reported at both low and high pH

Matthews and his co-workers[25] have carried out one of the most rigorous studies on the effect of anions on the rate of photomineralization of organic pollutants (salicyclic acid, aniline, and ethanol), sensitized by TiO_2 From the results of this work it appears that perchlorate and nitrate have very little effect, whereas sulfate, chloride, and phosphate at concentrations > 10^{-3} mol dm^{-3} can reduce the rate of photomineralization by 20–70%, due to their absorption at the oxidation sites on the TiO_2 We have recently found that nitrate, at concentrations of *ca* 0 4 mol dm^{-3}, can indeed reduce the rate of TiO_2-sensitized photomineralization of 4-chlorophenol by 50%, not by blocking oxidation sites, but rather by UV screening the TiO_2 particles [23]

2 2 8 *Wear Efficiency and Costings*

Most workers have not noticed an appreciable loss in the photocatalytic activity of TiO_2 with its repeated use as a photosensitizer for reaction 1 Figure 10 illustrates the results for a typical set of successive kinetic runs in which 4-chlorophenol (0 155 × 10^{-3} mol $dm^{\ 3}$) is the pollutant in reaction 1 and TiO_2 the photosensitizer [26] If semiconductor photocatalysis is to be used extensively as a method of water purification then much more significant extended wear tests will need to be carried out than have been to date

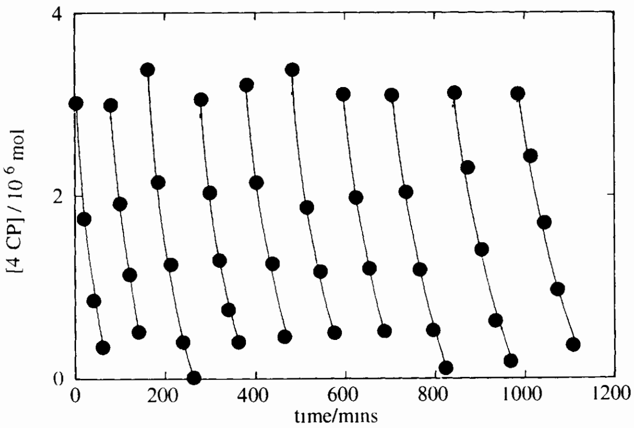


Figure 10 Ten successive photomineralization cycles involving 4-chlorophenol and the same portion of TiO_2 The dotted lines correspond to the readjustment of the 4-chlorophenol concentration to *ca* 0 155 × $10^{\ 3}$ mol $dm^{\ 3}$ and to a dark period of 20 min so that the adsorption equilibrium is attained exciting light ≥ 340 nm Data from reference 26

If semiconductor photocatalysis as a method of water purification is to have a viable commercial future its operating costs must compare favourably with those of its competitors A major component of these costs will be that of the electricity used to generate the necessary UV light The manufacturers of the 8 W blacklight (UVA) bulbs used in our work on the TiO_2-sensitized photomineralization of 4-chlorophenol quote a UV output at 344 nm of 0 8 W, *i e* 10% electricity to light conversion efficiency Ferrioxalate actinometry carried out using the batch photoreactor illustrated in Figure 6(a) showed[23] that one 8 W blacklight bulb generated 5 × 10^{16} photons $s^{\ 1}$ in the wavelength region 300–400 nm, if we assume, for the sake of simplicity, that all these photons are of wavelength 355 nm, then the electricity to light conversion efficiency is only 0 35% in our system, it is not at all clear why this figure should be so very different to that reported by the manufacturer

Using the photoreactor illustrated in Figure 6(a), with 11 lamps on, the initial rate of destruction of 4-chlorophenol was determined as 6 × 10^{15} molecules $s^{\ 1}$ and, therefore, the formal (maximum) quantum yield for the photomineralization of this pollutant is 0 011 In most photomineralization studies the reported quantum yield lies typically in the range (1—0 1)%

In 1987 Ollis carried out a preliminary comparison of the process economics associated with the removal of PCBs from waste water using activated carbon, UV–ozone, and a near-UV semiconductor photocatalysis system [27] The calculated operating costs, updated from 1987 to 1993, for a range of system sizes are given in Table 2 Although it is just a preliminary study, the calculations do indicate that heterogeneous semiconductor photocatalysis could be economically comparable with activated carbon systems on intermediate to large size water purification systems

2 2 9 *4-Chlorophenol/TiO_2/Air A Standard Test System*

As can be seen from Table 1, research into the photomineralization of organic compounds sensitized by semiconductors has progressed to such an extent that there is a real need to define a standard test system, since it would help facilitate a comparison of results between groups using different experimental con-

Table 2 Estimated process costs for different water purification systems[a]

System size MGD[b]	0.029	0.115	0.23	0.92	2.44
Carbon	$7.79	4.25	3.19	2.21	1.95
UV ozone	$13.00	6.32	4.92	3.83	3.10
UV photocatalysis[f]	$9.85	4.36	3.21	2.32	2.00

The 1993 costs have been estimated from Ollis s original 1987 costs[27] by assuming a 10% per year rise giving a multiple of 1.77 Ollis assumed that the labour maintenance requirements will only be 2.4h/day [b] MGD = million of gallons per day Incinerative regenerator included in larger sizes only No carbon disposal costs included in small units [f] UV ozone process minus ozone generation dissolution

ditions, such as alternative semiconductors, pollutants, reactant concentrations, irradiation sources, and temperatures At present so disparate are the conditions used by the different groups in their research on semiconductor photocatalysis that such comparisons are usually meaningless

As noted before, the commonly accepted standard form of TiO_2 for such work is Degussa P25 TiO_2, and this is usually used under air-saturated conditions Of the many organics studied in the photomineralization of pollutants sensitized by TiO_2, 4-chlorophenol has attracted particular attention and appears a good candidate for a standard test organic pollutant We have suggested that Degussa P25 TiO_2/4-chlorophenol/air-saturated aqueous solution at pH 2 should be adopted as a standard test system for water purification by semiconductor photocalysis, and in order to characterize this system thoroughly we have carried out a detailed study of the kinetics of photomineralization[23] and the intermediates[20] involved in this standard test system

2.2.10 *Methylene Blue/TiO_2/Air A Simple Visual Demonstration of Semiconductor Photocalysis*

Methylene blue is a brightly coloured, commonly available, water-soluble dye which is stable in air-saturated solution when irradiated with light of wavelength > 300 nm It has been established[28] that TiO_2 is able to photocatalyse the complete oxidative mineralization of methylene blue by O_2, *i e*

$$\underset{\text{methylene blue}}{C_{16}H_{18}N_3SCl} + 25\tfrac{1}{2}O_2 \xrightarrow[h\nu > 3.2\ \text{eV}]{TiO_2\ \ \text{air}} 16CO_2 + 6H_2O + 3HNO_3 + H_2SO_4 + HCl \qquad (7)$$

Because of the bright colour of the dye ‘pollutant’, the methylene blue/TiO_2/air system provides a simple visual demonstration of the mineralization of organic pollutants by O_2, photosensitized by TiO_2 In a typical demonstration using the batch irradiation system illustrated in Figure 6(a), 10 mg of Degussa P25 TiO_2 are dispersed in 100 cm^3 of air-saturated water containing 1.05×10^{-5} mol dm^{-3} methylene blue, which is sufficient to turn the TiO_2 dispersion very blue This reaction solution is then placed in a 100 cm^3 Dreschel bottle and then irradiated with the 12 × 8 W UVA lamps of the photoreactor The variation of the absorbance due to the dye *versus* irradiation time is illustrated in Figure 11 and shows that the dye has apparently all been photomineralized within 6 min In fact it can be shown that the dye is bleached within 6 min and colourless intermediates have been generated, quantitative evolution of CO_2 according to the reaction stoichiometry in equation 7 takes about three times as long as the bleaching

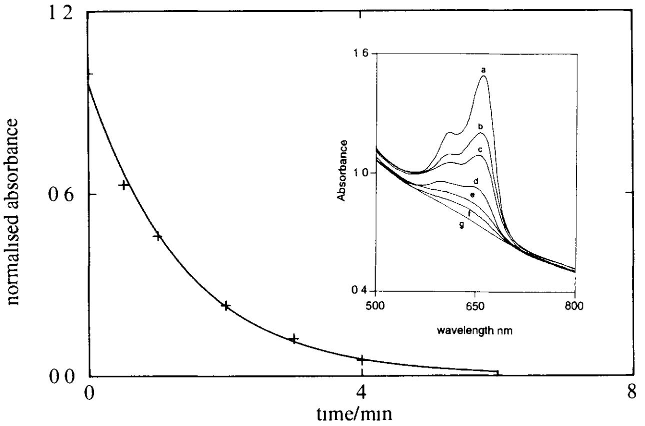


Figure 11 Plot of absorbance at 660 nm due to methylene blue (1.05×10^{-5} mol dm^{-3}) recorded as a function of irradiation time in the presence of TiO_2 (10 mg in 100 cm^3 of air saturated water) where the normalized absorbance of 1 is equivalent to a true dye absorbance of 0.78 In this work the methylene blue samples were taken from the reaction solution at regular intervals and both absorbance and absorption spectra were recorded (see inset)

2.2.11 *Other Novel Applications of TiO_2 Photocatalysis*

There is a growing interest in the application of TiO_2 photocatalysis in areas other than the photomineralization of organic pollutants and some of these other uses are listed in Table 3 Thus, Matthews and his co-workers have reported that a TiO_2 photocatalyst for reaction 1 can be used to carry out total organic carbon analysis (0.1—30 μg cm^{-3}) in < 10 min, the CO_2 generated being detected quantitatively using a conductivity cell In this work it appears to be assumed that all organics will be totally mineralized by this technique, despite the fact that there are known exceptions An instrument for the rapid determination, based on TiO_2 photocatalysis, of organic carbon in water has just been made commercially available – the SGE ANATOC™

Another intriguing use of TiO_2 as a photocatalyst is in mediating the destruction of cancer cells[30] Not surprisingly, the workers involved believe that the photoinduced death of the cancer cells was due to attack from photogenerated hydroxyl

Table 3 Other novel applications of TiO_2 photocatalysis

Application	Ref
Solar to chemical energy conversion	*a*
Photoelectrochemical detector (photocurrent measured) for flow injection analysis and liquid chromatography	*b*
Photocatalytic oxidation system for total organic carbon analysis	*c*
Photoinduced cytotoxic action towards cancer cells	*d*
Photodeodorizer for kitchens and bathrooms	*e*
Photo-oxidation of oil slicks using TiO_2 coated hollow glass microbeads	*f*
Recovery of platinum group metals from industrial wastes or dilute solution	*g*
Photoinduced detoxification of cyanides	*h*

K Kalyanasundaram in Energy Resources through Photochemistry and Catalysis ed M Gratzel Academic Press New York 1983 Chapter 7 [b] G N Brown J W Birks and C A Koval *Anal Chem* 1992 **64** 427 434 R W Matthews M Abdullah and G K C Low *Anal Chim Acta* 1990 **233** 171 179 [d] R Cai Y Kubota T Shuin H Sakei K Hashimoto and A Fujishima *Cancer Research* 1992 **52** 2346—2348 T Ogawa T Saito T Hasegawa H Shinozaki K Hashimoto and A Fujishima in The First International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air Book of Abstracts London Ontario Canada November 1992 p 192 [f] I Rosenberg J R Brock and A Heller *J Phys Chem* 1992 **96** 3423 3428 [g] E Borgarello R Harris and N Serpone *Nouv J Chim* 1985 **9** 743 [h] N Serpone E Borgarello and E Pelizzetti in Photocatalysis and Environment Trends and Applications ed M Schiavello Kluwer Academic Publishers Dordrecht 1988 p 499 radicals and hydrogen peroxide It is surprising that more work is not in progress in the general area of photocatalytic sterilization by TiO_2 as a means of destroying bacteria, viruses, and cancer cells

TiO_2 photocatalysis can be used to destroy volatile organics in air, thus, it has potential as a photodeodorant It has been suggested[31] that TiO_2 could be used to deodorize cars, kitchens, and bathrooms Some research workers have even gone as far to develop an interior tile with a *ca* 1 μm thick TiO_2 film for this purpose

It has also been suggested[32] recently that TiO_2 photocatalysis could be used to assist in the clean-up of oil spills To this end TiO_2 has been coated in part onto low-cost, hollow glass microbeads (50—200 μm diameter) which float on water and are readily separated These oleophilic TiO_2 photocatalyst coated beads clean up small-scale experimental oil spills by (i) stripping and aggregating the oil, followed by mechanical clean-up, (ii) photoassisting the oxidation of the oil, and (iii) controlling the combustion of the oil films on water

3 Conclusion

The purification of water by semiconductor photocatalysis is a rapidly growing area of interest to both research workers and water purification companies In this process, invariably, the pollutant is organic and the semiconductor is TiO_2 The range of organic pollutants which can be completely photomineralized by oxygen, using TiO_2 as the sensitizer, is extensive and includes many aliphatics, aromatics, detergents, dyes, pesticides, and herbicides TiO_2 photocatalysis can also be used in (i) the measurement of total organic carbon, (ii) the killing of cancer cells, (iii) the removal of unwanted odours and (iv) the cleanup of oil spills

4 Appendix

4.1 Photochemical Reaction Schemes

Excitation

$$\mathrm{TiO_2} \xrightarrow{h\nu \geqslant 3\ 2\ \mathrm{eV}} \mathrm{e} \quad + \mathrm{h^+} \tag{A1}$$

Back Reaction

$$\mathrm{e} \quad + \mathrm{h^+} \longrightarrow \mathrm{heat} \tag{A2}$$

Trapping

$$\mathrm{Ti^{IV}(OH\quad /H_2O) + h^+ \longrightarrow Ti^{IV}{-}OH^\bullet} \tag{A3a}$$

$$\mathrm{Ti^{IV}{-}OH^\bullet \longrightarrow Ti^{IV}(OH\quad /H_2O) + h^+} \tag{A3b}$$

$$\mathrm{Ti^{IV} + e} \quad \underset{}{\overset{K_{\mathrm{A4a}}}{\rightleftharpoons}} \mathrm{Ti^{III}} \tag{A4a}$$

$$\mathrm{Ti^{III} + O_2} \overset{K_{\mathrm{A4b}}}{\rightleftharpoons} \mathrm{Ti^{IV}{-}O_2^{\bullet}} \tag{A4b}$$

In the absence of O_2 no photomineralization occurs, thus the efficiency of trapping e , δ_T, is a function of $[O_2]$ (which is thought to be noncompetitively adsorbed onto the surface of the TiO_2 at Ti^{III} sites) If $K_{A4b}\,[O_2] \gg 1$, it can be shown that δ_T $(= \{[Ti^{III}] + [Ti^{IV}{-}O_2^{\bullet}\ ]\}/\{[e\ ] + [Ti^{III}] + [Ti^{IV}{-}O_2^{\bullet}\ ]\})$ is given by the following expression

$$\delta_T = f(O_2) = K(O_2)\,[O_2]/(1 + K(O_2)\,[O_2]) \tag{A4c}$$

where $K(O_2) = K_{A4a}[Ti^{IV}]K_{A4b}$

Absorption of organic pollutant (S) and photogenerated intermediates (Q_j)

$$\mathrm{site + S \rightleftharpoons S_{ads}} \tag{A5}$$

$$\mathrm{site + Q_j} \overset{k_{\mathrm{Qj\ ad}}}{\rightleftharpoons} \mathrm{Q_{j\ ads}} \tag{A6}$$

Hydroxyl radical attack on the initial organic pollutant generating intermediates

$$\mathrm{Ti^{IV}{-}OH^\bullet + S_{ads} \longrightarrow Ti^{IV} + Q_{j\ ads}} \tag{A7a}$$

$$\mathrm{Ti^{IV}{-}OH^\bullet + S \longrightarrow Ti^{IV} + Q_j} \tag{A7b}$$

Hydroxyl radical attack on intermediates generating other intermediates

$$\mathrm{Ti^{IV}{-}OH^\bullet + Q_{j\ ads}} \xrightarrow{k_{\mathrm{Qj\ ad}}} \mathrm{Ti^{IV} + Q_{j+1\ ads}} \tag{A8a}$$

$$\mathrm{Ti^{IV}{-}OH^\bullet + Q_j} \xrightarrow{k_{\mathrm{Q}}} \mathrm{Ti^{IV} + Q_{j+1}} \tag{A8b}$$

where the different intermediates are identified by the different integer values of j The parameter j will have all values which lie in the range m (= total number of intermediates generated) $\geqslant j \geqslant 1$

Other reactions

$$\mathrm{e} \quad \mathrm{+ Ti^{IV}{-}O_2^{\bullet} \quad + 2H^+ \rightleftharpoons Ti^{IV}\,(H_2O_2)} \tag{A9}$$

$$\mathrm{Ti^{IV}{-}O_2^{\bullet} \quad + H^+ \rightleftharpoons Ti^{IV}(HO_2^{\bullet})} \tag{A10}$$

$$\mathrm{Ti^{IV}(H_2O_2) + Ti^{IV}{-}OH^\bullet \rightleftharpoons Ti^{IV}(HO_2^{\bullet}) + Ti^{IV}(H_2O)} \tag{A11}$$

Reactions (A9—A11) indicate that the reduction of O_2 by e can lead to the formation of radicals, such as $Ti^{IV}(HO_2^{\bullet})$, which may be capable of oxidizing the organic pollutant S As a result, under steady state conditions (of electron $[e\ ]_{ss}$ and hole $[h^+]_{ss}$ concentration) the overall rate of formation of oxidizing radicals, which is usually taken to be $= \delta_T k_{A3a}\,[Ti^{IV}(OH\ /H_2O)][h^+]_{ss}$, may be best expressed as $= \alpha\delta_T k_{A3a}[Ti^{IV}(OH\ /H_2O)][h^+]_{ss}$, where for any irradiation system the term α is a constant with a value which lies in the range $1 \leqslant \alpha \leqslant 2$

4.2 Kinetic Equations

High absorbed light intensity I_{abs}

$$[h^+]_{ss} = (k_{A1} I_{abs} \phi A_c / k_{A2} V_p)^{\frac{1}{2}} \tag{A12}$$

where ϕ is the quantum yield for reaction A1, A_c is the area of a TiO_2 particle normal to the illumination, and V_p = volume of a TiO_2 particle

Low absorbed light intensity

$$[h^+]_{ss} = k_{A1} I_{abs} \phi A_c / k_{A3a}[Ti^{IV}(OH\quad /H_2O)]A_s \tag{A13}$$

where A_s is the surface area of a TiO_2 particle

Case A: The destruction of S occurs *via* hydroxyl radical attack on adsorbed S, *i e* equation 7a, and, in the other major reactions, all intermediates are adsorbed on the surface of the TiO_2

$$[Ti^{IV}{-}OH^\bullet]_{ss} = \frac{\alpha\delta_T k_{A3a}[Ti^{IV}(OH\quad /H_2O)][h^+]_{ss}}{k_{A3b} + k_{A7a}[S_{ads}] + \sum_{j\ 1}^{m} k_{Qj\ ads}[Q_{j\ ads}]} \tag{A14}$$

$$-\,d[S]/dt = k_{A7a}[S_{ads}][Ti^{IV}{-}OH^\bullet]_{ss} A_S \tag{A15}$$

$$-\,d[S]/dt = \frac{k_{A7a}[S_{ads}]\alpha\delta_T k_{A3a}[Ti^{IV}(OH\quad /H_2O)][h^+]_{ss} A_S}{k_{A3b} + k_{A7a}[S_{ads}] + \sum_{j\ 1}^{m} k_{Qj\ ads}[Q_{j\ ads}]} \tag{A16}$$

Case B: The destruction of S occurs *via* hydroxyl radical attack of the non-absorbed S, *i e* equation A7b, and, in the other major reactions, all intermediates and S are not absorbed on the surface of the TiO_2

$$-\mathrm{d[S]/d}t = k_{\mathrm{A7b}}[\mathrm{S}][\mathrm{Ti^{IV}{-}OH^{\bullet}}]_{\mathrm{ss}}A_{\mathrm{S}} \qquad \text{(A17)}$$

$$-\mathrm{d[S]/d}t = \frac{k_{\mathrm{A7b}}[\mathrm{S}]\alpha\delta_{\mathrm{T}}k_{\mathrm{A3a}}[\mathrm{Ti^{IV}(OH^-/H_2O)}][\mathrm{h^+}]_{\mathrm{ss}}A_{\mathrm{S}}}{k_{\mathrm{A3b}} + k_{\mathrm{A7b}}[\mathrm{S}] + \sum_{j=1}^{m} k_{\mathrm{Qj}}[\mathrm{Q_j}]} \qquad \text{(A18)}$$

Summary

The final rate equations for both cases A and B have the same form, *i e*

$$-\mathrm{d[S]/d}t = \frac{\delta_{\mathrm{T}}k_{\mathrm{obs}}\kappa_{\mathrm{S}}[\mathrm{S}]}{1 + \kappa_{\mathrm{S}}[\mathrm{S}] + \sum_{j=1}^{m} \kappa_{\mathrm{Qj}}[\mathrm{Q_j}]} \qquad \text{(A19)}$$

where the different parameters are defined as follows

$$\delta_{\mathrm{T}} = f(\mathrm{O_2}) = K(\mathrm{O_2})[\mathrm{O_2}]/(1 + K(\mathrm{O_2})[\mathrm{O_2}])$$

low I $k_{\mathrm{obs}} = \alpha k_{\mathrm{A1}} I_{abs}\phi A_{\mathrm{c}}$

high I $k_{\mathrm{obs}} = \alpha A_{\mathrm{S}} k_{\mathrm{A3a}}[\mathrm{Ti^{IV}(OH^-/H_2O)}](k_{\mathrm{A1}} I_{abs}\phi A_{\mathrm{c}}/k_{\mathrm{A2}} V_{\mathrm{p}})^{\frac{1}{2}}$

	CASE A	**CASE B**
κ_{S}	$k_{\mathrm{A7a}}K_{\mathrm{A5}}[\mathrm{site}]A_{\mathrm{S}}/k_{\mathrm{A3b}}$	$k_{\mathrm{A7b}}/k_{\mathrm{A3b}}$
κ_{Qj}	$k_{\mathrm{Qj\ ads}}K_{\mathrm{Qj\ ads}}[\mathrm{site}]A_{\mathrm{S}}/k_{\mathrm{A3b}}$	$k_{\mathrm{Qj}}/k_{\mathrm{A3b}}$

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