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Photobleaching of methylene blue sensitised by TiO_2: an ambiguous system?

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Abstract

The photobleaching of methylene blue MB, sensitised by TiO_2, in an aqueous solution is studied in the absence and presence of oxygen. In the absence of oxygen and in the presence of a sacrificial electron acceptor (SED), MB is photoreduced to its colourless *leuco* form, LMB, by the TiO_2 photocatalyst. This same photoreduction process is observed even if an SED is not present, indicating that MB itself can act as an SED. The oxidation of LMB by oxygen to regenerate MB is significantly slower if the aqueous solution is acidified (0.01 mol dm^{-3} $HClO_4$) and, at low partial pressures, the rate of reaction depends directly upon the concentration of dissolved oxygen. The TiO_2-sensitised photobleaching of MB is irreversible in an oxygen-saturated aqueous solution, as expected, since the bleaching was due to an oxidative process. However, in an acidified solution (0.01 mol dm^{-3} $HClO_4$), the photobleaching process, in an oxygen-saturated solution, generates LMB initially. The latter situation arises because, under acidic conditions, LMB reacts only very slowly with oxygen to form MB. The significance of these findings with respect to the popular use of photobleaching of MB as a demonstration of semiconductor photomineralisation is discussed. ©1999 Elsevier Science S.A. All rights reserved.

1. Introduction

Methylene blue, MB, is a brightly coloured ($\varepsilon_{660} = 10^5$ dm^3 mol^{-1} cm^{-1}) [1], blue cationic thiazine dye, with λ_{max} values [2] at 660, 614 and 292 nm. The uses of MB include being an antidote for cyanide poisoning in humans, antiseptic in veterinary medicine and, most commonly, in vitro diagnostic in biology, cytology, hematology and histology [3]. The doubly reduced form of MB, *leuco*-methylene blue, i.e., LMB, is colourless (typically, $\lambda_{max} = 256$ nm) [2] and stable in de-aerated aqueous solutions [4]. The singly reduced form of MB, the semi-reduced radical, $MB^{\bullet -}$, is pale yellow ($\lambda_{max} = 420$ nm) and readily disproportionates ($k = 3 \times 10^9$ dm^3 mol^{-1} s^{-1}) [4] to form MB and LMB, i.e.,

$$2MB^{\bullet -} \rightarrow MB + LMB \qquad (1)$$

Less research has been conducted into the oxidised form of MB, i.e., $MB^{\bullet +}$, $\lambda_{max} = 520$ nm, which appears to be quite stable and is easily reduced back to MB in acidic solution [5], but decomposes irreversibly in slightly alkaline (pH = 9.1) solution [6].

MB readily forms dimers in aqueous solution, i.e.,

$$2MB \overset{K_D}{\rightleftharpoons} (MB)_2 \qquad (2)$$

A typical value for K_D, the equilibrium constant associated with the dimerisation process [7], is 3970 dm^3 mol^{-1}. The structures of most of the methylene blue-type compounds highlighted above are illustrated in Table 1 along with the associated pK_a and redox potential data [2,5–12].

The photochemistry of MB has been widely studied. In the early 1980s, MB was a common sensitiser in Fe^{2+} thiazine dye photogalvanic cells — a once very active area of research in the field of solar to electrical energy conversion [13]. Although photogalvanic cells appear to have had their day, MB remains a popular dye sensitiser in photochemistry, especially in the areas of singlet oxygen production [14] and reductive electron transfer [15]. The wide and varied use of MB in photochemistry is attributable to its relatively long-lived, triplet state, $\iota_T = 450$ µs, with its high probability of formation, $\phi_T = 0.52$, large energy (1.44 eV above the ground state) and high triplet oxidation potential ($E^0(MB^T/MB^{\bullet -}) = 1.21$ V versus NHE. The major photophysical and redox characteristics of MB are summarised in Table 2 [15,16].

Given the well-established photochemical activity of MB, initially it might appear surprising to note that MB has often been used as a reactant in semiconductor photocatalysis. This surprise may well increase when it is realised that the semiconductor most often employed in such studies is TiO_2, a UV absorber (i.e., $\lambda < 380$ nm). However, a brief inspection of the UV–Vis absorption spectra of MB, illus-

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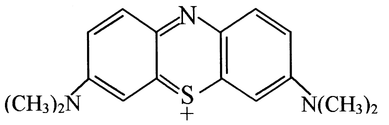
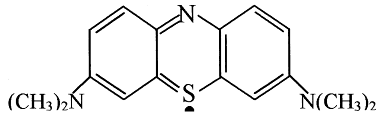
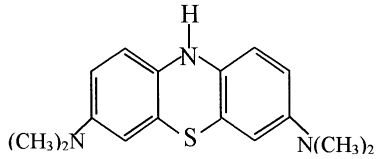
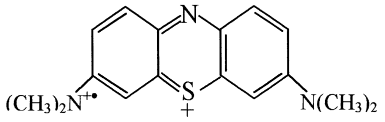
Table 1
Structure and UV–Vis absorption characteristics of methylene blue and its common reduced and oxidised forms

Species	Structure	Abbreviation	pK_a	E^0 vs. NHE (V)	λ^{max}/n	Other properties	References
Methylene blue		MB	0		660, 614, 292	$K_D = 3970\,dm^3\,mol^{-1}$	[2,7,8]
Semi-reduced methylene blue		$MB^{\bullet -}$	−3,2,9	$(MB/MB^{\bullet -}) = -0.23^8$	420	Readily disproportionates to form MB and LMB	[4,8,9]
Leuco methylene blue		LMB	4,5,5.8	(MB/LMB) = 0.011 (pH 7) and 0.532 (pH 0)	2562		[2,10]
Oxidised methylene blue		$MB^{\bullet +}$		$(MB^{\bullet +}/MB) = 1.08$	52012	Stable in acid (pH 1) and unstable at pH 9	[5,6,11,12]

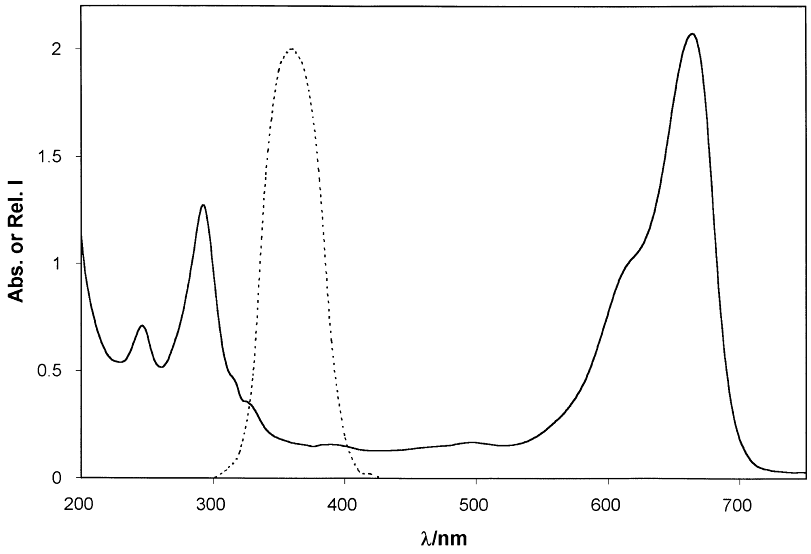


Fig. 1. UV–Vis absorption spectrum of a $2.10^{-5}\,mol\,dm^{-3}$ MB aqueous solution (solid line) and the relative emitted light intensity (I) versus λ profile (broken line) for an 8 W blacklight bulb.

Table 2
Photophysical properties of methylene blue. [15,16]

	Singlet: MB^1	Triplet: MB^3
ϕ_T	–	0.52
E (excited state) ($kJ\,mol^{-1}$)	180	138
τ	30–390 ps	450 μs
ϕ (fluorescence)	0.04	–
E^0 (Excited state/$MB^{\bullet -}$) vs. NHE (V)	1.60	1.21

trated in Fig. 1 (solid line), reveals that MB absorbs little light between 300 and 400 nm. The latter wavelength region is usually the region of illumination in TiO_2-sensitised semiconductor photocatalysis, since most UV irradiation sources used in such work are designed to emit light of $\lambda < 400$ nm, and most of the glassware used is Pyrex, which cuts off at 300–310 nm. To emphasise the latter point a little further, the relative emission intensity versus λ profile for one of the most common light sources in use in semiconductor photocatalysis, the blacklight bulb (λ_{max} (emission) = 355 nm), is also illustrated in Fig. 1 (dotted line). A brief inspection of the two spectra in Fig. 1 reveals a marked lack of overlap. As a result, it is not surprising that most workers find that aqueous solutions of MB show little evidence of bleaching upon UV irradiation (300–400 nm) in the absence of TiO_2 and in the absence or presence of oxygen.

The major studies involving MB as a reactant in TiO_2-sensitised photocatalysis fall largely into two categories: (i) the reduction of MB to LMB by an SED, such as methanol or sodium citrate, under anaerobic conditions, i.e.,

$$\mathrm{MB} + \mathrm{SED} \underset{h\nu \geq 3.2\,\mathrm{eV}}{\overset{\mathrm{TiO_2}}{\rightarrow}} \mathrm{LMB} + \mathrm{SED}^{2+} \qquad (3)$$

where SED^{2+} is unstable and decomposes rapidly and irreversibly; and (ii) the mineralisation of MB by O_2, i.e.,

$$\underset{\mathrm{(MB)}}{\mathrm{C_{16}H_{18}N_3SCl}} + 25\tfrac{1}{2}\mathrm{O_2} \underset{h\nu \geq 3.2\,\mathrm{eV}}{\overset{\mathrm{TiO_2}}{\rightarrow}} \mathrm{HCl} + \mathrm{H_2SO_4} + 3\mathrm{HNO_3} + 16\mathrm{CO_2} + 6\mathrm{H_2O} \qquad (4)$$

Typical examples of these two types of semiconductor-sensitised photochemical reactions, i.e., (3) and (4), are given in Table 3, [2,17–21] and Table 4, [2,18,22–29], respectively.

At first, it might appear that the two photochemical reactions, i.e., (3) and (4), have little in common. Reaction (3) appears to require anaerobic, or nitrogen-saturated, conditions and an SED, whereas (4) simply requires aerobic, or oxygen-saturated, conditions. However, both reactions give the same superficial result, namely, with *ultra*-band gap irradiation of the semiconductor the MB dye is bleached, the difference being that the process is reversible in reaction (3) (upon the addition of O_2 to the anaerobic system, which oxidises LMB back to MB), but irreversible in reaction (4). There is the clear possibility for overlap and misidentification between the two systems. This possibility has not been recognised before, and is of some concern, since, from Table 4, we can see that reaction (4), firstly, has been the subject of numerous studies; secondly, it has been cited as a good visual demonstration of semiconductor-sensitised photomineralisation reactions; and, lastly, is the subject of an often-cited measurement of the true quantum yield of a heterogeneous, semiconductor-sensitised photocatalytic mineralisation reaction.

One way to distinguish between reactions (3) and (4) is to monitor the evolution of carbon dioxide, which is generated only by reaction (4). However, as illustrated by the results of Matthews [22] from his study of reaction (4), using a flow-reactor based on TiO_2 coated on a glass spiral tube, CO_2 evolution occurs at a much slower rate than MB bleaching. This finding is not too surprising, given that many different intermediates will be involved in oxidative mineralisation of MB. Because of the simplicity and ease associated with the measurement of dye bleaching, as opposed to CO_2 evolution, and the apparent safety in the assumption that dye bleaching is indicative of dye oxidation and, so, is irreversible, most studies of reaction (4) have used dye bleaching as a gauge with which to measure the kinetics of dye mineralisation. Clearly, there is a great deal of scope for misinterpreting results if, in fact, some, or all, of the observed semiconductor-sensitised photobleaching of MB is due to the formation of LMB, rather than an irreversibly oxidised form of the dye.

A typical example of what we believe is an unrealised overlap between reactions (3) and (4), is provided by the study, ostensibly of reaction (4), sensitised by TiO_2 in a foamed polyethylene sheet [19]. As in so many of the studies of reaction (4), bleaching of the dye was taken as an indication of mineralisation by Naskar et al. [19], who noted that the rate of bleaching of MB, photo-sensitised by TiO_2, was the same in the absence and presence of O_2. These workers assumed that in both cases mineralisation occurs, and that in the absence of dissolved oxygen, the source of oxygen must be the lattice oxygen! However, a simpler, more likely explanation is that in the absence of oxygen, reaction (3), rather than (4), takes place, with the polyethylene acting as the SED. Indeed, there is no reason why this photochemistry, i.e., reaction (3), does not also take place to some extent in aerobic solution, alongside reaction (4). This is easily tested, as the addition of oxygen to the anaerobic, irradiated solution should lead to some, if not total, recovery in the blue colouration due to MB as the colourless LMB is oxidised back to MB by oxygen. This test does not appear to have been conducted by Naskar et al. [19].

In this paper, reactions (3) and (4) are examined in some depth. An attempt is made to identify reaction conditions that could lead to possible misidentification of the major process involved in these two photobleaching processes. The ramifications of the results of this work with respect to those from previous studies are discussed.

2. Experimental

2.1. Materials

The TiO_2 used throughout this work was Degussa P25 TiO_2. The methylene blue (~85%), zinc granules (−10 + 50 mesh 99.8%) and citric acid (99+%) were obtained from Aldrich Chemicals, and the sodium citrate (99–100%) and perchloric acid (AnalaR grade) from BDH Chemicals. The gases O_2 and N_2 were obtained from BOC. In all this work, the water used to make up solutions was doubly distilled and de-ionised.

2.2. Methods

Details of the photochemical reactor have been reported elsewhere [30,31]. In brief, the photoreactor comprised two half cylinders, each containing six 8 W Black Light UVA lamps set against a half-cylinder aluminium reflector. Each of the lamps (Coast Air®); emitted a broad range of UVA light, typically 320–390 nm, with λ_{max} (emission) = 355 nm. Unless stated otherwise, in this work only two of the 8 W bulbs were used in any irradiation experiment. The photochemical reaction vessel used in this work comprised a 125 cm^3 borosilicate glass Dreschel bottle (i.d. 4 cm) fitted with a rubber septum to allow samples from the reaction

Table 3
Typical TiO_2-sensitised systems for the reduction of MB to LMB via reaction (3) [2,17–21][a]

TiO_2 source	Irradiation source	$[TiO_2]$	[MB]/ (μmol dm^{-3})	SED: nature and [SED]	Comment	References
Powder dispersion, home made by the hydrolysis of $TiCl_4$ by NH_4OH	–	–	–	none	one of the first examples of this process, but with few details	[17]
TiO_2 rutile crystal	390 nm light provided by 350 W Xe arc lamp plus monochromator	single TiO_2 crystal ($6 \times 6 \times 2.5$ mm)	10	methanol or water	claims that water can be used as a SED and is oxidised to oxygen. However, methanol proves most effective	[18]
Degussa P25 on foamed polyethylene sheet	125 W medium pressure Hg lamp + Pyrex filter	97 mg in 21.6×6.5 cm sheet	625	polyethylene sheet?	the researchers report that the rate of bleaching of MB is the same in the absence and presence of O_2. They appear to assume that in both cases bleaching is due to mineralisation. In contrast we have assumed that LMB is formed in the absence of O_2.	[19]
Colloidal dispersion, made by the hydrolysis of Ti(IV)*iso*-propoxide in PrOH	200 W Xe/Hg lamp	2×10^{-4} mol dm^{-3}	5	0.4% propan-2-ol in acetonitrile	LMB stable in anaerobic solution, but rapidly converted back to MB upon exposure to air.	[20]
Degussa P25 powder dispersion	75 W Xe arc lamp	0.08 g dm^{-3}	40	Citric acid/Nacitrate (0.5 mol dm^{-3}) or neat MeOH	very clear reduction of MB to LMB with the latter converted back to MB slowly in the dark and more rapidly upon exposure to air. The former result is a real oddity and will be discussed further	[2]
Degussa P25 powder dispersion	250 W Xe arc lamp	0.12 g dm^{-3}	9.6	none	rate of bleaching of MB is the same in the absence and presence of O_2, but in the former case LMB is formed, whereas in the latter mineralisation takes place	[21]

[a] Experiments carried out under anaerobic conditions.

solution to be withdrawn and analysed spectrophotometrically, using a Perkin Elmer Lambda 3 UV–Vis spectrophotometer. The vessel had an outer water jacket that was always thermostatted at 30°C.

A typical reaction solution placed in the photochemical reaction vessel comprised 10^{-5} mol dm^{-3} MB dissolved in 100 cm^3 of 0.01 mol dm^{-3} $HClO_4$ or water containing 10 mg TiO_2. The reaction solution was continually purged with oxygen or nitrogen and magnetically stirred (600 rpm) at least 15 min before, as well as throughout, any irradiation. Samples of the reaction solution were taken regularly as a function of irradiation time, placed in a 1 cm spectrophotometer cell, sealed with a rubber septum to maintain the gaseous environment from where they were taken, and the UV–Vis absorption spectrum recorded. A typical collection of these spectra is illustrated in Fig. 2. From the difference between the absorbance of a blank (no MB, just TiO_2) solution, and that of the MB/TiO_2 reaction solution irradiated for time t, with both absorbances recorded at 660 nm, a value of ΔAbs.(t) was calculated; ΔAbs.(t) was taken as a direct measure of the concentration of MB at time t. The basis of the calculation of ΔAbs.(t) used throughout this work is illustrated in Fig. 2.

In one set of experiments, the oxidation of LMB to MB by dissolved oxygen, fixed at different concentrations, was monitored as a function of time. In this work, the different levels of dissolved oxygen were generated using a gas blender (Signal Instruments, model: Series 850).

Table 4
Typical TiO_2-sensitised systems for the mineralisation of MB by oxygen via reaction (4) [2,18,22–29][a]

TiO_2 source	Irradiation source	$[TiO_2]$	$[MB]/(\mu mol\,dm^{-3})$	Comment	Ref.
Degussa P25 coated on to a borosilicate glass spiral	20 W blacklight bulb	75 mg on 7 m of 6 mm o.d glass tubing	10	the first, notable study of the mineralisation of MB via reaction (4) Some MB is adsorbed on the TiO_2 in the dark ($K_{ad} = 2980\,dm^3\,mol^{-1}$). rate of bleaching first order with respect to [MB] and dependent upon flow rate (thus, some mass transport control in the kinetics). Quantum yield ca 0.0092. CO_2 evolution is much slower than dye bleaching.	[22]
Degussa P25 deposited onto sand	100 W medium pressure Hg lamp ± Pyrex filter	0.5 g on 100 g sand in 250 ml solution	10	rate of bleaching first order with respect to [MB] and dependent upon flow rate (thus, some mass transport control in the kinetics). Photobleaching enhanced with the addition of H_2O_2.	[23]
Various, including Aldrich Chemicals (anatase) and Degussa P25	concentrated solar light	typically $2\,g\,dm^{-3}$ in 250 ml	80	attempt to identify the problems which must be addressed before a commercially viable water purification system based on this technology can be developed.	[24]
Degussa P25 powder dispersion	sunlight	$1\,g\,dm^{-3}$	100	a simple demonstration of semiconductor photocatalytic mineralisation	[25]
Aldrich Chemicals (Gold label, anatase)	not specified	$0.05\,g\,dm^{-3}$	27	an attempt to establish the quantum yield for photobleaching of MB via reaction (4). A maximum quantum yield of 0.056 was established for the system. Amongst other things the reaction kinetics were examined as a function of [MB], $[TiO_2]$ and λ (irradiation). Possible concerns about this work are described later in this paper.	[26]
Degussa P25 powder dispersion	125 W medium pressure Hg lamp	$0.67\,g\,dm^{-3}$	6–36	a study of the kinetics of reaction (4) as a function of [MB] (first order), $[TiO_2]$ and pH (increases from pH 2.5–7, then plateau's off).	[27]
TiO_2 on glass fibre mesh	15 W blacklight bulb	glass mesh has 16.5 wt. % TiO_2	33	development of a kinetic model for a novel flow photoreactor. A very appreciable (>75%) adsorption of MB on the TiO_2 impregnated mesh is observed.	[28]
Degussa P25 on foamed polyethylene sheet	125 W medium pressure Hg lamp + Pyrex filter	97 mg in 21.6 × 6.5 cm sheet	625	TiO_2 containing sheet about as photoactive as a TiO_2 dispersion ($0.44\,g\,dm^{-3}$). Rate of COD reduction is less than the rate of photobleaching of the dye. See also Table 3 for comments.	[18]
Degussa P25 powder dispersion	250 Xe arc lamp	$0.12\,g\,dm^{-3}$	9.6	rate of bleaching of MB is the same in the absence and presence of O_2, but in the former case LMB is formed, whereas in the latter mineralisation takes place. In the presence of oxygen, mineralisation (as measured by CO_2 evolution) is much slower than dye bleaching.	[20]
Degussa P25 powder dispersion	high pressure Hg lamp	$1.38\,g\,dm^{-3}$	670	rate of photobleaching of MB is increased with increasing $[TiO_2]$ and with the addition of ozone.	[29]

[a] Experiments carried out under air or oxygen saturated conditions.

3. Results and discussion

3.1. Dimerisation and adsorption

As noted earlier, like many thiazine dyes, MB has a tendency to dimerise, see reaction (2), and has a value of $K_D = 3970\,dm^3\,mol^{-1}$. The dimer of methylene blue, $(MB)_2$, has an absorption maximum at band 614 nm [7]. If dimerisation is the only aggregation process MB can undergo, it is possible to calculate the fractions of monomer ($f_M = [MB]/[MB]_{TOTAL}$) and dimer ($f_D = 2[(MB)_2]/[MB]_{TOTAL}$), where $[MB]_{TOTAL} = [MB]$

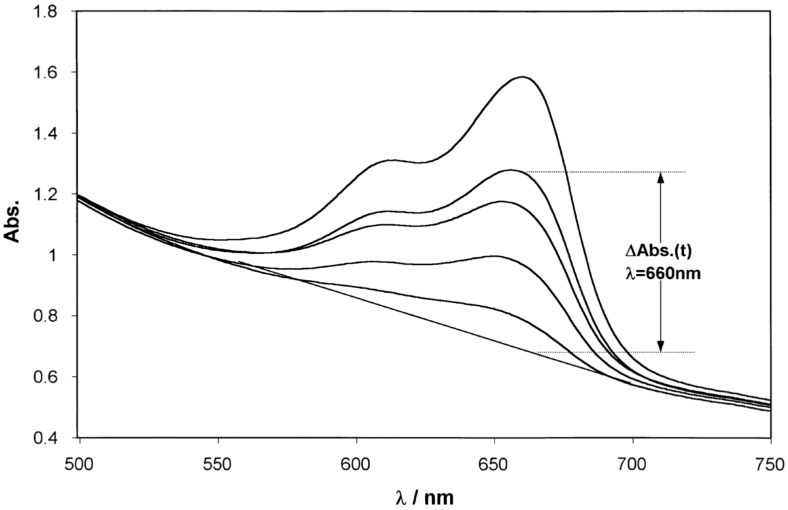


Fig. 2. Variation in the UV–Vis absorption spectrum of a typical MB/TiO_2/0.01 mol dm^{-3} $HClO_4$ system, saturated with oxygen. The following typical reaction conditions were used: [TiO_2] = 0.1 mg cm^{-3}; [MB] = 10^{-5} mol dm^{-3}. Two 8 W blacklight bulbs were used in irradiation and the solution was continuously stirred (600 rpm) and purged with gas (oxygen in this case). The absorption spectra correspond to the following irradiation times (from top to bottom): 0, 5, 10, 20, 30 min and no MB (just TiO_2), respectively. The diagram also shows how typically the measure of the concentration of MB still present after an irradiation time, *t*, i.e., the parameter ΔAbs.(*t*), was obtained from such plots.

+ 2[$(MB)_2$], at any total MB concentration, i.e., any value of $[MB]_{TOTAL}$, by solving the following quadratic equation for the concentration of the monomer [MB]:

$$2K_D[MB]^2 + [MB] - [MB]_{TOTAL} = 0 \qquad (5)$$

In our work, typically $[MB]_{TOTAL} = 10^{-5}$ mol dm^{-3}; thus, upon solving Eq. (5), it appears that ~93% of the dye is in its monomer form and the amount of dimer present can be considered negligible.

MB has also a tendency to adsorb onto metal oxides, such as TiO_2. Matthews [22] examined this adsorption process, using 75 mg of Degussa P25 TiO_2 coated onto glass, and found that the adsorption fitted the Langmuir adsorption isotherm, i.e.,

$$[MB]_{ads} = \frac{\sigma K_{ads}[MB]_{eq}}{1 + K_{ads}[MB]_{eq}} \qquad (6)$$

where, σ is the maximum concentration of MB that can be adsorbed on 75 mg of TiO_2 from 500 ml of solution of the dye, K_{ads} is the adsorption constant and $[MB]_{ads}$ is the concentration of MB adsorbed when the bulk, equilibrium concentration of MB is $[MB]_{eq}$. Matthews [22] reported values of σ and K_{ads} of 5.08 μmol dm^{-3} and 29 800 dm^3 mol^{-1}, respectively. Given $[MB]_{TOTAL} = [MB]_{eq} + [MB]_{ads}$, the following quadratic equation can be derived from Eq. (6) in terms of $[MB]_{eq}$:

$$-K_{ads}[MB]_{eq}^2 + [MB]_{eq}(K_{ads}\{[MB]_{TOTAL} - \sigma\} - 1) + [MB]_{TOTAL} = 0 \qquad (7)$$

In our system, $[MB]_{TOTAL} = 10^{-5}$ mol dm^{-3} and, since we have 100 ml of solution in contact with 10 mg TiO_2, $\sigma = 5.08 \times 500 \times 10/(75 \times 100) = 3.39$ μmol dm^{-3}. Solving Eq. (7), using the latter values for $[MB]_{TOTAL}$ and σ, yields a value of 9.26 μmol dm^{-3} for $[MB]_{eq}$; thus, only ~7.4% of the dye is adsorbed onto the TiO_2 in our work. From the work of Matthews [22] and others [2], the process of adsorption occurs within 1–3 min and both dimer and monomer forms absorb roughly to the same extent, i.e., there are no shifts in the relative intensities of the bands at 660 (due to monomer) and 614 nm (due to dimer).

3.2. Photobleaching of MB under anaerobic conditions

Several studies have already demonstrated that *ultra*-bandgap irradiation of TiO_2 in the presence of MB and an SED, such as sodium citrate or methanol, leads to the photobleaching of MB, forming as it does LMB. The overall process is summarised by reaction (3). This process is the subject of an article by de Tacconi et al. [2], in which, primarily, citric acid/sodium citrate (0.05 mol dm^{-3}) were used as the SED. Although there is little novelty in the author's [2] claim that MB is reduced to LMB upon irradiation of the system, the subsequent claim that the LMB re-oxidies back to MB in the dark and *in the absence of oxygen* is novel and unexpected. The apparent reversibility of this system in the dark under anaerobic conditions appears to indicate that citrate does not act like an SED, but rather once oxidised, can be re-reduced by LMB, i.e., after reaction (3), the following back reaction appears to be able to occur:

$$SED^{2+} + LMB \rightarrow MB + SED \qquad (8)$$

As an alternative explanation, de Tacconi et al. [2] suggest that reverse electron transfer takes place from the LMB into the TiO_2 conduction band or nearby trap states.

In an attempt to reproduce the novel findings of de Tacconi et al. [2], an experiment was carried out under very similar reaction conditions, namely, an aqueous solution containing MB (10^{-5} mol dm^{-3}), TiO_2 (0.1 g dm^{-3}) and citric acid/sodium citrate (0.05 mol dm^{-3}) was irradiated under anaerobic conditions. Upon irradiation of this solution, the MB was seen to bleach; however, when left in the dark subsequently, the colourless LMB solution appeared stable under anaerobic conditions and the blue colour associated with MB was only regenerated when oxygen was bubbled through the solution, i.e., when the following reaction took place:

$$2LMB + O_2 \rightarrow 2MB + 2H_2O \qquad (9)$$

Fig. 3 illustrates the typical variation in ΔAbs.(t) versus time observed for the above experiment. It should be noted that, upon bubbling oxygen into the irradiated solution, reaction (9) appears to regenerate almost, if not all, of the MB within a matter of minutes. Similar ΔAbs.(t) versus time profiles were generated using methanol or triethanolamine (TEOA), instead of citrate, as the SED. These results cast serious doubts on the novel claim by de Tacconi et al. [2] of the reversibility of reaction (3) in the dark under anaerobic conditions. Instead, the most likely cause for their [2] observed recolouration of the LMB solution, photogenerated by TiO_2 using citrate as an SED, is a slow leak of oxygen into the system.

The work of Yoneyama et al. [18] on reaction (3), using a single crystal of rutile TiO_2 (see Table 3), indicates that the SED can be water, which is duly oxidised to oxygen. Although these workers did not look for any oxygen production, they did observe the photoreduction of MB to LMB, sensitised by the TiO_2 in water [18]. The results of this work may have worrying implications for those that use the photobleaching of MB as a gauge of its irreversible mineralisation.

Thus, in an attempt to reproduce the effects observed by Yoneyama et al. [18], an irradiation was carried out under anaerobic, but otherwise typical, reaction conditions (i.e., 10 mg TiO_2 dispersed in 100 ml aqueous solution and containing 10 mol dm^{-3} MB). The variation of ΔAbs.(t) versus time observed for this system is illustrated in Fig. 4a and shows that MB is indeed bleached, and forms a significant amount of LMB, since with the subsequent introduction of oxygen into the system ~63% of the MB is regenerated. The results illustrated in Fig. 4a indicate that the TiO_2/MB/N_2-purged water system is an example of reaction (3), but, if this is the case, what is acting as the SED? Yoneyama et al. [18] suggest that the SED is water, however, it appears more likely that, initially at least, MB acts to some extent as the SED. As the [LMB] increases with irradiation time, then it, too, could begin to act as the SED, along with MB and/or water. The LMB does not appear as efficient as MB as an electron donor towards TiO_2, possibly because it may be even more weakly adsorbed than the latter. (If LMB were a facile electron donor towards TiO_2, then the irradiation would, if anything, lead to the slow irreversible bleaching of MB, with little evidence for any LMB formation — this is not what is observed). A similar ΔAbs.(t) versus time profile to that illustrated in Fig. 4a was observed in 0.01 mol dm^{-3} $HClO_4$, as illustrated by the results in Fig. 4b, and, under the latter conditions, the re-oxidation of LMB to MB by oxygen appears slower.

In support of the suggestion that MB acts as the SED in the TiO_2/MB/N_2-purged water and 0.01 mol dm^{-3} $HClO_4$ systems, it should be noted that in both Fig. 4a and b, the recovery of the MB, with the introduction of oxygen, is ca. 63–68%. If water was the sole SED, then a total recovery of the MB colour would have been observed. To totally mineralise, MB requires 102 oxidising equivalents (i.e., from Eq. (4): 25.5 O_2 molecules, where each O_2 molecule requires 4 electrons to reduce it to H_2O). Thus, if MB had acted as an SED with this number of oxidising equivalents, only 2% of the dye would have been irreversibly bleached, instead of the 32–37% observed. From the latter numbers, it appears that MB, initially at least, acts as a source of 2–4 electrons for each MB bleached to form LMB. Mild oxidation of MB, provided by photogenerated holes on CdS particles for example [32], usually causes it to demethylate, and eventually leads to the formation of thionine (λ_{max} = 600 nm) [12]. If demethylation is a major route in the oxidation of MB sensitised by TiO_2 in de-aerated solution, the colour of the original MB solution would be expected to change, as the thionine is formed; however, the solution would not be expected to bleach, as thionine is not colourless. In all our experiments, there appeared little evidence for the formation of thionine with the irradiation of TiO_2 in the presence of MB; instead, the solution bleached with irradiation. Unlike CdS, TiO_2 photocatalyst particles are believed to generate very strong oxidising agents, such as adsorbed hydroxyl radicals, upon *ultra*-bandgap irradiation. Thus, from our results, it appears that such radicals are the cause for the extensive (32–37%) irreversible photobleaching undergone by MB in the TiO_2/MB/N_2-purged water and 0.01 mol dm^{-3} $HClO_4$ systems upon 30 min irradiation with the light of two 8 W blacklight bulbs. Some support for the latter suggestion is provided by the results of Ohno et al. [33], carried out on the oxidative bleaching of MB using ^{60}CO$-\lambda$ radiation, that indicate that only three hydroxyl radicals are needed to bleach MB irreversibly.

The TiO_2-sensitised photobleaching of the absorbance due to MB and its subsequent recovery upon exposure to oxygen is best illustrated using the TiO_2 in the form of a film on glass. This is because when TiO_2 is used as a powder dispersion, the dispersion must be filtered, before a full (200–750 nm) UV–Vis absorption spectrum of the reaction solution (i.e., without TiO_2) can be recorded. In contrast, if a film of TiO_2 is used as the photocatalyst, no filtering of TiO_2 particles is required and the reaction solution can simply be sampled and its full absorption spectrum recorded. In previous work [34], we established a method for depositing Degussa P25 onto the glass walls of the photoreactor. This

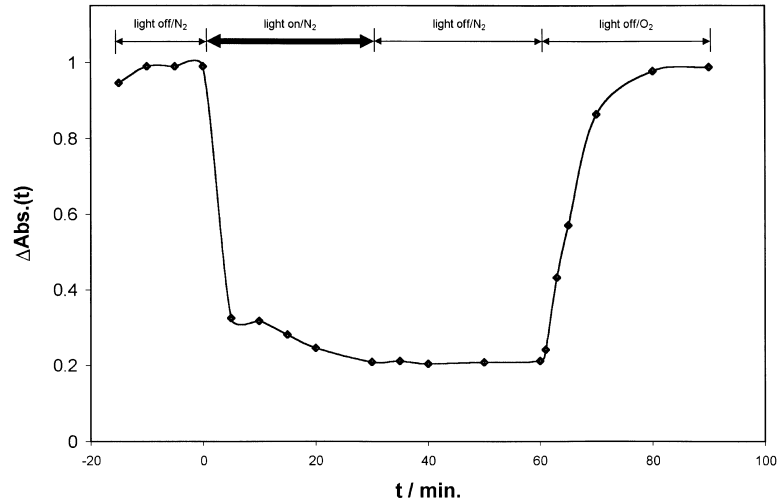


Fig. 3. Observed variation in ΔAbs.(t) versus irradiation time, t, for a typical MB/TiO_2 system in which the solvent was water containing 0.05 mol dm^{-3} citric acid/sodium citrate. The solution was initially nitrogen-purged, and all other conditions were as was in Fig. 2.

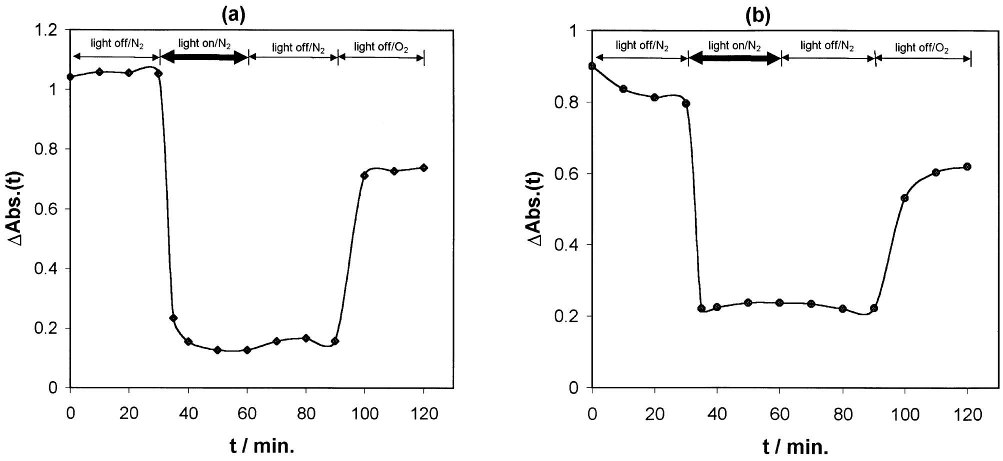


Fig. 4. Observed variation in ΔAbs.(t) versus irradiation time, t, for a typical MB/TiO_2 system, in which the solvent was (a) water and (b) 0.01 mol dm^{-3} $HClO_4$. The solution was initially nitrogen-purged and all other conditions were as was in Fig. 2.

TiO_2 film comprised 3 wash coats of Degussa P25 and was used to study the photomineralisation of 4-chlorophenol. From the results of this work, it was established that the mechanism for 4-CP mineralisation by oxygen, sensitised by TiO_2, is largely unaffected by using the TiO_2 powder as a dispersion or as a film. Assuming this is the case for reaction (3), a three-coat TiO_2 film was used to photoreduce MB (2.10^{-5} mol dm^{-3}) to LMB under anaerobic conditions. The results of the observed variation in the full UV–Vis absorption spectrum of MB as a function of time of irradiation of the TiO_2 film/MB/N_2-purged water photosystem, are illustrated in Fig. 5a. The change in UV–Vis absorption spectrum as a function of time of bubbling oxygen through the photobleached system is illustrated in Fig. 5b. A similar set of experiments were carried out in 0.1 mol dm^{-3} $HClO_4$ and the results of this work are illustrated in Fig. 6a and b.

From the results illustrated in Fig. 6a and b, it appears that the absorption spectrum of LMB has a wavelength of maximum absorption of $\lambda_{max} = 262$ nm in water and 257 nm in 0.1 mol dm^{-3} $HClO_4$ and, in the latter medium, the absorbance was about twice as large. It appears that LMB is in a more protonated form in 0.1 mol dm^{-3} $HClO_4$ than it is in water. This finding was confirmed by reducing an aqueous de-aerated solution of MB to LMB, chemically, using zinc granules, and titrating the LMB with $HClO_4$. From the results of this work, a value for the pK_a of LMB of 1.7 was obtained. To our knowledge, this pK_a transition has not been reported before for LMB, although others [35] have reported evidence that *leuco*-thionine has a pK_a of ca. 2, involving a protonated and deprotonated form which differ spectrophotometrically in much the same way as observed above for LMB.

As noted earlier, the rate of re-oxidation of LMB to MB, via reaction (9), appears slower in acidic solution than it does in water. Using zinc granules to reduce MB to LMB in a de-aerated solution, the recovery of the absorbance due to

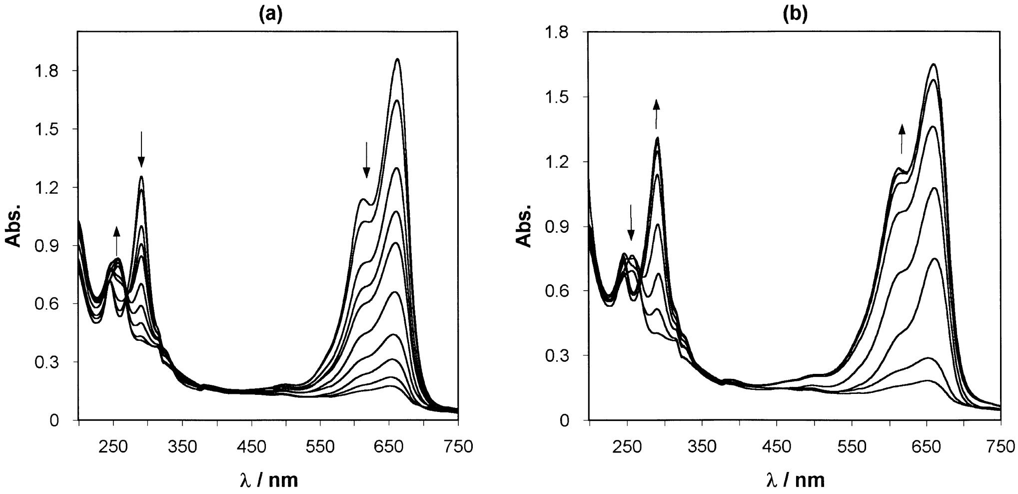


Fig. 5. (a) Variation in the UV–Vis absorption spectrum of an 2.10^{-5} mol dm^{-3} MB aqueous solution, purged continuously with nitrogen and irradiated in the presence of a 3-wash coat film of TiO_2 deposited onto the walls of the photoreactor [34]. The spectra were recorded after the following irradiation times (from top to bottom at 660 nm): 0, 1, 3, 5, 7, 10, 15, 20, 25 and 30 min, respectively; (b) variation in the UV–Vis absorption spectrum of the bleached reaction solution generated in (a) upon purging with oxygen. The spectra were recorded at the following oxygen purge times (bottom to top 660 nm): 0, 0.5, 1, 2, 3, 4 and 5 min, respectively.

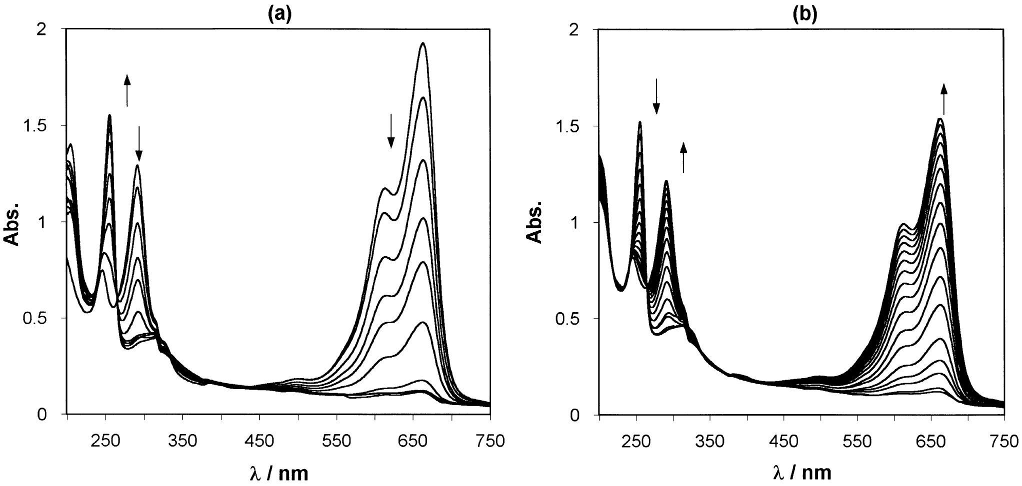


Fig. 6. (a) Variation in the UV–Vis absorption spectrum of a 2.10^{-5} mol dm^{-3} MB aqueous solution containing 0.1 mol dm^{-3} $HClO_4$, purged continuously with nitrogen and irradiated in the presence of a 3-wash coat film of TiO_2 deposited onto the walls of the photoreactor [34]. The spectra were recorded after the following irradiation times (from top to bottom at 660 nm): 0, 3, 5, 7, 10, 15, 20 and 25 min, respectively; (b) variation in the UM–Vis absorption spectrum of the bleached reaction solution generated in (a) upon purging with oxygen. The spectra were recorded from $t = 0$, every 0.5 min of oxygen purging.

MB was monitored as a function of time purging with oxygen. From the results of this work, it appears that reaction (3) is much slower in 0.01 mol dm^{-3} $HClO_4$ ($t_{1/2} = 105$ s) than it is in water ($t_{1/2} = 15$ s). Separate experiments showed that this significant decrease in rate was not due to an ionic strength effect. The apparent decrease in rate of reaction (9) with increasing acidity may simply be due to an associated decrease in the thermodynamic driving force for the reaction. Evidence that this is indeed the case, is provided by the work of Clark [10], who reported that the redox potential for the MB/LMB couple is 0.532 V and 0.011 V versus NHE at pH 0 and pH 7, respectively. In contrast, the oxidation potential for the H_2O/O_2 couple is 1.23 V and 0.817 V versus NHE at pH 0 and pH 7, respectively, thus the driving force for reaction (9) decreases from 0.806 to 0.698 eV on changing the pH from 7 to 0. Alternatively, it may be associated with the pK_a of LMB, which is 1.7, with the protonated form of LMB being less reactive in reaction (9) than its deprotonated counterpart; further work is required before a full understanding can be gained.

In a separate set of experiments, the rate of reaction (9) was studied as a function of the percentage oxygen in the purging gas. In this work, the same amount of LMB was photogenerated each time using a de-aerated solution (100 cm^3) containing MB (10^{-5} mol dm^{-3}) and TiO_2 (10 mg). The observed ΔAbs.(t) versus purging time profiles, associated

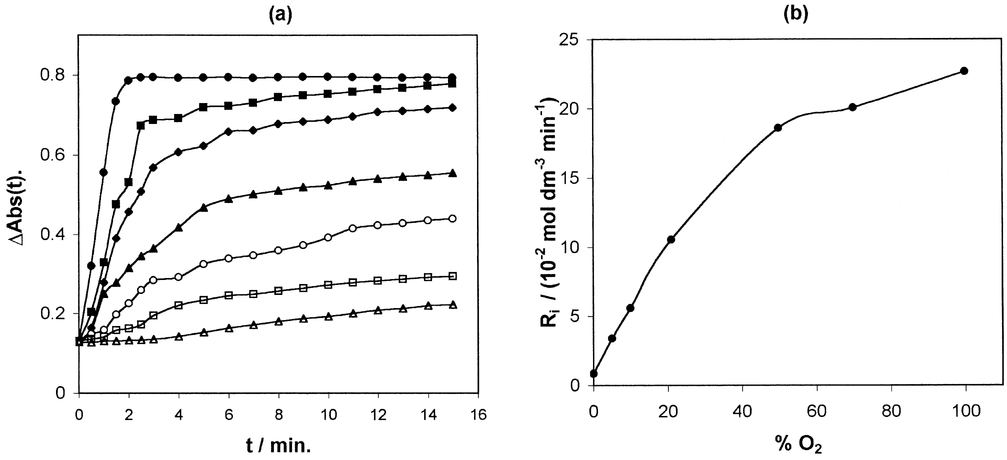


Fig. 7. (a) Observed variation in ΔAbs.(*t*) versus purge time, *t*, profiles for typical LMB/TiO_2 aqueous solutions, in which the LMB was generated by irradiating each system to the same extent, prior to purging with a different level of oxygen. The different levels of oxygen in the purge gas were as follows (from bottom to top): 0, 5, 10, 21, 50, 70 and 100% oxygen. (b) Variation in the initial rate of recovery in the absorbance of MB upon purging, calculated using the data illustrated in (a), as a function of the %O_2 in the purge gas.

with the oxidation of LMB to MB by a purging stream containing different levels of oxygen, are illustrated in Fig. 7a and show that the rate of reaction (9) is strongly dependent upon the level of oxygen present. Using this data, the initial rate of recovery was calculated for each level of oxygen (used to purge the reaction solution) and the results are illustrated in Fig. 7b. From this latter data, the rate appears to depend directly on the percentage of O_2 present in the purging gas stream at levels <60%, but becomes increasingly insensitive to any increase in percentage of O_2 above a level of 60. The latter effect may be due to the process of gas-to-liquid mass transfer [36], which at the flow rates used (ca. 100 cm^3/min), would be expected to be of the order of 1–3 min [36]. Thus, in the above system, gas-to-liquid mass transfer would be expected to become the rate determining step as the level of oxygen is increased to a level at which the kinetics of reaction (9) had a reaction time <1–3 min; in our work this level appears to be >60% O_2. At low levels of O_2, the kinetics of reaction (9) will be much slower than gas-to-liquid mass transfer and, under these conditions, the 'true' kinetics (i.e., no gas-to-liquid mass transfer effects) of reaction (9) will dominate. From the results illustrated in Fig. 7b, the rate of reaction (9) appears to depend directly upon the percentge of O_2 at low levels of O_2 (i.e., <60% O_2), and this appears consistent with the findings of others [33].

3.3. Photobleaching of MB under oxygen-saturated conditions

A quick comparison of Tables 3 and 4 reveals that most studies involving the photobleaching of MB, sensitised by TiO_2, have been carried out under oxygen or air-saturated conditions, usually in water. The overall process assumed to take place in such studies is the photomineralisation of MB by oxygen, sensitised by TiO_2, this process is summarised by reaction (4) and reported examples are listed in Table 4. There appears to be little doubt that with prolonged irradiation of the MB/TiO_2/O_2-saturated water or acid system with *ultra*-bandgap light, reaction (4) does occur. However, as noted earlier, many workers have used the photobleaching of MB as a gauge of the initial kinetics of reaction (4); most recognising that CO_2 evolution is delayed significantly compared to dye photobleaching.

The visual nature of this system has led to the promotion of the MB/TiO_2/air-saturated water system as a suitable demonstration of semiconductor photocatalysis [25]. Others have used the same system to determine the true quantum yield (reported as 0.056) for the photobleaching of MB, via reaction (4) [26]. And yet, from our previous work, it appears that reaction (3) will also bring about the photobleaching of MB, via reaction (3). However, competition between reaction (3) and (4) can only occur if the rate of reaction of MB with the photogenerated conductance band electrons, i.e.,

$$\mathrm{MB} + e_{\mathrm{CB}}^{-} \rightarrow \mathrm{MB}^{\bullet -} \qquad (10)$$

and the subsequent disproportionation of the semireduced MB radical, i.e., reaction (1), are significantly faster than electron trapping by oxygen, i.e.,

$$\mathrm{O_2} + e_{\mathrm{CB}}^{-} \rightarrow \mathrm{O_2}^{\bullet -} \qquad (11)$$

If reactions (10) and (1) are much faster than reaction (11), then reaction (3) will compete with reaction (4) and this will become particularly apparent if the level of dissolved oxygen is low, or the rate of reaction (9) is slow. Conditions that favor the undesirable creation of a low level of oxygen in any study of semiconductor-sensitised photomineralisation by oxygen are (i) use of air-saturated solutions that are not purged continuously with air/oxygen and (ii) insufficient agitation of the reaction solution, for example, by stirring or continual purging, resulting in a low gas-to-liquid mass transfer rate.

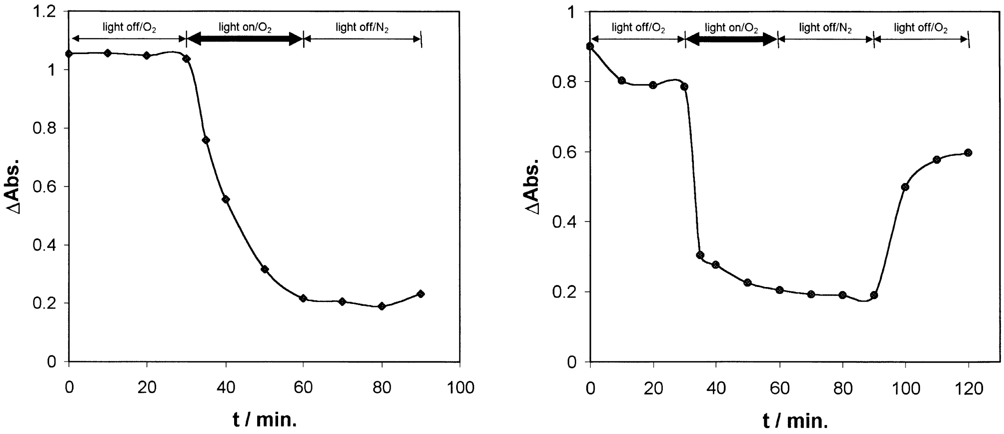


Fig. 8. Observed variation in ΔAbs.(t) versus irradiation time, t, for a typical MB/TiO_2 system in which the solvent was (a) water and (b) 0.01 mol dm^{-3} $HClO_4$. The solution was initially oxygen-purged and all other conditions were as for Fig. 2.

For those studying reaction (4), clearly conditions (i) and (ii) are best avoided, although this does not always appear to be recognised. For example, in making the measurement of the 'true' quantum yield for reaction (4), Bolton and his co-workers [26] do not report if the solution is stirred or purged or, if pre-saturated, whether the gas used was air or oxygen. Matthews [22] rather nicely notes that even at the modest concentration of 10^{-5} mol dm^{-3}, the complete mineralisation of an aerated MB solution would require all the dissolved oxygen present in the solution (2.5×10^{-4} mol dm^{-3}) and some more. It comes as no surprise, therefore, to note that in his [22] work on reaction (4), using a film of TiO_2 as the photocatalyst in a circulating flow photoreactor, the kinetics of reaction (4) appeared to depend upon flow rate. The latter finding was attributed to a depletion in the level of dissolved oxygen level in the photoreactor upon irradiation that was reduced by increased agitation of the reaction solution caused, in turn, by an increased solution flow rate.

In a simple experiment, the photobleaching of MB, sensitised by TiO_2, in oxygen saturated water was studied under standard reaction conditions (10 mg TiO_2 in 100 ml of solution, [MB] = 10^{-5} mol dm^{-3}; stirred and purged continuously),. The resulting recorded variation in ΔAbs.(t) versus irradiation time is illustrated in Fig. 8a and shows that the MB is bleached upon irradiation of the system and that, once photobleached, no recovery of the absorbance due to MB is observed in the dark, despite continued purging of the system with oxygen. Thus, under these conditions, it seems reasonable to assume that reaction (4) is the dominant process. Indeed, on the face of these results, there appears little evidence that reaction (3) does compete with reaction (4) under these conditions.

However, similar observations to those illustrated in Fig. 8a would be expected even if reaction (3) did compete with reaction (4), if the rate of re-oxidation of LMB to MB by oxygen, i.e., reaction (9), is rapid. From the results of an earlier study it was noted that the rate of reaction (9) is significantly slower in acidic solution than in water. Thus, it may be possible to obtain evidence for competition between reactions (3) and (4), even in oxygen saturated solution, by conducting the irradiation of a MB/TiO_2/O_2-saturated solution in 0.01 mol dm^{-3} $HClO_4$. The results of such an experiment, carried out under otherwise standard conditions, are illustrated in Fig. 8b. These results show that MB is bleached upon irradiation, and that the reaction solution remains colourless when the irradiation light is turned off and the solution purged with nitrogen, instead of continuing with the oxygen purge. However, when the oxygen purge is reintroduced into the system a substantial (68%) amount of the original colouration due to MB recovers. It should be note that the fraction of MB that appears to be bleached permanently is the same in oxygen-saturated as it is in nitrogen-saturated solution (cf Figs. 4b and 8b). This latter finding indicates that reaction (3) dominates over reaction (4) and that oxygen is a much poorer scavenger of photogenerated conductance band electrons, via reaction (11), than MB, via reaction (10) in acidic solution, and probably neutral solution as well. The oxidised radical of MB, i.e., $MB^{\bullet +}$ may be more stable in acidic than in neutral (see Table 1and references therein) and this may also facilitate the dominance of reaction (3) over (4) in acidic solution.

4. Conclusion

The phtotobleaching of MB, sensitised by TiO_2, in aqueous solution is revealed to be a quite ambiguous system in terms of mechanism. Whilst prolonged irradiation leads to the eventual complete mineralisation of the dye, the initial observed photobleaching of the dye, so often favoured by researchers studying this system as an example of semiconductor photomineralisation, is not necessarily due to the dye oxidation, expecially if the reaction is carried out under conditions that favour the formation of LMB, i.e., conditions which include: a low, easily depleted dissolved oxygen level and a low pH.

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