



Adsorption and photocatalytic and photosensitised bleaching of acid orange 7 on multilayer mesoporous films of TiO₂

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ABSTRACT

A series of mesoporous films of titania of different thicknesses are prepared and their surface areas and porosities determined by physical adsorption using Kr as the adsorbate. The amounts of acid orange 7 (AO7) adsorbed by these films are found to be proportional to their measured surface areas and so the possibility of using this as a method of determining the surface area of thin titania films is discussed. The initial rates of UV-driven photocatalytic- and visible-driven photosensitised-bleaching of AO7 in solution, upon UVA and visible light irradiation, respectively, are also directly dependent upon the measured surface areas of the titania films. The quantum efficiencies for the UV photocatalytic- and visible photosensitised-bleaching of AO7 by the thickest of the AO7 films were estimated to be 0.08 and 0.01%, respectively.

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1. Introduction

In recent years, much attention has been devoted to preparation of organized mesoporous thin films, of both crystalline and amorphous nature, of a variety of inorganic oxides, such as SiO₂, TiO₂, SiO₂/TiO₂, SnO₂, ZnO, ITO and ATO. Their preparation is based on the evaporation-induced, self-assembly mechanism which operates when the films are deposited by dip-, spin- and spray-coating [1–3]. Such films have potential application in a number of advanced technologies, such as photocatalysis, electrochemistry, photoelectrochemistry, photovoltaics, sensors and membrane separation.

Photocatalysis is an area of increasing interest for the destruction of environmentally hazardous materials and there is a growing interest in the use of mesoporous titania films for effecting this process. They have been used recently to promote the photomineralisation of volatile pollutants, such as NO [4] and toluene [5], organic films (such as stearic or oleic acid [6,7]) and water-based pollutants, such as 4-chlorophenol [8] and dyestuffs [9].

In order to provide a deeper insight into the properties of those films and their successful application in such diverse fields, it is crucial to understand their sorption properties both in gaseous and liquid phases. The analysis of their gas sorption properties provides fundamental data about the porosity features of the films, such as

the surface area, pore volume and pore size. Using this information, the adsorption of other species, such as dyes in solution, can be more fully understood. This information, in turn, helps reveal the role of surface area and adsorption in important processes, such as the photocatalytic or photosensitised bleaching of dyes mediated by semiconductor photocatalyst materials, such as titania.

The use of semiconductor photocatalysis for the remediation of dye-contaminated water is a major research area [10], which is possibly not surprising given the dyestuff industry is a recognised major source of pollution. Indeed, it is estimated of the ca. 0.9 million tonnes of organic dyes produced annually, ca. 15% is lost to the environment during their synthesis and production [10,11].

In order to demonstrate the efficacy and controlling factors of the destruction of dyes by semiconductor photocatalysis in this paper the preparation and characterisation of a series of mesoporous films of titania are described, particularly with regard to film surface area, porosity and dye adsorption. This information is then used to rationalize the observed kinetics of the photocatalytic and photo-sensitisation bleaching of a typical dye used as a test pollutant in dye removal studies, using films of different thicknesses, surface areas and porosities.

2. Experimental

2.1. Film preparation

Mesoporous films of TiO₂ were prepared using a reaction mixture which contained: 14.4 mL of titanium(IV) ethoxide, 56 mL of

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Table 1

An overview of the texture parameters of 1–4-layer films prepared by dip-coating, respectively, obtained from adsorption isotherms of krypton at ca. 77 K.^a

No of layers	$S_{\text{BET}}(\text{cm}^2)$	$S_{\text{BET, SPEC}}(\text{cm}^2/\text{cm}^2)$	$S_{\text{BET, MASS}}(\text{m}^2/\text{g})$	$V_{\text{PORE}} \times 10^3 \text{ cm}^3$	$V_{\text{PORE, SPEC}} \times 10^4 \text{ cm}^3/\text{cm}^2$	$D(\text{nm})$	Porosity (%)	Thickness (nm)
1	3681	147	92	0.686	0.274	10	69	400
2	6822	273	85	1.168	0.467	10	68	690
3	7714	309	64	1.297	0.519	10	45	1150
4	9093	364	57	1.303	0.521	9.5	40	1290

^a The BET surface area, S_{BET} , and pore volume, V_{PORE} , were calculated from the krypton data at ca. 77 K using the average area occupied by each krypton molecule in the completed monolayer and the density conversion factor of 0.210 nm² and 0.0012743, respectively, as provided by the Micromeritics software. The pore volume corresponds to the plateau at the relative pressure approaching 1. The specific BET surface area, $S_{\text{BET, SPEC}}$, and the specific pore volume, $V_{\text{PORE, SPEC}}$, are related to a unit surface area of the support. The surface area $S_{\text{BET, MASS}}$ is related to a unit of the TiO₂ mass (i.e., 1 g). The pore width, D , corresponds to the maximum of the pore size distribution. The porosity was calculated by dividing the pore volume by the total volume of a film (determined by multiplying the area of the support by the film thickness).

butan-1-ol, 10.2 mL of HCl and 5 g of Pluronic P123 (BASF). The films were deposited by dip-coating glass slides at a speed of 1 mm s⁻¹ at a relative humidity of 20%. Afterwards the films were aged at room temperature for 24 h and then calcined in air at 350 °C for 3 h. Films of increasing thickness (up to 4 layers) were prepared by repeating the deposition procedure. All the chemicals were obtained from Sigma–Aldrich (except for the Pluronic copolymer).

2.2. Characterisation of the multilayer films

The thicknesses of the different multilayer films were measured using a Dektak profilometer and are reported in Table 1. For each film, there was some variation in thickness across the film, thus the values reported in Table 1 are average values.

In order to determine the texture parameters of thin porous films deposited on supports with total surface areas in the range of several tens cm², a high-sensitive krypton adsorption technique was used. Note: the most frequently used adsorbing gases, namely, nitrogen and argon at ca. 77 and 87 K, respectively, cannot be applied to materials, such as thin films, having very small surface areas. This is because the saturation pressures of nitrogen and argon at 77 and 87 K, respectively, are very high, reaching ca. 760 Torr, which leads to an extremely large number of molecules being trapped within the void volume of the sample cell. Because of the very small total pore volumes and surface areas of such thin porous films, the pressure changes due to gas adsorption cannot be measured with sufficient precision. As an alternative, an adsorbing gas with a substantially lower saturation vapor pressure needs to be used, such as krypton, at the boiling point of liquid nitrogen, whose saturation pressure equals 1.63 Torr and 2.63 Torr as a solid and a super-cooled liquid, respectively. Thus, in this work the adsorption isotherms of krypton were measured using a Micromeritics ASAP 2010 apparatus and liquid nitrogen (ca. 77 K) as the coolant. Prior to the adsorption experiment, the films were evacuated at 150 °C overnight. The specific surface areas of the different films were determined by the BET method using the molecular cross-sectional area of Kr of 0.21 nm².

Information on the pore volume was obtained from the limiting adsorption at a pressure near to the saturation pressure. As the analysis of adsorption isotherms of Kr at 77 K is far from straightforward, and a well-established procedure (e.g. DFT) has not yet been devised, a simple method based on comparative plots was used to determine the mean pore size and the pore size distribution [12,13]. A non-porous sample of anatase (Aldrich) was used, with a surface of 11.2 m²/g, as a reference material. Comparison plots for each sample were constructed, in which the adsorption of the sample under study was plotted against that of the reference material. The differentiation of the obtained plots provided an assessment of the pore size distribution for each film. To obtain a true pore size distribution, the x-axis of the differentiated comparison plot was converted to the pore width using an equation based on the adsorption properties of a series of TiO₂ powders,

whose texture was reliably known [12,13]. The results of this work are summarised in Table 1.

XRD performed on the films revealed the material to be mostly anatase (about 60%), the rest being amorphous TiO₂ (40%). It is expected that the particle size will be compatible with the thickness of the pore walls, i.e. About 5–10 nm in size.

2.3. Dye adsorption

The adsorption of dye on the TiO₂ sol-gel films (over 24 h) was carried out using the schematic procedure illustrated in Fig. 1. The dye-containing staining solution (100 mL) comprised: a dye concentration of 1.5 mM, with 0.01 M of NaCl, to ensure a fixed ionic strength, and 0.001 M HCl, to ensure the titania film was sufficiently protonated so as to bind strongly – via electrostatic attraction – the anionic dye, acid orange 7, AO7 [14]. Note: little or no AO7 will adsorb onto these, or other titania films, at pHs \gg point of zero charge, pzc, of titania (ca. 6.6) [15]. The TiO₂ film on glass slide under test was then carefully lowered into the staining solution which was agitated continuously via a magnetic stirrer. The film was then left in the solution in the dark for 24 h to ensure the adsorption of the dye onto the film was complete. When removed, the UV/Vis absorbance spectrum of the film was recorded. The film was then lowered into 100 mL of a 0.001 M NaOH (pH 11) solution. This change in ambient pH produced a change in charge on the titania (from positive to negative) with the result that the adsorbed AO7 was rapidly (within 1–5 min) released from the surface of the titania due to electrostatic repulsion of the anionic dye from the now negatively charged surface. Once all the dye was desorbed in this manner into the 0.001 M NaOH solution, the UV/Vis absorbance spectrum of the solution was measured and used to derive how much AO7 was adsorbed onto the titania.

This process was employed on all the mesoporous titania films so as to determine the amount of dye that was adsorbed on each on them under the staining conditions, namely: pH 3, [AO7] = 1.5 mM and [NaCl] = 0.01 M.

2.4. Photocatalysis

All UV irradiations, i.e. photocatalytic dye bleaching reactions, were conducted using two 8 W black light blue (BLB) fluorescent tubes with an output maximum at 365 nm and a typical UV irradiance of 2 mW cm⁻². All visible irradiations, i.e. photo-sensitised dye bleaching reactions, were carried out using a 150 W Xe arc lamp fitted with a 400 nm cut-off filter to remove the UV component of the light (irradiance at 475 nm = 21 mW/cm²). The lamp irradiance levels were measured using an OL 750D spectroradiometer (Optronic Labs, USA).

In all cases, one side of the coated glass slide was wiped clean of titania in order to improve the absorption measurements. A fluorescence cell with part (ca. 1.5 cm²) of one face removed was used as the reaction cell containing 3.5 mL of the AO7 reaction solution (0.048 mM AO7, 0.01 M NaCl, 0.001 M HCl). The titania coated glass

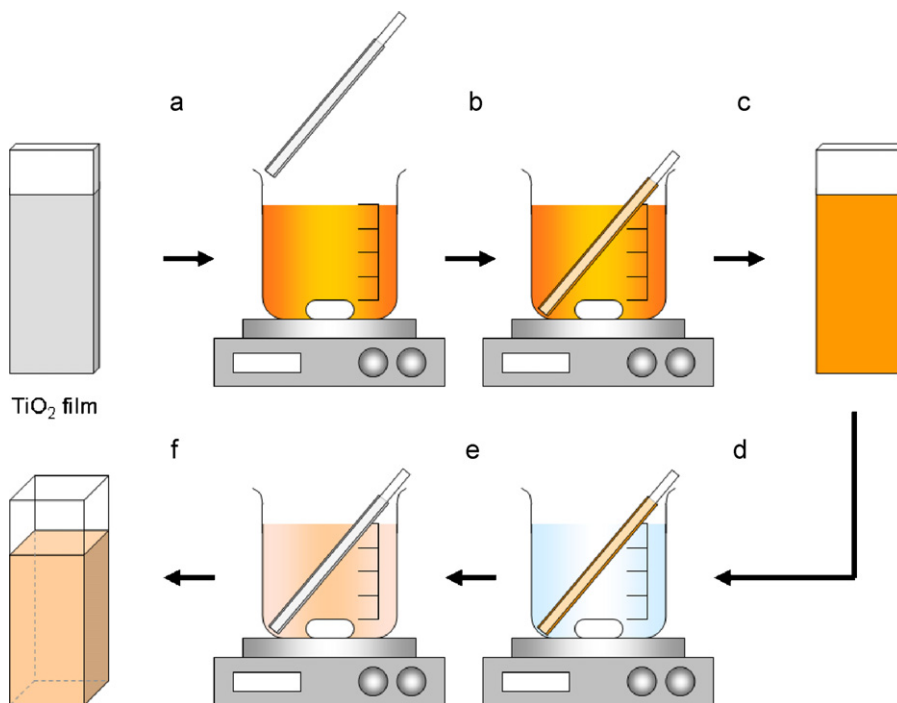


Fig. 1. (a) The film is carefully lowered into the staining solution; (b) the film is left in there for 24 h to ensure equilibrium is reached; (c) after 24 h, the film is removed and then; (d) lowered in alkali solution to desorb the dye; (e) all the dye is desorbed into the alkali solution after 1–5 min; (f) the absorbance spectrum of the resulting solution is then used to calculate the amount of dye adsorbed on the film.

slide was used to replace the missing face of the fluorimeter cell and held in place by a clamp, with a thin silicone rubber gasket between cell and slide to ensure a good seal. The cell allowed the solution to be irradiated through the titania film and for the UV/Vis absorption spectrum of the continuously stirred reaction solution to be monitored as a function of irradiation time.

3. Results and discussion

3.1. Morphological and texture properties of the films

The krypton adsorption isotherms measured at 77 K for the series of 1–4-layers of mesoporous titania on glass films are illustrated in Fig. 2(a) and were used to calculate the surface area and porosity data in Table 1. From this data it is clear that the surface area and overall pore volume increase with the increasing number of deposited layers; as does the average thickness of the films (also given in Table 1). When the pore volume is related to the total film volume, as it is in the value of the porosity, it is apparent that there is a deterioration in the porosity of the film with increasing layers, as noted previously by others [8,16,17] and presumably brought about by the increased number of annealing cycles, and therefore sintering, associated with an increased number of layers. The deterioration of the porous nature of the films with increasing number of layers is illustrated most graphically by the change in the shape of the pore size distribution calculated from the adsorption isotherms, as illustrated in Fig. 2(b). Thus, while the 1- and 2-layer films exhibit a very narrow distribution, the 3- and 4-layer films are notably broader. However, all the distributions are centered at ca. 9–10 nm, i.e. there is only very slight shift of the average pore size due to the increasing number of layers.

3.2. AO7 adsorption on the multilayer films

In the absence of AO7 the mesoporous titania films were colourless and increasingly frosted-looking, i.e. opaque due to light

scattering, with increasing number of layers. However, after staining with AO7, all the films were highly coloured. Photos and UV/Vis absorption spectra of the 1–3 layered films are illustrated in Fig. 3 (the UV/Vis spectrum of the adsorbed dye on the 4-layered film could not be recorded due to the highly light-scattering nature of the underlying film of titania). These results show not only the efficacy of the staining process but also that the adsorbed dye appears very different from its monomeric form. Interestingly, unlike many dyes, most aggregates of AO7 have very similar absorption spectra to that of the monomer [18]. Indeed, even colloids of AO7 exhibit spectra that are not dissimilar to the monomer [19]. The significant hypsochromic shift in the absorption maxima (480 nm for monomer, 460 nm for adsorbed dye) suggests something more than aggregation is responsible. Others have found evidence from FT-IR spectra and adsorption isotherm data [20,21], to suggest that AO7 forms a bidentate inner sphere complex with two protonated hydroxy groups via its sulfonate group, as illustrated in Fig. 4. Similar FT-IR spectra were found in this work, implying the same complex formation. Thus, it is possible this strong binding, as well as some degree of aggregation is responsible for the markedly different absorption spectrum of AO7 on titania, compared to that of its monomeric and simple aggregated forms in solution.

3.3. AO7 desorption on the multilayer films

The dye adsorbed on each film was then desorbed using a pH 11 NaOH solution. Complete desorption, as shown by a lack of any colouration of the titania film, took between 1 and 5 min, depending on the thickness of the film. Further, more quantitative, evidence that the mass balance of the dyes in the adsorption–desorption process was 100%, i.e. the stained films released all the dye in the desorption process, was provided by the identical nature of the UV/Vis spectra of the films before staining and after desorption, i.e. comparison of the two spectra for each film revealed no evidence of any retention of the dye after the desorption process. Once desorbed, the UV/Vis absorption spectrum of each of the solutions was

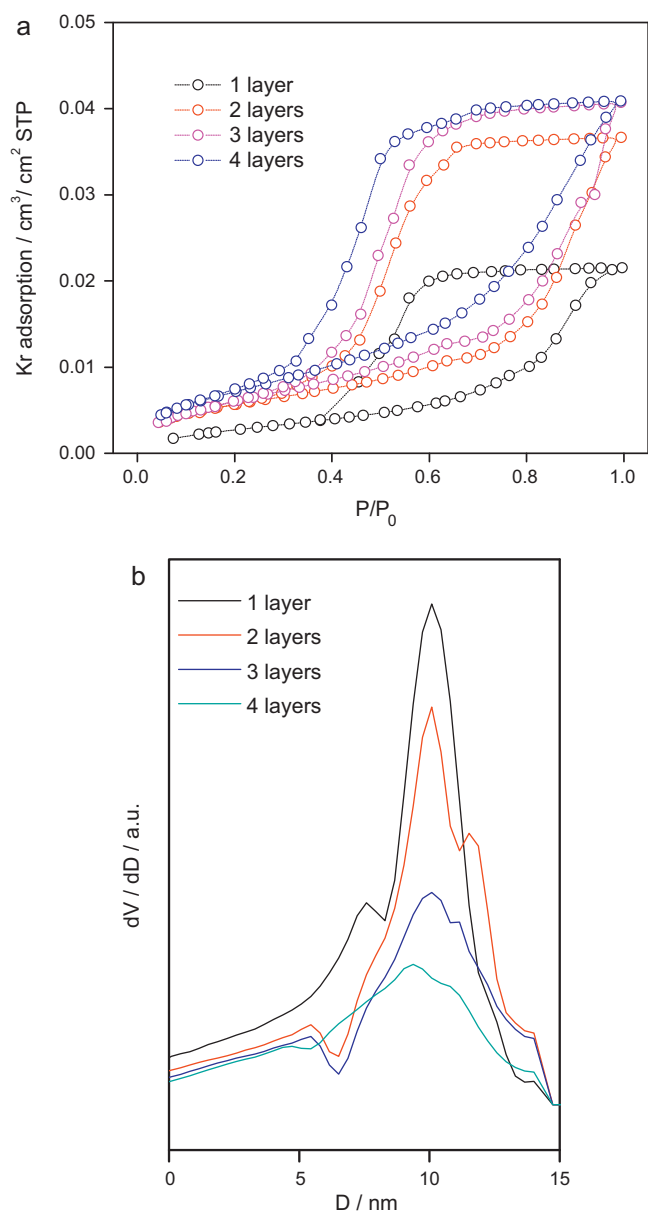


Fig. 2. (Above) (a) Adsorption isotherms of Kr at ca. 77 K on 1–4-layer films per unit of geometric area of the support and to a unit of the total volume of the film, respectively and (b) pore size distribution for 1–4-layer films calculated from the comparative plots based on Kr adsorption data at ca. 77 K.

recorded and the results are illustrated in Fig. 5. From these spectra the concentrations (and so the number in moles per geometric cm^2 of titania film) of the AO7 desorbed were determined and the plot constructed of these values versus the measured surface area per geometric cm^2 of titania film, $S_{\text{BET,SPEC}}$ which is the insert diagram in Fig. 5. This plot suggests the amount of AO7 adsorbed is proportional to the available surface area, which is not too surprising and from the gradient of the line of best fit to data in the insert diagram ($0.036 \times 10^{-8} \text{ mol cm}^{-2}$) it would appear that there are ca. 2.2 AO7 molecules per nm^2 of titania.

This would suggest that the total number of sites available for AO7 to bind onto was $= 2 \times 2.2 = 4.4$ sites per nm^2 , assuming each adsorbed AO7 molecule binds to two OH sites on the titania. Encouragingly, this value is not far off the number of appropriate sites often cited for titania for such binding, namely 5.6 per nm^2 . As a consequence, it would seem that one possible way to determine approximately the surface area of titania would be to adsorb

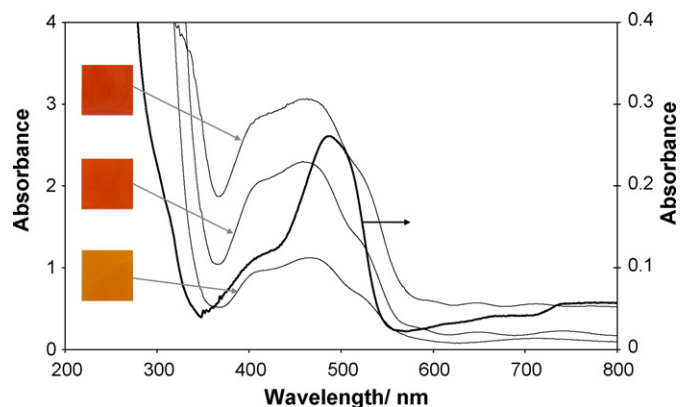


Fig. 3. UV/Vis absorption spectra of the stained 1–3 mesoporous titania layers on glass and photographs of their appearance; staining conditions: 24 h in contact with 1.5 mM AO7, 0.01 M of NaCl and 0.001 M HCl). The solid line is the absorption spectrum of a monomeric AO7 aqueous solution (10^{-5} M).

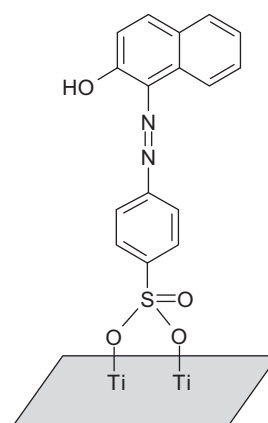


Fig. 4. AO7 bidentate binding onto titania [10,11].

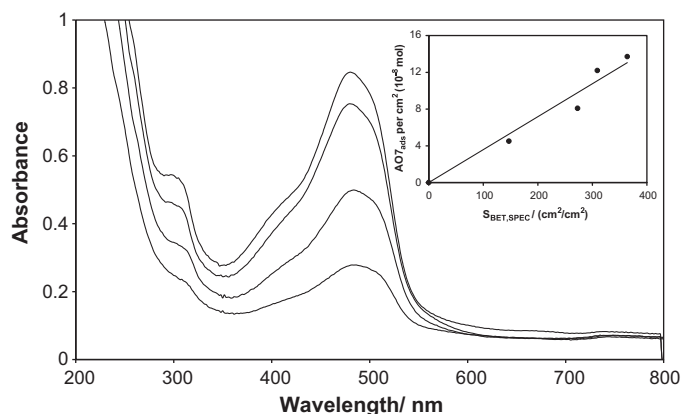


Fig. 5. UV/Visible absorption spectra of desorbed AO7 solutions from the 1–4 layer titania films and (insert diagram) of the number of moles of AO7 desorbed per geometric cm^2 of titania film versus the measured surface area per geometric cm^2 of titania film, $S_{\text{BET,SPEC}}$; gradient of line $= 0.036 \times 10^{-8} \text{ mol cm}^{-2}$.

AO7 onto its surface, using the conditions reported above, and desorb the dye and determine the amount adsorbed. From this value (assuming 2.2 AO7 molecules will adsorb per nm^2 of titania) the surface area of the titania can be gleaned. This would be especially useful in the determination of the surface areas of titania films.

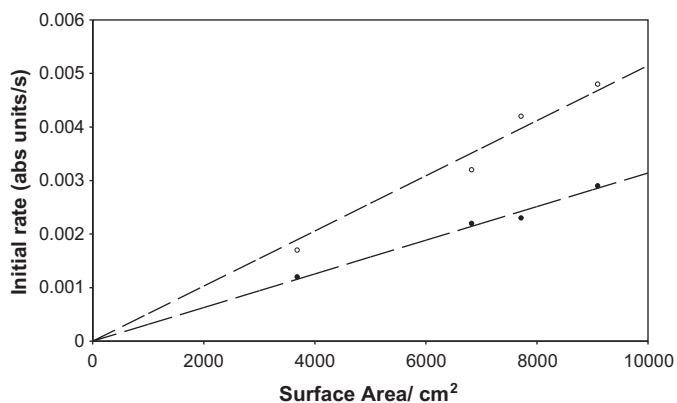
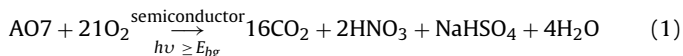


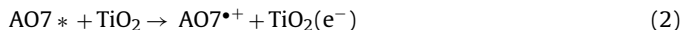
Fig. 6. Plots of initial rate of AO7 dye bleaching (reaction solution: 0.048 mM AO7, 0.01 M NaCl, 0.001 M HCl) under UV (2 mW/cm² at 365 nm) (●) and visible (21 mW/cm² at 475 nm) (○) illumination, respectively.

3.4. Photocatalytic and photosensitised bleaching of AO7 mediated by multilayer films

In the photocatalytic bleaching of AO7 the process involves the oxidation of the dye by either photogenerated holes or adsorbed hydroxyl radicals generated by the holes. The overall photomineralisation process can be summarised as follows [14,22]:



However, it is well known that in such systems dye photobleaching can also occur via a dye photosensitised process in which the electronically excited state of the dye, AO7* in this case, injects an electron into the conduction band of the semiconductor to produce an oxidised dye radical (AO7*⁺) which is unstable and capable of decomposing to colourless products [14,23,24], i.e.



Discrimination between the two mechanism of photobleaching is made easier by the fact that AO7 has a minimum in its UV absorption spectrum around the wavelength of UV light usually used (365 nm from a BLB lamp) for assessing the activity of UV-absorbing semiconductor photocatalysts, such as the mesoporous titania films used in this work. The quantum efficiency (= rate of photoreaction per cm²/incident irradiance) of the dye-sensitised reactions (2) and (3) is also much lower than that for photocatalytic reaction (1). For example, in contrast to work with BLBs, when using the same wattage visible fluorescent tubes as BLBs, but filtered to remove the UV, there is little evidence of bleaching via dye sensitisation when studying the AO7/mesoporous titania system. Since AO7 does not absorb strongly in the UV, this dye-sensitised process is most easily and usually demonstrated using an intense visible light, such as that provided by a Xe-arc light. With this in mind the photocatalytic and photosensitised bleaching of AO7, mediated by the different mesoporous titania films, was studied using two UV 8 W black light blue (BLB) fluorescent tubes and a 150 W Xe arc visible lamp fitted with a 400 nm cut-off filter to remove the UV component of the light, respectively. In both studies the initial rate (as measured by the change in absorbance at 480 nm per min) of dye bleaching was determined for the different layers of mesoporous titania. The results of this work are illustrated in Fig. 6, i.e. plots of initial rate versus mesoporous titania film surface area under UV (photocatalytic) and visible (photosensitised) irradiation conditions.

The results of this work show that the rates of dye bleaching by either mechanism are proportional to the film surface area, which is much as expected given that the higher the surface area of the photoatlyst, the greater the number of adsorption and photocatalytic sites. Other work, conducted on P25 TiO₂, using methylene blue as the dye, suggests that dye adsorption is a necessary pre-requisite for AO7 photobleaching via a photosensitised reaction mechanism as summarised by reactions (2) and (3). In contrast, the level of dye photo-bleaching via a photomineralisation mechanism, reaction (1), is not negligible even when little dye is adsorbed onto the titania, presumably due to indirect oxidation by desorbed hydroxyl radicals, rather than direct oxidation by photogenerated holes or adsorbed hydroxyl radicals. Given the data in Fig. 6 it is possible to estimate the quantum efficiency of the UV photocatalytic bleaching of AO7 via reaction (1) as ca. 0.08%. Similarly, the quantum efficiency of the visible photosensitised bleaching of AO7 via reactions (2) and (3) can be estimated to be ca. 0.01%, confirming the much lower photon efficiency of the latter process.

4. Conclusions

AO7 adsorbs readily on mesoporous titania films at pH 3. The amount of AO7 adsorbed per cm² (geometric area) increases with increasing surface area of the films. The estimated number of bidentate binding sites available for AO7 to bind (4.8 nm⁻²) is sufficiently close to the oft reported value (5.6 nm⁻²) that it suggests that AO7 adsorption could provide a simple, alternative method, to Kr gas adsorption, for determining the surface area of thin titania films. The rate of the UV-driven photocatalytic bleaching of AO7 is directly related to the available surface area, as is the rate of the visible-light driven photosensitised bleaching of AO7. The quantum efficiencies of these two processes are estimated as: 0.08 and 0.01%, respectively. From the results of this work it is clear that both the photocatalytic and photosensitised bleaching of AO7 are able to occur within the pores of mesoporous titania films and that the kinetics of both process are directly dependent upon the total surface area.

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