Study of the conditions affecting dye adsorption on titania films and of their effect on dye photodegradation rates

Nikoleta Strataki, Vlasoula Bekiari, Panagiotis Lianos *

Engineering Science Department, University of Patras, 26500 Patras, Greece

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Abstract

Nanocrystalline titania films have been deposited on glass slides by the sol–gel technique in the presence of surfactant, which plays the role of template of the nanostructure. Several different dyes, both anionic and cationic, have been adsorbed on these films from aqueous solutions. Some of these dyes were adsorbed at large quantities some at lower quantities. Some of them were adsorbed in monomeric form and others formed aggregates. Aggregates are easily distinguished by absorption spectrophotometry, since absorption of light is observed at a different wavelength than monomer absorption in a dilute solution. In all cases, aggregation demonstrated a hypsochromic shift, indicating repulsive interactions, which are justified in view of the fact that titania surface is charged and that adsorbed molecules are aligned in parallel. The above titania films are hydroxylated. Therefore, cationic dyes were readily adsorbed. Anionic dyes could be adsorbed only from aqueous solutions brought at low pH. Photodegradation rates of adsorbed dyes were generally fast since these films are efficient photocatalysts. Nevertheless, photodegradation of an adsorbed dye was faster when the quantity of the dye was smaller. When the adsorbed dyes formed aggregates, aggregation had adverse effect on photodegradation rates.
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1. Introduction

Titania is the best-known catalyst for dye photodegradation in aqueous solutions or in air. In both cases, immobilization of titania on solid substrates in the form of thin transparent films composed of titania nanocrystallites is a preferred method for both increasing efficiency and providing the means for catalyst recuperation and reuse [1–5]. It is obvious that photocatalytic degradation of dyes depends to a large extent on the ability of the titania nanoparticles to adsorb dye molecules and thus make photodegradation processes more efficient [6,7]. So far, the question of dye adsorption has been studied only with titania powders and studies were exclusively connected with the nanostructure of titania and the properties of the particle surface. Very few studies have dealt with the chemical structure of the dye itself [8] whether it is an ion or a neutral molecule or where lies its hydrophobic/hydrophilic balance, which is very crucial for adsorption, especially, on thin films. This work studies these aspects and relates them with photodegradation efficiency. Pre-liminary results have shown that some crucial factors affecting photodegradation are dye aggregation on titania films, the effect of humidity on the aggregation state of the dye [9] and radiation screening phenomena. Further to the immediate influence of dye aggregation on the photodegradation reactions one has to take into account photosensitation processes in the visible, which are affected by dye-aggregation and which are bound to further affect photodegradation rates.

2. Experimental

All chemicals were purchased from Aldrich and Merck, were of the best quality available and were used as received. *N-n*-Alkyl-4-(dimethylaminophenylethenyl) pyridinium bromide (HnHC) of different alkyl chain lengths was synthesized by condensation of the corresponding *N*-alkylated 4-methylpyridines with 4-dimethylaminobenzaldehyde and were purified by repeated recrystallization from ethanol. These last reagents were graciously donated by Professor A. Laschewsky, Potsdam University, Germany. Water was purified by using a millipore installation. The chemical structures of the dyes used in this work are shown in Fig. 1. The following additional abbreviations were employed: pyrenetetrasulfonate (PTS); acid orange

* Corresponding author.
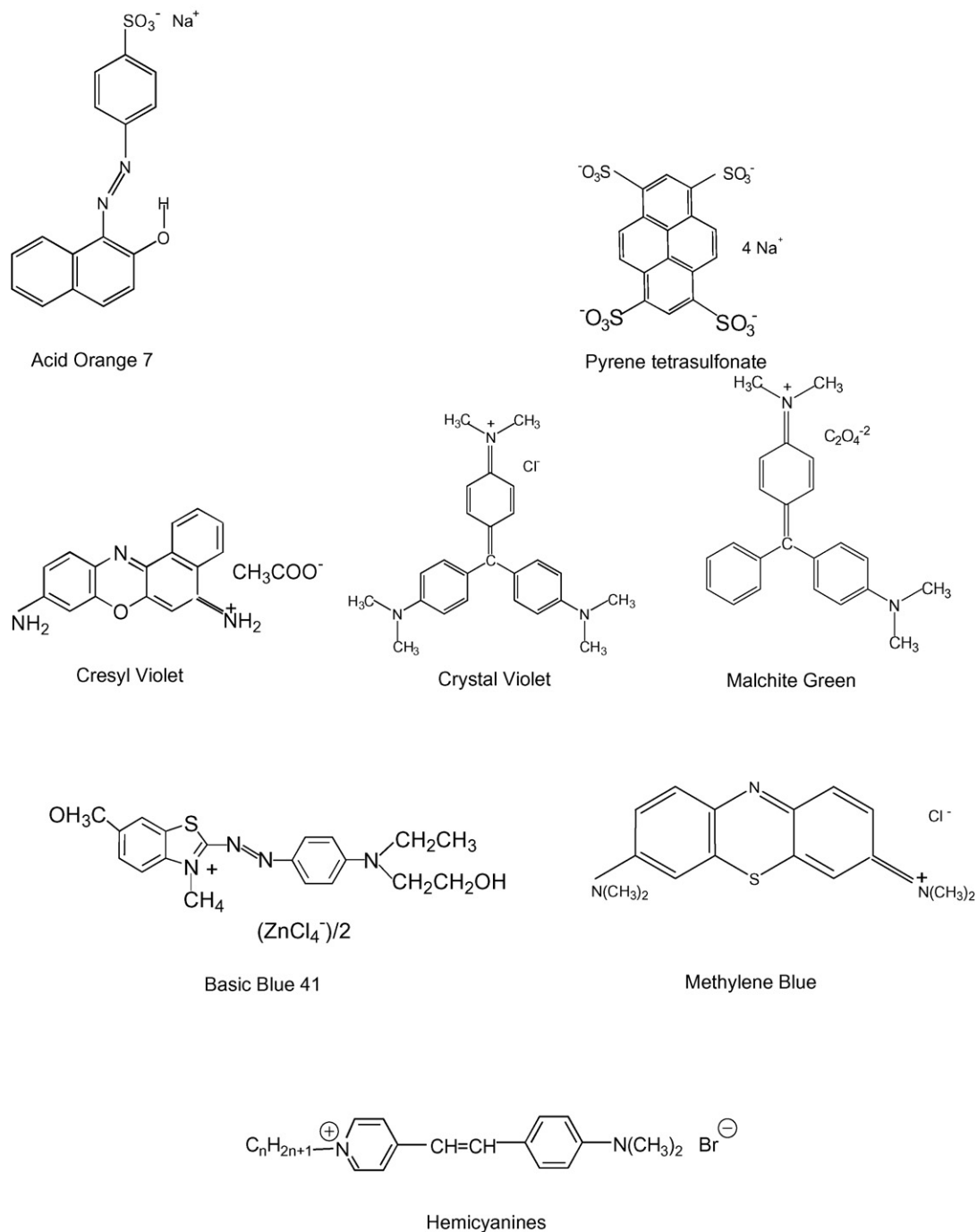 *E-mail address:* lianos@upatras.gr (P. Lianos).

Fig. 1. Chemical structure of some dyes used in the present work.

7 (AO7); cresyl violet (CreV); crystal violet (CryV); malachite green (MG); basic blue (BB); and methylene blue (MB).

Titania films were deposited by following the previously reported procedure [3,4,10]. Briefly, 1.4 g of the non-ionic surfactant Triton X-100 [polyoxyethylene-(10) isooctylphenyl ether] was mixed with 7.6 ml of ethanol, followed by addition of 1.36 ml of glacial acetic acid and 0.72 ml of Titanium isopropoxide under vigorous stirring. Self-organization of the surfactant in this original sol creates organized assemblies that act as templates defining nanoparticle size. The surfactant is burned out during calcination. After a few minutes stirring, a glass slide, which was previously thoroughly washed, sonicated in ethanol and dried in a N_2 stream, was dipped in the above sol and withdrawn fast by hand. After leaving the film to dry in air for a few minutes, it was calcined in an oven. The temperature was raised with a heating rate of 20 °C/min–550 °C and left at that temperature for about 10 min. When the film was taken out of the oven it was transparent and optically uniform. The above procedure was repeated six more times. The mass of titania deposited on the slide after seven dipping and calcination steps

was approximately 2.7 mg (that is about 1.35 mg on each side of the slide). The area of the slide covered by titania film was $4.9 \times 1.2 = 5.9\,cm^2$.

Dyes were deposited on the surface of the titania films by adsorption from aqueous solutions containing 5×10^{-4} M of each dye. The pH of the solution was controlled by adding drops of either concentrated HCl (37%) or concentrated ammonia (25%) solutions. In the case of AO7, because the above chemical agents seem to have adverse effects on the dye, pH was controlled by using concentrated nitric acid (65%) or NaOH. After the last layer of titania was deposited and immediately after the film was taken out from the oven, the slide was submerged in the solution of the dye and was left there for half an hour in the dark. Then it was washed, dried and in this form was used for absorption measurements and photodegradation.

Photodegradation experiments were carried out by exposing films to radiation from a 450 W xenon lamp. Only one side of the slide was facing the lamp but since the films were transparent, light was absorbed by films on both sides. The intensity of light at the position of the slide was approximately $100\,mW/cm^2$ and it was regulated by using multiple wire grids. Other experiments were also carried out by putting sample within a cavity illuminated by low intensity black light tubes. The radiation produced is contained in a single band centered around 355 nm. In this case the total intensity of the incident radiation was approximately $2\,mW/cm^2$. Intensities were measured with an Oriel 70260 Radiant Power meter. Photodegradation rates were measured by monitoring discoloration by absorption spectrophotometry at regular time intervals. UV–vis absorption measurements were made with a varian cary 1E spectrophotometer.

3. Results and discussion

The characteristics of the titania films used in the present work have been described in previous publications [3,4,10]. Briefly, films consist of anatase nanocrystals of about 12–15 nm average size. Size polydispersity is limited and the active surface area is around $110\,m^2/g$. These films demonstrate enhanced adsorption capacities for several organic and inorganic species.

Table 1
Position of the absorption maximum for low-concentrated solutions of various dyes in various solvents and pH values of aqueous solutions containing 5×10^{-4} M of various dyes

Dye (Solvent)	Wavelength of maximum absorbance (nm)	pH value of a dye aqueous solution at concentration 5×10^{-4} M
PTS (water)	375	6.2
AO7 (water)	484	6.0
BB (water)	603	6.5
MB (water)	663	5.6
MG (water)	617	4.5
CryV (water)	590	6.0
CreV (water)	584	4.8
H12HC (water)	450	6.8[a]
H12HC (ethanol)	484	–
H12HC (chloroform)	495	–

[a] The concentration of H12HC was only 10^{-4} M since it is not soluble at higher concentrations in water.

3.1. Adsorption of dyes on titania films

Several dyes have been studied differing in structure and charge. In general, cationic dyes are better adsorbed on titania films because the surface of the films is hydroxylated and for this reason it attracts cations and repels anions. In this work we present some characteristic examples of cationic and anionic dyes and we follow the different steps from the preparation of dye solutions till dye photodegradation.

Low concentrated aqueous solutions of the dyes produce the absorption spectra of Fig. 2. Hemicyanines constitute a special case. The absorption spectra of the homologue bearing a chain with 12 carbon atoms (H12HC) was studied in several different solvents. Some examples are shown in Fig. 2C. The behaviour of other homologues was similar. The absorption maxima for dilute solutions and for all studied dyes are listed in Table 1. Table 1 and Fig. 2C show that the absorption spectrum of H12HC changes from one solvent to the other due to the tendency of this substance to aggregate [11] thus causing hypsochromic shift of its excitation energy (repulsive interaction). We consider the spectrum in chloroform as the representative monomer absorption (maximum at 495 nm) since H12HC does not form aggregates
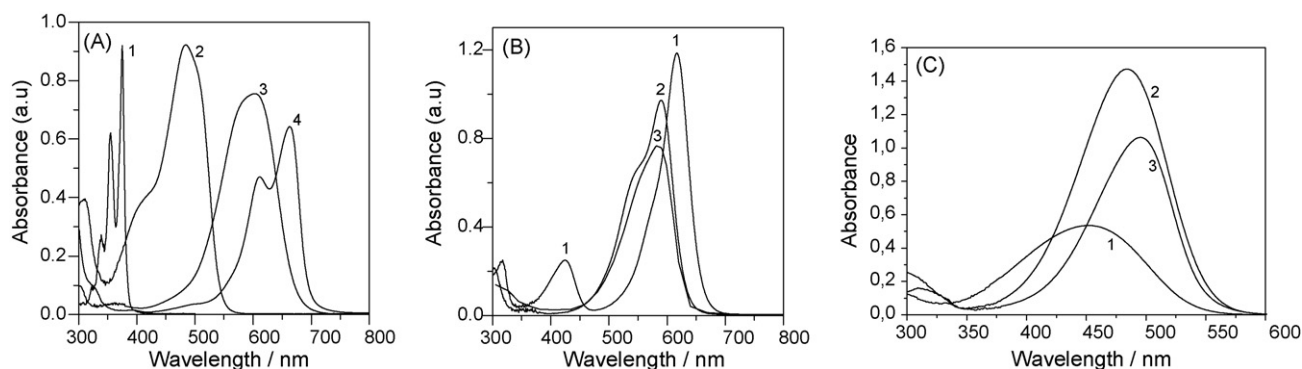

Fig. 2. Absorption spectra of aqueous solutions of: A1 2×10^{-5} M PTS; A2 5×10^{-5} M AO7; A3 2.5×10^{-5} M BB; A4 10^{-5} M MB; B1 0.8×10^{-5} M MG; B2 1.2×10^{-5} M CryV; B3 5×10^{-5} M CreV; and absorption spectra of 2.5×10^{-5} M H12HC in C1 water; C2 ethanol; and C3 chloroform.

Table 2
Absorbance of titania films with adsorbed dyes at different pH values of the dye aqueous solutions

Dye	Wavelength of maximum absorbance (nm)	Absorbance		
		pH 2.0	Solution's own pH	pH 10.0
PTS	375	0.75	0.00	0.00
AO7	471	0.80	0.00	0.00
BB	530	0.00	2.20	1.80
MB	564	0.00	1.70	1.80
MG	617	0.15	0.75	0.80
CryV	590	0.00	1.30	1.90
CreV	520	0.00	0.35	—[a]
H12HC	447	0.00	0.50	0.55

[a] CreV suffers irreversible changes at alkaline pH.

in chloroform, which is a good solvent for this molecule. The absorption spectra of the rest of the molecules of Table 1 are considered to represent absorption by monomers.

Adsorption of the dyes on titania films from aqueous solutions demonstrated a different behaviour from one dye to the other. Anionic dyes were not adsorbed on titania unless the pH of the solution was brought to highly acidic values. This is expected since only at low pH values the surface of Titania becomes positively charged. The opposite happens with cationic dyes, which were adsorbed at high pH and were not adsorbed at very low pH values. This rule was slightly broken by MG, but this exception enhances the rule. The pH values of the solutions used for adsorption, without addition of any acid or base, are listed in the third column of Table 1. All dye solutions were slightly acidic, that is pH ranged from 4.5 to 6.8. Table 2 lists the maximum absorbance of the various dyes adsorbed on identical titania films at three different pH values: strongly acidic pH, solution's own pH and strongly alkaline pH. Cationic dyes were slightly or not at all adsorbed at strongly acidic pH but were adsorbed at maximum at alkaline pH. Furthermore, they were also well adsorbed at solution's own pH. Fig. 3 also shows some characteristic examples of dye adsorption, as represented by the absorption spectra of titania films bearing adsorbed dyes. As in the case of Table 2, absorption spectra have been recorded with samples obtained at three different pH values: solution's own pH (Table 1); acidic pH 2.0; and basic pH 10.0. Curves 4 of Fig. 3A–C correspond to monomer absorptions in dye dilute

solutions, put there for comparison. The features of the spectra of Fig. 3 and the data of Table 2 lead to several interesting conclusions. The fact that cationic dyes, like BB, are strongly adsorbed at solution's own pH means that the surface of the titania film is negatively charged, that is hydroxylated, even at solution's own pH, which is slightly acidic. Indeed the isoelectric point of titania is known to be around 5.8–6.0 [12,13] but it may vary depending on the method of preparation, doping, etc. [13–15]. It is interesting, as seen in Fig. 3C, that AO7 was not at all adsorbed at medium and high pH, which is in line with adsorption data of the oppositely behaving cationic dyes. In the case of curve 1 of Fig. 3A and B and curves 2 and 3 of Fig. 3C, the spectrum simply shows the absorbance of titania itself. The oscillating part of the spectrum in the visible is due to interference fringes. Another important feature of the spectra of Fig. 3 is the position of the absorption maximum of the adsorbed dye compared with the absorption maximum of the dye in solution (Curves 4). A large blue shift was obtained both in the case of BB $(603 - 530 = 73\,\mathrm{nm})$ and H12HC $(495 - 447 = 48\,\mathrm{nm})$. A smaller shift was observed in the case of AO7 $(484 - 471 = 13\,\mathrm{nm})$. The largest was observed in the case of MB $(663 - 564 = 99\,\mathrm{nm})$. For some dyes no shift was registered at all, as can be seen by comparison of Column 2 of Table 2 with Column 2 of Table 1. These shifts in absorption spectra are indicative of aggregate formation between the dyes, when they are adsorbed on the surface of the titania film. All shifts were hypsochromic, that is they are due to repulsive interactions. This was expected. Since the dyes are
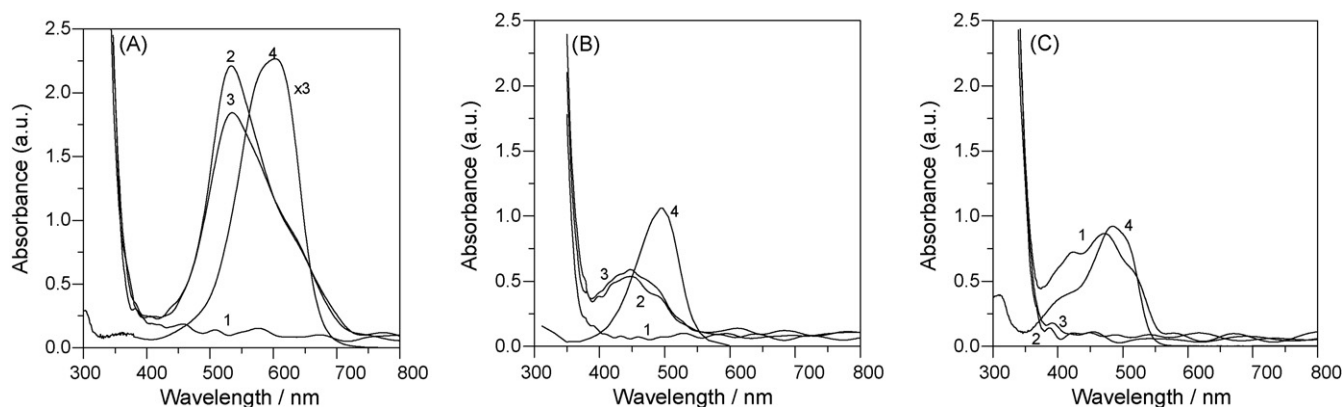

Fig. 3. Absorption spectra of titania films with adsorbed dyes at three different pH values: (1) pH 2.0; (2) solution's own pH; and (3) pH 10.0: (A) BB; (B) H12HC; and (C) AO7: The curves (4) correspond to the absorption spectra of the corresponding dyes in dilute solutions: water for BB and AO7 and chloroform for H12HC.
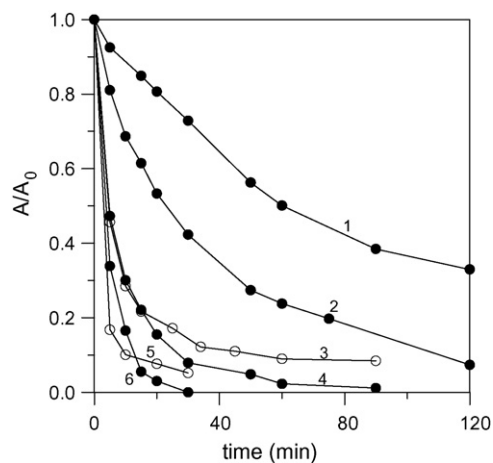
Fig. 4. Discoloration of various dyes adsorbed on titania films by irradiation with a xenon source: (1) MB; (2) BB; (3) AO7; (4) CryV; (5) CreV; (6) H12HC.

adsorbed on a charged surface they are placed parallel to each other with their dipole moments parallel to each other. Therefore interactions are repulsive. Finally, a third important feature of the spectra of Fig. 3 and of the data of Table 2 is the large absorbance observed with certain of the studied dyes, particularly the aggregate-forming ones. Indeed, maximum absorbance of BB at 530 nm was 2.20, which means that transmittance of light at this wavelength is only 0.63%. In a large range of the visible spectrum, from about 480 to 630 nm, absorbance is ≥1.00, which means that transmittance of light is ≤10% in the visible. In the case of MB, the latter range is placed between 500 and 700 nm. Even though, transmittance in the visible was very low, almost all these dyes have relatively small absorbances in the near UV, where the band-gap excitation of Titania takes place. In any case, the large absorbance of light indicates that large quantities of the dyes are retained on the surface of these Titania films. This analysis is useful to interpret photodegradation data presented in the following paragraph.

3.2. Photocatalytic degradation of dyes on titania films

Fig. 4 gives the discoloration rates of various dyes adsorbed on identical titania films by illumination with a xenon lamp. Discoloration rates are also shown by the data of Table 3. Discoloration of AO7, PTS (not shown), CryV, CreV, MG and H12HC was very rapid while that of BB and MB was relatively slow. No data are shown for PTS since the absorption of light by this dye overlaps titania film absorption and thus the extracted val-

Table 3
Kinetic data on the photodegradation of various dyes

Dye	k (min^{-1})	$t_{1/2}$ (min)	R^2
AO7	0.113	6.1	0.975
BB	0.026	26.7	0.993
MB	0.011	63.0	0.997
MG	0.109	6.3	0.979
CryV	0.101	6.9	0.982
CreV	0.255	2.7	0.952
H12HC	0.169	4.1	0.989

ues contain a lot of error. In order to rationalize conclusions, it is necessary to review a few possible reasons for this marked difference in discoloration rates.

First, the photocatalytic efficiency may be different for dyes of different chemical structure. This difference may demonstrate itself by the site and the nature of first attack but it cannot be monitored in photodegradation experiments carried out on films where intermediate products are hard to detect. Photodegradation then and simple discoloration are hardly distinguished one from the other. Consequently, it is expected that the net result of photodegradation will only depend on the number of titania active sites and the number of dyes. Therefore, we are of the opinion that chemical structure is not an issue in the present case.

Second, photosensitization of titania by absorption of light by the dye in the visible and injection of excited electron into the conduction band of the semiconductor [16] may be carried out with different efficiencies by different dyes. We have avoided photosensitization by direct band-gap excitation of titania using black-light tubes (emission centered around 353 nm). In that case, the semiconductor is directly excited independently of the adsorbed dye. Photodegradation was generally slower this time, since the light source was of much weaker intensity (see Section 2). By referring to the two characteristic cases, MB and CryV were again discolored at very different rates, as can be seen in Fig. 5 and discoloration was again much faster in the case of CryV. Similar was the behaviour with the rest of the dyes. Therefore, different photosensitization efficiency is not the cause of the large difference in discoloration rates.

Third, radiation-filtering effects due to absorption of light by the dyes may also be an issue in some cases but this would happen in the visible part of the spectrum and would have negligible effects with band-gap excitation. Indeed, as already said, band-gap excitation still distinguishes CryV from MB.

A fourth and most plausible reason for the difference in discoloration rates is related with the quantity of the adsorbed dye, which must not be what is derived by light-absorbance measurements. As already said, MB is in aggregated form when
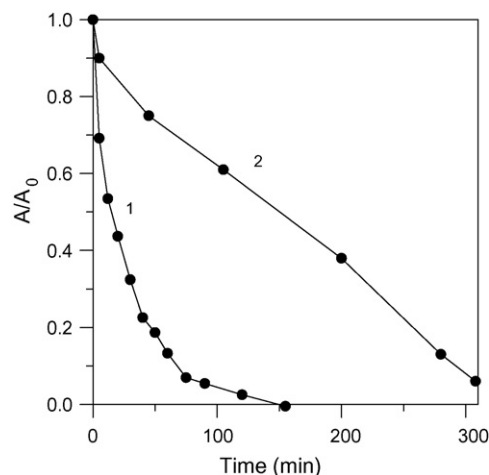

Fig. 5. Discoloration of CryV (1) and MB (2) adsorbed on titania films by illumination with Black Light.

adsorbed on titania. Aggregates, absorb light as a single entity, therefore they cannot provide a linear relationship between the number of molecules and the corresponding optical density. In fact, we believe that the quantity of MB adsorbed on titania film is a multiple of what is extracted by absorbance calculations. It is then expected that the photodegradation rate for MB will be much slower than for CryV, since the quantity of adsorbed MB is much higher for the same quantity of catalyst. Therefore, we consider the quantity of the adsorbed dye as one main cause of the difference in discoloration rate.

A fifth reason for the observed different rates, should derive from the different physicochemical states of the adsorbed molecules. Aggregates should not be degraded at the same rate as single molecules. We have observed in the present and in a previous work [7], particularly with BB, that as the dye was discolored, its optical density, of course, decreased but its absorption maximum was simultaneously blue shifted. The number of monomers in an aggregate affects the extent of the hypsochromic shift in excitation energy. Aggregates with a larger aggregation number suffer a larger blue shift in absorption. Thus blue shift of absorption maximum during photodegradation means that smaller aggregates are first consumed, followed by larger aggregates. We may then conclude that CryV, which was in monomer form, was consumed faster than MB, which was in aggregate form. In this sense, H12HC makes a special case. This dye was in aggregate form when adsorbed on titania films, as already said, but its photodegradation rate was still fast. There are two reasons for this behaviour.

First, the quantity of adsorbed H12HC was small, so that it was faster consumed.

Second, the aliphatic chain born by this molecule makes well-ordered aggregates with the chromophore attached and the aliphatic chain exposed. This geometry facilitates photosensitization and photodegradation processes since the chromophore group is in contact with active titania sites. Similar reasoning can be followed also in the case of CreV, which constitutes a second special case. Again aggregates were observed but the adsorbed quantity of the dye was very small. Therefore, photodegradation came faster.

As a overview of the above data, it is suggested that systematic photophysical characterization of titania films with adsorbed dyes can lead to a protocol that may be useful for optical sensing of waste waters polluted by dye stuffs.

4. Conclusions

Cationic dyes are easily adsorbed on titania nanocrystalline films since the surface of these films is hydroxylated. Anionic dyes are adsorbed only at highly acidic pH. The physicochemical state of the adsorbed dye affects photodegradation rates. Molecules, like BB and MB, which are adsorbed at high quantities and form aggregates are more slowly photodegraded. Other molecules, adsorbed at substantially smaller quantities, no matter whether they form or not aggregates, are discolored at much faster rates. The adsorption capacity of nanocrystalline titania films was very high for some substances like BB and MB. In that case, the films could play the double role of retaining and photodegrading water pollutants.

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