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Journal of Photochemistry and Photobiology A: Chemistry 191 (2007) 13–18
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Effect of aggregation of dyes adsorbed on nanocrystalline titania films on the efficiency of photodegradation

Nikoleta Strataki, Vlasoula Bekiari, Elias Stathatos, Panagiotis Lianos*

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

Received 18 January 2007; received in revised form 16 March 2007; accepted 22 March 2007
Available online 27 March 2007

Abstract

The conditions of adsorption of some dyes from aqueous solutions on nanocrystalline titania film have been studied. Adsorption follows Langmuir kinetics. Ionic dyes have the tendency to aggregate in the adsorbed state. 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 with dipole moments in parallel. For a given titania film, the extent of dye aggregation and shift of absorption spectrum varies from one dye to the other. Some blue dyes demonstrate very large shifts. Photodegradation rates were slow in the case of aggregated dyes. It is concluded that the main cause for this deficiency is dye aggregation, which apparently inhibits interaction with photocatalyst. These results may be useful in the photocatalytic treatment of waste waters, in particular, from textile industry.

Keywords: Nanocrystalline titania films; Dye aggregation; Photodegradation

1. Introduction

Heterogeneous photocatalysis by employing transition-metal oxide semiconductors as photocatalysts is a very popular method aiming at environmental remediation. In this respect, nanocrystalline titania is the most popular and most studied photocatalyst. Light absorption by the semiconductor creates charge carriers, i.e. electrons and holes, which are scavenged by molecular oxygen and hydroxyl anions and thus create reactive radicals, which attack and degrade organic pollutants. Physical contact of the pollutant with the photocatalyst is, in principle, not necessary for photodegradation in aqueous phase, since the radical mediators can displace themselves to reach target, however, it is realistic to assume that efficient photodegradation can take place only when photocatalyst and pollutant are in close proximity or in contact. Contact is brought about by adsorption of pollutants on the surface of the photocatalyst. Many authors support the idea that adsorption on titania surface is a prerequisite of photodegradation [1–3]. Of course, this is absolutely true in the case of photosensitization, that is, when visible light is absorbed by a dye sensitizer and photocatalysis proceeds by injection of excited electron into the conduction band of the semiconductor [4,5]. Dye-adsorption on the surface of titania nanoparticles results to removal of surface traps and increase of charge carrier diffusion [6] with beneficial consequences on photodegradation rates. Furthermore, hydroxyl groups, typical hole scavengers, are abundant on the surface of the photocatalyst, in particular, anatase titania. Nevertheless, in some cases, it has also been shown that part of photodegradation, in particular the final stages, may occur in the bulk phase [5]. In any case, it is necessary to study the conditions and the consequences of pollutant adsorption on the surface of the photocatalyst before any other parameter is taken into account. Some aspects of the physicochemical state of adsorbed pollutants have actually been studied and related with photocatalytic efficiency. As a matter of fact, the mode of pollutant adsorption is expected to affect the photodegradation pathway [7]. However, little attention has been paid to the physical state and the organization of pollutant molecules on the surface of the photocatalyst as related with photocatalysis rates. In the present work, which tries to fill the void, titania nanocrystalline films are used as photocatalyst and adsorption and photophysical behavior of various dyes on

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

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doi:10.1016/j.jphotochem.2007.03.023

these films are studied. Dyes have been chosen as model pollutants for four reasons: first, they are indeed the major pollutants found in waste waters released by textile and leather industry; second, the photophysical aspects of dyes can be easily studied by spectrophotometry in the UV–vis spectral range; third, dyes are usually molecules with rich chemical structure leading to a large variety of chemical processes during photodegradation; and fourth, because dyes are strong light absorbers in the UV–vis spectral range they allow examination of a crucial factor affecting photocatalysis, i.e. radiation screening effects. Adsorbed pollutants may be found in monolayer or they may form multilayers [8], they may be monomers or they may be aggregated. It is natural to expect that a molecular cluster will be degraded at a different rate than a monomer. Photosensitization in the visible may be also affected by molecular self organization. Such matters are treated in the present work.

2. Experimental

All chemicals were purchased from Aldrich and Merck, were of the best quality available and were used as received. 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 abbreviations were employed: Acid Orange 7 (AO7); Crystal Violet (CryV); and Methylene Blue (MB).

Titania films were deposited by following the previously reported procedure [9–11]. 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,

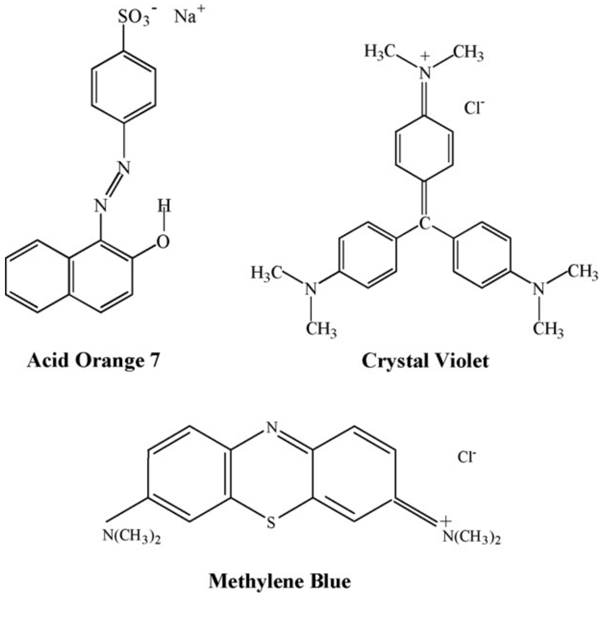

Fig. 1. Chemical structures of the ionic dyes used in the present work. Figure also shows the corresponding counter ion in each case.

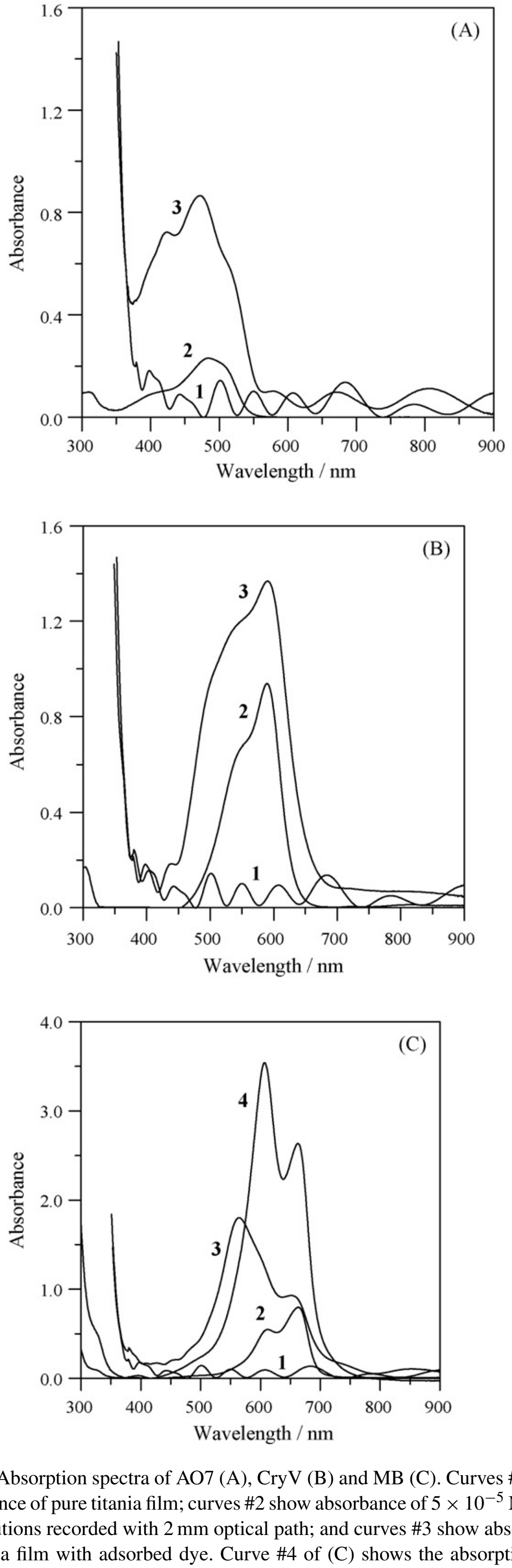

Fig. 2. Absorption spectra of AO7 (A), CryV (B) and MB (C). Curves #1 show absorbance of pure titania film; curves #2 show absorbance of 5×10^{-5} M aqueous solutions recorded with 2 mm optical path; and curves #3 show absorbance of titania film with adsorbed dye. Curve #4 of (C) shows the absorption of a concentrated aqueous solution of 5×10^{-4} M MB recorded with 2 mm optical path.

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 to 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 dippings 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 $4.9 \times 1.2 = 5.9\,\mathrm{cm}^2$. The above film was transparent. Its absorption profile is seen in Fig. 2. The energy band gap, as revealed by the absorption onset, was 3.39 eV. The oscillating part of the spectrum is due to interference fringes. By assuming an index of refraction of about 2.0–2.1, a value usually found in nanocrystalline titania films, the film thickness was calculated to be about 1.2–1.3 μm.

Dyes were deposited on the surface of the titania films by adsorption from aqueous solutions containing various concentrations 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 and was left there for about 1 h in the dark. Then it was washed, dried and in this form was used for absorption measurements or for photodegradation.

Photodegradation experiments were carried out by exposing films with adsorbed dye 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 the films on both sides. The intensity of light at the position of the slide was approximately $100\,\mathrm{mW/cm}^2$ 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 by Black Light is contained in a single band centered around 353 nm. In that case, the total intensity of the incident radiation was approximately $2\,\mathrm{mW/cm}^2$. 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

It is well known that titania surface is charged. At low pH the predominant species are $\mathrm{Ti{-}OH_2}^+$ and become Ti–OH at neutral and $\mathrm{T{-}O}^-$ at alkaline pH [3]. Aqueous solutions of common dyes, including the ones of Fig. 1, give pH values (natural pH), which are slightly acidic (around 6.0). As a consequence, cationic dyes, like the present CryV and MB are readily adsorbed while anionic dyes, like AO7, can only be adsorbed at strongly acidic pH, that is, when the titania surface is positively charged. Thus, CryV and MB were adsorbed on titania at the natural pH of the solution or at alkaline pH while AO7 was adsorbed only from aqueous solutions where the pH value was around 2.0. Table 1 and Fig. 2 show light absorption data of dyes in dilute aqueous solutions and adsorbed on titania films. Column 2 of Table 1 shows the wavelength of maximum absorbance of dyes adsorbed on the titania film and (in the same column, in parentheses) the corresponding maximum of dilute aqueous solutions. It is seen that adsorbed dyes may suffer a blue shift in absorption, which varies from dye to dye. It was zero in the case of CryV, 12 nm in the case of AO7 and 100 nm in the case of MB. Other dyes have also been tried (not shown), which also gave a variety of (always blue) shifts [12]. The shift of absorption maxima can be also seen in the spectra of Fig. 2. Columns 4–6 of Table 1 give estimates of the quantity of dye adsorbed on the titania film as can be extracted by absorption spectrophotometry. Absorbance is not linearly related with quantity of adsorbed dye because, as it will be seen below, the physical state of the adsorbed dye varies from one case to the other. However, the obtained light-absorption data of Table 1 reveal that AO7 is only adsorbed at strongly acidic pH while CryV and MB are readily adsorbed at the natural pH of the solution and even more strongly adsorbed at alkaline pH. As expected, cationic dyes were not adsorbed at strongly acidic pH.

The kinetics of adsorbance of the three dyes on the present titania films have been studied by recording adsorption isotherms. For this purpose, the quantity of titania was kept constant but the concentration of the dyes in aqueous solutions was varied in the range of 5×10^{-5} to 5×10^{-4} M. This concentration range was limited by the need to assure a linear relationship between concentration and absorbance. Indeed, the concentration of the dye remaining in solution after adsorption was monitored by absorption spectrophotometry. For this purpose, we took care to use the proper optical path (i.e. appropriate cell thickness) so that absorbance would stay at non-saturated levels. Fig. 3 shows Langmuir isotherms, that is, the variation

Table 1
Light absorbance of titania films with adsorbed dyes

Dye	Wavelength of maximum absorbance (nm)[a]	Extinction coefficient ($\times 10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$)	Absorbance		
			pH 2.0	Natural pH of the solution	pH 10.0
AO7	472 (484)	1.9	0.87	0.00	0.00
CryV	590 (590)	7.5	0.00	1.37	1.90
MB	563 (663)	6.7	0.00	1.70	2.00

[a] In parentheses, absorption maxima of dilute aqueous solutions.

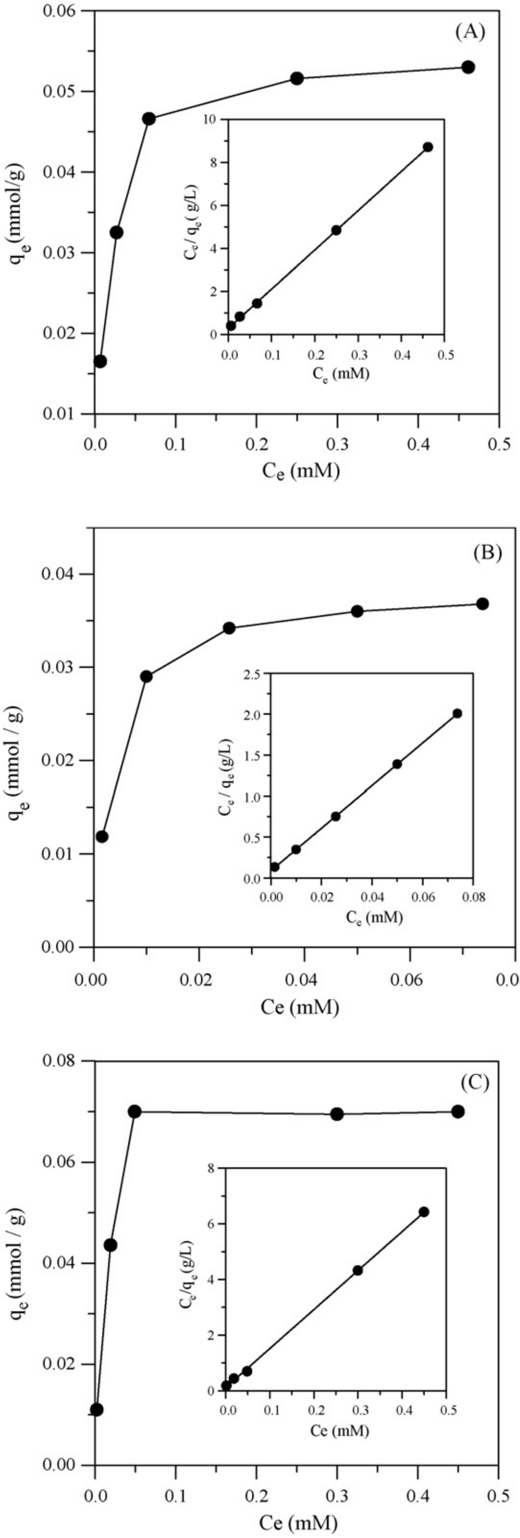

Fig. 3. Langmuir isotherms for the adsorption of AO7 (A), CryV (B) and MB (C) on titania films. The inserts show corresponding C_e/q_e vs. C_e plots.

Table 2
Calculated q_e max and K_L values from Langmuir isotherms

Dye	q_e max (mmol/g)	K_L (l/g)
AO7	0.05	1.5
CryV	0.04	11.4
MB	0.07	8.7

of the quantity q_e of the adsorbed dye per gram of the adsorbent versus the concentration C_e of dye remaining in solution. q_e was calculated by Eq. (1) [13–15]:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 is the initial dye concentration (in mmol/l), V the volume of the solution (in liters) and m is the mass of the adsorbent (in grams). The inserts in Fig. 3 also show the variation of the ratio C_e/q_e versus C_e. It represents an analysis of the Langmuir isotherm and it produces the binding constant K_L by Eq. (2) [14–17]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right) C_e \tag{2}$$

where K_L is the binding constant (in l/g) and α_L is a Langmuir constant. The straight lines obtained in the Inserts of Fig. 3 show that adsorption obeys Langmuir kinetics. Table 2 shows the values of q_e and K_L measured for the three dyes studied. These data have been obtained by fixing pH value at 2.0, in the case of AO7, and at 6.0, in the case of CryV and MB. The second column of Table 2 shows the values of q_e max, i.e. the saturation value of the Langmuir isotherm. The higher the q_e max the larger the quantity of adsorbed dye for the same quantity of adsorbent. q_e max varied from one dye to the other, the largest value measured in the case of MB. This variation was rather limited, since the capacity of adsorbance mainly depends on adsorbent material and secondarily on the adsorbed dye, other conditions been met (e.g. pH). On the contrary, the K_L values of the third column of Table 2 dramatically changed from one dye to the other. K_L values mainly show how fast a dye is adsorbed and this is better demonstrated when the dye concentration is low. Among the two cationic dyes, CryV is more rapidly adsorbed than MB while both are much more rapidly adsorbed than AO7. Similar behavior was detected with other anionic and cationic dyes (not shown) indicating that surface hydroxyl groups, which are abundant at neutral pH, provide better conditions for adsorption. As seen in Fig. 2 (curves #3) and Table 1 (columns 4–6), the absorbance of adsorbed AO7 is much lower than that of CryV and MB, even though, as already found, the q_e max values do not justify such difference. This is due to the difference in extinction coefficient, as can be seen in the third column of Table 1. The values of the extinction coefficient were measured in dilute aqueous solutions. Absorbance of AO7 is low (Fig. 2A), mainly, because it has the lowest extinction coefficient. On the other hand, the higher values of absorbance obtained with MB as compared with CryV can be justified in terms of q_e max, which was much higher in the case of MB.

The above data show the conditions and the extent of adsorption of the three dyes on a given titania film. In this paragraph, we examine the physicochemical state in which the absorbed dyes find themselves. In the case of AO7 and, particularly, in the case of MB, as shown in Fig. 2, we observed a blue shift in the absorption spectrum in going from dilute solution to adsorption. In the case of CryV, the absorption maximum was not shifted but the enhanced shoulder on the left indicates a small broadening on the blue side of the spectrum. This effect, which seems to be common in all adsorbed dyes, both those studied here [18–21] and others not shown, demonstrates itself at a different extent by different dyes. The shift was very large for some blue dyes, like MB and Basic Blue [12], which absorb at long wavelengths. In all cases, the shift is hypsochromic (towards the smaller wavelengths). This is justified by the fact that the titania surface is charged and the adsorbed molecules are oppositely charged. Consequently, they are aligned with their dipole moments in parallel so that interaction is repulsive and thus absorption energy increases. Shift of absorption spectrum of the above type indicates aggregate formation. Obviously, this phenomenon is very intense in the case of MB, less important in the case of AO7 and almost negligible in the case of CryV. This difference may be explained by structural considerations (see Fig. 1). CryV, which has a symmetric structure, is incapable to develop intermolecular interactions. On the contrary, AO7, which is an elongated molecule and carries a hydroxyl group, can form complexes by loose bonding through this chemical group [cf. Ref. 21]. MB is also known to form aggregates, which are also observed in concentrated aqueous solutions (cf. Ref. [19] and Curve #4 of Fig. 2c). Indeed, blue shift in absorption was observed in both adsorbed and concentrated MB. Both AO7 and MB are expected to form aggregates by placing dipole moments in parallel [20]. This situation corresponds to repulsive interaction (H-aggregates) [22–24]. The shift in the absorption spectrum is accompanied by a change in color, which is very intense in the case of MB. This change of color is sometimes called Metachromacy and can be exploited for sensing or staining in various applications [12].

The difference of behavior demonstrated by the adsorbed dyes on the titania film is not without consequences. Photodegradation of the adsorbed dyes was studied in air and the extent of discoloration is shown in Fig. 4. Photodegradation was very fast in the case of CryV and AO7 but it was much slower in the case of MB. We believe that this difference is related with the state of the dye on the surface of the catalyst. There are a number of reasons that could make photodegradation rates faster or slower: (1) the chemical structure of the dye is expected to have an influence on mineralization pathways. However, since the early stage of the photocatalytic mechanism depends only on the catalyst itself and the availability of reactive radical species, chemical structure should not play a role on the rates of discoloration itself. Consequently, AO7 and CryV were discolored, practically, at the same rate. (2) Radiation screening effects are expected to be very important with dyes. Titania by itself is transparent. When dyes are adsorbed, light transmittance in the visible is limited in a large part of the spectrum. However, screening effects are not important for band gap excitation of titania in the near UV, particularly, for dyes with low optical density in the near UV. As a matter of fact, MB and CryV, which are strong light absorbers in the visible have relatively low absorbance in the near UV. Indeed, photodegradation experiments carried out by using Black Light (emission centered at 353 nm) gave, as seen in Fig. 5, again much faster photodegradation rates for CryV than for MB. Radiation screening effects is then not an important issue in the present case. (3) The number of photodegradable molecules as compared with the number of catalyst nanoparticles should play an important role in photodegradation rates. Since the quantity of catalyst is in all cases the same, the quantity of adsorbed dye, expressed by the value q_e max given above, should be a determining factor defining rates. However, the similarity of behavior between AO7 and CryV as well as the marked difference from MB is not compatible with the values of the second column of Table 2. Dye concentration is not an issue in the present case either. (4) Photosensitization of the catalyst by visible absorption by the dye itself may be an issue [25] but it does not explain the data of Fig. 5. (5) Dye aggregation is apparently the only persuasive explanation of the present data. MB is extensively aggregated when adsorbed on the surface of titania. It is highly probable that aggregation could lead to the formation of multilayers. Stacking of dyes will prevent immediate contact with titania surface and this will extensively affect photodegradation

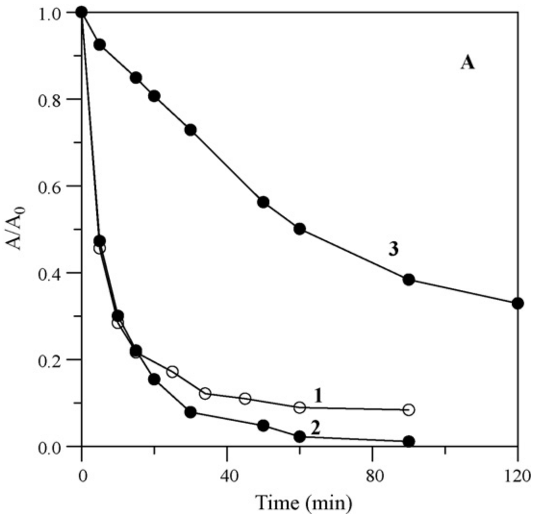

Fig. 4. Discoloration of various dyes adsorbed on titania films by irradiation with a Xenon light source: (1) AO7; (2) CryV; and (3) MB.

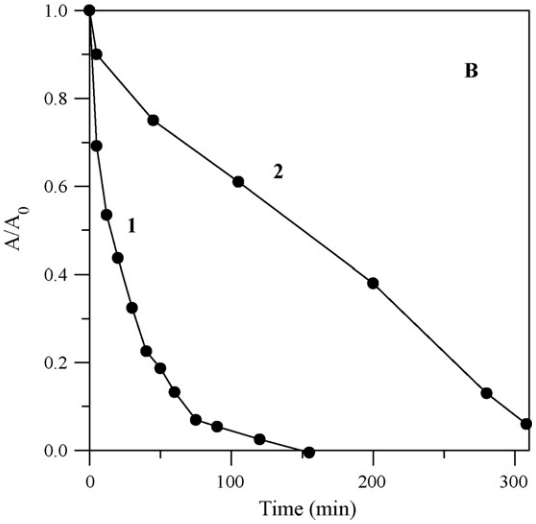

Fig. 5. Discoloration of CryV (1) and MB (2) adsorbed on titania films by illumination with Black Light.

rate. The above data show that CryV is not aggregated while AO7 is slightly aggregated. Therefore, their photodegradation rates were much faster.

4. Conclusion

Photodegradation rates of pollutants adsorbed on titania photocatalyst might be extensively reduced when the photodegradable molecules are aggregated, since in that case, interaction with photocatalyst is inhibited. MB is aggregated in the adsorption state and this is demonstrated by a large shift in its absorption spectrum. MB photodegradation was much slower compared with other model dyes, which were adsorbed without or with limited aggregate formation.

Acknowledgements

We thank the European Social Fund (ESF), Operational Program for Educational and Vocational Training II (EPEAEK II), and particularly the Program PYTHAGORAS II, for funding the above work.

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