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Determination of the photocatalytic efficiency of TiO_2 coatings on ceramic tiles by monitoring the photodegradation of organic dyes

Vladimira Petrovič [a], Vilma Ducman [a], Srečo D. Škapin [b,*]

[a] *Slovenian National Building and Civil Engineering Institute, Dimičeva 12, 1000 Ljubljana, Slovenia*[1]
[b] *Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*[2]

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Abstract

A method for the evaluation of the photocatalytic effectiveness of nanotitania coatings on ceramic substrate was established. Decolourization of three organic dyes, including methylene blue (MB), rhodamine B (RB) and crystal violet (CV), was investigated under different experimental conditions. The results showed that the UV light spectrum and light intensity are important parameters when establishing this method.

The effect of TiO_2 on the percentage degradation of the dyes was examined by varying its concentration in the suspensions between 0.1% and 4.5 wt%, which resulted in different thicknesses of the TiO_2 layers, and as expected higher percentages of nanotitania resulted in higher photocatalytic efficiencies. However higher amounts of titania lead to the formation of cracks on the surface, which might detrimentally affect adhesion and thus also long-term durability. The applicability of all the dyes used in the present study was proved, and there is good correlation between MB, RB and CV in the evaluation of self-cleaning efficiency.

Keywords: D. TiO_2; Photocatalysis; UV/vis spectra; Organic dye decolourization

1. Introduction

Industrial pollution is an important global problem, and has effects on the quality of urban and rural environments, including water, air and soil. The development of new materials that can be easily applied to facades, roofs, glass, tiles, pavements, textiles and similar surfaces with photocatalytic and self-cleaning, de-polluting properties would significantly contribute to a decrease in environmental pollution and its irreparable consequences. The use of materials with self-cleaning properties will not be just eco-friendly to the environment, but may also be able to prolong the life-time of buildings and a variety of exterior subjects. The initial aesthetics and mechanical properties of new buildings often deteriorate due to attack by environmental pollution (i.e. car fumes which coat building exteriors with grime or moss, fungi that stain roofs, etc.) [1–3].

In order to decrease environmental pollution, the photocatalytic degradation of organic pollutants in the presence of TiO_2 as photo-catalysts appears to be a rapidly growing decontamination process.

So far numerous experimental methods have been reported for the determination of the photo-catalytic activity of TiO_2, as well as studies related to the use of semiconductors in the photo-mineralization of coloured organic substances. As model pollutants dyes are commonly used because their concentration can be easily monitored using a spectrometer. Among them, methylene blue (MB) has been widely studied due to its highly coloured nature, good chemical stability, and inexpensiveness. The method which employs MB dye dissolved in water in the presence of TiO_2 has been considered as a standard test for photo-catalytic surfaces by the International Organization for Standardization (ISO) [4,5].

A major advantage of using heterogeneous photo-catalysis, which are based on the generation of very reactive species such as hydroxyl radicals (OH·) and others, is the total mineralization of organic dyes, which results in CO_2, H_2O and corresponding mineral acids. The semiconductor-sensitized photo-oxidative degradation of dye test reagents is considered

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* Corresponding author. Tel.: +386 1 477 3708; fax: +386 1 477 3875.
E-mail address: sreco.skapin@ijs.si (S.D. Škapin).

[1] http://www.zag.si.

[2] http://www.ijs.si/.

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to proceed via the following general mechanism.

$$TiO_2 + h\nu \rightarrow TiO_2\,(h^+ + e^-) \quad (1)$$

$$h^+ + \text{dye} \rightarrow \text{oxidation products} \quad (2)$$

$$h^+ + H_2O \rightarrow HO^{\cdot} + H^+ \quad (3)$$

$$HO^{\cdot} + \text{dye} \rightarrow \text{degradation products} \quad (4)$$

$$e^- + O_2 \rightarrow O_2{\cdot}^- \quad (5)$$

$$O_2{\cdot}^- + \text{dye} \rightarrow \text{degradation products} \quad (6)$$

$$e^- + \text{dye} \rightarrow \text{reduction products} \quad (7)$$

The photo-generated holes are able to oxidize the dye either directly (2) or indirectly via the production of adsorbed $HO^{\cdot}$ radicals and via reactions (3) and (4). The photo-generated electrons are able to reduce adsorbed oxygen to superoxide radical anions (5), which may then also react with the dye, reaction (6), or undergo subsequent reduction to H_2O_2 and subsequently, water may also act as a source of $HO^{\cdot}$ radicals to oxidize the dye. The dye can also be directly reduced by the photo-generated electrons (7) [6]. As well as methylene blue (MB), other organic pigments, too, can be used as model pollutants [7].

In this paper the degradation of the organic dyes: MB, RB and CV, as a model pollutant in an aqueous solution in a presence of a TiO_2 photo-catalytic surface irradiated with UV light, was studied. The research was focused on determining the parameters like light spectra/wavelength and intensity, as well as the amount of the photo-catalyst which influences the degradation rate of the dye and the photo-catalytic activity of the photo-catalyst. The influence of these parameters was examined on laboratory prepared samples, consisting of ceramic tiles coated with commercially available TiO_2 sol.

2. Experimental

2.1. Materials and preparation

Titania coatings were prepared from four TiO_2 suspensions with different concentration (4.5%, 1%, 0.5%, and 0.1 wt%). They were prepared in advance based on Hombikat XXS 100 (Sachtleben Chemie GmbH) sol of nanosized (declared size 7 nm) anatase form in isopropanol (Sigma–Aldrich). The resulting suspensions were stirred for 24 h at room temperature and then deposited on the ceramic tile with a smooth surface by the spray technique. The titania films were dried at room temperature and then fired up to 700 °C at a rate of 100 °C/h, and maintained at this temperature for 30 min.

Three different types of cationic organic dyes were selected as test reagents for assessing photo-catalytic activity: methylene blue (MB) as thiazine dye (Kemika), rhodamine B (RB) (Kemika) as xanthene dye, and crystal violet (CV) (Kemika) as triphenylmethane dye. In all cases the concentrations of the dye solutions were 10 μM, and they were prepared in double deionized water.

2.2. Characterization of the samples

The morphology of the films was examined using Field Emission-Scanning Electron Microscopy, Supra 35 VP, Carl Zeiss (FE-SEM).

Raman spectra were recorded using a Raman spectrometer LabRam HR800 (HORIBA Jobin Yvone) equipped with an Olympus BXFM optical microscope and an air-cooled CCD detector. The samples were excited with the 514.45 nm line of an Argon ion laser operating at a power of 17 mW, using neutral density filters.

2.3. The photo-catalytic test

Samples were first pre-irradiated in an irradiation chamber equipped with two parallel UV-A bulbs (40 W, Osram Eversun, λ_{max} = 360 nm, 10 W/m^2); the aim of this pre-radiation was to decompose any possibly remaining organic contaminants by photo-catalytic oxidation. A cylindrically shaped glass cell (with an inner diameter of 40 mm) was attached to each sample using silicon glue. Since the substrates showed a tendency to adsorb the dye molecules, pre-adsorption of the surface was performed, using 20 μmol/L solutions. The tests were then performed using a test solution of 10 μmol/L. 40 mL of the dye adsorption solution was poured into the test cell and the dye was adsorbed in the dark for 24 h. If the remaining concentration of the dye in the solution was larger than that of the test solution, the adsorption was considered to be complete. Otherwise, the procedure was repeated for another 12 h employing a fresh adsorption solution. After the adsorption process of the dye was complete, the adsorption solution was replaced by the test solution and the samples were exposed to UV-A light in an irradiation chamber using Osram Eversun bulbs (40 W, λ_{max} = 360 nm, 10 W/m^2). The decomposition rate of the dye under the UV-A light irradiation was determined by measuring its absorption spectrum using a UV/vis spectrophotometer (Ocean Optics Inc.) every 2 h. The photo-catalytic activity of TiO_2 was defined as the degree of photo-degradation rate of the dye (i.e. the decrease in the dye concentration) and is calculated using following equation [8]:

$$\text{Photo-degradation efficiency } (\eta) = \frac{A_0 - A_t}{A_0} \times 100\% \quad (8)$$

where A_0 is the initial absorption of the dye, and A_t is the absorption of the dye at a given UV irradiation time.

Photocatalytic measurements by MB were performed on at least two parallel test specimens; the reproducibility of results was within error of measurement (less than 3%).

In order to assess the photocatalytic efficiency of the TiO_2 coated samples, measurements were also performed on inert laboratory glass, as well as on non-coated ceramic tiles, which were designated as ‘‘blank’’ samples.

3. Results and discussion

3.1. Influence of the light spectra and light intensity

The fact that dyes absorb light in the UV and visible light spectra indicates that a photoreaction can be induced by UV/vis light photo-absorption (dye sensitization) as well as by the photo-absorption of a photo-catalyst. Fig. 1 shows that all three types of dyes absorb UV light below $\lambda = 350$ nm and in the visible region, with maximum absorption peaks at 664 nm for MB, at 553 nm for RB and at 590 nm for CV. In order to avoid any type of photolysis reaction of the dyes the wavelength for the excitation of the photo-catalyst has to lie within the range of $\lambda = 350$–480 nm [5].

The emission spectra of the illumination light source in the UV-A range (Osram Eversun) with the maximum irradiation peak of the lamp in the range of 320–380 nm is shown in Fig. 1. RB and CV can absorb UV-light in this area, while MB does not absorb significantly in the UV-A region, so that MB decomposition in this region can be mainly ascribed to the band-gap photo-excitation of TiO_2 [9].

Fig. 2 confirms the stability of the MB solution under experimental conditions (UV light) on blank samples. It can be noticed that the sample with 4.5% TiO_2 is highly efficient, and that the tile without TiO_2 coating as well as glass do not cause decolourization of MB under UV light.

Beside the physico–chemical properties of TiO_2 which might influence the rate of the dye degradation since the MB photoreaction could proceed mainly through adsorption and electron injection, light intensity, too, can greatly influence the photo-catalytic activity of TiO_2 and thus affect the degradation rate of the dye [5,10,11]. Under higher light intensities the formation of electron-hole pairs is predominant, so that recombination is negligible. At lower light intensities, electron–hole pair separation competes with recombination, which in turn decreases the formation of free radicals. The result is a smaller effect on the percentage degradation of the dye [12].

In Fig. 3 the influence of light intensity (Osram Eversun) on the MB degradation in the presence of TiO_2 is presented using an initial test solution concentration of 10 μM. The decolourization process progresses proportionally with the irradiation time. As expected, at higher light intensities the percentage of MB degradation increases.

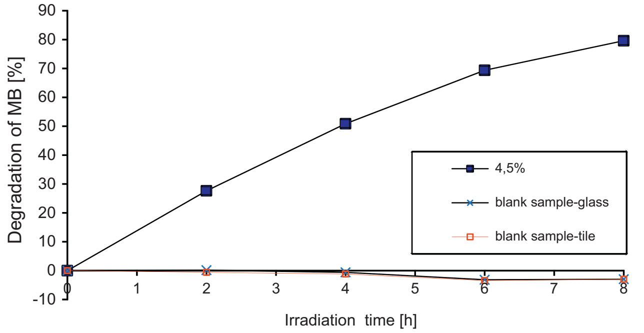


Fig. 2. Photo-degradation of the MB aqueous solution as a function of irradiation time (laboratory sample (4.5% TiO_2)) and blank samples (non-coated glass and non-coated tile) after 8 h of exposure under UV light (Osram Eversun); light intensity: $I = 10$ W/m^2.

3.2. Effect of amount of the photo-catalysts on the surface

The assumption that a higher amount of TiO_2 corresponds to enhance photo-degradation of the dye can be explained as follows. As the amount of catalyst is increased, the number of absorbed photons and adsorbed dye molecules is increased. The rate of degradation is enhanced as a consequence of the increased density of TiO_2 particles in the area of illumination [8,13].

In order to examine the effect of the amount of catalyst on the decolourization of MB dye, active titania layers of different thickness were prepared using different concentration of the TiO_2 particles in the suspension, between 0.1% and 4.5 wt%.

This is evident from the SEM images shown in Fig. 4a, d and g, where it can be seen that in the case of 4.5%, 1% with an approximate thickness of 700 nm and 550 nm (Fig. 4b and e), respectively, and 0.5% of TiO_2, the substrate surface is completely covered, whereas in the case of 0.1% of TiO_2 (Fig. 4i) the surface remains partly uncovered.

Due to the considerable thickness of the TiO_2 coatings, and probably also because no binder had been added to the spraying solution, cracks formed after firing at 700 °C (Fig. 4c and f).

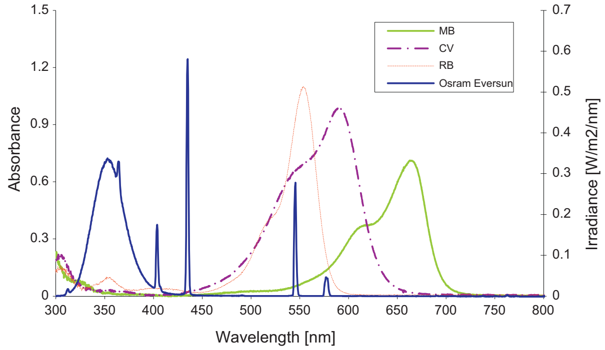


Fig. 1. Absorption spectra of the dyes MB, RB and CV and the emission spectrum of the illumination light source – an Osram Eversun bulb.

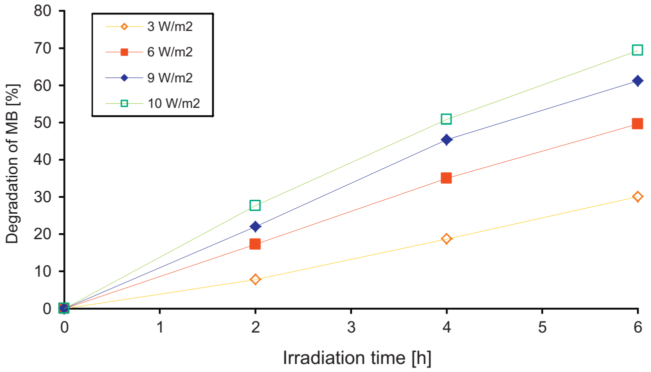


Fig. 3. Degradation of MB as a function of the irradiation time under different light intensities of the UV light; $C_0 = 10$ μM.

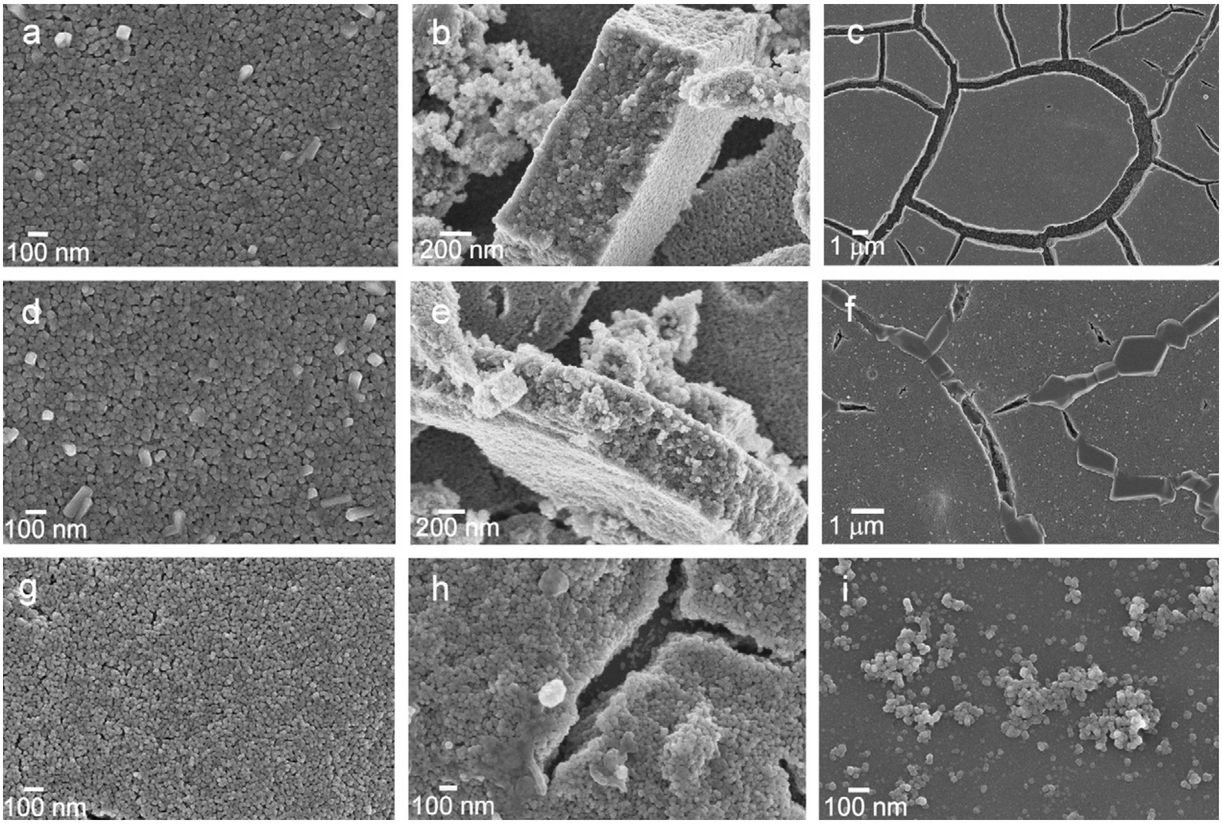


Fig. 4. FE-SEM micrographs of TiO_2 film on a ceramic tile fired at 700 °C: (a–c) 4.5% of TiO_2, (d–f) 1% of TiO_2, (g and h) 0.5% of TiO_2 and (i) 0.1% of TiO_2.

The photo-catalytic activity of the so-prepared samples was monitored by the change in absorbance of MB as a function of irradiation time employing the UV/vis spectrophotometer. As can be seen from Fig. 5, the highest degradation of MB was recorded in the case of the sample with 4.5% of TiO_2. By prolonged irradiation for 24 h almost total decomposition, 99%, was achieved in the case of the sample with 4.5% TiO_2. The results given in Table 1 indicate that increasing thickness enhances the photo-catalytic process and with a certain amount of the photo-catalysts can almost totally decompose the organic pollutant.

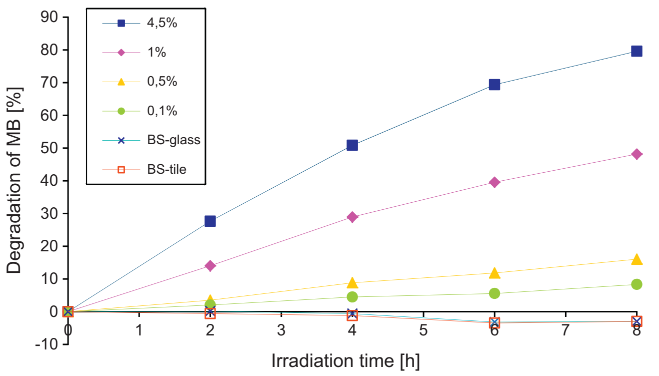


Fig. 5. Photodegradation of MB as a function of irradiation time for the following samples (■) 4.5% TiO_2, (◆) 1% TiO_2, (▲) 0.5% TiO_2, (●) 0.1% TiO_2, (×) blank sample-glass. Experimental condition: light intensity: $I = 10\ W/m^2$.

The Raman spectra (Fig. 6) confirmed the presence of the anatase after firing the samples at 700 °C; the spectra of the anatase form of TiO_2 with characteristics peaks at 143 cm^{-1}, 197 cm^{-1}, 396 cm^{-1}, 516 cm^{-1} and 640 cm^{-1} was recorded.

3.3. Investigation of the photo-catalytic activity of TiO_2 films with other organic dyes and their suitability as a model organic pollutant

The photo-catalytic decomposition of dyes depends on their different molecular structures and on the functional groups (Scheme 1) which influence the initial pH of the solution and, due to adsorbed dyes at different amounts onto the photoactive surface. During the reaction water-insoluble organic intermediates are generated that can also affect the photo-catalytic process by inhibiting the covering of active sites [4,5].

Table 1
Photodegradation efficiency of MB, RB, and CV ($C_0 = 10\ \mu M$) after 24 h of irradiation under UV light (light intensity $I = 10\ W/m^2$) on photocatalytic films with different thickness of TiO_2 layer.

Concentration of TiO_2	4.5%	1%	0.5%	0.1%
Approx. thickness [nm]	700	550	100	[a]
Degradation of MB after 24 h [%]	99%	88%	33%	18%
Degradation of RB after 24 h [%]	96%	86%	48%	28%
Degradation of CV after 24 h [%]	99%	93%	54%	20%

[a] Only partially covered.

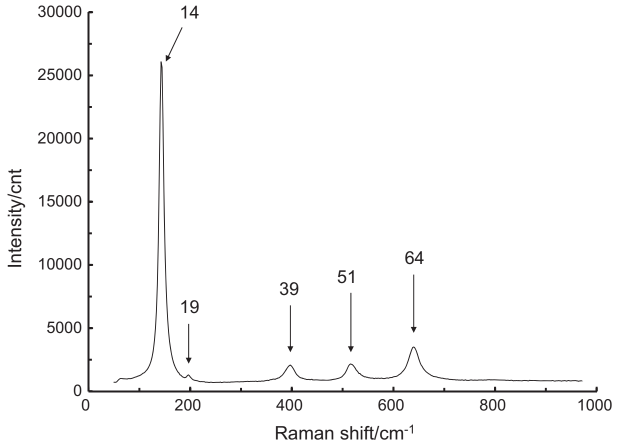
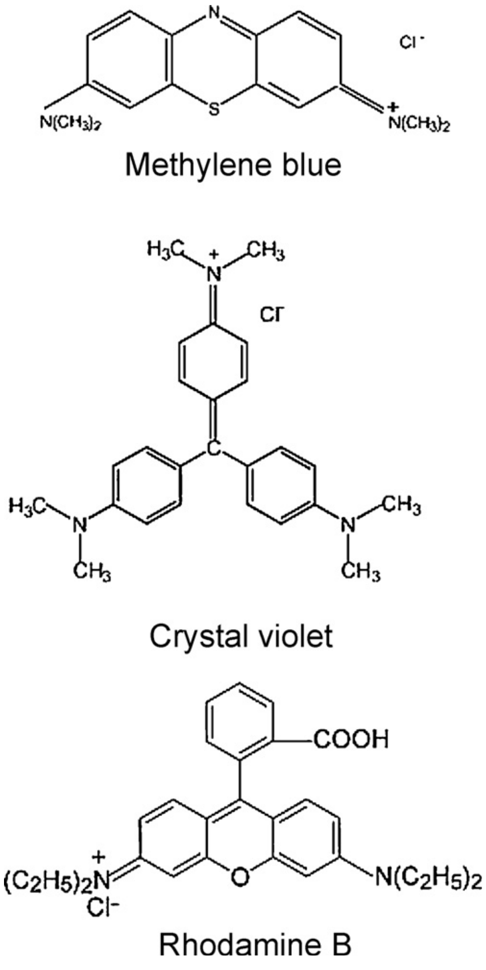


Fig. 6. Raman spectra of the laboratory sample–a ceramic tile coated with TiO_2 (4.5%) fired up to 700 °C; $\lambda_{ex} = 514.45$ nm.

The feasibility of the degradation by a UV/TiO_2 treatment of dyes having different chemical structures is now presented. The photo-catalytic degradation of RB and CV was investigated in aqueous solutions under the same conditions as the MB dye and was monitored by the change in absorbance as a function of irradiation time employing the UV/vis spectrophotometer. This is shown in Figs. 7 and 8.



Scheme 1. Chemical formulae of the applied organic dyes.

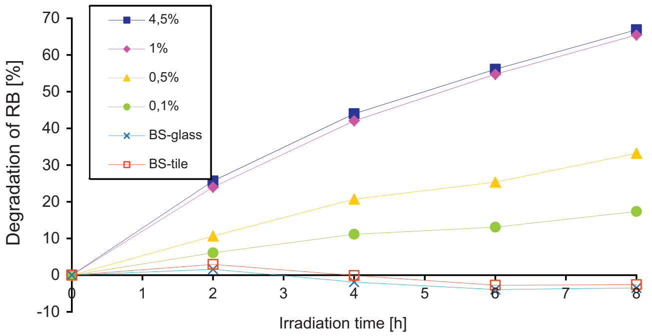


Fig. 7. Photo-degradation of RB as a function of irradiation time for the following samples (■) 4.5% TiO_2, (◆) 1% TiO_2, (▲) 0.5% TiO_2, (●) 0.1% TiO_2, (×) blank sample-glass. Experimental condition: light intensity: $I = 10$ W/m^2.

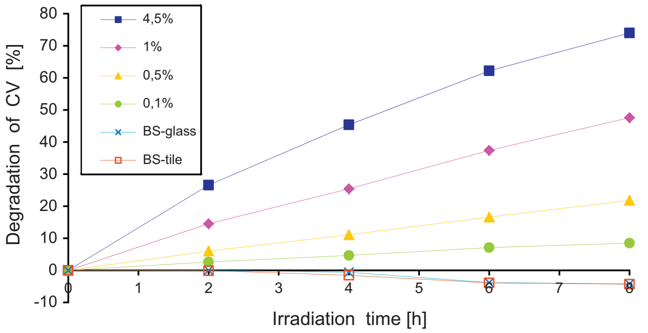


Fig. 8. Photo-degradation of CV as a function of irradiation time for the following samples (■) 4.5% TiO_2, (◆) 1% TiO_2, (▲) 0.5% TiO_2, (●) 0.1% TiO_2, (×) blank sample-glass. Experimental condition: light intensity: $I = 10$ W/m^2.

Similarly to the results in Fig. 5, where the results for the decolourization of MB are presented, also from Figs. 7 and 8 for the decolourization of RB and CV respectively, it can be concluded that (i) both colour solutions are stable on blank samples, and (ii) the efficiency of decolourization greatly depends on the amount of the applied TiO_2 coatings.

Zita et al. [14], who studied the degradation of two model compounds, also found that the mass of the titania layer is decisive in photocatalytic degradation.

The results of photocatalytic efficiency for all three colours are summarized in Table 1; where it can be seen that there is good correlation between the results for all three colours solutions.

4. Conclusions

A test method to determine the discolouration of organic dyes on photo-catalytic surfaces was established in laboratory. It was found that light spectra and light intensity greatly influence the photo-catalytic activity. When varying the amount of TiO_2 on the surface it was noticed that if the concentration of titania was too high (in our case equal to or higher than those prepared from the 1% TiO_2 solution), then the applied layer shows cracks after firing.

MB dye has been proved to be a suitable dye for the established test method by many researchers, but the other used dyes RB and CV proved their suitably in the test method and showed good correlation with the MB.

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