

# Surface Photocatalysis: A Study of the Thickness of TiO<sub>2</sub> Layers on the Photocatalytic Decomposition of Soluble Indigo Blue Dye

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*The effect of the thickness of a TiO<sub>2</sub> layer coated on glass slides, obtained by the use of a simple multiple soaking method, was tested evaluating its effect on the efficiency of photodegradation of adsorbed soluble indigo blue dye on it. Photodegradation was undertaken on a laboratorial bench top photoreactor, equipped with a mercury lamp covered by a glass bulb, and photodegradation results were monitored directly on the photocatalytic surface by ground state diffuse reflectance.*

*Keywords: photocatalysis, glass coated / immobilized TiO<sub>2</sub>, Soluble Indigo Blue dye, ground state diffuse reflectance*

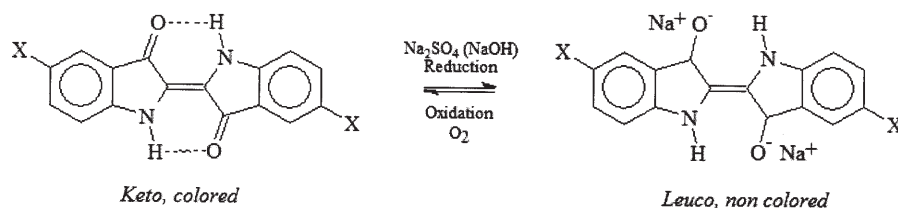
Since the discovery by Fujitsu and Honda [1] of the photoinduced water cleavage titanium dioxide (TiO<sub>2</sub>) heterogeneous photocatalytic oxidation using semiconductors as catalysts has been continuously investigated to be used on environmental remediation [2-6]. The first photocatalytic studies were conducted on aqueous media with TiO<sub>2</sub> powders suspended on the liquid but although this method appeared to be extremely efficient on a laboratorial scale [2-6] it soon revealed concrete scale up problems mostly related with the need of removal of powdered TiO<sub>2</sub> following the treatment of the contaminated solution. This is a technically difficult and extremely costly step due to the energy consumed in the removal process [7-9]. To overcome this technical difficulty several proposals for the use of immobilized TiO<sub>2</sub> layer on several types of reactors appeared as a promising solution for this problem furthermore enabling the reuse of photocatalyst [7-9].

Diffuse reflectance techniques, namely ground state diffuse reflectance (GSDR), are suitable spectroscopic techniques to follow the photodegradation of probes adsorbed on surfaces [10,11], since it enables the measurement of ground state absorption spectra directly from opaque solid surfaces.

Nowadays, indigoid vat dyes continue to be the most widely used dyes to impart blue colour to jeans, cotton

work cloths and wool [12-15]. Vat dyes once in their coloured occurring forms (*keto*, coloured insoluble oxidized form) are most often water insoluble, reason why they require a somewhat complicated dyeing procedure [12,16]. In fact, to be applied to cotton fibers, vat dyes have to be reduced to their water soluble forms (*leuco*, colourless soluble reduced form), which ones are substantives towards cellulose, once they readily become adsorbed on fiber surface through hydrogen bonding (scheme 1). After adsorption, vat dyes can then be readily oxidized by simple air contact to their original *keto* forms [12, 16]. Since vat dyes are not covalently bound to fibers, they are easily subject to removal by abrasion. This is the reason why, blue jeans rapidly turn white at knees or other pressured zones and also accounts for the popular production of “stone washed” jeans clothes [12].

At several textile industries locations the intensive use of indigoid vat dyes for blue jeans dyeing and production poses a serious challenge of waste water treatment [13-16]. At those locations the deep blue wastewater colour is a strongly imposing sign of water pollution and has to be removed prior to effluent discharge in the water bodies in order to avoid the common strong public opposition [13-16]. In fact, the presence of small amounts of any dye (below 1 ppm) in water is easily identified and affects not



Scheme 1. Dyeing procedure of indigoid vat dyes

X<sub>1</sub> = H; Indigo Blue

X<sub>2</sub> = SO<sub>3</sub><sup>-</sup> Na<sup>+</sup>; Soluble Indigo Blue

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only the water aesthetic aspect but also its transparency [13-16]. Although usually ignored, the later mentioned effect causes serious problems to both local fauna and flora [13-16]. Colour removal from textile effluents is often considered to be more urgent than any other non coloured contaminant of the same effluent [13-16].

In the present work we will use  $\text{TiO}_2$  layers immobilized on glass slides to test the effect of the thickness of the  $\text{TiO}_2$  coated layer on its photocatalytic ability to decompose a common textile indigoid vat dye, soluble indigo blue (for structure see scheme 1) [14,15].

## Experimental part

### Materials

$\text{TiO}_2$  (DeGussa P25, gift from DeGussa Brasil), Acetilacetone (Aldrich 99%) and Triton X-100 (for cationization from Vetec Química fina Ltda) were used as received.

Soluble Indigo Blue (technical grade, formulation for cloth dyeing) was a gift from SENAI, CETIQT, Rio de Janeiro, Brazil and was also used as received. Water used to prepare dye solutions was MiliQwater.

### Methods

#### Preparation of the coating photocatalytic emulsion

A  $\text{TiO}_2$  coating emulsion was prepared according to the method previously used by us [17, 18] by mixing 12 g of  $\text{TiO}_2$  powder with 4 mL of water and 0.4 mL of acetilacetone in a beaker. The mixture was homogenised in an ultrasonic bath (Bandelin Sonorex RK 156) for 10 minutes. Finally another 25 ml of water and 0.2 ml of Triton X-100 were added to the mixture to yield a white  $\text{TiO}_2$  emulsion.

#### Preparation of the glass slides coated with photocatalyst

This emulsion was applied to common microscope glass slides (750 mm x 250 mm ie. 18,75 cm<sup>2</sup>) one or several times (according to the desired number of deposited  $\text{TiO}_2$  layers) simply by emersion of the glass slide in the  $\text{TiO}_2$  suspension. After immersion of the slide and drain off of the exceeding suspension the  $\text{TiO}_2$  layer was allowed to dry at room temperature for at least 30 min before a new photocatalytic layer was deposited by the same method.

After the desired number of  $\text{TiO}_2$  layers coated on glass was attained the glass slides were finally dried for 1 h at 100°C. The amount of  $\text{TiO}_2$  coated on the glass on each deposition was measured by weighing each glass slide before and after each  $\text{TiO}_2$  deposition. Slides with one up to ten  $\text{TiO}_2$  coated layers were prepared. The average amount of  $\text{TiO}_2$  coated per glass slide and per deposition is listed in table I. Up to layer number five 16 mg of  $\text{TiO}_2$  suspension were coated in average on each deposition. For more than six coated layers, the amount of  $\text{TiO}_2$  by layer progressively increased, being ~ 50 mg for layer number six and ~ 100 mg for layers seven to ten. Therefore the total amount of  $\text{TiO}_2$  coated on the glass slides was 16.4 mg, 29.4 mg, 415 mg, 60.0 mg, 71.7 mg, 119.3 mg, 200.5 mg, 286.3 mg, 384.7 mg and 476.7 mg respectively for layer one to ten. The durability of the  $\text{TiO}_2$  coating was evaluated by visual observation and weighting of all glass slides after slide preparation, dye deposition, contaminated slide irradiation and post irradiation spectroscopic measurements and no significant  $\text{TiO}_2$  lost were observed up to 5 layers. For high number of layers the  $\text{TiO}_2$  deposited on the glass slides a general tendency for cracking and lost of the  $\text{TiO}_2$  coating was observed. It appears that for high number of layers the  $\text{TiO}_2$  coating tended to behave more as  $\text{TiO}_2$  powder deposited on  $\text{TiO}_2$  rather than  $\text{TiO}_2$  coated on glass. This is

also consistent with the observed increase on the amount of the  $\text{TiO}_2$  coated, per layer, for more than five layers.

#### Contamination of glass slides coated with photocatalytic layer with soluble indigo blue dye

Each glass slide was contaminated with 200  $\mu\text{L}$  of a  $6 \times 10^{-3} \text{M}$ , i.e.  $1,2 \times 10^{-6} \text{mol}$ , solution of soluble indigo blue dye in water, independently of the amount of  $\text{TiO}_2$  coated on its surface. The optimal volume of solution containing the dye was optimized for the complete impregnation / coverage / wetting of the slides with the thickest  $\text{TiO}_2$  coating (ten layers) in a single deposition, with the aid of a micropipette. This implies that for thinner  $\text{TiO}_2$  coatings the same total volume had to be carefully deposited on several steps followed by solvent evaporation to avoid any accidental lost of the solution containing the dye.

#### Irradiation of the contaminated glass slides

Each layer thickness was prepared six times and the experiment performed in triplicate for each thickness. For every thickness the first slide was kept in the dark and the second was irradiated for 6 h. The glass slides coated with different amounts of  $\text{TiO}_2$  and impregnated with a constant amount of soluble indigo blue dye ( $1,2 \times 10^{-6} \text{mol}$ ) were irradiated with a 125 watts mercury vapour lamp (HQL 125 watts E27, from Osram). In this type of commercial lamps, the filament is protected by a glass bulb that cuts all UV-A and UV-B radiation. The glass bulb presents a white colour due to the internal phosphor coating that improves the radiation of the lamp on the visible region [19]. This type of lamps with glass bulb is appropriated to selectively illuminate and exclusively excite  $\text{TiO}_2$  band gap, avoiding direct photolysis of the dye molecules that could be simultaneously promoted if all the lamp emission profile was available.

The photoreactor is composed of an elliptical cover that supports the irradiation source described above and of a base containing a sliding tray, where the samples to be irradiated are placed. The internal surface of the reactor was totally covered with aluminium foil in order to maximise the efficiency of the sample irradiation. The light arising from the mercury lamp was measured at 366 nm (the wavelength of  $\text{TiO}_2$  bandgap [2]) with the help of a Cole Parmer radiometer (series 9811-50) placed above the lamp, inside the photoreactor. The intensity of the lamp was measured placing the radiometer probe in six different positions of the tray and within experimental error the measured values were constant and equal to 1.35mW/cm<sup>2</sup>. In order to avoid overheating of the glass slides the global temperature of the laboratory were the irradiation experiments were performed was kept at 18°C and during all the irradiation process the photoreactor was placed between two fans.

#### Equipment

UV-Visible spectra of soluble indigo blue in water were measured in a CamSpec M501 Single Beam Scanning UV/Visible Spectrophotometer, at 20°C. Spectra of different concentrations of the dye in water were recorded with the help of 1 cm and 1 mm quartz cuvettes.

Diffuse Reflectance Ground State Absorption Spectra of the glass slides were registered in the UV-VIS regions using a Cary OLIS 14 UV/VIS/NIR spectrophotometer with a diffuse reflectance attachment from 200 to 900 nm. Further experimental details and a complete description of system calibration used to obtain accurate reflectance (R) measurements are given elsewhere [10, 11].

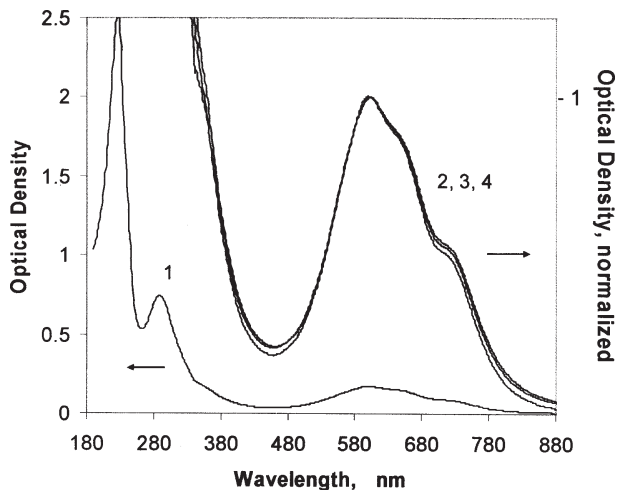


Fig. 1. UV-Visible absorption spectra of soluble indigo blue dye in water. The concentrations are  $6 \times 10^{-5}$  M (curve 1),  $6 \times 10^{-6}$  M (curve 2),  $6 \times 10^{-4}$  M (curve 3),  $6 \times 10^{-3}$  M (curve 4). Curve 1 presents the optical density of the sample (y axis on the left hand side) and curves 2 to 4 present values of optical density normalized to the absorption maxima (y axis on the right hand side).

## Results and discussion

### UV-Vis absorption of soluble indigo blue dye in water

Soluble Indigo blue dye presents high solubility in water and it is totally insoluble in ethanol. Figure 1 presents the absorption spectra of increasing concentrations (from  $6 \cdot 10^{-6}$  up to  $6 \cdot 10^{-3}$  M) of soluble indigo blue dye in water. The dye presents two strong and sharp absorption bands in the ultra-violet region, peaking respectively at 225 nm and 294 nm. In the visible region, the dye strongly absorbs from 480 nm to 880 nm, with maxima at around 600 nm. This band also presents two shoulders, respectively at 650 nm and 720 nm. This later band can be clearly seen at curves 2 to 4, which present spectra normalized to the absorption maxima (please refer to y axis on the right hand side of fig. 1) for concentrations from  $6 \times 10^{-6}$  M to  $6 \times 10^{-3}$  M. Absorption spectra for diluted samples ( $OD_{604 \text{ nm}} < 0.05$ ) were measured and the spectra presented always the same shape, with the primary maxima at 600 nm and shoulders at 650 nm and 720 nm. From this result we can conclude that on water soluble indigo blue is on its monomeric form on the all range of concentrations studied [14].

Once dye absorption presents the same shape for all the investigated concentration range we decided to choose a concentration similar to the one presented in a real industrial effluent containing soluble indigo blue dye. Like that, we considered that a suitable concentration to be deposited in the photocatalytic glass slides containing different thicknesses of coated  $\text{TiO}_2$  is  $6 \times 10^{-3}$  M since the concentration of the dye present in a real effluent is usually very high, producing a deep blue coloured effluents. This concentration is also the most adequate from the technical point of view since when this type of dyes are used in dyeing processes they are usually applied in very high concentrations that results on their presence in the water bodies, used as final destination of their wastes, also in high loading.

### Irradiation of the contaminated photocatalytic glass slides

Samples were subject to 6 h of irradiation. During the irradiation period the photodegradation was visually inspected and noticeable changes were observed. By this visual monitoring was possible to observe that:

- for the non irradiated samples the blue colour of the contaminated slides is stronger for slides with 1 to 5 layers;

Table 1  
AVERAGE AMOUNT OF  $\text{TiO}_2$  DEPOSITED ON EACH GLASS SLIDE ON EACH PHOTOCATALYST ( $\text{TiO}_2$ ) DEPOSITION

N° of $\text{TiO}_2$ layers	Average amount of $\text{TiO}_2$ deposited per glass slide and per deposition (g)
1	0.0164
2	0.0117
3	0.0159
4	0.0170 (*0.016)
5	0.0194
6	0.0496 (**0.050)
7	0.0864
8	0.0953
9	0.1115
10	0.1117 (***0.101)

Average amount of  $\text{TiO}_2$  deposited per glass slide and per deposition \*up to the 5<sup>th</sup> deposited layer; \*\* on the 6<sup>th</sup> deposited layer; \*\*\* from the 7<sup>th</sup> to the 10<sup>th</sup> deposited layer

Table 2  
AVERAGE CONCENTRATION OF SOLUBLE INDIGO BLUE DYE OVER  $\text{TiO}_2$  DEPOSITED ON EACH GLASS SLIDE

N° of $\text{TiO}_2$ layers	Average concentration of soluble indigo blue dye over $\text{TiO}_2$ deposited on each glass slide ( $\mu\text{molg}^{-1}$ )
1	73.2
2	42.7
3	27.3
4	19.6
5	14.9
6	9.2
7	5.5
8	3.8
9	2.8
10	2.2

The curve plotted in dotted gray is from the dye in water. Insets show a) Percentage reflectance and b) Remission function values at 450 nm (circles), 606 nm (triangles), 650 nm (squares) and 720 nm (losangles) for the different number of  $\text{TiO}_2$  layers before irradiation with a 125W mercury lamp.

- for glass slides with 6 to 10 layers the blue colour changes from deep blue to light blue, reflecting the increase of the amount of  $\text{TiO}_2$  where the dye was effectively adsorbed (see below fig, 2a). In fact there is a neat decrease on the concentration of the dye adsorbed per gram of  $\text{TiO}_2$  since the amount of the later effectively increases for every new added layer. Taking in account the average amounts of  $\text{TiO}_2$  deposited per layer presented in table 1, the average concentration of  $\text{TiO}_2$  per number of layers deposited on glass was calculated (see values on table 2). We found that the concentration of soluble indigo blue dye varied from values as high as  $\sim 120 \mu\text{molg}^{-1}$  for only one  $\text{TiO}_2$  layer to only approximately  $4 \mu\text{molg}^{-1}$  for 10  $\text{TiO}_2$  layers; concentrations of 10 to  $25 \mu\text{molg}^{-1}$  were observed between 5 to 7 layers of the photocatalyst;



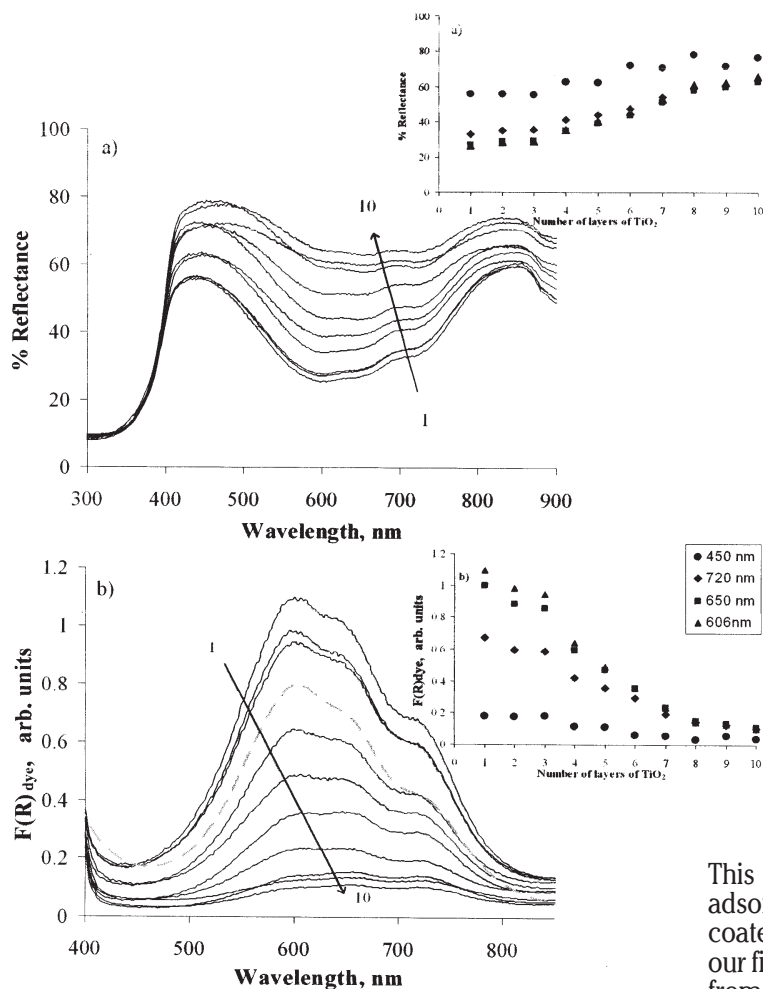


Fig. 2. Ground state diffuse reflectance spectra for each of the  $\text{TiO}_2$  layers after contamination with a constant amount of  $1,2 \times 10^{-6}$  mole of soluble indigo blue dye and before irradiation. a) Percentage Reflectance b) Remission Function of the dye. The number of  $\text{TiO}_2$  deposited layer increases from 1 to 10 as indicated by the arrows

- for irradiated samples the effect of disappearance of the colour of the soluble indigo blue dye was observed from early irradiation times (only 1 h) for the slides with higher amount of  $\text{TiO}_2$  and smaller concentration of soluble indigo blue per gram of  $\text{TiO}_2$  (8 to 10 layers). At 3 h of irradiation time (observed during irradiation) this effect visibly extended to all the slides from 6 to 10 layers, with the almost complete disappearance of the blue colour and with an increased yellowish colour of the coated layer. For 3 h of irradiation the same effect started also to be perceivable for plates 3 to 5. At the end of this time the neat decrease of the deep blue colour of the dye was only not easily observed for the glass slides with less than 2 or 3  $\text{TiO}_2$  layers. By the end of 6 h irradiation all glass slides presented noticeable colour lost (i.e., photodegradation changes).

#### UV-Vis absorption of soluble indigo blue dye over $\text{TiO}_2$ before and after irradiation

Figure 2 presents the UV-Visible ground state diffuse reflectance spectra for each of the  $\text{TiO}_2$  layers contaminated before irradiation with a constant amount of soluble indigo blue dye. For comparative purposes a typical absorption of the dye in water is also plotted (gray dotted line).

From figure 2 we can observe that the ground state absorption of soluble indigo blue adsorbed on  $\text{TiO}_2$  is very similar to the absorption of the same dye in water (compare also with the results from fig. 1). In fact the shape of the spectra of the dye over  $\text{TiO}_2$  (full black lines) is the same of that exhibited by the dye (dotted gray line) in water, and their wavelength maxima are the same ( $\sim 600$  nm). We can observe also that the absorption is always more intense for the glass slide with only one layer of  $\text{TiO}_2$  coating.

This means that the concentration of soluble indigo blue adsorbed on  $\text{TiO}_2$  is higher when only one layer of  $\text{TiO}_2$  is coated on the glass slide. This result is in accordance with our first visual inspection that showed that the blue colour from the dye was more intense for one layer and confirms also the average concentrations calculated for soluble indigo blue deposited on  $\text{TiO}_2$  for the different number of layers, as presented in Table 2. In this way, it is not surprising that the percentage reflectance, %R, of soluble indigo blue dye adsorbed on coated  $\text{TiO}_2$  increases (or the remission function,  $F(R)$ , decreases) with the increase of the number of layers, once the concentration of the dye actually decreases, as seen in figure 2.

Another point to remark is that in the case of the samples of soluble indigo blue dye deposited on  $\text{TiO}_2$  it is only possible to observe the soluble indigo blue absorption spectra for wavelengths higher than 360 nm. For lower wavelength the spectra is totally dominated by the strong  $\text{TiO}_2$  absorption and it is not possible to observe the absorption bands characteristics of the dye that were previously registered for the dye in water at those wavelengths (fig. 1).

In the insets of figure 2 a and b we can further observe the evolution of the percentage reflectance (inset in fig. 2a) and of the remission function (inset in fig. 2b) at the most relevant spectral wavelengths. In the inset of figure 2a we can observe that the reflectance progressively increases with the increase in the amount of the  $\text{TiO}_2$  coated in the glass slide, closely in the same way (nearly from 20 to 60%) for 606 nm, 650 nm and 720 nm, respectively the three wavelength maxima of the main absorption curve of the soluble indigo blue dye, traducing the above mentioned decrease on the concentration with the increase of the number of  $\text{TiO}_2$  layers. The fact that the curves for the three wavelengths closely follows for all the different numbers of coated  $\text{TiO}_2$  layers indicates that in the all range of concentrations herein investigated it is always the same species that is responsible for the absorption. Between 420 nm and 450 nm, the change in percentage reflectance is

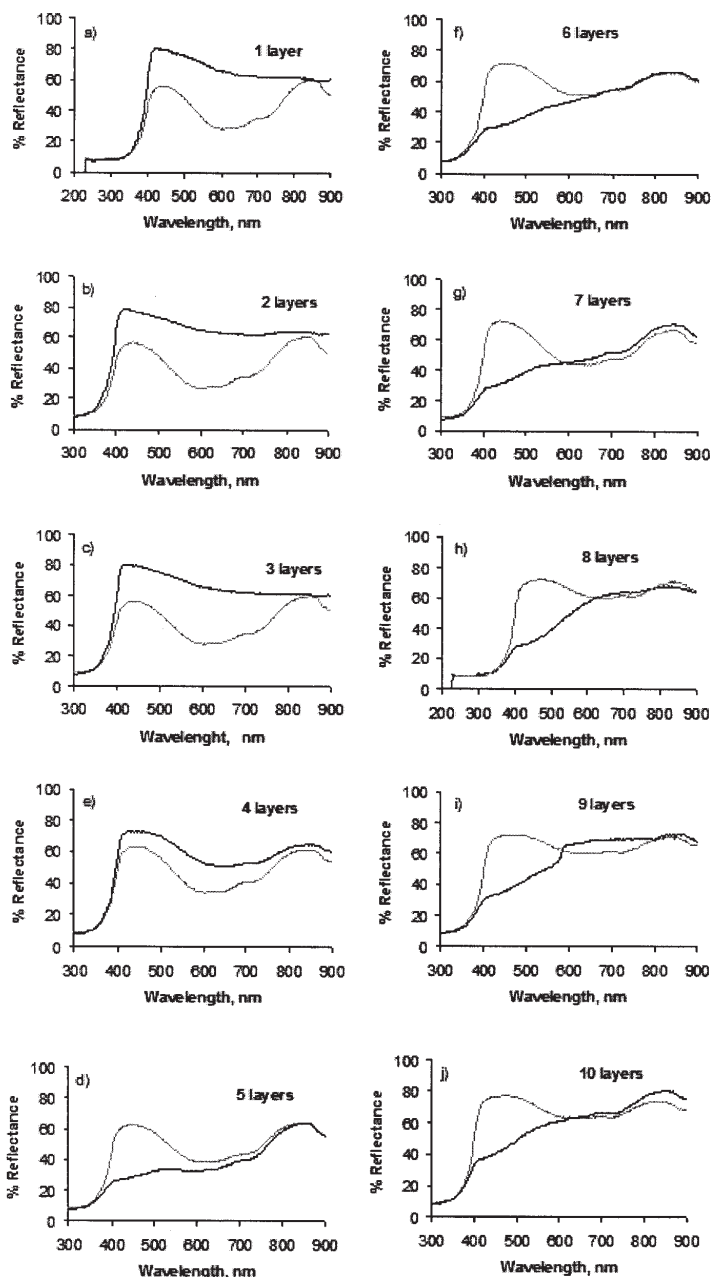


Fig. 3. Percentage Reflectance for each of the  $\text{TiO}_2$  layers contaminated with a constant amount of  $1,2 \times 10^{-6}$  mole of soluble indigo blue dye before (—) and after 6 h of irradiation with a 125W mercury lamp(—). Figures a) to j) present curves from 1 to 10 layers.

much smaller, varying only from  $\sim 60\%$  to  $70\%$ , since those are wavelengths out of those of the absorption band of the dye. In the inset of figure 2b, we present the same variation in terms of remission function, with similar conclusions.

The results observed after 6 h of irradiation are presented in figures 3 to 5.

Figure 3 presents the percentage reflectance, %R, for each layer number of the soluble indigo blue dye contaminated glass slide after 6 h of irradiation curves in black. For comparative purposes the spectra of each contaminated layer number before irradiation, (already presented at fig. 2) is also superimposed in each figure (curves in light gray). In figures 3a to 3c, respectively for 1 to 3 layers of coated  $\text{TiO}_2$  we observed the decrease (or the disappearance) of the band of the soluble indigo blue dye for the irradiated samples. In fact there is a neat decrease on the primary maximum absorption wavelength of the dye at  $\sim 600$  nm. To wavelengths shorter than 360 nm, the disappearance of absorption of the dye is completely masked by the intense  $\text{TiO}_2$  absorption, and so it is not possible to follow the photodegradation of the dye at those wavelengths. For wavelengths higher than 400 nm,  $\text{TiO}_2$ , a white highly reflecting powder, doesn't absorb and so does not interfere with the spectra of the dye. For

figures 3d to 3g, respectively for 4 to 7 layers of  $\text{TiO}_2$ , it is still possible to distinguish the above mentioned absorption maxima for soluble indigo blue but it is also possible to observe a new spectral feature. In fact, a new absorption band appears in the region located from 400 to 600 nm. For figure 3h to 3j that band increases in the same time when the absorption between 600 and 800 nm decreases even more. This phenomena is very much evident from the comparison of the spectra after 6 h of irradiation (curves plotted in black) and those of the correspondent glass slide before irradiation (curves plotted in light gray). In fact, from the comparison of the superimposed curves it is evident the disappearance of the compound from 600 to 800 nm and the appearance of something new absorbing in the region from 400 to 600 nm.

These same results can be more clearly observed at figure 4, where we plot the remission function of the irradiated slides. For comparative purposes the remission function of some of the non irradiated glass slides (1, 4, 6 and 10 layers of  $\text{TiO}_2$ ) are plotted (again in light gray) in this figure (to see all remission functions for non irradiated samples please refer to fig. 2b)).

With one layer of  $\text{TiO}_2$  and a neat concentration of soluble indigo blue dye of  $\sim 120 \mu\text{molg}^{-1}$ , a big decrease of the  $\text{TiO}_2$  absorption maxima was observed (reduction of

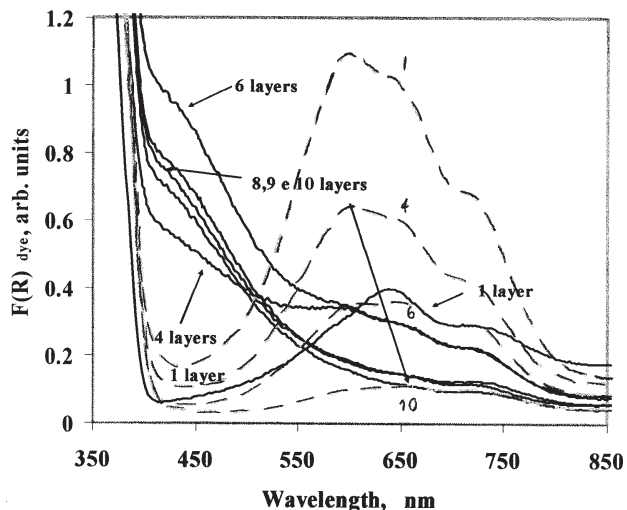


Fig. 4. Remission function from the  $\text{TiO}_2$  layers contaminated with a constant amount of  $1,2 \times 10^{-6}$  mole of soluble indigo blue dye after 6 hours of irradiation with a 125W mercury lamp (—). The number of layer of each curve is indicated in the curve. For comparative purposes the spectra of the non irradiated glass slides with 1, 4, 6 and 10 layers are also plotted in light gray (—)

~ 80 – 85 % on the remission function of the dye; based on the spectra measured for the non irradiated glass slides after contamination with  $1,2 \times 10^{-6}$  moles of the dye we can estimated that following irradiation the concentration decreased from ~  $120 \mu\text{molg}^{-1}$  to ~  $20 - 25 \mu\text{molg}^{-1}$ . For one layer no other spectral change was observed. However, for 4 layers of  $\text{TiO}_2$ , and for a neat concentration ~  $30 \mu\text{molg}^{-1}$  of soluble indigo blue, the decrease of the

absorption maxima of the soluble indigo blue at 600 nm, 650 nm and 720 nm is already accompanied by the appearance of the new absorption from 400 to 600 nm. For 6 layers (~  $20 \mu\text{molg}^{-1}$  of soluble indigo blue) the remission function for the wavelength maxima of the soluble indigo blue remain approximately constant but the absorption from 400 to 600 nm increases even more. This behaviour traduces the breakdown of the soluble indigo blue structure with the simultaneous formation of photodegradation products, which ones absorb at shorter wavelengths since they are smaller molecules. Finally for 8 to 10 layers, respectively with concentrations from ~  $3.7 \mu\text{molg}^{-1}$  to ~  $6.4 \mu\text{molg}^{-1}$ , we observed that the absorption in the dye region was minimal and the absorption from 400 to 600 nm reached approximately a constant value of remission function.

Figure 5 further presents the evaluation of the percentage reflectance, %R, (fig. 5a) and of the remission function,  $F(R)$ , (fig. 5b) of the irradiated samples at the most relevant wavelengths to following the photo-degradation process. The figure displays the spectral variations observed at the maxima of absorption of the dye, at ~ 600 nm, and at 420 - 430 nm, wavelength where the maximum absorption increase due to photoproducts formation was observed. For easier comparison the correspondent values for the non irradiated samples are plotted together in the same figure (in light grey). Although for the irradiated samples the behaviour of the dye under degradation (at ~ 600 nm) it is not as easy to follow as that of the non irradiated samples, it is always still possible to observe clearly that, for the smaller numbers of  $\text{TiO}_2$  deposited layers (from 1 to 5 or 6) there is a strong decrease of the dye absorption. For the higher number of layers, although the smaller values of  $F(R)$  observed either for

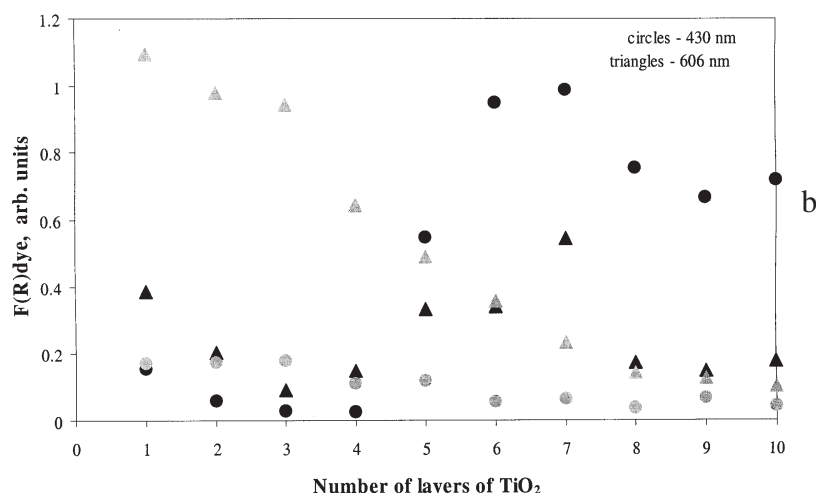
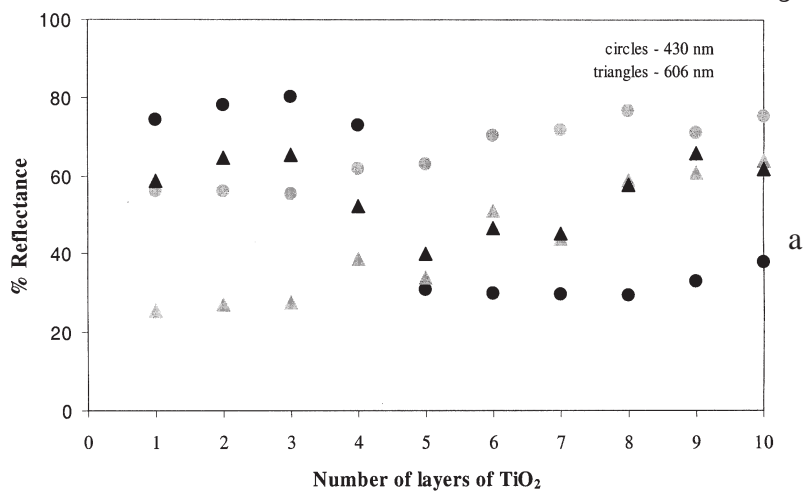


Fig. 5a) Percentage reflectance and b) remission function values at 430 nm (circles) and 606 nm (triangles) for the different number of  $\text{TiO}_2$  layers contamination with a constant amount of  $1,2 \times 10^{-6}$  mole of soluble indigo blue dye and after 6 hours of irradiation (closed symbols) with a 125W mercury lamp. The reference values for the non irradiated samples are plotted in light gray.



non irradiated or irradiated samples makes difficult to follow the dye behaviour, the continues decrease on the concentration of the dye adsorbed on the different coated TiO<sub>2</sub> layers following irradiation is very much evident from the variation of the percentage reflectance plotted in figure 5a. In what concerns the variations at 420 - 430 nm, traducing the formation of photodegradation products after irradiation of the glass slides, is clear from observation either of percentage reflectance or remission function curves for the different glass slides, that photoproducts formation it is not significant bellow five TiO<sub>2</sub> coated layers. For TiO<sub>2</sub> coated layers equal or higher than 6 photoproducts formation it is very significant. For 9 and 10 layers we could further observe a decrease on the photoproducts absorption. This result can indicate that for the higher number of coated TiO<sub>2</sub> layers also photodegradation products start already to be decomposed. However, the fact that the spectra of a certain irradiated sample result for the sum of dye spectra at its actual photodecomposition stage plus those of all the decomposition products being formed (and maybe also already being photodegraded), makes the analysis of the ground state absorption of the solid irradiated sample sometimes rather difficult. In fact, on the sample surface we have simultaneously products disappearing and others being formed. Although dye photodegradation usually takes place thought break down of the dye chromophore with the concomitant formation of smaller photodegradation products, which usually absorb at shorter wavelengths than those of the parent chromophore, frequently the lower edge of the absorption of the dye is superimposed with the upper edge or the absorption band of one or more of the photoproducts. For wavelengths where that happen, frequently it is extremely difficult to account for the accurate absorption of the dye, since we easily observe the formation of the photoproducts by the increase of their absorption but it is rather difficult to observe the photodegradation of the dye since the absorption of the later seems not to decrease as much as expected. So, in the present case these phenomena can be responsible, both for the apparent small decrease on the remission function of the soluble indigo blue dye for the higher numbers of layers, and for the apparent decrease on the amount of photoproducts absorbing in the 430 nm region. It may be that in the latter case, the photoproducts formed are approximately constant and that its apparent decrease comes from an effective decrease of the parent soluble indigo blue dye. This last hypothesis is further reinforced by the observation of a decrease of the remission function of the soluble indigo blue for 9 and 10 deposited layers.

The confirmation of each of the above mentioned hypothesis would require to repeat the experiments with longer irradiation times and/or to analyse the results with other complementary techniques of analysis. We also need to clarify if the apparent non formation of photoproducts observed for layer coating numbers equal or smaller to 5, simply traduces a smaller photodegradation ability of the coated TiO<sub>2</sub> layer, due to small amount of coated photocatalyst or if instead it traduces a different photodegradation pathway that directly leads to the mineralization of the soluble indigo blue dye with minimal photoproduct formation.

## Conclusions

In this work we investigated the effect and the efficiency of the number of TiO<sub>2</sub> layers deposited on glass slides on the degradation of a constant amount of soluble indigo blue dye. Glass coated TiO<sub>2</sub> layers showed to be extremely

efficient on soluble indigo blue degradation over an extended range of concentrations of the dye. Ground state diffuse reflectance showed once more to be particularly suitable for direct monitoring of photodegradation process on the glass coated TiO<sub>2</sub> surface.

*Acknowledgments: Equipment was financed by project Praxis/P/Qui/10023/98 and Praxis/P/Qui/10023/2004. L.F.V.F. and J.C.M. thank ICCTI/CAPES for past financial support. A.S.O. gratefully acknowledges Fundação para a Ciencia e Tecnologia for grant SFRH /BPD/26798/2006 and project PTDC/QUI/65510/2006. E.M.S. thanks PIBIC/FioCruz/CNPq and CAPES respectively for science initiation and master grants.*

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Manuscript received: 25.11.2010