

# Comparison of photocatalytic efficiencies of TiO<sub>2</sub> in suspended and immobilised form for the photocatalytic degradation of nitrobenzenesulfonic acids

Anita Rachel<sup>a</sup>, Machiraju Subrahmanyam<sup>b</sup>, Pierre Boule<sup>a,\*</sup>

<sup>a</sup> *Laboratoire de Photochimie Moléculaire et Macromoléculaire, Université Blaise Pascal, CNRS UMR 6505 (Clermont-Ferrand), F-63177 Aubière cedex, France*

<sup>b</sup> *Catalysis and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India*

Received 19 July 2001; received in revised form 25 November 2001; accepted 28 December 2001

## Abstract

The photocatalytic efficiency of TiO<sub>2</sub> immobilised on various supports (glass, cement, red brick and inorganic fibres), using different techniques (sputtering, sol–gel dip-coating, patented method for inorganic fibres), are compared with the photocatalytic efficiency of TiO<sub>2</sub> Degussa P25 in suspension 2 g l<sup>-1</sup>, for the degradation of 3-nitrobenzenesulfonic acid (3-NBSA) and 4-nitrotoluenesulfonic acid (4-NTSA). In all cases, the fixation of TiO<sub>2</sub> on solid supports appreciably reduces the photocatalytic efficiency. The best results were obtained with TiO<sub>2</sub> on inorganic fibres. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Photocatalytic efficiency; Titanium dioxide; TiO<sub>2</sub> immobilisation; 3-Nitrobenzenesulfonic acid; 4-Nitrotoluenesulfonic acid

## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) is a well known for its advantage as a photocatalyst. It has often been proposed for the elimination of organic pollutants [1,2]. Another advantage is its absence of toxicity. TiO<sub>2</sub> Degussa P25 is extensively used as a standard in photocatalysis, even though other types such as Hombikat and Millennium were also proposed. However, the use of aqueous suspensions limits practical applications because of problems of separation of fine particles of TiO<sub>2</sub> and the recycling of the photocatalyst. The micrometric size of particles makes it difficult to be separated from water after use, particularly with waste waters. Many techniques were proposed for the immobilisation of TiO<sub>2</sub> on solid supports to eliminate this problem. Most of the general methods are reported

in a recent review [3], but some practical techniques are protected by patents. Various supports were experimented in particular different classes of glass [3,4], quartz [5], silica, activated carbon [6], zeolites [6,7], etc. Glass fibres were also proposed [8]. Brezová et al. reported that commercial fiberglass covered with TiO<sub>2</sub> and suspended TiO<sub>2</sub> P25 have comparable activities for the photocatalytic transformation of phenol [9]. The activity of fiberglass decreases during repeated experiments and becomes significant after 20 h, but they can be regenerated [10].

Often the fixation of TiO<sub>2</sub> on solid supports reduces its efficiency due to various reasons (reduction of the active surface, a more difficult exchange with solution, introduction of ionic species [11], etc.) and a direct comparison of efficiency between suspensions and catalysts on support is not usually reported. Fernández et al. compared the efficiencies of TiO<sub>2</sub> on glass, on quartz and on stainless steel [11]. Quartz

\* Corresponding author.

gave better results but the comparison was not made with TiO<sub>2</sub> in slurry.

This work was carried out to develop photocatalysts that can be used to eliminate non biodegradable pollutants contained in waste waters after bio-treatment. The aim is to compare the efficiencies TiO<sub>2</sub> Degussa P25 in aqueous suspension and TiO<sub>2</sub> immobilised on inexpensive supports. Results obtained with several types of supports of commercial commodity, such as red brick and cement, are presented since supports such as quartz are not really appropriate for application in a sunlight photocatalytic plant for decontamination of waste waters. Commercial TiO<sub>2</sub> on inorganic fibres was also used for comparison. The study was carried out using benzenesulfonic acids as substrates since these compounds are by-products in dye industry and they are highly soluble in water [12]. A special attention is focused on the photocatalytic transformation of 3-nitrobenzenesulfonic acid (3-NBSA), which is chosen as a model compound, since it transforms very slowly in sunlight [13].

## 2. Materials and methods

### 2.1. Catalyst and reagents

Photocatalyst used as reference is Degussa P25, anatase/rutile ca. 70/30, surface area  $55 \pm 15 \text{ m}^2 \text{ g}^{-1}$ . Inorganic fibres coated with TiO<sub>2</sub> Degussa P25 were provided by Iover Saint-Gobain company. Because of confidentiality, they are reported as “TiO<sub>2</sub> on inorganic fibres”.

#### 2.1.1. Reagents for coating

Titanium(IV) isopropoxide 97%, titanium(IV) ethoxide, tech. and titanium diisopropoxide bis(acetylacetonate), 75 wt.% solution in 2-propanol, were provided by Sigma-Aldrich.

#### 2.1.2. Substrates

3-Nitrobenzenesulfonic acid sodium salt >95% (3-NBSA), Fluka; 4-Nitrotoluene-2-sulfonic acid dihydrate >90% (4-NTSA), TCI; Phenol 99.5%, Merck.

Water used for experiments was purified with Milli-Q system and its purity controlled by measurement of its resistivity (>18 MΩ cm).

#### 2.1.3. Supports

Several supports were used for the deposition of TiO<sub>2</sub>: common glass, borosil glass (“Pyrex”), red brick (with a plain surface) and white cement.

### 2.2. Methods adopted for TiO<sub>2</sub> immobilisation

The methods most commonly used for deposition of TiO<sub>2</sub> on supports are sputtering and sol-gel dip-coating or spin-coating (see, for example, [14–22]). Techniques used in the present work are given in detail below. Some other methods are patented and consequently not available in scientific literature. So, is the case for “TiO<sub>2</sub> on inorganic fibres” used in the present. Another method was used in the present study which consists of mixing TiO<sub>2</sub> (20–30%) with powdered white cement. Water was added to this mixture in order to form a paste which was then spread as a thin layer on a preformed round brick of cement (diameter 52 mm, thickness 5 mm). It may be noted that the introduction of such a cement brick in a dilute solution of 3-NBSA significantly increases the pH of the solution.

#### 2.2.1. Sputtering

The thin films of TiO<sub>2</sub> were spread by cationic sputtering with a radiofrequency (13.56 MHz) using a cold plasma (argon 98%, oxygen 2%) under a pressure equal to 0.2 Pa. Power of  $2.5 \text{ w cm}^{-2}$  used. It maintains the temperature below 70 °C. The amorphous layers were converted into anatase by calcination at 470 °C during 5 h. The conversion was controlled by XRD. Thickness was in the range 0.2–1 μm. Supports used were glass, red brick, white cement and ceramic tiles.

#### 2.2.2. Sol-gel dip-coating

Three methods were used. In the first one (preparation P<sub>1</sub>), titanium tetraisopropoxide (30 ml) was dissolved in isopropanol (200 ml). The mixture was stirred during 15 min and kept aside for half-hour period before use. For the second (P<sub>2</sub>), titanium tetraethoxide (18 g) was stirred with acetic acid (18 ml) and then 200 ml of ethanol/water mixture was added. The mixture was stirred half-hour and allowed to equilibrate overnight before use. In the third preparation (P<sub>3</sub>), titanium diisopropoxide bis(acetylacetonate) (24 ml) was mixed with isopropanol (171 ml) and

water 5 ml. The resulting yellow mixture was stirred for about 30 min and used immediately. In all cases, the film of TiO<sub>2</sub> was deposited by dip-coating. Its thickness depends on dip-withdrawal speed (usually 3.4 mm s<sup>-1</sup>) and by the number of cycles (3, 6 or 9). The samples were represented by the nature of the support (Gl for glass, Rb for red brick, Wh cem for white cement), the type of preparation used (P<sub>1</sub>, P<sub>2</sub> or P<sub>3</sub>) and the number of layers (L<sub>3</sub>, L<sub>6</sub> or L<sub>9</sub>). For example, Rb P<sub>1</sub>L<sub>6</sub> for six layers of preparation 1 on red brick. After dip-coating supports were dried at 100 °C during 12 h and calcined at 450 °C for 5 h to obtain the anatase form of TiO<sub>2</sub>. The thickness of the film obtained is in the range 0.1–1.0 μm [3].

Only some of the typical results obtained are reported here since the different methods used in dip-coating lead to results not significantly different.

### 2.3. Irradiation devices

The device used consists of two identical crystallizers (i.d. 53 mm) exposed to two fluorescent lamps Philips TLD 15 W/05. Three or four crystallizers can be exposed to UV light under similar conditions. The advantage of this device is not only the possibility of studying any kind of catalysts on any kind of support, but also catalysts in suspended form with the same flux of incident light. The flux of incident light was evaluated to be 3.4 × 10<sup>15</sup> photons cm<sup>-2</sup> s<sup>-1</sup> (i.e. 5.6 × 10<sup>-9</sup> einstein cm<sup>-2</sup> s<sup>-1</sup>) with chemical actinometry (potassium ferrioxalate).

The solid supports used for catalysts were most often cut as round disks (∅ 52 mm) consistent with the diameter of the crystallizers. The magnetic stirrer screened less than 3% of the surface. This effect was neglected. With TiO<sub>2</sub> on solid supports the magnetic stirrer was above the support. In the case of fibres, the layer of fibres was maintained on glass rods with the stirrer beneath it. Smaller supports may also be used. It may be necessary when it is difficult to cut a round disk, or in the case of soft catalysts to prevent from abrasion by magnetic stirrer. With supports smaller than the round disk (as it is with TiO<sub>2</sub> on glass), it may be assumed that light intensity received is proportional to the area and the rate of transformation may be normalised as

follows:

$$\text{standard rate} = \text{measured rate} \times \frac{\text{disk area}}{\text{support area}}$$

(disk area = 21.2 cm<sup>2</sup>)

In all cases initial volumes were 32 ml, which corresponds to 1.5 cm depth. Water evaporation is not negligible, but this concentration effect was easily eliminated by weighing before and after irradiation and making up the volume with pure water. It is worth noting that sampling (0.5–1.0 ml) does not modify photon flow received, but it is not negligible with respect to irradiated volume. It results a systematic modification of apparent kinetics, but this phenomenon is not a disadvantage for the comparison of initial transformation rate induced by different photocatalysts irradiated in the same conditions. In fact, the kinetics becomes more linear and this facilitates the determination of initial slope.

### 2.4. Analyses

Irradiated solutions were analysed by HPLC on a column C<sub>18</sub> using UV detection and methanol/water mixture of 40/60 v/v as the eluent. Tetrabutylammonium hydrogen sulfate (TBA) 10<sup>-2</sup> M was added to water in order to obtain a correct retention time. In the absence of it retention times are too short due to the ionic character of the substrates. Spectrophotometric titration was experimented, but results with this method were less precise.

## 3. Results and discussion

### 3.1. Direct phototransformation

The pK<sub>a</sub>'s of 3-NBSA and 4-NTSA were evaluated to be 1.6 using a conductometric method. In unbuffered solution 10<sup>-4</sup> M<sup>-1</sup> or less, 3-NBSA is in the anionic form. It absorbs UV light approximately up to 340 nm with a maximum at 260 nm (ε<sub>max</sub> ≈ 7500 M<sup>-1</sup> cm<sup>-1</sup>). In the same conditions 4-NTSA absorbs up to 360 nm with a maximum at 276 nm (ε<sub>max</sub> ≈ 8600 M<sup>-1</sup> cm<sup>-1</sup>). In spite of a significant overlap with sunlight spectrum, the phototransformation in sunlight was found to be negligible after one

week in October. The quantum yield of 3-NBSA was measured at 254 nm. It is in the range  $(0.6\text{--}2.0) \times 10^{-4}$  according to the method used [13,23]. It is consistent with values reported for 3-nitrophenol [24]. This low value is due to the electron-withdrawing effect of nitro group. Consequently, photocatalysis is useful for the elimination of 3-NBSA and 4-NTSA and these substrates were chosen to test supported photocatalysts.

### 3.2. Phototransformation with $\text{TiO}_2$ slurries

In order to evaluate the photonic efficiency of immobilised  $\text{TiO}_2$ , solutions of the same concentration ( $2 \times 10^{-5}$ ) of phenol, 3-NBSA and 4-NTSA were photocatalytically transformed using Degussa P25 in suspension  $2 \text{ g l}^{-1}$ . This value of  $\text{TiO}_2$  concentration was chosen after studying the influence of the concentration on the rate of transformation [13]. Phenol is transformed more rapidly than 3-NBSA and 4-NTSA. The relative photonic efficiency  $\zeta_r$  was defined by Serpone et al. by taking phenol as the reference [25]. It was evaluated to be 0.72 and 0.45 for 3-NBSA and 4-NTSA respectively. It reflects the fact that the rate constant of reaction of  $\bullet\text{OH}$  radicals with 3-NBSA [23] is significantly lower than with phenol [26].

### 3.3. Photocatalytic transformation of 3-NBSA on immobilised $\text{TiO}_2$

Several kinds of supports and deposition methods were used in order to select a technique that can be used in photocatalytic plants for depollution of waste waters.

#### 3.3.1. Sputtering

This technique was used on common glass, Pyrex glass, red brick and white cement. Photocatalytic effect was negligible in spite of formation of anatase as revealed by XRD. This may be due to the fact that the thin film formed on the surface has probably a low surface area and insufficient porosity for the adsorption of hydrophilic 3-NBSA. Hence, this technique is not appropriate for the utility of waste water treatment.

#### 3.3.2. $\text{TiO}_2$ mixed with cement

A layer consisting of a mixture cement/ $\text{TiO}_2$  was spread on a round cement brick as described in Section 2.2. Several percentages of  $\text{TiO}_2$ , 20%, 30% and 40%

were adhered on cement. The latter was given up since the layer was not sufficiently strong to be bound on the cement. With titanium dioxide P25 20% and 30%, we obtained 9% transformation in 12 h with a solution of 3-NBSA of  $2 \times 10^{-5}$  M. It is not negligible, but not better than the results of sol-gel dip-coating and the graph was not reported in Fig. 1, for simplification. It may be noted that the presence of cement significantly increases the pH of the solution. The drastic loss of efficiency (a factor of  $>200$  compared to slurry), cannot be attributed only to the reduction of active area, but the high concentration of ionic species in the support which probably contributes to recombination of charges in the photocatalyst leading to its deactivation.

#### 3.3.3. Sol-gel dip-coating deposition of $\text{TiO}_2$

Several methods were used for coating  $\text{TiO}_2$  on different supports. They are described in Section 2.2. Only some typical results are reported in Table 1, Figs. 1 and 2. It appears that the photocatalytic efficiency of photocatalysts obtained by coating on red brick (Rb) or white cement (Wh cem) is relatively low compared to slurries. It can be noted that preparation P<sub>1</sub> gave better results on red brick than on white cement and that the number of layers slightly increases the efficiency. On Wh cem, preparation P<sub>3</sub> gave better results than preparation P<sub>1</sub>, but this difference was not observed with red brick.

The most outstanding feature with dip-coating method is that photocatalytic activity is higher when glass is used as the support, than with red brick

Table 1  
Transformation rates of nitrobenzenesulfonic acids on suspended and immobilised  $\text{TiO}_2$  P25

Substrate	Catalyst	Initial transformation rate ( $10^{-5} \text{ M h}^{-1}$ )
Phenol	P25 (slurry)	6.3
3-NBSA	P25 (slurry)	4.5
Immobilised $\text{TiO}_2$ P25		
3-NBSA	Wh Cem P <sub>1</sub> L <sub>6</sub>	$\cong 0.01$
	Wh Cem P <sub>3</sub> L <sub>6</sub>	$\cong 0.02$
	Rb P <sub>1</sub> L <sub>6</sub> /Rb P <sub>1</sub> L <sub>9</sub>	0.02–0.03
	GIP <sub>3</sub> L <sub>3</sub>	0.074
	F <sub>1</sub> /F <sub>2</sub>	0.15–0.17
4-NTSA	P25 (slurry)	2.8
	Rb P <sub>1</sub> L <sub>6</sub> /Rb P <sub>2</sub> L <sub>6</sub>	$< 0.002$
	F <sub>2</sub>	0.18

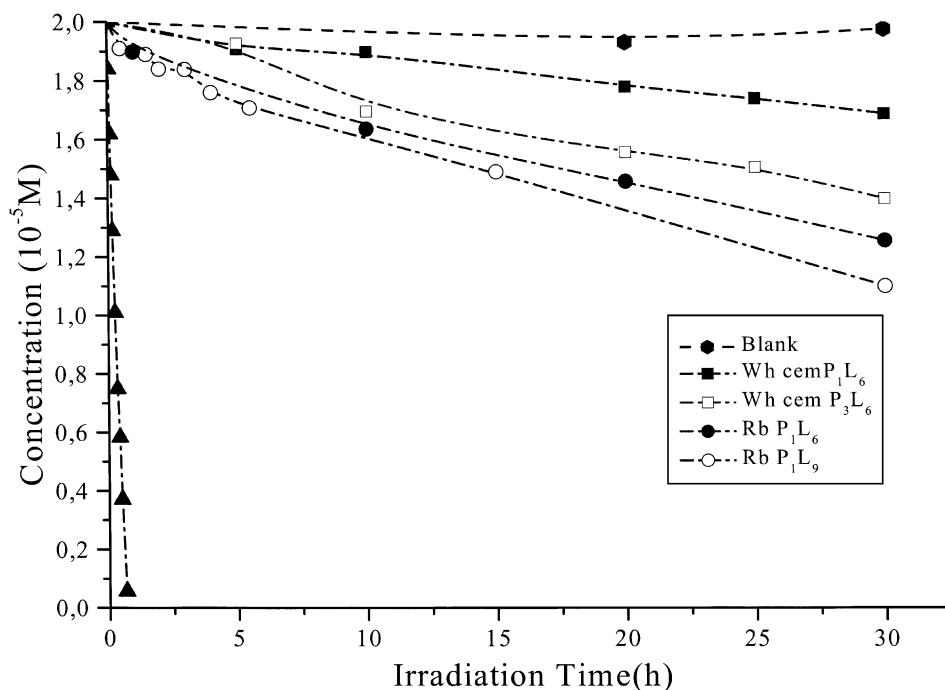


Fig. 1. Photocatalytic transformation of 3-NBSA with  $\text{TiO}_2$  on red brick and white cement (sol-gel technique) using the horizontal device: white cement with six layers of preparations 1 and 3 (Wh cem P<sub>1</sub>L<sub>6</sub> and Wh cem P<sub>3</sub>L<sub>6</sub>); red brick with six and nine layers of preparation 3 (Rb P<sub>1</sub>L<sub>6</sub> and Rb P<sub>1</sub>L<sub>9</sub>).

or cement, as it appears in Fig. 2. However, it can be noted that the coated glass sample was smaller ( $3.2 \text{ cm} \times 3.2 \text{ cm}$ ) than the other samples (disk  $\varnothing 5.2 \text{ cm}$ ) and for a quantitative comparison the amount of 3-NBSA transformed was standardized using the relation given in Section 2.2. For a more accurate comparison samples of the same size would be apt.

#### 3.3.4. Titanium dioxide on inorganic fibres

Inorganic fibres coated with  $\text{TiO}_2$  provided by Iover Saint-Gobain were used under similar conditions as the other catalysts in the horizontal device, with the difference that the layer(s) of fibres was (were) maintained at mid-height in the solution. With one layer the phototransformation of 3-NBSA ( $2 \times 10^{-5} \text{ M}$ ) was significantly higher than with all the supports previously used, but the initial rate of transformation is of course lower than with P25 slurry  $2 \text{ g l}^{-1}$ . Kinetics of transformation are reported in Fig. 2 and initial rate constants in Table 1. Two different samples fibres F<sub>1</sub> and F<sub>2</sub> correspond to different

fabrications. The second generation gave slightly better results, but the difference was not really meaningful. Most surprisingly, the use of two layers of fibres did not improve the efficiency of the photocatalytic transformation. This phenomenon may tentatively be explained by the fact that the first layer transmits less than 30% of incident light. Consequently, the second layer receives only a little proportion of light, but it reduces of convection current in the crystalliser and chemical exchanges at the surface of the photocatalyst.

Earlier literature reported a decrease of photocatalytic activity of  $\text{TiO}_2$  on glass fibres [10]. In order to observe if this phenomenon occurs with the present experimental conditions, a solution of 3-NBSA  $2 \times 10^{-5} \text{ M}$  was subjected to photocatalytic transformation with  $\text{TiO}_2$  on inorganic fibres provided by Iover Saint-Gobain for a period of 4.5 h and the initial transformation rate was measured. Then the same sample of fibres was used for the transformation of 3-NBSA  $10^{-3} \text{ M}$ . After 58 h, the catalyst was re-used on a solution  $2 \times 10^{-5} \text{ M}$ . The transformation rate was

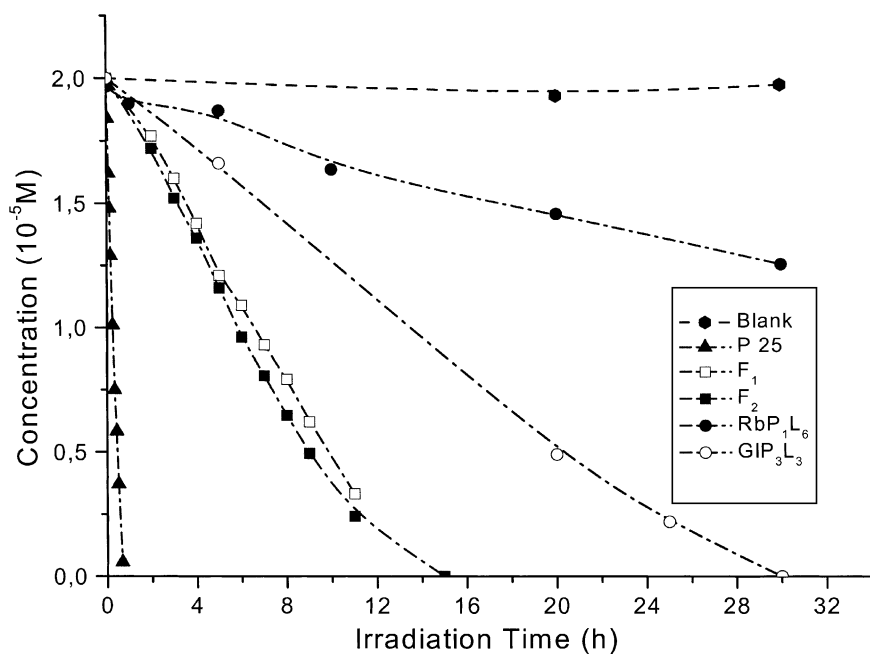


Fig. 2. Comparative photocatalytic transformation rates of 3-NBSA ( $2 \times 10^{-5} \text{M}$ ) with  $\text{TiO}_2$  P25 (slurry  $2 \text{g l}^{-1}$ );  $\text{TiO}_2$  on inorganic fibres (one layer of fibres F<sub>1</sub> and F<sub>2</sub>); red brick coated by sol-gel dip-coating method (six layers with preparation 1: Rb P<sub>1</sub>L<sub>6</sub>); glass with three layers of preparation 1 (GI P<sub>2</sub>L<sub>3</sub>), sample smaller, results normalised.

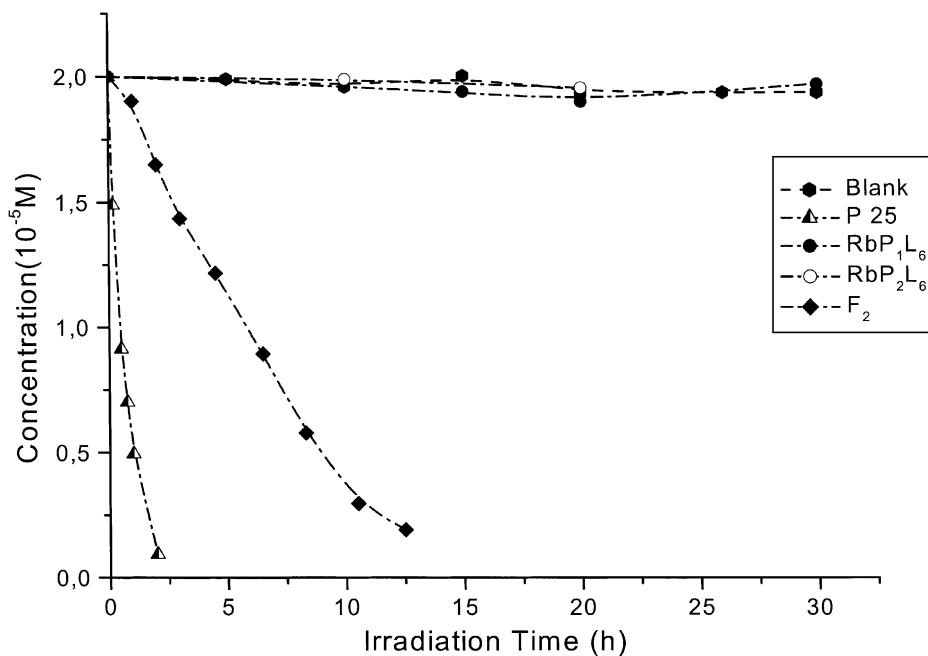


Fig. 3. Comparative photocatalytic transformation rates of 4-NTSA with  $\text{TiO}_2$  (slurry  $2 \text{g l}^{-1}$ ),  $\text{TiO}_2$  on inorganic fibres (F<sub>2</sub>) and coated red bricks (Rb P<sub>1</sub>L<sub>6</sub> and Rb P<sub>2</sub>L<sub>6</sub>).

found to be the same as before. It can be deduced that this photocatalyst maintains a good efficiency for the transformation of benzenesulfonic acids even after repetitive usage. It may be due to the absence of the accumulation of photoproducts on the its surface.

### 3.4. Photocatalytic transformation of 4-NTSA

The efficiencies of immobilised TiO<sub>2</sub> were also compared using 4-NTSA as the substrate. Most representative results are reported in Fig. 3 and Table 1. They are not much different from the results obtained with 3-NBSA. It confirms that TiO<sub>2</sub> on inorganic fibres is significantly more efficient than with bricks coated by sol-gel dip-coating technique.

## 4. Conclusions and perspectives

Direct photolysis of 3-NBSA and 4-NTSA is very low in spite of their absorption in UV range. The low quantum yield obtained for 3-NBSA is consistent with values obtained with nitrophenols. It may be attributed to the electron-withdrawing property of NO<sub>2</sub> group.

The photocatalytic activity of TiO<sub>2</sub> sputtered on glass or red brick is very low in spite of its anatase structure obtained by calcination. It might be due to a low surface area.

The fact that TiO<sub>2</sub>-cement mixture and TiO<sub>2</sub> spread on red brick or cement by sol-gel dip-coating method are significantly less efficient than TiO<sub>2</sub> slurries, cannot be attributed only to the reduction of the active surface, but also to the presence of ionic species that contribute to the charge recombination. Experiments will be carried out to improve the method of dip-coating by calcination after every layer.

At the present time, the best results were obtained with TiO<sub>2</sub> on inorganic fibres. The efficiency is not significantly increased by using several layers. It remained constant even after repetitive uses for the transformation of 3-NBSA.

The extension work of TiO<sub>2</sub> immobilisation to other kinds of support is in progress.

## Acknowledgements

The authors greatly acknowledge Indo-French Centre for Promotion of Advanced Research (IFCPAR)/

Centre Franco-Indien pour la Promotion de la Recherche Avancée (CEFIPRA) for its financial support (contract no. IFC/2205-2). They thank Isover Saint-Gobain for coated inorganic fibres. They are also very grateful to Dr. C. Guillard for her skillful assistance in sol-gel dip-coating and for helpful discussions. They are indebted to J. Cellier and M. Jacquet (University Blaise Pascal, Clermont-Ferrand) for sputtering TiO<sub>2</sub> on inorganic supports, for thermal treatment and for XRD analysis of some samples.

## References

- [1] D.F. Ollis, E. Pelizzetti, N. Serpone, in: N. Serpone, E. Pelizzetti (Eds.), *Photocatalysis Fundamentals and Applications*, Wiley, New York, 1989, pp. 603–637.
- [2] D. Bahnemann, in: P. Boule, O. Hutzinger (Eds.), *Environmental Photochemistry, The Handbook of Environmental Chemistry*, Springer, Berlin, 1999, pp. 285–351.
- [3] R.L. Pozo, M.A. Baltanás, A.E. Cassano, *Catal. Today* 39 (1997) 219–231.
- [4] N. Serpone, E. Borgarello, R. Harris, P. Cahill, M. Borgarello, *Solar Energy Mater.* 14 (1986) 121–127.
- [5] J.-M. Herrmann, Y. Tahiri, Y. Ait-Ichou, G. Lassaletta, A.R. González-Elipse, A. Fernández, *Appl. Catal. B: Environ.* 13 (1997) 219–228.
- [6] T. Torimoto, S. Ito, S. Kuwabata, H. Yoneyama, *Environ. Sci. Technol.* 30 (1998) 1275–1281.
- [7] M.A. Fox, K.E. Doan, M.T. Dulay, *Res. Chem. Intermed.* 20 (1994) 711–722.
- [8] M. Murabayashi, K. Itoh, S. Kuroda, R. Huda, R. Masuda, W. Takahashi, K. Kawashima, *Denki Kagaku* 8 (1992) 741.
- [9] M. Mikula, V. Brezová, L. Ceppan, L. Pach, L. Karpinský, *J. Mater. Sci. Lett.* 14 (1995) 615–616.
- [10] V. Brezová, A. Blazková, M. Breznan, P. Kottás, M. Ceppan, *Collect. Czech. Chem. Commun.* 60 (1995) 788–794.
- [11] A. Fernández, G. Lassaletta, V.M. Jiménez, A. Justo, A.R. González-Elipse, J.-M. Herrmann, H. Tahiri, Y. Ait-Ichou, *Appl. Catal. B: Environ.* 7 (1995) 49–63.
- [12] *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Edition, Vol. 17A, 1991, pages 440 and 442.
- [13] A. Rachel, M. Sarrakha, M. Subrahmanyam, P. Boule, *Appl. Catal. B: Environ.*, in press.
- [14] N. Negishi, K. Takeuchi, T. Ibusuki, *Appl. Surf. Sci.* 121/122 (1997) 417–420.
- [15] K. Kato, A. Tsuzuki, H. Taoda, Y. Torii, T. Kato, Y. Butsugan, *J. Mater. Sci.* 29 (1994) 5911–5915.
- [16] S. Sato, H. Koshihara, H. Minakami, N. Kakuta, A. Ueno, *Catal. Lett.* 26 (1994) 141–147.
- [17] Y. Takahashi, Y. Matsuoka, *J. Mater. Sci.* 23 (1988) 2259–2266.
- [18] P. Sawunyama, A. Yasumori, K. Okaba, *Mater. Res. Bull.* 33 (1998) 795–801.

- [19] R. Camprostrini, G. Carturan, L. Palmisano, M. Schiavello, A. Sclafani, *Mater. Chem. Phys.* 38 (1994) 277–283.
- [20] H. Tada, M. Tanaka, *Langmuir* 13 (1997) 360–364.
- [21] Y. Takahashi, Y. Matsuoka, *J. Mater. Sci. Lett.* 32 (1988) 2259–2266.
- [22] D. Robert, J.V. Weber, *J. Mater. Sci. Lett.* 18 (1999) 97–98.
- [23] A. Rachel, P. Mazellier, J. De Laat, in preparation.
- [24] A. Alif, P. Boule, J. Lemaire, *J. Photochem. Photobiol. A: Chem.* 50 (1990) 331.
- [25] N. Serpone, G. Sauvé, R. Koch, H. Tahiri, P. Pichat, P. Piccinini, E. Pelizzetti, H. Hidaka, *J. Photochem. Photobiol. A: Chem.* 94 (1996) 191–203.
- [26] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.