

## Use of porous lavas as supports of photocatalysts

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### Abstract

Porous lavas, more precisely pumice stone, are promising supports for TiO<sub>2</sub> used as a photocatalyst. TiO<sub>2</sub> deeply penetrates into pores that favours its retention. Its deposition is convenient and facile and the photocatalytic activity is not significantly affected by the erosion of the surface. The immobilization of TiO<sub>2</sub> on pumice stone gave better results for the photocatalytic degradation of 3-nitrobenzenesulfonic acid than conventional sol–gel dip-coating on cement and red brick. A layer of pumice stone as pellets, fixed on a cement layer and impregnated with TiO<sub>2</sub> is used in a thin film fixed bed reactor, for the photocatalytic treatment of water. © 2002 Published by Elsevier Science B.V.

*Keywords:* Immobilized photocatalyst; Pumice stone; Volvic lava; Nitrobenzenesulfonic acids

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### 1. Introduction

Photocatalysis is often proposed for the elimination of biorecalcitrant organic pollutants from waste waters. Titanium dioxide has the advantage of its absence of toxicity and low price. Its efficiency in suspension is widely recognized, but its use is limited by the necessity to separate it after treatment. To eliminate this problem many solutions were proposed for its immobilization [1]. Some methods are patented for instance the

deposition of TiO<sub>2</sub> on glass for self-cleaning window panes or mirror [2a,3], deposition on tiles for the elimination of bad smells and atmospheric pollutants [2b,2c,4], deposition on inorganic fibres for photocatalytic air-cleaning [5]. The technique most commonly proposed for the immobilization of TiO<sub>2</sub> is sol–gel, either dip-coating or spin-coating using organic Ti<sup>IV</sup> derivatives, often alcoholates (see for example [6–11]), but generally immobilization drastically reduces the efficiency of the photocatalyst. With some supports such as red brick and cement this deactivation may be partly attributed to the high superficial ionic concentration [12]. Anchoring TiO<sub>2</sub> may also be used but on flat supports such as glass where the layer is very thin and not very stable.

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The present paper is focused on the use of porous supports, that have a good retention of  $\text{TiO}_2$  without reducing too much the photocatalytic activity. Pumice stone is a particularly promising support because of its high porosity and its neutral pH.

## 2. Experimental

### 2.1. Reagents and materials

$\text{TiO}_2$  used as slurry or spread on supports was Degussa P25 (anatase:rutile 70:30, BET surface area  $\approx 55 \text{ m}^2 \text{ g}^{-1}$ ), various supports were used in particular pumice stone and Volvic lava. Pumice stone was provided by two firms Prolabo and Eyraud S.A. (Lyon, France). It is available as pellets or small pieces (maximum dimension about 10 cm). Volvic lava was provided as slices  $40 \times 20 \times 1 \text{ cm}^3$  by Mallet S.A. (Volvic, France). Other photocatalysts were used for comparison:  $\text{TiO}_2$  coated on solid supports (red brick and white cement) by sol-gel dip-coating method. For this method several  $\text{Ti}^{\text{IV}}$  alcoholates provided by Sigma-Aldrich were used:  $\text{Ti}^{\text{IV}}$  tetraisopropoxide and  $\text{Ti}^{\text{IV}}$  diisopropoxide bis(acetylacetonate), 75% solution in 2-propanol.

Substrates were 3-nitrobenzenesulfonic acid sodium salt > 95% (3-NBSA) Fluka and 4-nitrotoluene-2-sulfonic acid dihydrate > 90% (4-NTSA) TCI.

Water was purified by Milli-Q system and controlled by its resistivity (> 18  $\text{M}\Omega \text{ cm}$ ).

### 2.2. Irradiation devices

Two different devices were used for the comparison of photocatalysts: stirred crystalliser (D1) and thin film fixed bed reactor (D2). D1 consists of a crystalliser (i.d. 53 mm) covered with a Pyrex watch glass and exposed to UV light with two lamps TLD 15W/05 emitting between 300 and 450 nm. Irradiations were carried out in crystallisers containing either suspended photocatalyst or photocatalyst dispersed on solid support (disk  $\phi$  52 mm, area  $21 \text{ cm}^2$ , or smaller) with 32 ml of solution which was magnetically stirred. Most of-

ten 2 or 3 crystallizers were irradiated at the same time. In spite of the presence of watch glass evaporation of water was not negligible. To correct this effect crystallisers were weighed before and after irradiation and water was added to make up weight. For every sampling about 1 ml of solution was taken off and filtered for HPLC analysis. This volume is not negligible compared to the initial volume whereas the photon flow remains constant. Consequently, the disappearance of the substrate does not exactly obey a first order kinetics, but it does not matter for the comparison of photocatalysts. The photon flow was evaluated at  $5.6 \times 10^{-9} \text{ einstein cm}^{-2} \text{ s}^{-1}$  with chemical actinometry (potassium ferrioxalate).

Device D2 consists of a detachable rectangular slanting plank ( $40 \times 20 \text{ cm}^2$ ). Solutions were circulated with a peristaltic pump (flow  $35 \text{ ml min}^{-1}$ ). Irradiated samples were collected at the bottom of the tank. Supported catalyst may be covered with a glass pane to limit the evaporation. It can be irradiated either in UV light with four lamps TLD 15W/05 (300–450 nm) or in sunlight. Therefore it is possible to compare the efficiencies by both types of irradiations. This device can be easily extended to larger scale operation.

Some sunlight irradiations were also carried out in Clermont-Ferrand (latitude  $46^\circ \text{ N}$  altitude 420 m) in July. Temperature was relatively high ( $25\text{--}30^\circ$  in the shade).

### 2.3. Photocatalyst preparation

Several methods were used for the immobilization of  $\text{TiO}_2$ .

#### 2.3.1. Sol-gel dip-coating on red brick or cement

Two methods were used involving  $\text{Ti}^{\text{IV}}$  tetraisopropoxide (preparation  $\text{P}_1$ ) or  $\text{Ti}^{\text{IV}}$  diisopropoxide bis(acetylacetonate) (preparation  $\text{P}_2$ ), respectively. With the former  $\text{Ti}^{\text{IV}}$  tetraisopropoxide (30 ml) was dissolved in isopropanol (200 ml). The mixture was stirred during 15 min and kept for equilibration during half an hour before use. With the latter the commercial solution of  $\text{Ti}^{\text{IV}}$  diisopropoxide bis(acetylacetonate) (24 ml) was mixed with isopropanol (171 ml) and water (5 ml), stirred for 30 min and used immediately. The

thickness of the film was controlled by the withdrawing speed and the number of cycles (usually 6 or 9). Then the coated supports were dried overnight at 100 °C and calcined during 5 h at 450 °C to obtain the anatase form of TiO<sub>2</sub>.

### 2.3.2. Immobilization of TiO<sub>2</sub> on pumice stone and Volvic lava

A slurry of TiO<sub>2</sub> 20–100 g l<sup>-1</sup> was prepared and sonicated in order to improve the dispersion of TiO<sub>2</sub> in water. This slurry was impregnated on a slice of pumice stone 16.3 cm<sup>2</sup> or Volvic lava 14.0 cm<sup>2</sup> with a brush. The coated support was then subjected to reduced pressure ( $\cong$  100 mbar), for approximately 1 min in a container connected to a vacuum line to eliminate air from pores and improve the penetration of slurry on putting back under atmospheric pressure, but it is not absolutely necessary. With light slurry (20 g l<sup>-1</sup>), TiO<sub>2</sub> slurry was impregnated twice on the support. Then it was dried overnight at 100 °C, washed with water in order to eliminate unfixed TiO<sub>2</sub>. After this, it was dried once again and used as photocatalyst.

In the case of thin film fixed bed reactor a sheet of Volvic lava (40 × 20 cm<sup>2</sup>) was specially cut and coated with TiO<sub>2</sub> P25. The procedure is as described above for pumice stone. Unfortunately it was not possible to obtain a pumice stone that is large enough with an even surface. Hence a layer of pumice stone as pellets was fixed on a bed of white cement. In this purpose pellets of pumice stone (80–85 g) were spread on fresh cement layer (40 × 20 cm<sup>2</sup>) before its hardening, but pellets can also be fixed using an inorganic binder. Pumice pellets were impregnated with a slurry of TiO<sub>2</sub> (6 g in 60 ml water). The impregnation may be improved by using reduced pressure, as indicated before. After drying the support was washed to eliminate the excess of TiO<sub>2</sub> and dried again.

Another technique was also used: a sheet (40 × 20 cm<sup>2</sup>) of sliced pumice stone (approximate dimensions of each slice 5 cm) was assembled together (patch) on a cement layer impregnated with TiO<sub>2</sub> slurry and used in the thin film fixed bed reactor (D2).

Besides free pellets of pumice stone (150 g) were also impregnated with TiO<sub>2</sub> slurry (25 g l<sup>-1</sup>) with

similar technique and used for photocatalytic transformation of a solution of 3-NBSA contained in the tank of device D2 after removing the plank.

### 2.4. Analyses

After irradiation, suspensions and solutions were analysed by HPLC using a C<sub>18</sub>, 5  $\mu$ , 250 × 4.6 mm<sup>2</sup> column with a mixture water/methanol 40/60 v/v as the eluent. Tetrabutylammonium hydrogen sulfate (TBA) 10<sup>-2</sup> M was added to water to obtain a good separation (in the absence of TBA the retention time should be too short because of the ionization of substrates such as benzenesulfonic acids).

## 3. Results

### 3.1. Substrates

The pK<sub>a</sub> of 3-nitrobenzenesulfonic acid (3-NBSA) and 4-nitrotoluene-2-sulfonic acid (4-NTSA) was evaluated at 1.6 [12]. It means that in unbuffered solution 2 × 10<sup>-4</sup> M or less the molecular form can be neglected. Both substrates absorb approximately up to 350 nm with a maximum at 261 nm for 3-NBSA and 276 nm for 4-NTSA. In the absence of photocatalyst the direct photolysis is negligible after a few hours. It is attributed to a very low quantum yield. Actually the quantum yield was evaluated to be 6 × 10<sup>-5</sup> for 3-NBSA. It is consistent with value 2.0 × 10<sup>-4</sup> obtained using different method [13] and with the values published for 3-nitrophenol [14].

### 3.2. Preliminary study

In the first step pellets of pumice stone were impregnated with TiO<sub>2</sub> by immersion in a sonicated slurry (about 50 g l<sup>-1</sup>) and drying. About 3.3 g of these pellets with 32 ml of a solution of 3-NBSA 2 × 10<sup>-5</sup> M was irradiated in the device D1 (stirred crystalliser). It was observed that the photocatalytic transformation was almost as rapid as in the case of a suspension of TiO<sub>2</sub> 2 g l<sup>-1</sup>. It was previously controlled that disappearance by

adsorption on the catalyst is negligible and that no transformation occurs in the dark during the same time. No photoproducts were detected in treated solutions. Unfortunately the stirrer induced the erosion of pellets and the solution became blurred. The experiment was repeated after washing and it was noted that the photocatalyst had almost the same efficiency even after about 20% erosion. This interesting property is attributed to the fact that pumice stone has a high porosity and  $\text{TiO}_2$  deeply penetrates inside, that is not the case with common supports. Several methods were tested to reduce or eliminate the problem of erosion of the support:

- (i) to use a block (slice) of pumice stone with lateral stirring in the same device,
- (ii) to use an irradiating device without stirring but with a gentle flow of solution on the supported catalyst (device D2),
- (iii) to replace pumice stone by a hard support, for example Volvic lava. It is quite hard enough but presents only superficial pores.

### 3.3. Comparison of the efficiencies of $\text{TiO}_2$ on different supports

A slice of pumice stone  $16.3 \text{ cm}^2$  coated with  $\text{TiO}_2$  as described in Section 2.3.2 was irradiated in device D1 in the presence of 3-NBSA  $2 \times 10^{-5} \text{ M}$  (Fig. 1). The magnetic stirrer was placed on the side to prevent from erosion of the catalyst. The transformation was complete after about 8 h irradiation. For comparison a solution of the same concentration was irradiated in the presence of  $2 \text{ g l}^{-1}$  of  $\text{TiO}_2$  powder, in the presence of disks of red brick or white cement coated by dip-coating method (6 layers). The transformation rate was slower on pumice stone than with the suspension, as it appears in Fig. 1, but it is much faster than with disks of red-brick or cement, whatever the method used, in spite of the smaller size of pumice stone ( $16.3 \text{ cm}^2$  compared to  $21 \text{ cm}^2$ ). Similar results were obtained with  $\text{TiO}_2$  on Volvic lava. The rate of disappearance was a bit slower than with pumice stone, but the size was only  $14.0 \text{ cm}^2$ .

To be really useful a photocatalyst has to be recycled many times. To control the stability and

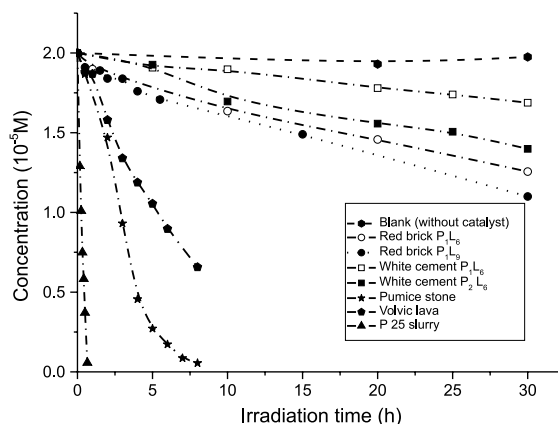


Fig. 1. Photocatalytic transformation of 3-NBSA in solution  $2 \times 10^{-5} \text{ M}$  on various supports: red brick ( $21 \text{ cm}^2$ ) dip-coated (6 and 9 layers) with  $\text{Ti}^{\text{IV}}$  tetraisopropoxide ( $\text{P}_1\text{L}_6$  and  $\text{P}_1\text{L}_9$ ); white cement ( $21 \text{ cm}^2$ ) dip-coated (6 layers) with  $\text{Ti}^{\text{IV}}$ , tetraisopropoxide and  $\text{Ti}^{\text{IV}}(\text{P}_1\text{L}_6)$  diisopropoxide bis(acetylacetonate) ( $\text{P}_2\text{L}_6$ );  $\text{TiO}_2\text{P}25$ , pumice stone ( $16.3 \text{ cm}^2$ );  $\text{TiO}_2 \text{P}25$ , Volvic lava ( $14.0 \text{ cm}^2$ );  $\text{TiO}_2 \text{P}25$ , slurry  $2 \text{ g l}^{-1}$ .

the efficiency of  $\text{TiO}_2$  on pumice stone and on Volvic lava, the rate of transformation of a solution of 3-NBSA  $2 \times 10^{-5} \text{ M}$  were compared before and after a 10-days use with a solution  $10^{-3} \text{ M}$ . In fact the solution  $10^{-3} \text{ M}$  was completely transformed after 5 days with  $\text{TiO}_2$  on pumice stone and after 6 days with  $\text{TiO}_2$  on Volvic lava. After this long irradiation the efficiency of  $\text{TiO}_2$  on pumice stone was only slightly reduced. It was a little more affected with Volvic lava. This difference may be attributed to a better retention of  $\text{TiO}_2$  on pumice stone which is a more porous material. A more precise study of this evolution is in progress with the device D2 (slanting plank), since stirring is not sufficiently reproducible with the device D1.

Experiments were also carried out with 4-NTSA ( $2 \times 10^{-5} \text{ M}$ ) as the substrate (Fig. 2). Similar results were obtained for the transformation on pumice stone even after a continuous usage with higher concentration for 10 days. The lower efficiency of  $\text{TiO}_2$  on Volvic lava compared to previous experiment is attributed to the fact that Volvic lava was used for several experiments in between. This effect was not prominent with pumice stone.

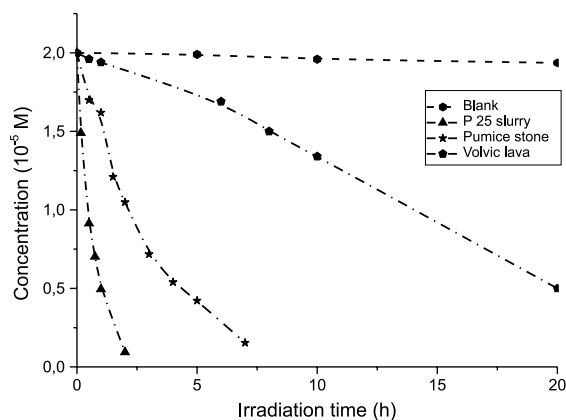


Fig. 2. Photocatalytic degradation of 4-NTSA ( $2 \times 10^{-5}$  M) on various supports: TiO<sub>2</sub> P25, pumice stone (16.3 cm<sup>2</sup>); TiO<sub>2</sub> P25, Volvic lava (14.0 cm<sup>2</sup>); TiO<sub>2</sub> P25, slurry 2 g l<sup>-1</sup>.

### 3.4. Thin film fixed bed reactor

The device used is described in Section 2.2. A solution of 3-NBSA ( $2 \times 10^{-5}$  M, 300 ml for UV irradiation, 350 ml for solar radiation) was allowed to flow gently at the top of the sloping sheet of Volvic lava coated with TiO<sub>2</sub> P25. The sheet was specially cut for this purpose. It was irradiated in artificial UV light 300–450 nm and in natural sunlight. In both cases the wavelength range was limited to  $\lambda > 310$  nm by a glass cover which was used to reduce evaporation. Hence it is possible to compare the efficiency for both the types of irradiations with the same device. The solution was completely transformed after 5 h in artificial UV light and after only 3 h in sunlight (July, bright sun).

Similar experiment was carried out with a layer of white cement of same dimensions covered with pumice stone in the form of pellets impregnated with TiO<sub>2</sub> P25 as explained before. However, the volume of treated solution was higher (400 ml) since the retention of solution on support was significant (about 200 ml). After 4 h the solution was 80% transformed in artificial UV light (Fig. 3) and completely transformed in bright sunlight. It can be concluded that with both supports the transformation is more rapid in summer time sunlight than with the indoors irradiation device. The rate of transformation was found to depend

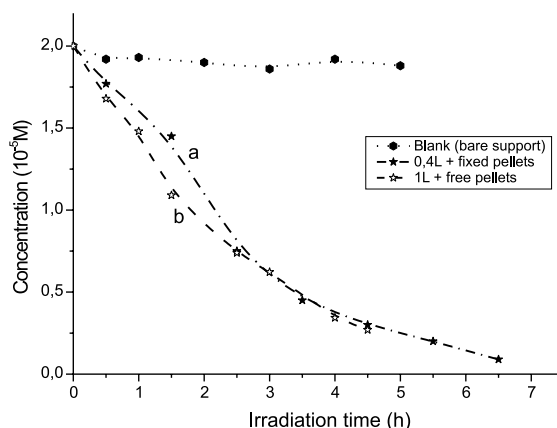


Fig. 3. Kinetics of photocatalytic transformation of 3-NBSA ( $2 \times 10^{-5}$  M) on TiO<sub>2</sub> on pumice stone. Irradiation in UV light (300–450 nm): (a) 400 ml solution treated with 80 g impregnated pellets immobilized on a slanting plank; (b) 1000 ml solution treated with 150 g free impregnated pellets of pumice stone.

on the size of pellets. It is higher with 2–3 mm than with 4–5 mm

Experiments were also performed on pumice stone in different mode of fixation with a solution of 3-NBSA  $2 \times 10^{-5}$  M l<sup>-1</sup>. Similar kinetics of transformation were obtained for 0.4 l of solution on the slanting plank and for 1 l with free pellets of pumice stone (150 g) impregnated with TiO<sub>2</sub> and irradiated at the bottom of the tank after removing the slanting plank (Fig. 3). The disadvantage of using unfixed pellets is that pellets settle toward one side of the device and there is a possible erosion due to friction. Larger pieces of pumice stone used in patch did not give better results than pellets of pumice stone fixed on cement layer. It was deduced that the fabrication of the patchwork, which is quite complicated, has no real advantage compared to pellets fixed on cement layer.

For comparison the device D2 with slanting plank was used for the photocatalytic transformation of phenol. Solutions  $2 \times 10^{-4}$  M and  $2 \times 10^{-5}$  M (500 ml) were completely transformed after 0.5 h in sunlight. It was controlled with the solution  $2 \times 10^{-5}$  M that the concentration stay unchanged when the bare support was exposed during the same time.

#### 4. Discussion

Pumice stone has a good retention for  $\text{TiO}_2$  due to its deep pores.  $\text{TiO}_2$  immobilized on pumice stone is more active than  $\text{TiO}_2$  fixed on cement and brick by sol–gel dip-coating method. It may be noted that dip-coating method could be improved by calcination between every layer, but then the procedure is quite time consuming. The activity of  $\text{TiO}_2$  on pumice stone is attributed to the fact that this support is neutral and does not contain high concentrations of ions as in the case of expanded cement tested for comparison. Other advantages: its coating with  $\text{TiO}_2$  is simple, easy, it does not involve any patented process and it does not introduce toxic by-products in solution. Unfortunately it is soft and not available in large enough surface. However, this problem can be eliminated by using a gentle flow of the solution to be treated on a fixed layer of pumice stone as pellets which are impregnated with  $\text{TiO}_2$ .

With hard supports, as Volvic lava, the photochemical efficiency is initially almost the same, but when the solution of pollutant is vigorously stirred some of superficial  $\text{TiO}_2$  is released and the activity decreases. Since the porosity is much lower than with pumice stone the residual photocatalytic efficiency is reduced. In order to maintain the same efficiency during a longer time gentle flow of solution on slanting plank can be used.

3-NBSA and 4-NTSA are photocatalytically transformed more slowly than phenol for two possible reasons: (i) the rate constant of reaction of 3-NBSA with  $^\circ\text{OH}$  is about 10-times less than with other benzenesulfonic acids [13]; (ii) the adsorption of 3-NBSA and 4-NTSA on  $\text{TiO}_2$  is very low due to their high solubility.

#### 5. Conclusion

Pumice stone is a promising porous support for the immobilization of  $\text{TiO}_2$ . It has a good retention and the photocatalytic efficiency is only slightly reduced after use during several days. (A more precise study of the evolution is in progress.) It can be used for different kinds of  $\text{TiO}_2$ , particularly for doped catalysts, since the immobiliza-

tion does not involve any thermal treatment. An appropriate device is proposed to take into account the softness of pumice stone and the fact that it is not available in large enough size with even surface. It consists in a slanting plank with a layer of pumice stone in pellets impregnated with  $\text{TiO}_2$ , the solution being gently spread at the top.

A harder porous support such as Volvic lava can also be used, but the long term retention of  $\text{TiO}_2$  is not so good and a decrease of photocatalytic efficiency is expected with solutions that are vigorously stirred. This disadvantage can be also eliminated by using a gentle flow of solution on a slanting plank.

The study of some other porous supports is programmed.

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