

Comparison of several titanium dioxides for the photocatalytic degradation of benzenesulfonic acids

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Abstract

The photocatalytic efficiency of several TiO₂ (namely Degussa P25 and Millennium PC50, PC100, PC105, PC500) used as suspensions are compared for the photocatalytic degradation of 3-nitrobenzenesulfonic acid (3-NBSA) and 2,5-anilinedisulfonic acid (2,5-ADSA). With 3-NBSA, P25 is clearly the most efficient and there is no apparent relationship between photocatalytic activity and specific surface area. This result is consistent with that obtained with phenol, but a contrast was noticed with 2,5-ADSA where PC500 is more efficient than P25 in spite of a higher adsorption of the latter. In the case of TiO₂ Millennium relative photonic efficiencies ζ_r are smaller with 3-NBSA than with 2,5-ADSA, that is consistent with the electron-withdrawing effect of nitro group. For the same reason the direct phototransformation in sunlight is much more rapid with 2,5-ADSA than for 3-NBSA and 4-nitrotoluene-2-sulfonic acid. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Aromatic sulfonated compounds are critical pollutants in aquatic environment [1,2]. They form a large group of industrial chemicals released with dyehouse effluents [3]. These compounds have low volatility and are highly water soluble. Consequently, it is difficult to remove them from water and they are transported from sewers to surface waters.

Organic pollutants can be eliminated by using photocatalysts [4,5]. Photocatalysis is based on the formation of pairs electron/positive hole (e^-/h^+), when the photocatalyst is subjected to UV light. The

electrons may induce reduction, but most often, in the presence of oxygen, they lead to the formation of superoxide anions. Positive holes oxidize adsorbed organic substrates or react with water leading to the formation of hydroxyl radicals which are very efficient oxidizers (the oxidation potential of $\bullet\text{OH}$ is as high as 2.80 V). The efficiency of slurries in water (usually $1\text{--}2\text{ g l}^{-1}$) was experimentally proved with most of the organic pollutants. It may be improved by doping with Pt or Fe(III) in particular [5] or by deposition on powdered inert supports, such as silica [6], activated carbon [7] and zeolite [6,7]. Titanium dioxide is the most commonly used photocatalyst since it is non toxic and therefore ecofriendly. Among the various kinds of TiO₂ that are commercially available, Degussa P25 is extensively used as a standard in photocatalysis, eventhough other

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types, such as Hombikat and Millennium are also proposed.

The objective of the present paper is to select efficient photocatalysts for the elimination of aromatic sulfonic acids, since these compounds are hydrophilic by-products of dye industry [8]. Titanium dioxides from Millennium were less studied than Degussa P25. They are expected to be photocatalytically as efficient as P25, or more, since they are 100% anatase which is the active form of TiO₂, whereas P25 contains only 70% of this form. For these reasons the efficiency of TiO₂ from Millennium are compared with that of P25 using two substrates 3-nitrobenzenesulfonic acid (3-NBSA) and 2,5-anilinedisulfonic acid (2,5-ADSA).

2. Materials and methods

2.1. Catalyst and reagents

Several kinds of titanium dioxide were used. They are described in Table 1. The main difference between TiO₂ lies in their surface areas.

2.2. Substrates

3-nitrobenzenesulfonic acid sodium salt >95% (3-NBSA), Fluka; 4-nitrotoluene-2-sulfonic acid dihydrate >90% (4-NTSA), and aniline-2,5-disulfonic acid monosodium salt (2,5-ADSA), 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).

2.3. Irradiation devices

Two different devices were used to compare the efficiencies of different types of photocatalysts. The first one is called “vertical device” and is represented in Fig. 1. It consists of a vertical Pyrex tube (20 mm i.d.)

with a water cooling jacket. It is located along one of the focal axes of a cylindrical mirror with an elliptic base. A fluorescent lamp TLD15 W/05 emitting between 300 and 450 nm is located along the other focal axis. TiO₂ is maintained in suspension by magnetic stirring. Irradiation conditions remain almost constant during sampling. When the initial volume is 50 ml or more, light mainly reaches the solution through the cylindrical surface and consequently the number of photons received by the suspension is almost proportional to the irradiated volume. Evaporation is found to be negligible. This device is appropriate to study and compare different suspended TiO₂ catalysts, but it is not convenient for catalysts immobilized on solid supports, such as glass, brick or cement.

The second device called “horizontal device” consists of two identical crystallizers ($\phi_i = 53$ mm) exposed to two fluorescent lamps Philips TLD15 W/05. Three or four crystallizers can be exposed to UV light under the same conditions. The advantage of this device is not only the possibility of studying any kind of catalysts on any kind of support, but also to study catalysts in suspended form with the same flux of incident light. The flux of incident light, determined by chemical actinometry using potassium ferrioxalate, was evaluated to be 3.4×10^{15} photons cm⁻² s⁻¹ (i.e. 5.6×10^{-9} einstein cm⁻² s⁻¹).

The quantum yield of 3-NBSA was measured at 254 nm using a low pressure mercury lamp located on one of the focal axes of a cylindrical mirror with an elliptic base, the reactor in quartz, being along the other focal axis. The incident photon flow was evaluated by chemical actinometry.

Sunlight irradiation of solutions were carried out in Clermont-Ferrand (latitude 46°N, altitude 420 m) during October and November. Solutions (100 ml) were exposed in Pyrex horizontal tubes ($\phi_i = 40$ mm, $L = 250$ mm), open at one end on a small tube for sampling.

There is a negligible effect of evaporation.

Table 1
Different types of titanium dioxide used and their physical properties

Origin	Type	Composition	Size of crystallites (nm)	Surface area (m ² g ⁻¹)
Degussa	P25	Anatase/rutile 70/30	30	55 ± 15
Millennium	PC50	Anatase	20–30	45 ± 5
Millennium	PC100	Anatase	15–25	80–100
Millennium	PC105	Anatase	15–25	75–95
Millennium	PC500	Anatase	5–10	>250

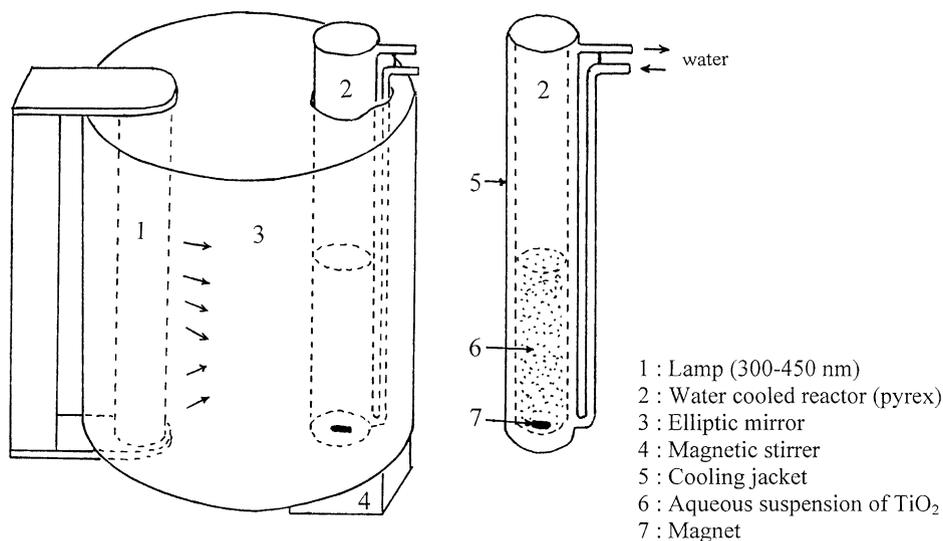


Fig. 1. Scheme of the "vertical device" used for the irradiation of TiO₂ slurries.

2.4. Analyses

Irradiated solutions were analyzed by HPLC on a column C₁₈ using UV detection and methanol/water mixture of 40/60 v/v as the eluent. However, a problem results from the low p*K*_a of substrates that are in the anionic form under normal experimental conditions. This problem was solved by adding tetrabutylammonium hydrogen sulfate (TBA) 10⁻² M to water. Tributylamine hydrochloride, obtained by acidification of tributylamine (less costly than TBA) can also be used.

With 3-NBSA a spectrophotometric titration is also possible since this substrate has a strong absorption band and only very little amounts of products are formed, but the results with this method were less reproducible.

3. Results and discussion

3.1. Direct phototransformation

The p*K*_a of 3-NBSA and 4-NTSA were evaluated to be 1.6 using a conductometric method. The UV spectra of 3-NBSA, 4-NTSA and 2,5-ADSA in unbuffered solution are given in Fig. 2. The three spectra have a significant overlap with sunlight spectrum which begins near 300 nm.

Solutions of 5 × 10⁻⁴ M were exposed to sunlight (October and November) in acidic, neutral and basic solutions (pH = 3.0, 6.3, 8.7; 3.0, 5.5, 7.8; 2.9, 5.4 and 7.8 for 3-NBSA, 4-NTSA and 2,5-ADSA,

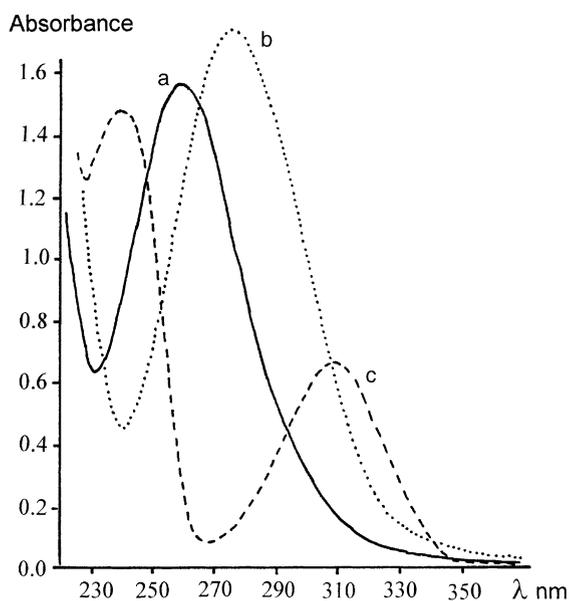


Fig. 2. UV-spectrum of unbuffered aqueous solutions of: (a) 3-NBSA sodium salt 2.1×10^{-4} M; (b) 4-nitrotoluene sulfonic acid (4-NTSA) 2.0×10^{-4} M; (c) aniline-2,5-disulfonic acid monosodium salt (2,5-ADSA) 2.0×10^{-4} M.

respectively). With 3-NBSA and 4-NTSA, no transformation was noted after 1 week in October, and only a little change after 1 month in November (about 1.5 and 9%, respectively, for the neutral solutions of 3-NBSA and 4-NTSA). In contrast, 2,5-ADSA was completely transformed after 4 days at pH = 2.9, after 8 days at pH = 5.4 and after 11 days at pH = 7.8. In all the three conditions solutions became yellow, but it was noted that the intensity of color decreased after several days in acidic solutions, but did not disappear after several weeks in neutral and basic solutions.

The quantum yield of 2,5-ADSA transformation was measured in air-saturated solution, pH = 3.9, irradiated in monochromatic light (310 nm): $\phi = 0.018$. It is much higher (0.46) in the absence of oxygen [9]. The quantum yield of 3-NBSA was measured at 254 nm with a device providing a higher light intensity of monochromatic light, since the rate of phototransformation at 310 nm need too long irradiation times. It was evaluated to be ca. 6×10^{-5} that is consistent with values reported for nitrophenols [10]. 3-NBSA and 4-NTSA were chosen to test photocatalysts in slurry or immobilized

form since they are almost photostable in direct photolysis.

From these experiments it can be concluded that:

- (i) direct photocatalysis in sunlight is efficient to eliminate 2,5-ADSA, but it leads to the formation of colored by-products;
- (ii) photocatalysis may be very useful for the elimination of 3-NBSA that is almost photostable in sunlight in spite of its UV absorption.

3.2. Photocatalytic transformation with TiO₂ slurries

3.2.1. Concentration of TiO₂

The two devices described in Section 2.3, named “vertical device” and “horizontal device” were used, respectively to compare the photocatalytic transformation of 3-NBSA and 2,5-ADSA with various TiO₂: P25 of Degussa, PC50, PC100, PC105 and PC500 from Millennium. A preliminary study was carried out to optimize the concentration of TiO₂. Results obtained with 3-NBSA 4×10^{-5} M in the horizontal device are reported in Fig. 3. It appears that the rate of transformation increases rapidly up

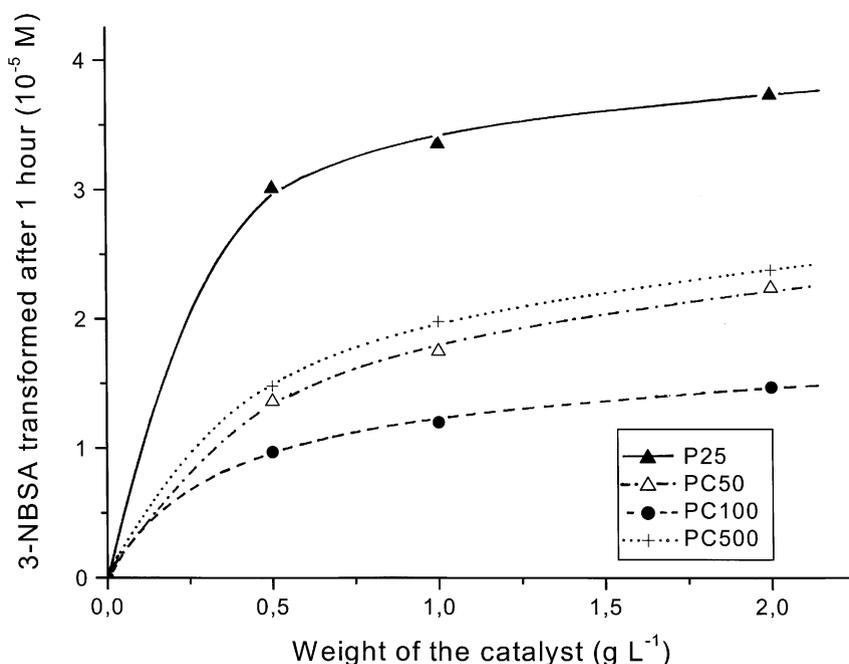


Fig. 3. Influence of the amount of TiO₂ on the rate of photocatalytic transformation of 3-NBSA (4×10^{-5} M).

to 0.5 g l^{-1} and it is not much different between 1 and 2 g l^{-1} . The same effect was observed with P25 irradiated in the vertical device. The influence of TiO_2 concentration, which may depend on the geometry of irradiation device used, is similar for all TiO_2 tested. This result is in good agreement with values generally reported in literature. Consequently, in all experiments described here TiO_2 2 g l^{-1} was used.

3.2.2. Adsorption

Influence of adsorption on TiO_2 was studied before irradiating the substrates. With 3-NBSA 4×10^{-5} , no change in concentration was observed after 30 min stirring. It fits well with the high solubility of 3-NBSA (more than 30 g in 100 ml water for the sodium salt). It is different with 2,5-ADSA 4×10^{-5} as it appears in Fig. 5. After 10 min stirring, approximately 50% of the substrate is adsorbed on the photocatalyst in the case of P25, but only a few percent with the TiO_2 from Millennium. No change was observed after 10 min that means that the equilibrium is rapidly reached. This difference of adsorption of 2,5-ADSA on P25 and TiO_2 Millennium was repeatedly observed, but not explained yet. Therefore a systematic study of the adsorption will be developed.

3.2.3. Photocatalytic transformation

3.2.3.1. 3-Nitrobenzenesulfonic acid. It appears in Fig. 4a and b that photocatalytic transformation of 3-NBSA $4 \times 10^{-5} \text{ M}$ is more efficient with P25 than with the different kinds of various TiO_2 from Millennium tested. The slightly different results obtained with both devices may be due to the reproducibility of stirring. A solution $2 \times 10^{-5} \text{ M}$ was also irradiated in the presence of TiO_2 2 g l^{-1} . It is noteworthy that the initial transformation rate is almost proportional to the concentration reflecting the fact that the surface of the catalyst is far from saturation. It can be also noted that for the different photocatalysts used for the degradation of 3-NBSA, there is no relationship between the transformation rate and the specific surface area of the catalyst.

To compare the efficiency of photocatalysts Serpone et al. [11] defined a relative photonic efficiency ζ_r taking the rate of transformation of phenol as reference. In the present work, we define the relative photonic

Table 2

Values of relative photonic efficiencies ζ_r for the transformation of 3-NBSA and 2,5-ADSA on various photocatalysts

	3-NBSA	2,5-ADSA	Phenol
P25	0.72 ± 0.06	–	1.00
PC50	0.27 ± 0.03	1.3 ± 0.2	–
PC100	0.21 ± 0.03	0.8 ± 0.1	–
PC105	–	3 ± 0.5	–
PC500	0.24 ± 0.03	10 ± 2	–

efficiency as:

$$\zeta_r = \frac{\text{initial transformation rate of substrate on TiO}_2}{\text{initial transformation rate of phenol on TiO}_2 \text{ P25}}$$

In order to evaluate ζ_r a solution of phenol of the same concentration ($4 \times 10^{-5} \text{ M}$) was irradiated in the presence TiO_2 P25 under the same conditions as 3-NBSA. Values of ζ_r calculated with horizontal device are gathered in Table 2. They are lower than 1, that fits well with the fact that the rate constant of $\bullet\text{OH}$ with 3-NBSA ($6.5 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$) is about 10 times smaller than with benzenesulfonic acids without nitro group ($(3\text{--}6) \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$) [12]. It is due to the electron-withdrawing effect of this group. Similar values of ζ_r were obtained with PC50, PC100 and PC500, in spite of a large difference in surface areas (ratio higher than 5). Value of ζ_r is significantly higher with P25.

When phenol was used as the substrate, it was also observed that the relative photonic efficiency is lower than 1 with PC50 and PC500 ($\zeta_r \cong 0.5$ for both).

3.3. 2,5-Anilinedisulfonic acid

The efficiencies of the different TiO_2 (slurries) were also compared using 2,5-ADSA $4 \times 10^{-5} \text{ M}$ as the substrate (Fig. 5). This compound slowly disappears without catalyst (“blank” in Fig. 5), but the degradation is much faster in the presence of TiO_2 . It is noteworthy that 2,5-ADSA adsorbs much more on P25 than on TiO_2 Millennium in the dark, before starting irradiation. In contrast with 3-NBSA, the photocatalytic degradation is more efficient with PC500 than with P25 and the rates of transformation are in the same order as the surface areas for PC50, PC105 and PC500. This phenomenon is probably related to the different photocatalytic behavior

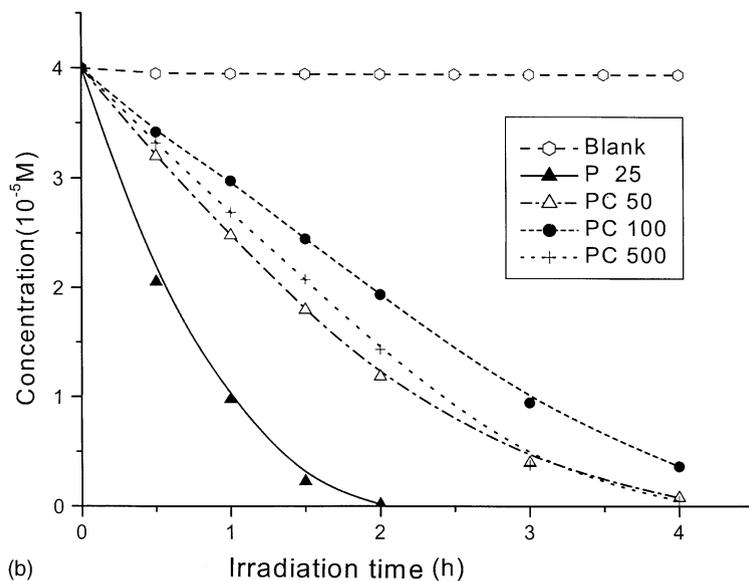
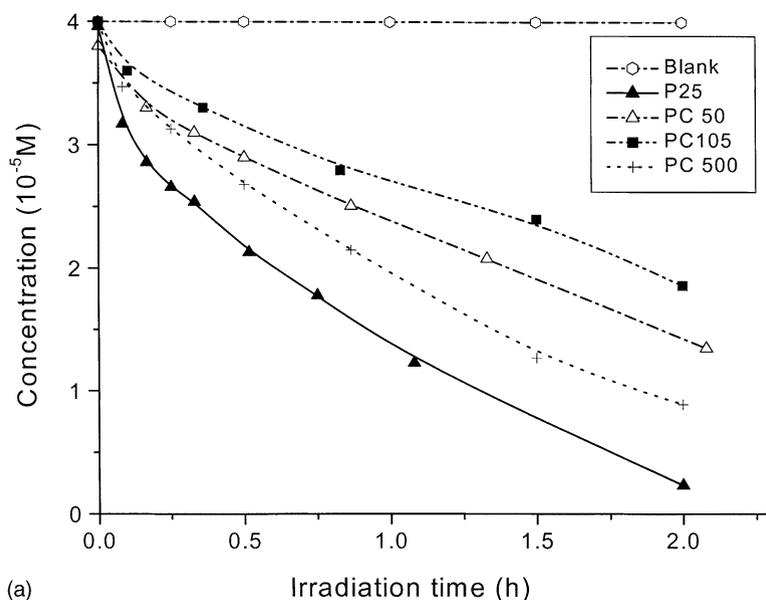


Fig. 4. Kinetics of photocatalytic degradation of 3-NBSA with various TiO_2 samples in suspension 2 g l^{-1} : (a) vertical device, initial concentration $C_0 = 4 \times 10^{-5} \text{ M}$; (b) horizontal device, $C_0 = 4 \times 10^{-5} \text{ M}$.

of both substrates. Values of ζ_r defined as before are reported in Table 2, except for P25 since the initial rate of photocatalytic transformation cannot be evaluated precisely because of the high proportion of 2,5-ADSA adsorbed. Values of ζ_r are near 1 or higher can be related to the fact that 2,5-ADSA

adsorbs better than 3-NBSA and phenol. A tentative explanation of the relatively low efficiency of P25 is the saturation of the surface of TiO_2 by 2,5-ADSA or a better adsorption of 2,5-ADSA on the rutile form present in P25 but absent in TiO_2 from Millennium.

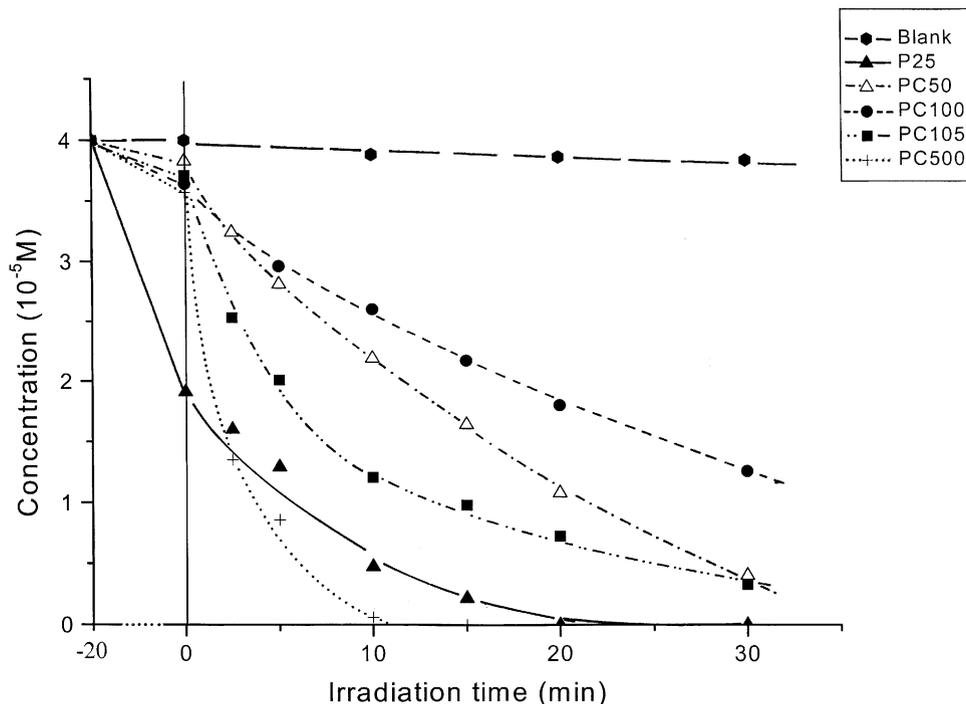


Fig. 5. Kinetics of photocatalytic degradation of 2,5-ADSA 4×10^{-5} M in the presence of several TiO₂ (horizontal device).

At the present time it appears clearly that the efficiencies of catalysts may depend on the substrate used for the test.

4. Conclusions

Direct photolysis of 2,5-ADSA is much more efficient than the photolysis of 3-NBSA. The low quantum yield obtained for 3-NBSA is consistent with values obtained with nitrophenols and may be attributed to the electron-withdrawing property of NO₂ group.

When TiO₂ P25 is used as a slurry, it is clearly more efficient than TiO₂ from Millennium for the degradation of 3-NBSA, and there is no simple relationship between surface area and photocatalytic activity. The same effect was observed with phenol with P25, PC50 and PC500. However, it is different with 2,5-ADSA since it is more easily transformed on PC500 than on P25. In the case of 2,5-ADSA the rate of photocatalytic transformation is approximately in the same order than surface areas.

From this study, it appears that the relative efficiencies of a photocatalysts depends on the substrate used for the test.

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