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On the "immobilization" of titanium dioxide in the photocatalytic oxidation of spent waters

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Abstract

The problems raised by the immobilization (or anchoring) of a photocatalyst, namely TiO_2, on a support are reviewed, from the standpoints of the procedure itself and of the structure, adherence, morphology and photocatalytic activity of the deposit. Some new experimental findings are also reported. It is concluded that the immobilized photocatalyst absorbs all the actinic light that it can, but the immobilization treatment generally lowers its activity. It would therefore be advisable to tailor a treatment which would at least maintain this activity, and even increase it, possibly by size quantization.

Keywords: Titanium dioxide; Immobilization; Photocatalysis; Oxidation; Spent waters

1. Introduction

Photocatalytic oxidation of dissolved impurities is an "advanced oxidation process" (AOP) which has reached the stage of pre-industrial development [1]. When the photocatalysis is heterogeneous, the catalyst is usually a powder suspended in a liquid medium, the photoreactor being a "slurry reactor". This simple arrangement has obvious advantages from the standpoint of the reactor itself: when it is perfectly mixed, there is no segregation of phases, and when the catalyst particles are small enough, their entire external surface can be illuminated during the reaction time (or the space time in a continuous reactor). In these circumstances, the reaction medium, albeit fundamentally heterogeneous, can be considered as "pseudo-homogeneous" and amenable, at least in a first approximation approach, to simple laws, such as the Beer–Lambert law [2]. However, in field applications, the reactor is only one part of the whole process, and it cannot be allowed that "purified" water can still contain particles of a solid catalyst, even as harmless as titanium dioxide. Therefore the reactor must be followed with a liquid–solid separator, the installation and operation of which enhance the costs of the whole process. This is why catalyst deposition on an inert support is of interest [3–6]. There are at least two obvious problems arising from this arrangement: the accessibility of the catalytic surface to the photons and the reactants. The way in which these problems have eventually been solved depends on the reactor assembly. Table 1 gives an overview of various photoreactors [3–22]. The quoted references deal exclusively with TiO_2 as photocatalyst, and this compound is the subject of this paper. One of the first questions which obviously arises from a change from suspended to immobilized catalyst is the possibility of rate limitation due to liquid to solid mass transfer. This effect is usually negligible for a suspension [2], whereas it has been shown [23] to explain the flow rate dependence of the photocatalytic reaction rate for an immobilized photocatalyst. This has been reviewed in Ref. [2]. In this paper, we deal with the characterization of the catalyst–support couple, the resulting solid being termed as the "contact mass" [24]. This characterization includes the support, the preparation of the photocatalyst proper, its structure, its adherence to the support, its morphology and, finally, its photocatalytic activity.

2. Photocatalyst supports

In conventional catalysis, the primary role of a support is to improve the textural properties of the contact mass (increase porosity, surface area, etc.). In photocatalysis, it should be borne in mind that the active component must be able to absorb light (except in the very special cases when the support can be a photoreceiver). This necessity renders useless the portions of the photocatalyst located in the pores of the support. Even when the latter is transparent to the

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Table 1
Overview of various photoreactors

Photoreactor type	Support of catalyst		Catalyst arrangement	Reference
	Nature	Physical appearance		
Batch	Glass	Beads	Fixed bed	[3]
Continuous flow	Glass	Spiral wound around the lamp	Wall of the glass spiral	[4–9]
Continuous flow	Glass	Beads	Fixed bed in the annular space between the lamp and the outer wall	[6,10]
Batch	Glass	Hollow beads	Floating bed	[11]
Batch (with recirculation)	Sand Silica gel	Grains Grains	Fixed bed on the reactor bottom	[12] [13]
Continuous	Silica based	Sand, glass beads, glass fibre mesh, glass wood fibre	Fixed bed	[14]
Flow injection	Teflon	Tubing wrapped around the lamp	Coating on the internal wall of the tubing	[15]
Batch (with recirculation)	Polymer	Membrane	Disc membranes sandwiched between optical "Pyrex" plates	[16]
Batch (with recirculation)	Glass	Fibre cloth	Coating on the surface	[17]
Batch (with recirculation)	Fused silica	Optical fibre	Coating on the surface	[18]
Batch	Activated carbon	Grains	Fixed bed	[19]
Batch	Ceramics	Plates	Fixed bed	[20]
Batch	Silicon, silica, "Pyrex" glass, stainless steel	Plates	Fixed bed	[21]
Batch (with recirculation)	Anodized iron	Plates	On the reactor bottom	[22]

incident light, the catalyst layer on the external surface absorbs the actinic light and therefore impedes penetration of the support. According to Teschner et al. [25] a few hundred angströms of TiO_2 are enough to absorb the incident light completely. Moreover, the mean diffusion length, l, of charge carriers in TiO_2 can be evaluated in the following way: $l \approx \sqrt{(D\tau)}$ [26], where D is the diffusivity of the charge carriers in the absence of an electric field and τ is the lifetime of these charge carriers. D can be computed from the well-known Einstein relation, $D = \mu[(kT)/e]$ [27], where μ is the mobility. According to Iwaki [28], the latter does not exceed, at room temperature, 0.4 $cm^2\ V^{-1}\ s^{-1}$, whence a value of D of $10^{-6}\ m^2\ s^{-1}$ can be derived. τ has been estimated to be 250 ns for the holes, which survive longer than the electrons after irradiation [29]. It follows that $l = 5 \times 10^3$ Å. This estimation, which is in agreement with the values given in Ref. [25] for undoped TiO_2, is certainly an overestimation. It seems improbable that a charge carrier can overcome the resistance due to grain limits (i.e. 300 Å in the case of Degussa P25 TiO_2). Therefore it can be concluded that the photocatalytic action is local, requiring the "triple encounter" of the surface, the reactant(s) and the photons. It follows that the primary role of a photocatalyst support is to provide, on its external surface, strong adherence of the photocatalyst. Surprisingly, there are very few studies which offer a rational approach to the improvement of adherence beyond the usual procedures of washing, scouring and etching. Jackson et al. [11] attempted to generate Si–O–Ti bonds on the glass surface by using triethoxysilane as a surface intermediate or by hydrolytic vapour phase deposition of TiO_2 from $TiCl_4$ as precursor.

3. Photocatalyst deposition

A priori two routes are open for photocatalyst deposition: (1) the use of a separately made solid designated as "SM", e.g. the commercially available Degussa P25 titanium dioxide of standard use in photocatalysis, and (2) preparation of a catalyst in situ from a precursor (the solid obtained is termed "ex-precursor").

3.1. Anchoring of SM TiO_2

Fig. 1 shows the sequence used for the immobilization of TiO_2 (experiments carried out in our laboratory [30,31]).

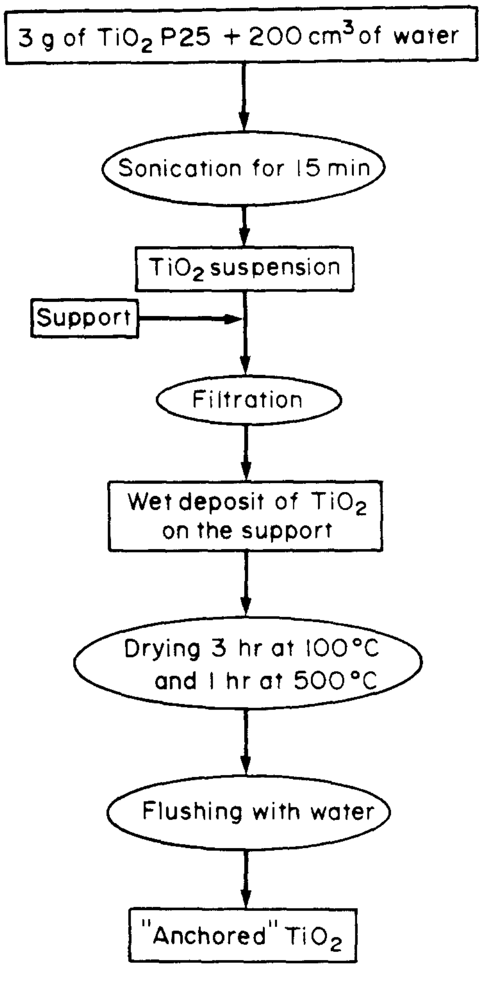

Fig. 1. Immobilization of SM TiO_2.

3.2. Anchoring of "ex-precursor" TiO_2

The precursor is a titanium salt, which is submitted to hydrolysis (passage to $Ti(OH)_4$) and to pyrolysis (passage to TiO_2) (sol–gel process). The initial salt is usually an alkoxide, since the hydrolysis of inorganic salts such as $TiCl_4$ in the liquid state is difficult to control. The widely used alcoholate is titanium tetraisopropoxide (TTP) $Ti(O\text{-}i\text{-}C_3H_7)_4$, although titanium tetraisobutoxide (TTB) $Ti(O\text{-}i\text{-}C_4H_9)_4$ can also be used as the starting material. The immobilization procedure differs only by details from a reference to another [32–37]. Fig. 2 shows the procedure adopted in our laboratory.

4. Photocatalyst structure

Rutile is the thermodynamically stable form of titanim dioxide, but is less photocatalytically active than anatase [38]. The irreversible transformation of anatase to rutile is noticeable at about 700 °C [39]. Although this temperature is not reached in the above described immobilization procedures, it is safer to check the crystal structure of the end product. In our case, we confirmed the structure of P25 TiO_2 in the former case (mixture of anatase (predominant) and rutile) and found only anatase in the latter case (ex-TTB oxide).

5. Photocatalyst adherence

Many studies neglect to check the photocatalyst adherence to the support. However, this adherence is of paramount

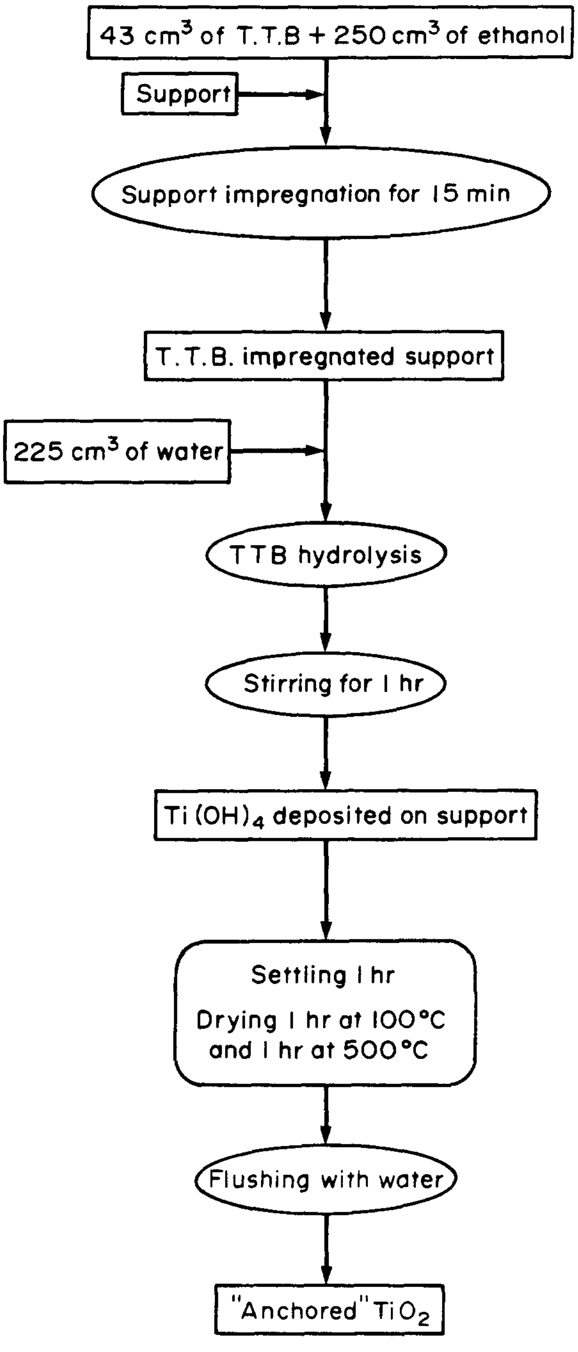

Fig. 2. Immobilization of ex-TTB TiO_2.

importance, since if it is not strong enough, some of (if not all) the catalyst grains will return to the liquid, where they can eventually act as a suspended catalyst. In this case, the immobilization has failed, at least partially. An initial precaution to eliminate this possibility involves flushing the contact mass with water at a flow rate at least equal to that used in the photocatalysis experiments, so that the most loosely bound particles will be removed. Secondly, the amount of attached titanium can be measured by a titration procedure as described in Ref. [11]. It involves the spectrophotometric determination of the peroxotitanate formed between titanium sulphate and hydrogen peroxide. Serpone et al. [3] washed their TiO_2-coated glass beads with aqua regia and checked by atomic absorption analysis the absence of TiO_2 in the washings.

6. Morphology of photocatalyst deposits

As usual, it is always advisable to view directly the contact mass obtained. Scanning electron microscopy (SEM) can be used to view TiO_2 deposits on various supports [5,11,20,36,40,41]. In most cases, the specks of photocatalyst are very irregular in shape, dimension and thickness with voids between them. A layer of uniform thickness of a few hundred angströms [25] would be ideal, but would require more elaborate deposition techniques [41].

7. Photocatalytic activity

The measurement of the photocatalytic activity of the TiO_2 deposit is the crucial test of the achievement of the immobilization procedure. Surprisingly, no studies are available which offer a systematic comparison between suspended and immobilized photocatalysts when the latter activity is taken before and after immobilization. This comparison not only gives a clue to the influence of this treatment, but also allows the photocatalytic activity due to the dispersion of detached particles to be taken into account. We report the results of our own experiments, where SF is the fresh catalyst in suspension, ST is the suspended photocatalyst after immobilizing treatment, but without support, IG is the catalyst immobilized on glass beads (2 mm in diameter) and IS is the catalyst immobilized on silica gel.

The test reaction studied with SF P25 TiO_2 is the oxidation of dissolved formic acid by oxygen

$$HCOOH + \tfrac{1}{2}O_2 \longrightarrow CO_2 + H_2O$$

Its rate is followed by acidimetric titration. The reactor design is inspired by a "solar pond" and is depicted in Fig. 3. The catalyst lies at the bottom and receives the light from a parallel beam (except for geometrical aberrations). The emitted light is filtered by a 3 mm thick glass plate which eliminates radiation with a wavelength shorter than 300 nm. As the photoreceiver is TiO_2, the absorption band edge of which is about 380 nm, the wavelength "window" open for light absorption lies between 300 and 380 nm. Standard uranyl oxalate actinometry allows the determination of the number of einsteins in this wavelength range falling in the reactor per unit time [42].

7.1. Suspensions of TiO_2

Fig. 4 shows the reaction rates for the following samples: SF P25 TiO_2 (a), ST P25 TiO_2 (b) and ST ex-TTB TiO_2 (c). This figure confirms the zeroth order with respect to

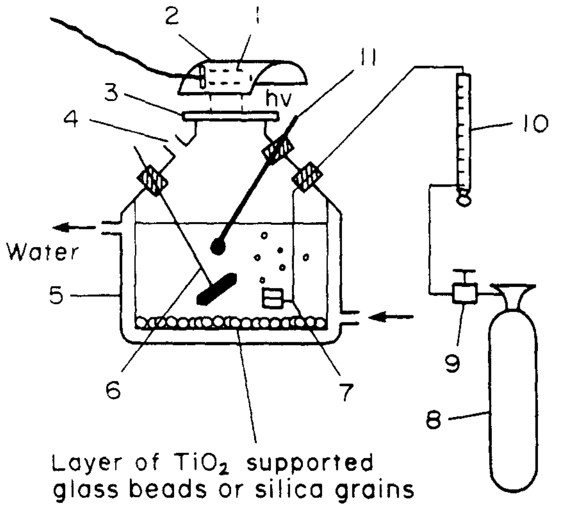

Fig. 3. Photocatalytic reactor: (1) mercury lamp (Philips HPK 125); (2) parabolic section reflector; (3) Pyrex glass filter; (4) sample collecting port; (5) jacketed reactor; (6) paddle stirrer; (7) oxygen-porous diffuser; (8) oxygen tank; (9) pressure reducer; (10) flow meter; (11) thermometer.

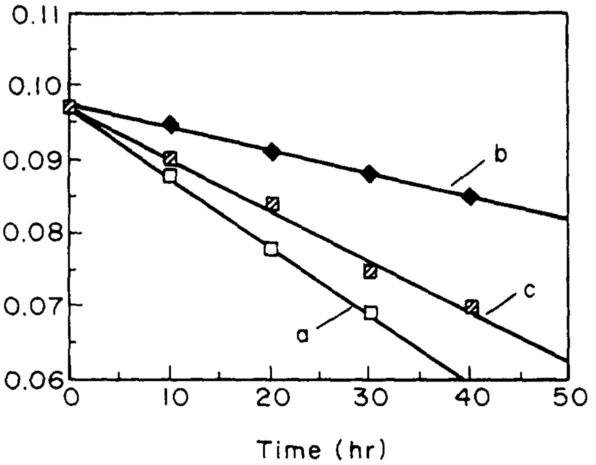

Fig. 4. Photocatalytic oxidation of formic acid with a 100 mg l^{-1} suspension of: (a) SF P25 TiO_2; (b) ST P25 TiO_2; (c) ST ex-TTB TiO_2. Acid concentration (mol l^{-1}).

formic acid (at least in the time span investigated) [42], and establishes that ST ex-TTB TiO_2 is a better photocatalyst than ST P25 TiO_2 for a given treatment procedure. We also studied the influence of the catalyst amount m and confirmed the trend already found in Ref. [42], namely an increase in r_v to a plateau $r_{v,max}$ obtained in the present experiments for an amount of TiO_2 close to 200 mg l^{-1} (Fig. 5). Of course, the value of $r_{v,max}$ depends on the origin of TiO_2. The dependence of r_v on m is amenable to the crude interpretation already given in Ref. [42] based on the Beer–Lambert law for the incident, almost parallel, beam.

The values of the Napierian absorption coefficients deduced from this figure are given in Table 2 together with the maximum quantum yields. The values in this table raise some comments.

(1) ϵ' and ϕ_{max} of SF P25 TiO_2 are in very close agreement with those determined previously [42].

(2) The maximum quantum yield does not vary in the same order as the absorption coefficient: ST ex-TTB TiO_2 is more active than ST P25 TiO_2, although it absorbs less.

(3) The knowledge of ϵ' allows the radiant power P_t transmitted over a path length of 5 cm (liquid thickness) to be evaluated for suspensions of m mg of TiO_2 in a volume of 0.5 l (Table 3).

The interpretation of the modification of the photocatalytic activity due to the immobilization treatment is difficult due to the lack of a precise knowledge of the surface characteristics of the TiO_2 samples. The fact that ST ex-TTB TiO_2 is more active than ST P25 TiO_2 may be ascribed to its crystallographic composition (anatase only detectable by X-ray diffraction). However, it is more difficult to explain the decrease in photocatalytic activity when a given sample (P25 TiO_2) is submitted to immobilization. This is probably related to the occurrence of adsorbed water and its dissociation fragments, e.g. OH groups (neutral or charged) [43]. OH^- ions have been assumed to be hole traps, giving rise to oxidizing species and thus to an enhancement of the photocatalytic

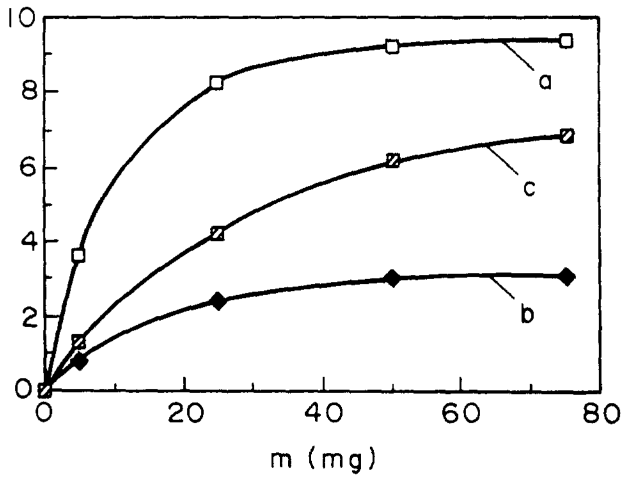

Fig. 5. r_v as a function of the catalyst mass (m). $r_v \times 10^4$ (mol l^{-1} h^{-1}).

Table 2
Napierian absorption coefficient and maximum quantum yields

Sample	ϵ' (l cm^{-1} mg^{-1})	ϕ_{max}
SF P25	10^{-2}	0.07
ST P25	7×10^{-3}	0.02
ST ex-TTB	4×10^{-3}	0.05

Table 3
P_t/P_0

Sample	m (mg)				
	1	3	4	6	156
ST P25	0.93	0.81	0.76	0.66	
ST ex-TTB	0.96	0.89	0.85	0.79	0.002

activity [44,45]. In addition, TPD experiments on water adsorbed on anatase and rutile have shown that all the adsorbed water species are desorbed at 400 °C [46]. It is therefore tempting to ascribe the loss of photocatalytic activity observed after immobilization to the loss of OH^- ions, which are not completely restored when the photocatalyst is exposed to formic acid solution.

7.2. Immobilized TiO_2

The zeroth order with respect to formic acid still holds. The values of $r_{v,exp}$ deduced are overall values since, as some TiO_2 passes into solution, $r_{v,exp}$ is considered to be the sum of the rate $r_{v,susp}$ due to the mass of TiO_2 in suspension and the rate $r_{v,imm}$ due to the immobilized photocatalyst (corrected for the absorption of radiant power in the supernatant suspension, assuming that the rate is proportional to the absorbed radiant power [42]). The amounts of TiO_2 fixed on the support have been determined by spectrophotometry of the peroxo complex formed with hydrogen peroxide [11] within an accuracy of 5% at best.

Table 4 shows the results obtained for various TiO_2 samples. Several comments can be made.

(1) The photocatalytic rate is reached with one row of support grains. The photocatalyst anchored in the underlying rows is ineffective.

(2) The prolonged duration of photocatalysis (several tens of hours) leads, in all cases, to the detachment of TiO_2, although all the samples had been subject to flushing. Although the small masses passed into solution are certainly inaccurate, ex-TTB TiO_2 is much less tightly bound to the support, either glass or silica gel, than P25 TiO_2. This is rather unexpected, since an oxide obtained from a liquid precursor is expected to be more likely to stick to the support than an oxide prepared separately. In this respect, ex-TTB TiO_2 supported by silica gel is certainly the worst catalyst, in spite of exhibiting the largest amount anchored at the beginning, since more than one-half of this returns to the solution. In this case, the contact mass is surrounded by a "swarm" of suspended particles, and the observed rate is practically due to this suspension.

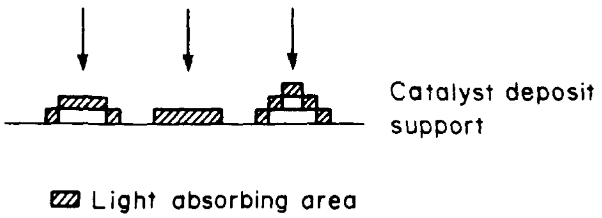

Fig. 6. The "bombarded city model".

(3) A rough estimation of the quantum yield attainable with the anchored catalyst can be made by assuming that all the incident intensity in the wavelength range 300–380 nm, namely 2×10^{-6} einstein s^{-1} in our experiments, is absorbed by the TiO_2 particles. If we take the case of IS P25 TiO_2, $r_{v,imm}=6.3\times10^{-8}$ mol s^{-1}. This gives a quantum yield roughly equal to 3%, larger than the maximum found for the suspension of treated P25 TiO_2 (Table 2). Given all the approximations and experimental uncertainties made in this estimation, this difference does not seem to be significant.

The following model can be tentatively proposed to account for the action of the anchored photocatalyst. A monolayer of TiO_2 particles (the diameter of which is 300 Å for P25) is sufficient to absorb the incident light. The fact that these particles are probably aggregated during immobilization enhances the catalyst layer thickness, *but not its activity*. The latter is reduced by the void spaces left between the catalyst layers. The corresponding model which could be named, by reference to the well-known BET model for multilayer physisorption, the "bombarded city model" is depicted in Fig. 6.

In such a model, the rate is reduced in that part of the external surface covered by the catalyst *irrespective of the layer number*. Unfortunately, the precision of our experiments does not allow a reliable estimation to be made of the surface coverage for comparison with an evaluation derived from microphotographs. But we think that at least this model is worth a check.

Table 4
Results for various TiO_2 samples

Sample	Bed thickness (numbers of layers of beads or grains)	Mass of TiO_2 (mg)			Fraction of transmitted radiant power	$r_{v,exp}$	$r_{v,susp}$	$r_{v,imm}$
		Fixed before photocatalysis	Fixed after photocatalysis	Passed into solution (0.5 l)		(mol l^{-1} h^{-1} $\times10^4$)		
IG P25	1	45	42	3 (7%)	0.81	3.0	0.6	2.9
IG ex-TTB	1	12	8	4 (33%)	0.85	2.5	1.0	1.8
IG ex-TTB	2	20	17	3 (15%)	0.89	2.2	0.8	1.6
IS P25	1	28	22	6 (21%)	0.66	4.1	1.1	4.5
IS ex-TTB	1	299	143	156 (52%)	2×10^{-3}	6.7	6.6	Indetermined

$r_{v,susp}$ is evaluated from $\ln[1-(r_{v,susp}/r_{v,max})]=-\epsilon' m(h/V)$ and $r_{v,imm}$ from $r_{v,imm}=(r_{v,exp}-r_{v,susp})/(P_t/P_0)$. The values of (P_t/P_0) are taken from Table 3 for the corresponding mass m in suspension.

8. Conclusions and perspectives

(1) A careful examination of the catalyst–support interaction, especially with regard to the adherence of the former, is needed to optimize the photocatalytic activity of the contact mass. This examination should include all the parameters which intervene in the many preparation steps: surface state of the support and the catalyst (especially with regard to the amount and ionicity of OH groups), crystal structure of the deposit, etc.

(2) When the photocatalyst adheres to the support, a very thin layer (a few hundred angstroms) is sufficient to absorb all the available light, and thus to reach a quantum yield close to the maximum obtained for a suspension of the photocatalyst *which has undergone the same immobilization treatment*. It would be useful to find a treatment which does not decrease the quantum yield and may even increase it. Such a treatment may involve a reduction in the size of the catalyst particles (''size quantization'' effect) [47].

(3) If the immobilization procedure is optimized, a very economical design for the solar purification of spent waters would be the solar pond, the immobilized catalyst being deposited on the bottom or, conversely, floating at the water surface. This design does not require any concentrating optics, and uses diffuse UV radiation (even through clouds) as well as direct radiation. Of course, it suffers from the obliquity of the solar radiation during the day. A rough calculation, based on our results for IG P25 TiO_2, shows that an area of the solar pond of 15 000 m^2 and a depth of 5 cm allow 5 m^3 of spent water to be treated per day. As is commonplace for such devices, a large irradiation surface is required for a small flow rate, but a reduction in the former and/or an increase in the latter is ruled by an increase in the quantum yield.

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Appendix: Nomenclature

D	diffusivity of charge carriers
e	charge of an electron
h	liquid depth (5 cm)
IG	immobilized on glass beads
IS	immobilized on silica gel
k	Boltzmann constant
l	mean diffusion length of charge carriers
m	catalyst mass (mg)
P	radiant power
r	reaction rate (mol h^{-1} or mol s^{-1})
SF	suspended fresh
SM	separately made
ST	suspended after treatment
TTB	titanium tetraisobutoxide
TTP	titanium tetraisopropoxide
T	temperature
V	reaction volume (0.5 l)

Greek symbols

ϵ	molar decadic absorption coefficient (l cm^{-1} mol^{-1})
ϵ'	Napierian absorption coefficient (l cm^{-1} mg^{-1})
μ	mobility of charge carriers
ϕ	quantum yield (%)

Subscripts

exp	resulting from experiments
imm	for the immobilized catalyst
max	maximum value
0	incident
susp	in suspension
t	transmitted
V	per unit volume

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