

Immobilized TiO₂ photocatalyst during long-term use: decrease of its activity

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Abstract

When TiO₂ is immobilized on organic fibres, pumice stone or polymer film, the photocatalytic efficiency decreases slowly during long-term use. The efficiency of immobilized photocatalysts were tested on 500 ml of a 5×10^{-5} M solution of acid orange-7 (a classical azo dye) before and after treatment of 10^{-3} M solution of acid orange-7 during 4 weeks. It was observed that the efficiency was reduced approximately four, five and 10 times with polymer film containing TiO₂, TiO₂ on organic fibres and TiO₂ on pumice stone, respectively, after 4 weeks of use. Volumes treated were 40, 45 and 60 l, respectively. Nevertheless, the decomposition rate stays a little higher with TiO₂ on pumice stone than with the two other catalysts tested. The photocatalytic activity of immobilized TiO₂ was significantly reduced also during treated with wastewaters. For immobilized photocatalysts used, the decrease of activity is considered to be caused by the elimination of some particles from the catalyst surface during use and also by fouling of catalyst surface by the formation of by-products during the course of degradation process. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Photocatalysis is often proposed for the elimination of organic pollutants from wastewaters. The efficiency of titanium dioxide photocatalyst, used as aqueous suspension, is experimentally proved for decomposition of most of organic substances in water [1–4]. It has several advantages, especially low price and absence of toxicity. However, it involves a difficult problem of filtration to eliminate and recycle the catalysts after use. It is the main limiting factor for practical use. The influence of catalyst recycling on its efficiency was not much studied so far. Al-Sayyed et al. [5] reported that the rate of transformation of 4-chlorophenol (0.15 mM) with TiO₂ progressively decreases for 2 g l^{-1} catalyst used and it is approximately twice less after 10 cycles. This effect was attributed to the inhibiting effect of chloride ions released in the solution, but according to Abdullah et al. [6], a 1.5 mM concentration of Cl⁻ present in the solution is not sufficient to explain this inhibition.

To avoid the problem of filtration, many methods were proposed to immobilize TiO₂, but in these conditions the photocatalyst is expected to be used for a relatively long time, especially for industrial applications. Such kind of tests are not often conducted probably because they require very long time of investigations (several weeks or a few months). Nevertheless, it was mentioned by Brezová et al. [7] that the degradation of phenol by using TiO₂ supported on glass fibres becomes slower and slower during repeated experiments (16 cycles of 90 min). This effect was attributed to the adsorption of by-products on the photocatalyst surface, since it does not occur when the photocatalyst is heated at 200 °C for 2 h. These reported experiments were relatively short. The use of TiO₂ catalyst for the depollution of industrial wastewaters has to be efficient during several weeks, if possible several months.

In a preliminary study, it was shown that the efficiency of TiO₂ on a porous support (pumice stone) was reduced by approximately 50% after 1 week of use with a solution of dye 10^{-3} M [8]. The aim of the present work is a systematic study of the photocatalyst efficiency during several weeks of use in order to evaluate how long the photocatalyst may be used with a reasonable efficiency. Two kinds of TiO₂ were

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used and three different methods of immobilization were applied. A solution of a dye and a real wastewater were used as the substrates. For comparison, the experiment was also carried out with TiO₂ in aqueous suspension.

2. Experimental

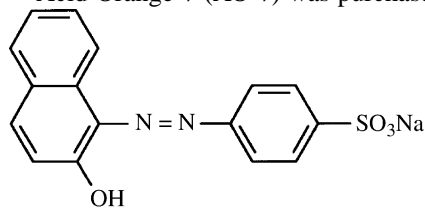
2.1. Reagents and catalysts

Three immobilized TiO₂ photocatalysts were used:

- TiO₂ PC500 from Millennium Inorganic Chemicals immobilized by the firm Ahlstrom on a sheet of organic fibres (mainly cellulose, with some polyester) at the dimensions of the irradiation device (20 cm × 40 cm). The initial weight spread was 20 g m⁻² but washing before the first use eliminated a small portion of TiO₂.
- TiO₂ Degussa P25 immobilized on pellets of pumice stone from Eyraud S.A., fixed on cement plate (20 cm × 40 cm). Pellets were impregnated with a slurry of TiO₂ 6 g/60 ml. Then, the support was let to dry and was washed with pure water to eliminate the excess of the catalyst. For comparison in sunlight/artificial UV light, a slurry of TiO₂ 4.6 g/60 ml was also used for impregnation.
- TiO₂ in “polymer” film obtained with a proprietary binder using a spray technique onto an inert support [9].

TiO₂ used for suspensions was Degussa P25.

Acid Orange-7 (AO-7) was purchased from Acros.



Acid Orange-7

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

Real wastewater from dyeing industry was collected after biological treatment. This treatment eliminated most of TOC (80–90%), but the photocatalytic decolorization was not completed and the TOC values were generally lower than 25 mg l⁻¹. It is worth to mention that they are not very accurate because they are obtained as the difference between total carbon (TC) and inorganic carbon (IC), approximately 70 mg l⁻¹. The pH was in the range of 7.2–8.0.

2.2. Irradiation devices

Solutions and wastewaters were exposed to UV light in a thin-film fixed-bed reactor. This device consisted of a detachable slanting plank 20 cm × 40 cm covered with the photocatalyst and exposed to the light of four lamps Philips TLD 15W/05 emitting the light of wavelength between 300 and 450 nm, i.e. in the range of UV radiations present in sunlight.

The scheme of this reactor has been presented in previous paper [8]. The solution was spread from the top by a peristaltic pump (35 ml min⁻¹ flow), and was collected at the bottom in a volumetric jar in order to evaluate the loss of solution by evaporation, or in a tank, for long time irradiation. In most of the experiments, the slanting plank was covered by a glass plate to reduce evaporation to 7 ml min⁻¹, but some experiments were carried out without cover (evaporation of 21–24 ml min⁻¹). The photon irradiance in the range of 300–450 nm was evaluated to be $3.2 \times 10^{15} \text{ photon cm}^{-2} \text{ s}^{-1}$ (i.e. $5.3 \times 10^{-9} \text{ einstein cm}^{-2} \text{ s}^{-1}$) using potassium ferrioxalate as the chemical actinometer [10]. In fact, the photocatalyst absorbed only the light at the wavelength shorter than ca. 380 nm and a significant portion of incident light is not absorbed.

Suspensions of TiO₂ Degussa P25 (2 g l⁻¹) were irradiated in the other device consisting of a vertical cylindrical Pyrex reactor and a Philips TLD fluorescent lamp. This device has been described elsewhere [11].

For comparison, some experiments were carried out in sunlight in Clermont-Ferrand (latitude 46°N, altitude 400) between late May and early July at 12 GMT \pm 3 h.

2.3. Analyses

The concentration of dye (AO-7) was measured spectrophotometrically at 485 nm after filtering the solution on PVDF membrane (dimension of pores 0.45 μm). The decolorization of wastewaters was monitored at 510 nm (for pink waters) or at 260 nm when no maximum was observed in the visible range. It was noticed that for the dye solutions the absorbance decreased with irradiation time without any modification in the shape of the spectrum, as it was shown in Fig. 1, which proves that no by-product of decomposition absorbs in the visible range.

Total organic carbon measurements were carried out on Shimadzu TOC-5050A analyzer.

2.4. SEM micrographs

SEM micrographs of catalysts with magnification of 250–1500 times, before and after irradiation were recorded on a scanning electron microscope Cambridge S 360 coupled with an Oxford EDS (energy dispersing spectrometer) Si(Li) detector X-ray detection 133 eV on Mn.

2.5. Procedures

Initially, $5 \times 10^{-5} \text{ M}$ solution of AO-7 (500 ml) was exposed to UV light in the thin-film fixed-bed reactor with glass cover, described above, and the initial decolorization rate was measured spectrophotometrically. In order to accelerate the ageing of catalyst, 2.5 l of 10^{-3} M solution was treated in this reactor and was changed after complete decolorization. Complete decolorization took initially less than 1 day, but several days after 3 weeks of use. Then, the catalyst

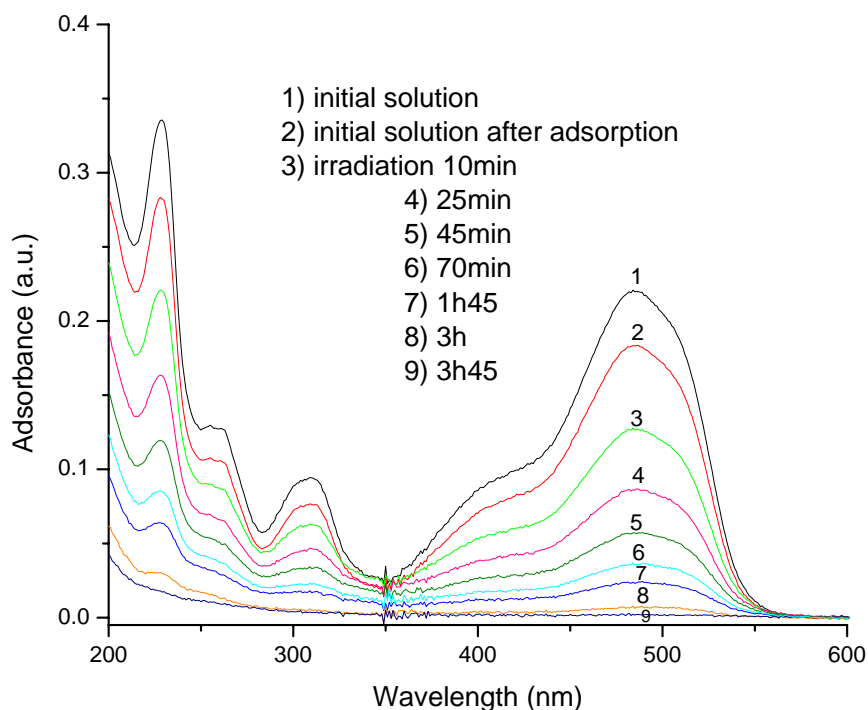


Fig. 1. Spectra of acid orange-7 after irradiation with suspended TiO₂.

was washed with water and dried. The kinetics of the dye decomposition in the diluted solution was measured and compared with the previous one. This procedure was repeated during several weeks in order to evaluate the decrease of the photocatalyst efficiency.

A similar procedure was used to study the ageing effect on TiO₂ immobilized on pumice stone with wastewater collected after biological treatment. The kinetics of decolorization was studied with 1 l of wastewater, with periodical addition of pure water (7 ml h⁻¹) to balance the evaporation loss. Then, the catalyst was aged by the treatment of 15 l of wastewater and then the kinetics with 1 l was compared with the first one.

In order to accelerate the test of kinetics and to work in conditions similar to the industrial applications, the ageing of TiO₂ on organic fibres and TiO₂ on “polymer” film were carried out without glass cover on the slanting plank, that roughly divides by 2 the decolorization rate but increases the evaporation of water. (The evaporation was evaluated as 24 ml min⁻¹ and was approximately three times higher in comparison to that with glass cover.)

For slurry, 60 ml of 5 × 10⁻⁵ M solution of AO-7 was irradiated in the presence of 120 mg TiO₂ P25 (suspension of 2 g l⁻¹), after 30 min adsorption in the dark. Actually, it was controlled that adsorption equilibrium was reached in 20 min. The decolorization of the dye was measured by UV absorption at 485 nm on samples filtered on 0.45 μm filter. A cuvette of 2 mm optical path was used to limit the volume of sampling. After irradiation and overnight decantation, water was removed with a pipette. A new solution (60 ml) was added together with 15 mg TiO₂ to balance the loss of TiO₂

due to the sampling, and irradiation was repeated in order to compare the kinetics of AO-7 decomposition with the initial one.

Another method of ageing was also used: after decolorization of the first solution (5 × 10⁻⁵ M), 0.6 ml of 5 × 10⁻² M solution of AO-7 was added in order to obtain a solution of 5 × 10⁻⁴ M. After photocatalytic decolorization, 0.6 ml of 5 × 10⁻³ M solution was added in order to obtain a solution similar to the initial one and to study the new kinetics of AO-7 decomposition. This procedure was repeated. Then, the catalyst was separated by filtration, calcined at 450 °C during 4 h to eliminate any organic matter remained on the catalyst surface and was reused for the kinetics tests with 5 × 10⁻⁵ M solution of AO-7.

3. Results and discussion

3.1. Kinetics of degradation of AO-7 and wastewater

3.1.1. Immobilized photocatalysts

The kinetics of degradation of 5 × 10⁻⁵ M solution of AO-7 with TiO₂ PC500 on organic fibres, TiO₂ P25 on pumice stone and TiO₂ immobilized in “polymer” film as described above, is reported in Figs. 2–4 respectively. No “blank” appears on Figs. 2 and 4 because fibres and “polymer” without catalyst were not available, but most probably it would be very similar to the blank obtained in Fig. 3 with support without catalyst. Initially, the photocatalytic efficiency was higher for TiO₂ on pumice stone than for TiO₂ on “polymer” and higher for TiO₂ organic fibres

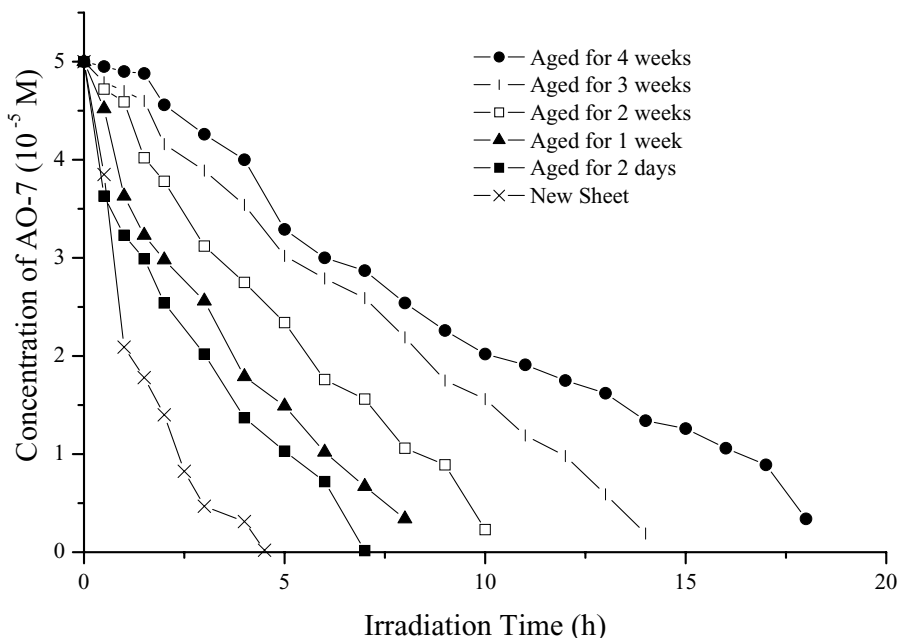


Fig. 2. Decolorization of acid orange-7 (5×10^{-5} M) with TiO_2 on organic fibres after treatment of a solution 10^{-3} M.

than on “polymer”. Decrease of AO-7 concentration was observed for all supported photocatalysts, but this decrease was a little less for TiO_2 on “polymer”. After 4 weeks of use, TiO_2 on “polymer” and TiO_2 on organic fibres were almost equivalent in efficiency and were a little less efficient than TiO_2 supported on pumice stone. Using TiO_2 on pumice stone, 60 l of 10^{-3} M solution AO-7 has been completely decolorized after 4 weeks that corresponded to 21 g of AO-7 decomposed. No formation of by-products absorbing in the UV range was observed. With TiO_2 on organic fibres and TiO_2 on “polymer” the volumes of decolorized

solution were 45 and 40 l, respectively. In the three cases, the catalysts were expected to be re-used during following weeks. It is a very good result for the laboratory use. However, for industrial application it means that the photocatalyst has to be changed (or regenerated) approximately every 1 or 2 months.

In order to know if this decrease of photocatalyst efficiency is due to the adsorption of organic by-products on the catalyst surface or to the degradation of these by-products in the solution, TiO_2 on pumice stone and TiO_2 on organic fibres were heated at 150°C during 3 h. After this treatment,

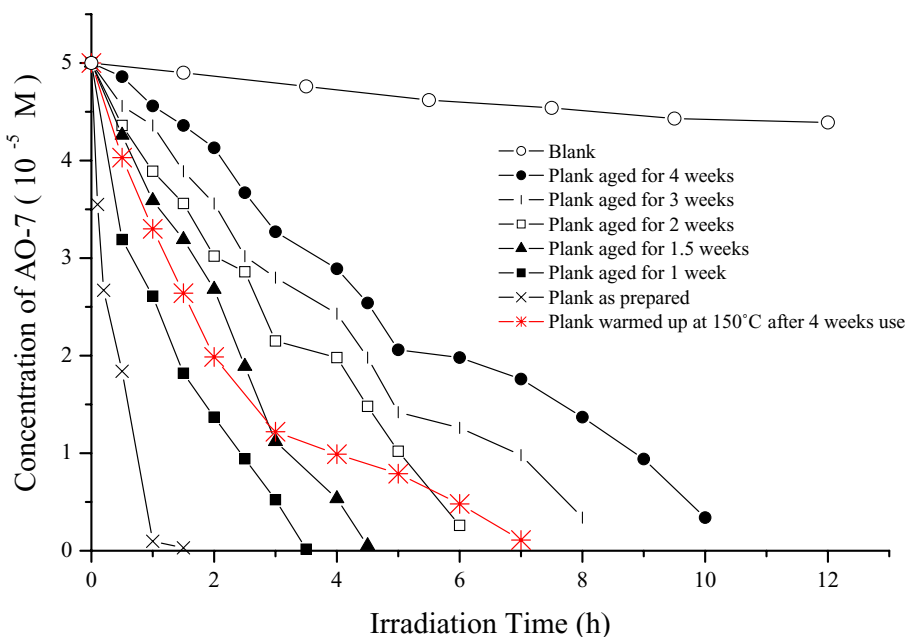


Fig. 3. Decolorization of AO-7 (5×10^{-5} M) with TiO_2 on pumice stone after treatment of a solution 10^{-3} M.

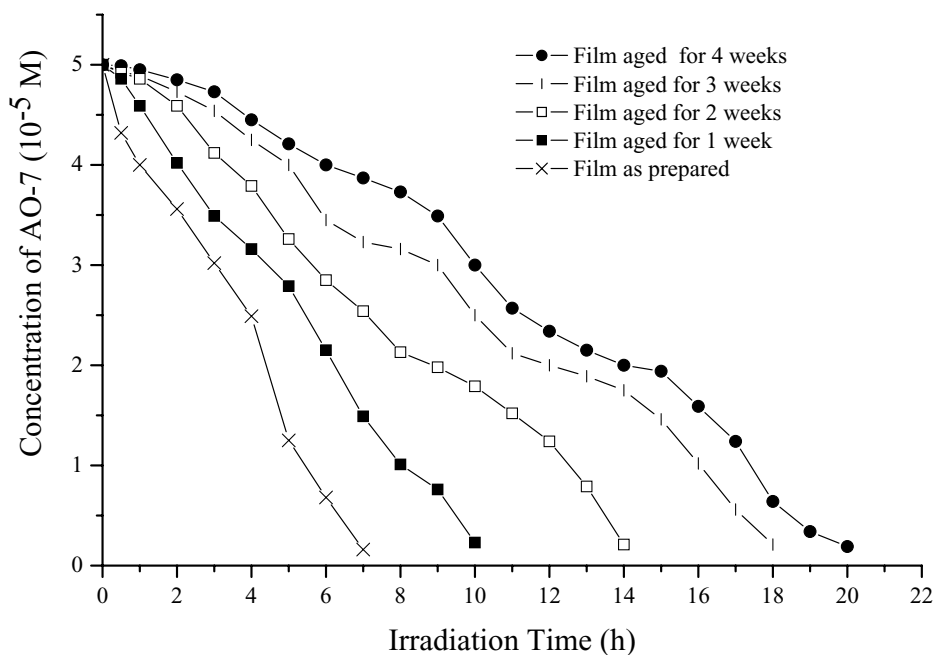


Fig. 4. Decolorization of AO-7 (5×10^{-5} M) with TiO₂ on “polymer” film after treatment of a solution 10^{-3} M.

the efficiency of TiO₂ on pumice stone was approximately 50% recovered (Fig. 3), but the catalyst on organic fibres was damaged with releasing of TiO₂. It was evidently seen that there is no possibility of using the same heat treatment of TiO₂ on “polymer” film to recover its activity.

Ageing was also studied using wastewater as the substrate. Procedure is described in Section 2.5 with TiO₂ immobilized on pumice stone. The photocatalyst efficiency observed was approximately 50% less after treatment with 15 l of wastewater, which took approximately 3 weeks. The experiment was planned to be continued during 1 month, but it had to be stopped before because the algae developed on the support and drastically reduced the photocatalytic efficiency. It may be deduced that this method is really not appropriate for biologically treated wastewaters.

The ageing of catalyst during the treatment of wastewater was studied with TiO₂ on organic fibres and with TiO₂ in “polymer” film also by using the same procedure but more rapid and more representative for possible industrial applications presented in Section 2.5 (i.e. without glass cover and without replacing of evaporated water). The rate of half-decolorization of 500 ml water with TiO₂ on organic fibres decreased as it is presented in Table 1. After 1 week and 9 l of treated water, the experiment was stopped because of the formation of algae on the catalyst surface, and because it was not possible to clean it up without damaging the catalyst.

The elimination of pollutants from wastewater with TiO₂ on “polymer” film in the same conditions was significantly slower. One of the reasons is that the film was not prepared in situ and its adhesion on the support was not perfect. Thus, the comparison with the other supports is not quantitatively valid. However, after 13 days and approximately 20 l of wastewater treated, the film was slightly damaged by

cracks, and the biological development was observed. It was necessary to clean up the catalyst with a diluted solution of hypochlorite before testing the decomposition rate. The efficiency was almost the same as initial, probably because of the cleaning process by using hypochlorite and followed by a long washing with pure water for the elimination of by-products. Then, the experiment was restarted with a new batch of 5 l of wastewater, which was changed after 3 days. The catalyst was washed every week. In these conditions, the catalyst efficiency was not significantly reduced and it was possible to treat approximately 70 l of wastewater. However, during the 7th week of this treatment, the “polymer” film became breakable and highly damaged. It had to be changed.

3.1.2. Solar irradiation

Most of experiments were carried out in artificial UV light which is more reproducible than sunlight, for the better comparison of photocatalyst efficiency. However, the same device was used in sunlight between May and July to com-

Table 1
Time taken for half-decolorization as a function of volume of treated wastewater for TiO₂ supported on organic fibres

Volume treated (l)	$\tau_{1/2}$ (min)
0.5 (initial)	34 (35)
1.0	39 (37)
3.0	70 (65)
5.0	80 (73)
7.0	140 (125)
9.0	160 (140)

In parentheses are values after approximate correction of evaporation effect.

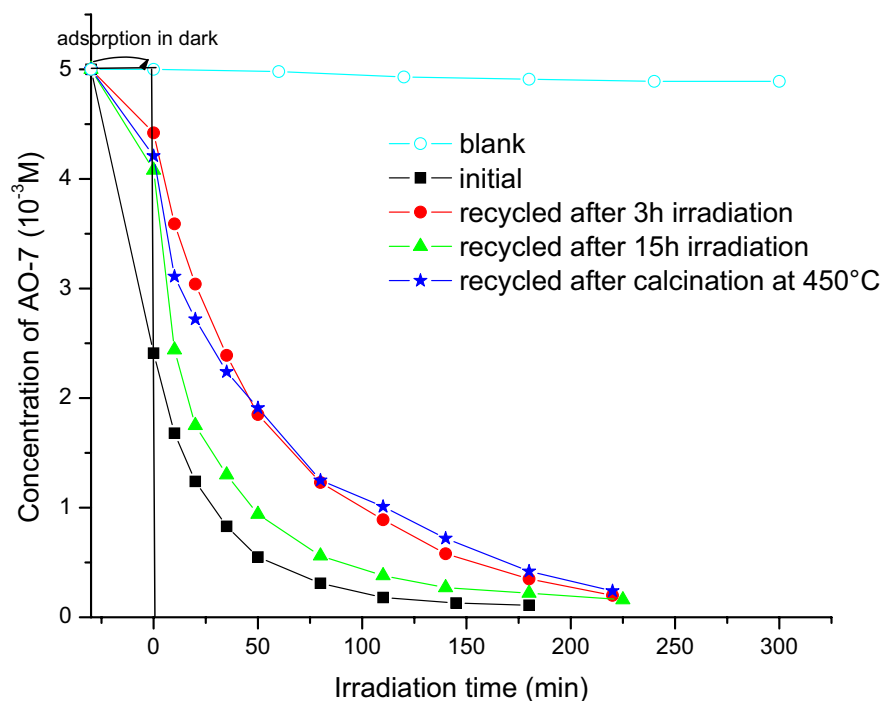


Fig. 5. Decolorization of AO-7 with irradiation time on suspended TiO_2 .

pare the rate of decomposition with both light sources. Substrates used were AO-7 ($5 \times 10^{-5} \text{ M}$) and real wastewater. Supported photocatalyst was P25 on immobilized pellets of pumice stone (4.6 g on a 20 cm \times 40 cm plank). With both substrates used, it was noted that the rate of photocatalytic degradation was approximately 1.5 times higher in sunlight than in artificial UV light. It was also noted that, in the case of AO-7, the direct photolysis plays a minor role in sunlight, but it is not completely negligible due to the strong absorp-

tion of the dye in the visible range. This phenomenon let understand why the ratio between the degradation rates in sunlight and in artificial UV light was a little higher with AO-7 solutions than with real wastewater.

3.1.3. Suspended photocatalysts

The decrease of photocatalyst efficiency observed for immobilized photocatalysts can have many causes, mainly the loss of catalyst by washing out and the fouling of the catalyst

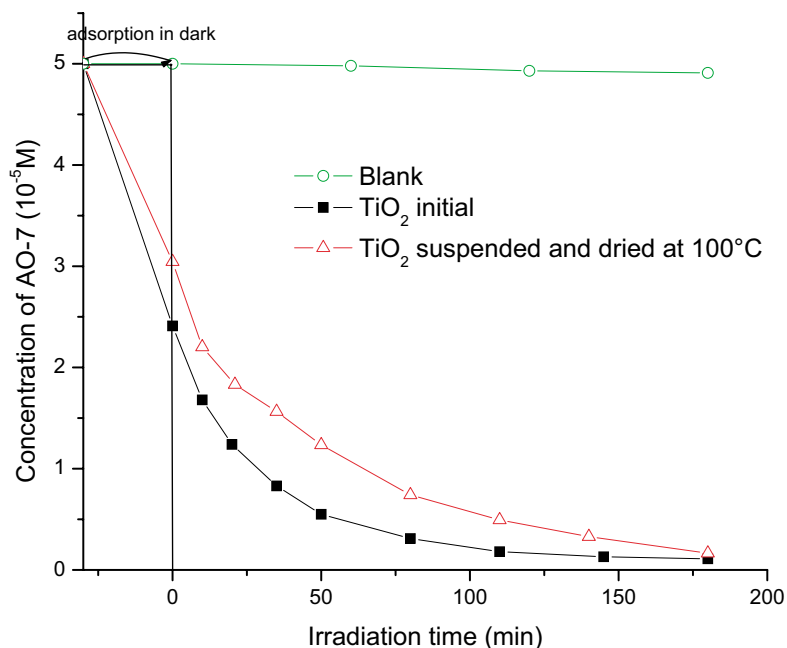


Fig. 6. Decolorization of AO-7 under UV irradiation for TiO_2 suspended and dried at 100°C after suspension.

surface. To prove this, experiments were carried out with suspended TiO_2 as described in Section 2.5 using AO-7 as the substrate. The rate of AO-7 decolorization was measured with a 5×10^{-5} M solution using a catalyst “as prepared”, TiO_2 recycled just after decolorization of the dye and TiO_2 irradiated several hours after decolorization. It is seen in Fig. 5 that adsorption of the dye is significantly higher for the new catalyst than for the recycled one and that this decrease in adsorption is more significant when the catalyst is reused just after decolorization than when the irradiation

is continued several hours later. It can be deduced that the competitive adsorption of by-products on the catalyst surface can be a reason of catalyst efficiency decrease. This effect is minimized when these by-products are destroyed, but it is difficult to control their complete elimination.

The experiment was carried out to eliminate by-products adsorbed on TiO_2 by the calcination of the catalyst at 450°C for 4 h and further irradiation during 3 h in the presence of 5×10^{-5} M solution of AO-7, i.e. just after elimination of the dye. The original efficiency of the catalyst was not recov-

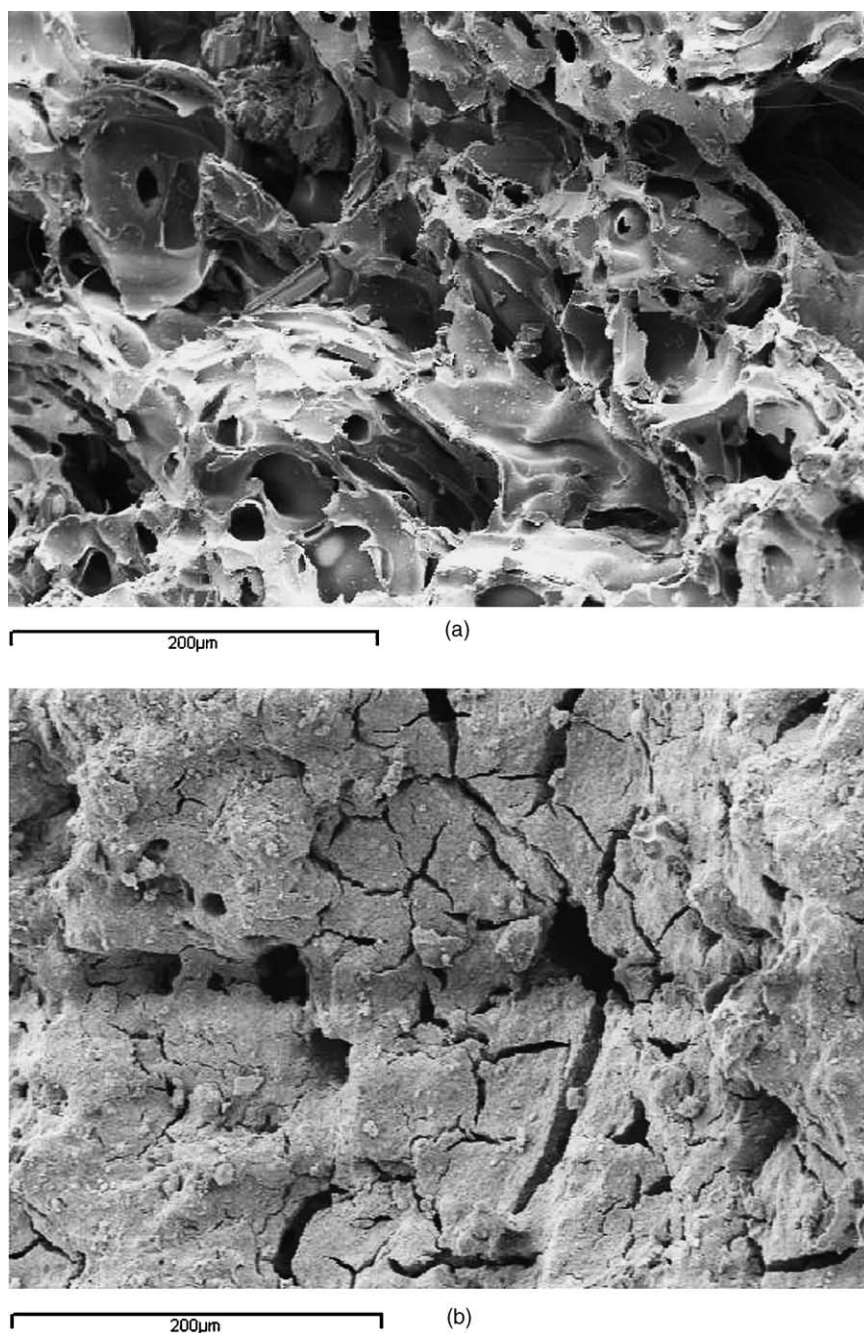


Fig. 7. Micrographs of supported catalysts “as prepared” and after 1 month of use: (a) pumice stone original (250 \times); (b) pumice stone with TiO_2 “as prepared”; (c) after 4 weeks of use; (d) TiO_2 on fibres (500 \times) “as prepared”; (e) after 4 weeks of use; (f) TiO_2 in “polymer” film (500 \times) “as prepared”; and (g) after 4 weeks of use.

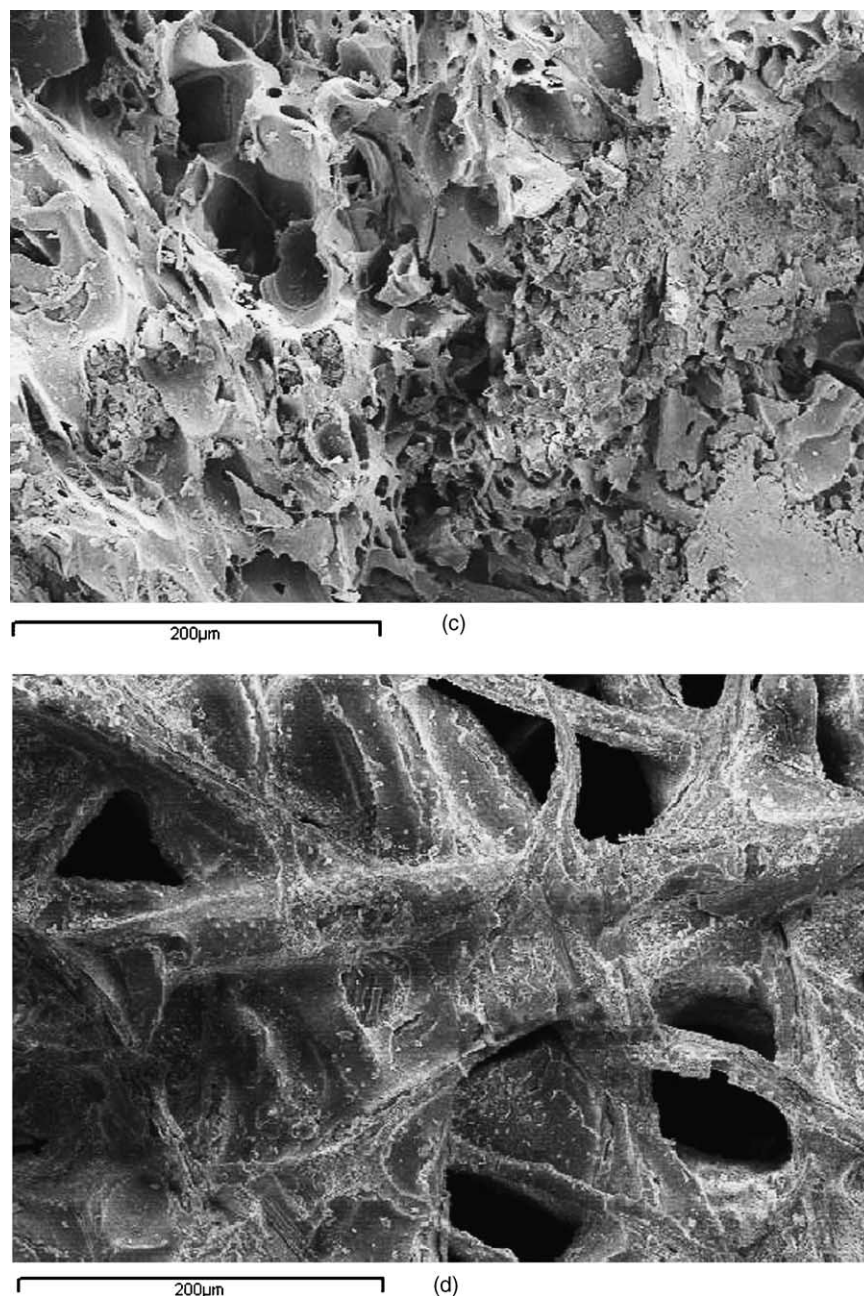


Fig. 7. (Continued).

ered, but in fact another phenomenon was observed: when TiO_2 was suspended in water and then dried (at 100°C) it formed agglomerates. Even when these agglomerates were ground in a mortar, the efficiency was not completely recovered and adsorption capacity became reduced, as shown in Fig. 6. In this case, the calcination of the catalyst causes two opposite effects: the elimination of organic by-products (beneficial effect) and physical damage of the catalyst (detrimental effect).

A drastic decrease in efficiency was also observed when the catalyst was aged with 5×10^{-4} M solution of AO-7, as described in Section 2.5 and was reused in situ with $5 \times$

10^{-5} M solution, but in these conditions the decrease in efficiency may be attributed to both adsorbed and dissolved by-products.

Ageing was also carried out with 5×10^{-3} M solution of AO-7, but the catalyst became dark and the solution was not completely decolorized after 50 days, probably due to the deposition of by-products on the catalyst surface.

3.2. Evaluation of total organic carbon (TOC)

TOC measurements were not used for monitoring the decomposition of AO-7 and wastewater, since these measure-

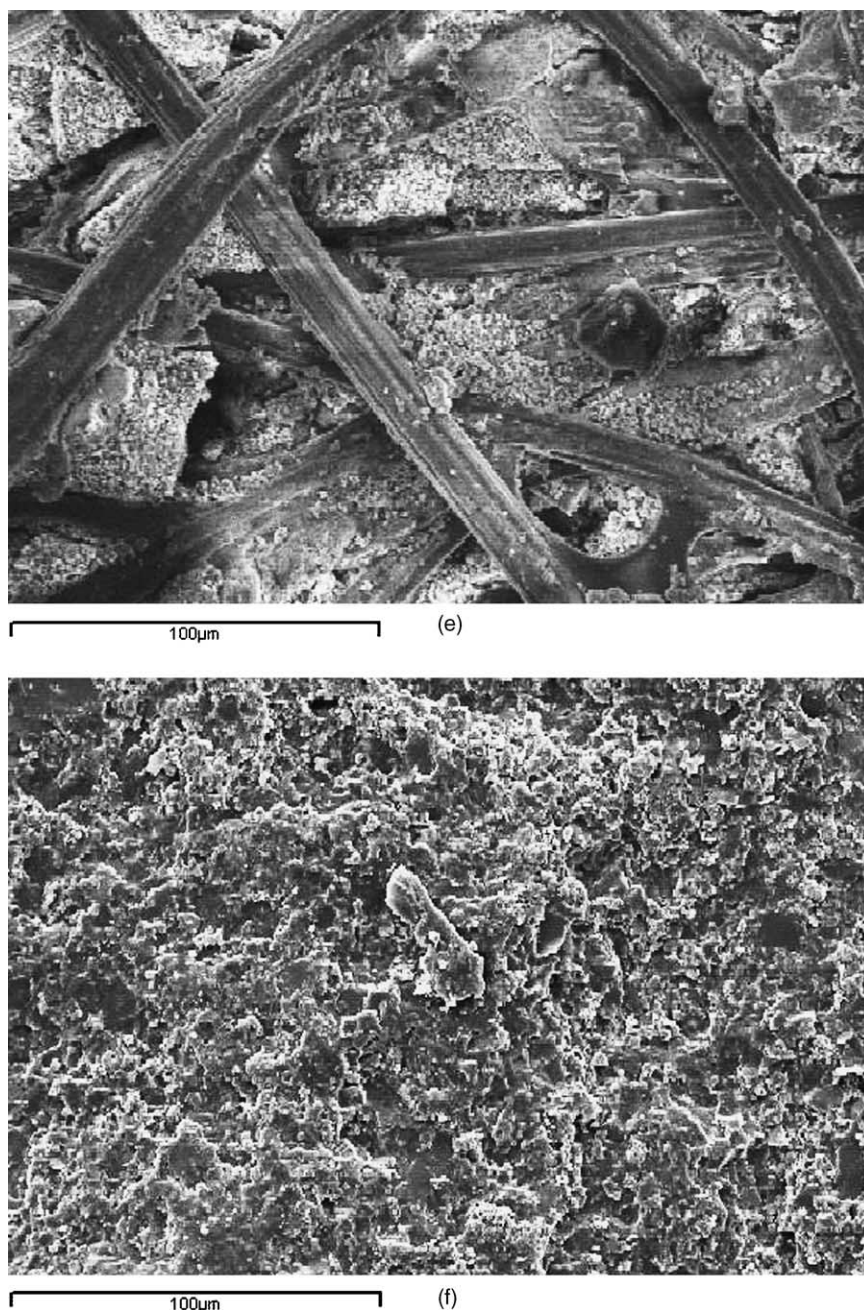


Fig. 7. (Continued).

ments were not so accurate than the measurement of UV-Vis absorbance. The reasons were that relatively low values of TOC were obtained as the difference between total carbon and inorganic carbon, and also because the degradation of the organic support may induce an increase of TOC. Nevertheless, measurements of TOC gave useful information.

When filtered wastewater was photocatalytically degraded with TiO₂ on organic (cellulosic) fibres the value of TOC was generally lower than 25 mg l⁻¹ and it decreased with the irradiation time. In contrast, when wastewater was treated with TiO₂ in “polymer” film the increase of TOC was observed, even when the evaporation was balanced with addi-

tion of pure water. The same increase was observed when AO-7 was degraded on that “polymer” film. It may be deduced that the measure of TOC is not a good method for evaluating the disappearance of the substrate in the presence of polymer. The observed increase of TOC value is attributed to a slow photocatalytic degradation of the “polymer” film.

3.3. Microscopic study

SEM micrographs of TiO₂ supported catalysts were taken “as prepared” and after 4 weeks of use (Fig. 7). In the case of TiO₂ supported on pumice stone and organic fibres, it

can be observed that some TiO_2 is removed from the catalyst surface. It is one of the reasons why photocatalytic activity decreased on the supported catalysts, but similar phenomenon was also observed for TiO_2 slurry. In the case of TiO_2 supported on “polymer” film, some cracks are formed after 1 month of use and the film became breakable, but the microscopic appearance at magnification $500\times$ is not significantly changed. The reduction in catalyst efficiency was observed when the surface was not periodically washed, so it can be attributed mainly to the presence of by-products on the catalyst surface.

3.4. Discussion

The photocatalytic efficiency of TiO_2 immobilized on pumice stone, organic fibres or polymer film was experimentally demonstrated. For presented device equipped with four lamps (15 W), 21 g of dye (AO-7) was decomposed in 4 weeks using ca. 5.5 g TiO_2 on pumice stone, 15.7 g with 1.6 g of TiO_2 on organic fibres and 14 g with 3.8 g of TiO_2 in “polymer” film. Higher decomposition is expected for longer irradiation time. It is a proof of a photocatalytic mechanism. However, for long-term use, a decrease of catalyst efficiency was observed. The elimination of TiO_2 from the support by washing, was observed as it is shown on micrographs, and also fouling of catalyst is involved in decreasing of catalyst efficiency, since the efficiency can be partly regenerated by heating the catalyst at 150°C when it is supported on pumice stone (temperature is limited by the cement layer). This ageing effect also appears with suspended TiO_2 . It should be noted that the ageing of TiO_2 on “polymer” film was not studied in the best conditions, since the film was not prepared in situ. The initial efficiency of TiO_2 on “polymer” is lower than in the case of the other supports used, but the retention of TiO_2 on the support is better, and the decrease of activity is less than that for pumice stone and organic fibres. However, the increase of TOC during irradiation time appears and it is related to a slow degradation of the “polymer” film. This phenomenon was confirmed by the observation of the mechanical damage of the film after several weeks of use.

From the obtained results on suspended TiO_2 and from the SEM micrographs of immobilized catalysts, it may be deduced that the observed decrease of efficiency during long-term use have two main causes: the elimination of some TiO_2 particles from the surface, especially with pumice stone and organic fibres and the fouling of the surface by accumulation of by-products. In the case of suspended TiO_2 adsorbed by-products can be eliminated by calcination, but after it is more difficult to suspend the catalyst in water. The regeneration of the catalyst by long irradiation does not damage the catalyst, but it is time consuming. In the thin-film fixed-bed reactor, it may be assumed that products are formed more rapidly than they are decomposed and their accumulation on the catalyst surface induces a reduction of catalyst efficiency for the degradation of incoming substrate.

The degradation of 60 l of 10^{-3} M solution of AO-7 in 4 weeks with TiO_2 on pumice stone corresponds to the elimination of 11.5 g of organic carbon on 0.08 m^2 of photocatalyst, i.e. $214\text{ mg m}^{-2}\text{ h}^{-1}$. It was investigated that for the presented device, the rate of photocatalytic decomposition is approximately 1.5 times higher in full sunlight than in artificial light and that the glass cover used to limit evaporation also reduces the decomposition rate approximately by a factor 2. The order of magnitude of the degradation rate is too low for the treatment of most of rough wastewaters (TOC of $500\text{--}1000\text{ mg l}^{-1}$ or more). The photocatalytic degradation of wastewater after biological treatment (TOC $< 80\text{ mg l}^{-1}$) in order to eliminate non biodegradable pollutants might be considered, but the volume of treated wastewater per m^2 of catalyst is still small (a few $1\text{ m}^{-2}\text{ h}^{-1}$) and two problems appear: evaporation of water and biological development (algae or other bio-organisms) on the catalyst surface.

4. Conclusion

Immobilization of TiO_2 on pumice stone, organic fibres or “polymer” film gave good results for a short term use (a few weeks). However, a long-term use of immobilized TiO_2 causes a significant decrease of photocatalytic efficiency for elimination of dyes or decontamination of wastewater. This effect is attributed to two main reasons: the elimination of some TiO_2 from the surface (mainly with TiO_2 on pumice stone and on organic fibres), and to the fouling of the catalyst by the by-products of degradation. Such fouling of catalyst surface also occurs for suspended TiO_2 and it can be partly cleaned by exposing the catalyst for a long time of irradiation. By-products adsorbed on catalyst surface may be also eliminated by calcination of catalyst, but it is detrimental to the photocatalytic properties of the suspended catalyst. The main phenomenon that limits the use of “polymer” film is its long-term degradation.

The photocatalytic treatment of a large volume of wastewater is problematic for several reasons: (i) too much organic matter in rough wastewaters; (ii) evaporation of wastewater from the large surfaces exposed to the sunlight; (iii) slow degradation of organic supports; and (iv) development of algae or other biological organisms, with bio-treated wastewaters. However, photocatalytic treatment may be proposed for the decontamination of small volumes of highly toxic waters such as the effluents of pesticides or pharmaceutical industries.

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