



Immobilization of TiO₂ on pumice stone for the photocatalytic degradation of dyes and dye industry pollutants

K. Venkata Subba Rao^a, A. Rachel^a, M. Subrahmanyam^b, P. Boule^{a,*}

^a *Laboratoire de Photochimie Moléculaire et Macromoléculaire, Université Blaise Pascal, CNRS UMR 6505 (Clermont-Ferrand), 63177 Aubière, France*

^b *Catalysis and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India*

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Abstract

An easy method is proposed to immobilize TiO₂ for photocatalytic transformations of organic pollutants in aqueous solution. It consists of impregnation of pumice stone pellets with commercially available TiO₂. Pumice stone is a soft material, but this disadvantage can be eliminated by fixing pellets on a hard surface (cement or polycarbonate) and using a thin-film fixed bed reactor. Examples of application are given with 3-nitrobenzenesulfonic acid (3-NBSA), Acid Orange-7 (AO-7, a dye) and real wastewaters collected after biological treatment.

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1. Introduction

One of the more pressing environmental problems that has been facing textile industry is the removal of colour from dyebath effluents prior to discharge to the local sewage. Many synthetic dyes, such as azodyes, are resistant to microbial degradation under usual aerobic conditions. This is because dyestuffs are designed to be resistant to chemical fading and light-induced oxidative fading. It was experimentally proved that TiO₂ in aqueous suspension is an efficient photocatalyst for the elimination of biorecalcitrant organic pollutants. Most of organic substances can be transformed since the oxidizing species involved, specially •OH, has a very high oxidation potential (1.9–2.7 V) [1]. Other

significant advantages of TiO₂ is the absence of toxicity and its low price. The main disadvantage that limits the development of this method is the need of a difficult and costly step of filtration to eliminate thin particles and recycle the catalyst. Consequently, only a few publications deal with the evolution of the catalyst after several recycling processes. Filtration can be eliminated by immobilizing the photocatalyst on a solid support [2]. Many supports were suggested, i.e. quartz, silica, different kinds of glass, ceramics [3], activated carbon [4], zeolites [4,5], glass fibres [6,7], stainless steel [8]. Most often the photocatalytic efficiency of immobilized TiO₂ was not compared to that of suspensions. Nevertheless, it was reported that commercial glass fibres covered with TiO₂ and suspended TiO₂ have comparable activities for the transformation of phenol [6a]. A decrease of activity was observed during repeated experiments and became significant after 20 h use. However, this activity can be recovered

* Corresponding author. Tel.: +33-473-40-7176;

fax: +33-473-40-7700.

E-mail address: pierre.boule@univ-bpclermont.fr (P. Boule).

by heating at 200 °C [6b]. Such a deactivation was not observed using 3-nitrobenzenesulfonic acid (3-NBSA) as the substrate [7], probably because adsorption is less than with phenol and products do not accumulate much on the surface. Commercial inorganic fibres coated with TiO₂ were reported to be less efficient than suspended TiO₂, but much more efficient than TiO₂ deposited by sol-gel dip coating on red brick, cement or glass [7]. This phenomenon may be due to the presence of ions in brick and cement, but also to a problem of exchange between solution and solid phase, easier with separated particles than with plain surfaces.

More recently, it was shown in a preliminary work that porous supports such as pumice stone can be impregnated with TiO₂ and used as immobilized photocatalyst. The efficiency is satisfactory for the transformation of nitrobenzenesulfonic acids, but the use of thin-film fixed bed reactor is recommended to prevent from damaging the support by stirring [9].

The aim of the present work is to compare different types of immobilized photocatalysts using the same device and different substrates, especially a model dye Acid Orange-7 (AO-7) and real industrial wastewaters after biological treatment. Acid Orange-7 was chosen as a substrate since it was experimentally proved that its direct photolysis in sunlight is not efficient. Actually, photocatalysis cannot be recommended for rough wastewaters that contain too much organic matter, but for the elimination of compounds that resist to biologic treatment.

2. Material and methods

2.1. Photocatalysts and supports

TiO₂ Degussa P25 anatase 70–80%, rutile 20–30% with a surface area of 55 m² g⁻¹ was immobilized according to different methods.

- On “inorganic fibres” provided by the firm Isover Saint-Gobain. The process is patented.
- On “polyacrylonitrile” sheet. The catalyst contains 50% TiO₂ and 50% polymer, but the preparation is confidential. Samples were provided by Dr. K.V. Peinemann from Germany.
- In acrylic emulsion spread on a glossy surface of Cuddapah stone. The acrylic sheet was peeled and

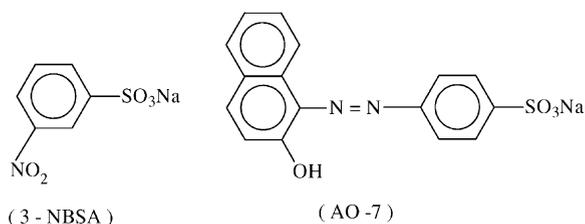
used in the thin-film fixed bed reactor. The proportion of TiO₂/polymer was approximately 50%. The weight of TiO₂ was evaluated at 48 g m⁻².

- Impregnation on pumice stone pellets fixed either on cement or on polycarbonate sheet. On cement, pellets were added before hardening of cement and on polycarbonate they were pasted using chloroform to dissolve the superficial layer of the polymer. Then, the pellets were impregnated with a sonicated suspension of TiO₂ (6 g/60 ml) dried, washed to eliminate the excess of titania and let to dry again before use. The weight of TiO₂ retained was 50–60 g m⁻². Micrographs of bare and impregnated pellets of pumice stone are given in Fig. 1. These micrographs were obtained on Cambridge S 360 coupled with an Oxford energy dispersing spectrometer with Si(Li) detection. It clearly appears that the rough and porous surface of pumice stone is covered with TiO₂ with small cracks as a dry clay.
- TiO₂ Millennium PC 105 (pure anatase—surface area 80–100 m² g⁻¹) was immobilized on organic fibres (mainly cellulosic) provided by the firm Ahlstrom was also used. The amount of TiO₂ was 20 g m⁻². The process is patented.
- TiO₂ Millennium PCs 50 and 500 (pure anatase), surface areas 45 ± 5 and >250 m² g⁻¹, respectively, were immobilized on pumice stone.

Pellets of pumice stone 2–3 mm and ≅5 mm were kindly provided by S.A. Eyraud (Lyon, France).

2.2. Substrates

Experiments were carried out with two pure substrates and with real wastewaters. Pure substrates were 3-nitrobenzenesulfonic acid sodium salt >95% provided by Fluka and a dye Acid Orange-7 of high purity grade from ACROS.



Wastewaters containing textile dyes were also collected before and after biological treatment for the

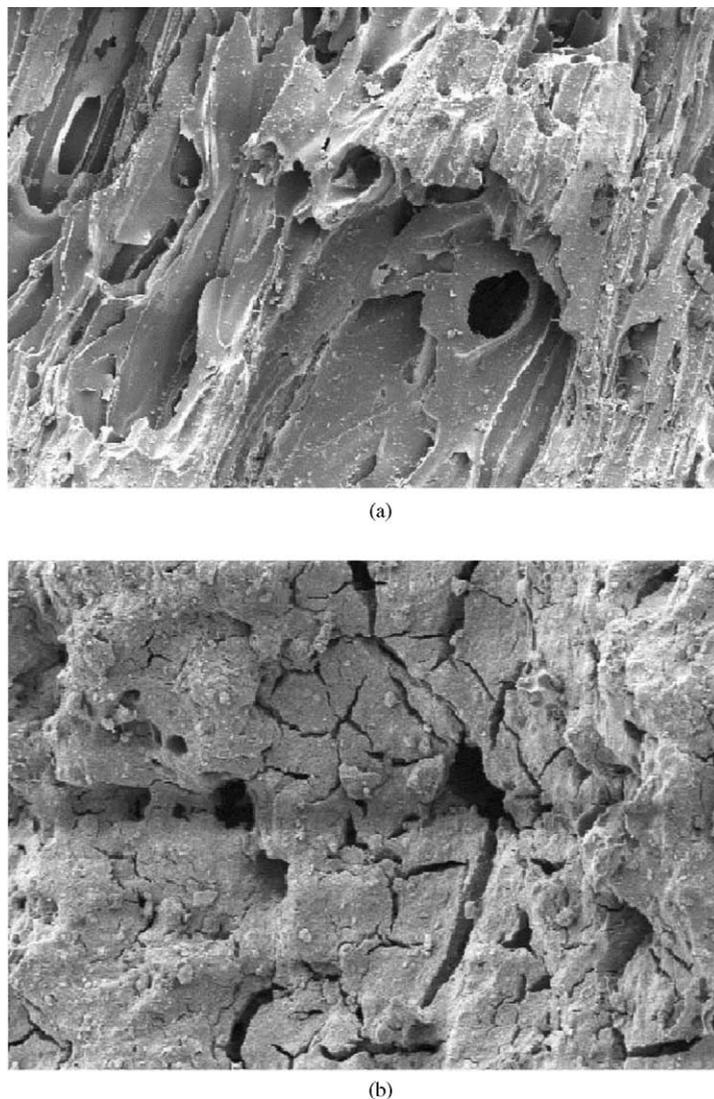


Fig. 1. Micrographs of a pellet of pumice stone (magnification 250): (a) bare pumice; (b) impregnated with TiO₂ P25.

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

2.3. Irradiation device

Solutions were exposed either to artificial UV light or to sunlight using the device presented in Fig. 2. It consists of a detachable slanting plank $20\text{ cm} \times 40\text{ cm}$ covered with a photocatalyst. The solution is spread

at the top with a peristaltic pump (35 ml min^{-1}) and collected at the bottom in a volumetric jar that permits to correct the evaporation by making up the volume with purified water. The slanting plank was covered with a glass to reduce the evaporation. In a typical experiment it was 7 ml h^{-1} . For indoor experiments the light source consists of four lamps Philips TLD 15 W emitting between 300 and 450 nm. Light intensity was evaluated by chemical actinometry with ferrioxalate at $3.2 \times 10^{15}\text{ photons s}^{-1}\text{ cm}^{-2}$.

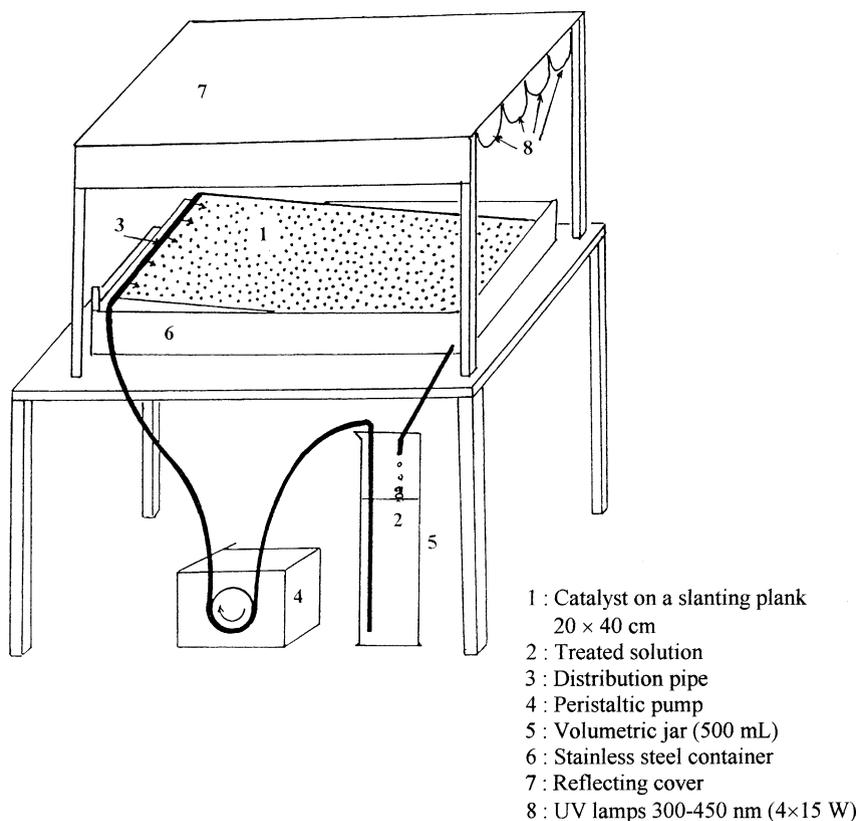


Fig. 2. Thin-film fixed bed reactor used for the irradiation of solutions in artificial UV light or sunlight. Dimensions of slanting plank 20 cm × 40 cm.

The order of magnitude of the power received was $10\text{--}20\text{ W m}^{-2}$.

2.4. Analyses

The disappearance of AO-7 was monitored by UV-Vis spectrophotometry on Cary 3 (Varian) at 485 nm. It was previously controlled that spectrophotometry and HPLC gave similar results. It proves that no photoproduct absorbing at this wavelength is formed. Then, spectrophotometry was preferred because it is more reproducible and rapid to use.

The disappearance of 3-NBSA was quantified by HPLC using Waters chromatograph equipped with a photodiode array detector and column C₁₈ 250 mm × 4.6 mm. Eluent was methanol/water (35:65 (v/v)). The addition of tetrabutylammonium hydrogen sulfate (TBA) $5 \times 10^{-3}\text{ M}$ to water was necessary to obtain a good resolution of the chromatogram.

The disappearance of pollutants in real wastewaters was monitored by total organic carbon (TOC) analysis on Shimadzu TOC analyser 5050A. Initial value of TOC was $89\text{--}91\text{ mg l}^{-1}$.

3. Results and discussion

3.1. Direct photolysis

It was controlled that the direct photolysis of Acid Orange-7 and 3-nitrobenzenesulfonic acid is very slow in sunlight in the absence of photocatalyst. With a $5 \times 10^{-5}\text{ M}$ solution of AO-7, 2% were transformed after 2 months exposure in sunlight near equinox. The disappearance of 3-NBSA was evaluated at 1.5% in a solution $5 \times 10^{-4}\text{ M}$ exposed to sunlight during 1 month (October–November). After only 1 week transformation was negligible. In artificial UV light

disappearance was negligible in the absence of photocatalyst during the time required for the photocatalytic transformation.

3.2. Acid Orange-7

A 500 ml solution of AO-7 (5×10^{-5} M) was photodegraded in artificial light (300–450 nm) using a thin-film fixed bed reactor on different kinds of immobilized photocatalysts: TiO₂ Degussa P25 on inorganic fibres provided by Isover Saint-Gobain, TiO₂ Millennium PC 105 on organic fibres provided by Ahlstrom, P25 on a sheet of polyacrylonitrile, P25 mixed with acrylic emulsion and spread on a flat surface, and pellets of pumice stone impregnated with a suspension of P25 as described in Section 2.1. Results are reported in Fig. 3. The “blank” was obtained with bare pellets of pumice stone fixed on white cement. It clearly appears that the best efficiency is obtained with impregnated pumice stone irrespective of the support (cement or polycarbonate). TiO₂ P25 on polyacrylonitrile lead to a less efficient catalyst. With all catalysts used it was controlled that adsorption effect on the concentration is negligible.

3.3. 3-Nitrobenzenesulfonic acid

The same device was used for the photocatalytic transformation of 3-NBSA. The volume treated was smaller (400 ml) except with TiO₂ on organic fibres (500 ml), the initial concentration was smaller (4×10^{-5} M) and nevertheless, half-lives are larger than with the dye. It is consistent with the electron withdrawing effect of NO₂ group that reduces the oxidability of the aromatic ring. The rate constant of the reaction of \bullet OH with 3-NBSA was evaluated at $6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, i.e. approximately 10 times less than with benzenesulfonic acids without nitro group [10].

As it is with AO-7, the fastest reaction occurs with TiO₂ on pumice stone fixed on white cement. It can be noted that the reaction is not so fast when pellets of pumice stone are fixed on polycarbonate, but this difference may be attributed to the fact that the catalyst was reused several times in between (see Section 3.5). Actually, as it appears in Fig. 4, when organic fibres with titania were used for a second experiment the transformation rate was a little smaller than for the first use.

With all catalysts used adsorption has a negligible effect on the concentration.

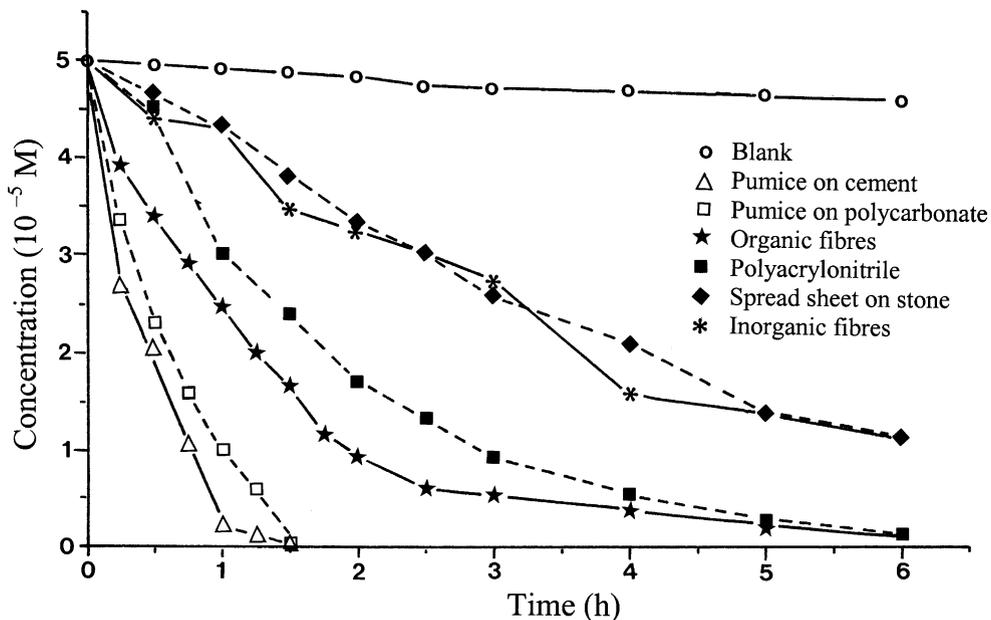


Fig. 3. Photocatalytic transformation of Acid Orange-7 on TiO₂ immobilized on various supports. Volume treated, 500 ml; initial concentration, 5×10^{-5} M. TiO₂ P25 except for organic fibres (PC 105).

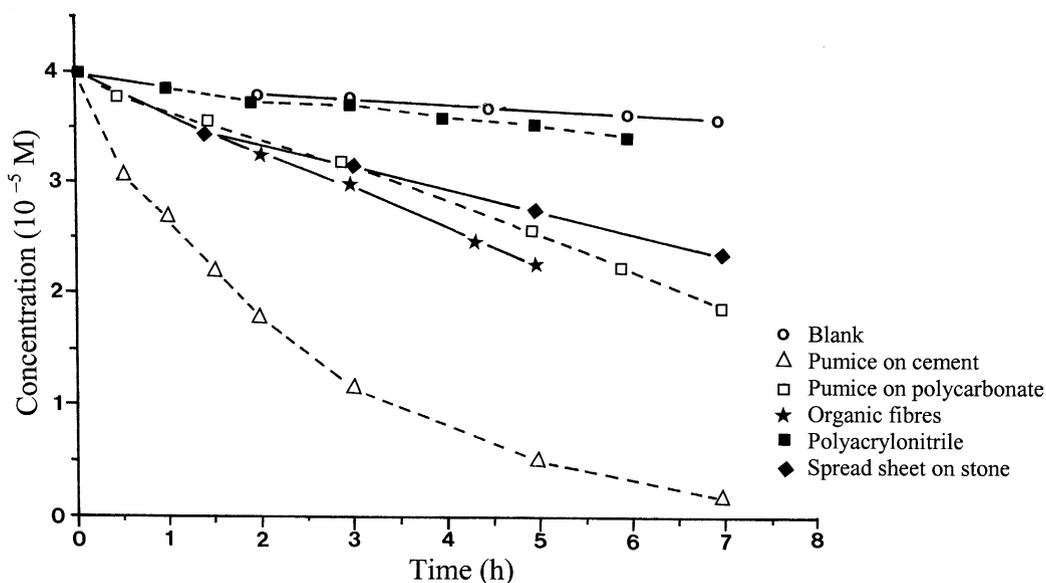


Fig. 4. Photocatalytic transformation of 3-NBSA on TiO_2 immobilized on various supports. Volume treated 400 ml except with TiO_2 on organic fibres (500 ml). Initial concentration, 4×10^{-5} M. TiO_2 P25 except for organic fibres (PC 105).

3.4. Real wastewaters

Real wastewaters from dye industry collected after biological treatment (light pink colour) were photocatalytically treated with the same device using various titanium photocatalysts immobilized on pellets of pumice stone. The degradation was monitored by UV absorption at 260 nm since aromatic and quinonic derivatives absorb at this wavelength. Results are reported in Fig. 5a and b for sunlight and artificial UV light, respectively. It appears that P25 is more efficient than PCs 50 and 500 immobilized in the same conditions on pumice stone. PC 50 gave slightly better results than PC 500. No meaningful difference was observed when pellets are fixed on white cement or on polycarbonate. It is also noteworthy that degradation is more rapid in sunlight (bright sunlight in April, latitude 46°N , altitude 400 m) than in artificial UV light (four lamps, 300–450 nm). It means that the half-lives evaluated in indoor experiments are surely longer than that of half-lives in summer sunlight.

Photocatalytic elimination of pollutants present in wastewaters were also monitored by the determination of total organic carbon. Results are depicted in Fig. 5c.

Real wastewaters collected before biological treatment were also treated in the same manner. Colour disappeared after 4 h (in place of 2 h), but the main problem is the formation of insoluble products that appear as suspended matter in the solution. Consequently, photocatalysis is not so convenient for the treatment of rough wastewaters.

3.5. Long term evolution of the photocatalyst

With immobilized photocatalysts that may be reused many times or used for long time, ageing is an important problem. The influence of reusing on the photocatalytic efficiency if titania immobilized on pumice stone was controlled in drastic conditions: The kinetics of transformation of a solution of AO-7 (5×10^{-5} M) was measured with a slanting plank covered with pellets of pumice stone impregnated with P25 titania and used for the first time. Then, the catalyst was used for the degradation of 5 l of solution (10^{-3} M) during a full week. It was observed that a solution of 10^{-3} M was completely decolourised after 1 week. After washing with pure water the same catalyst was used with a dye solution 5×10^{-5} M and the kinetics were compared with the first one (Fig. 6). The transformation

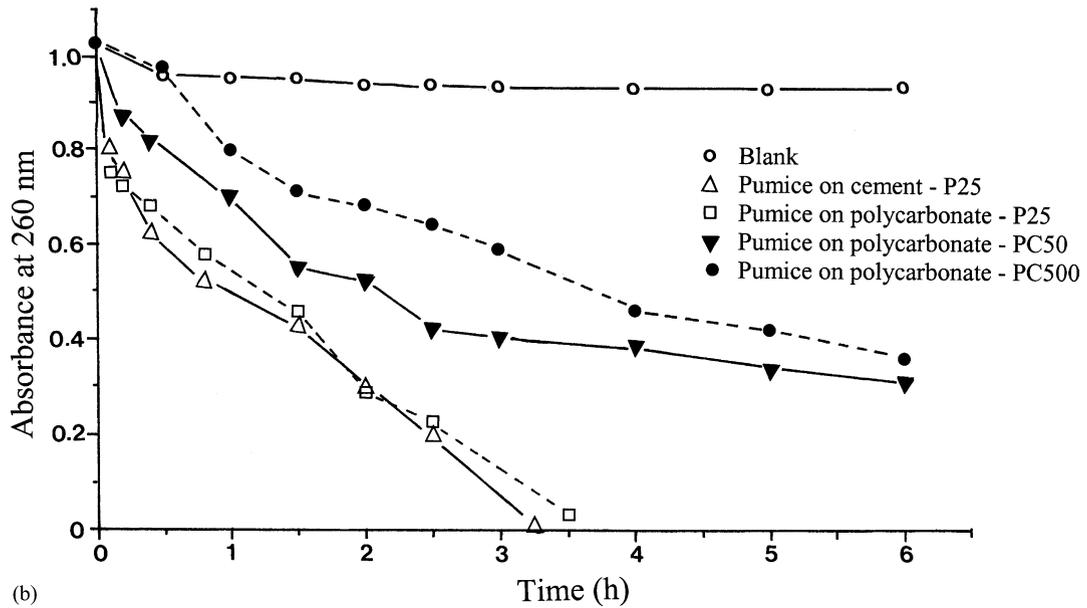
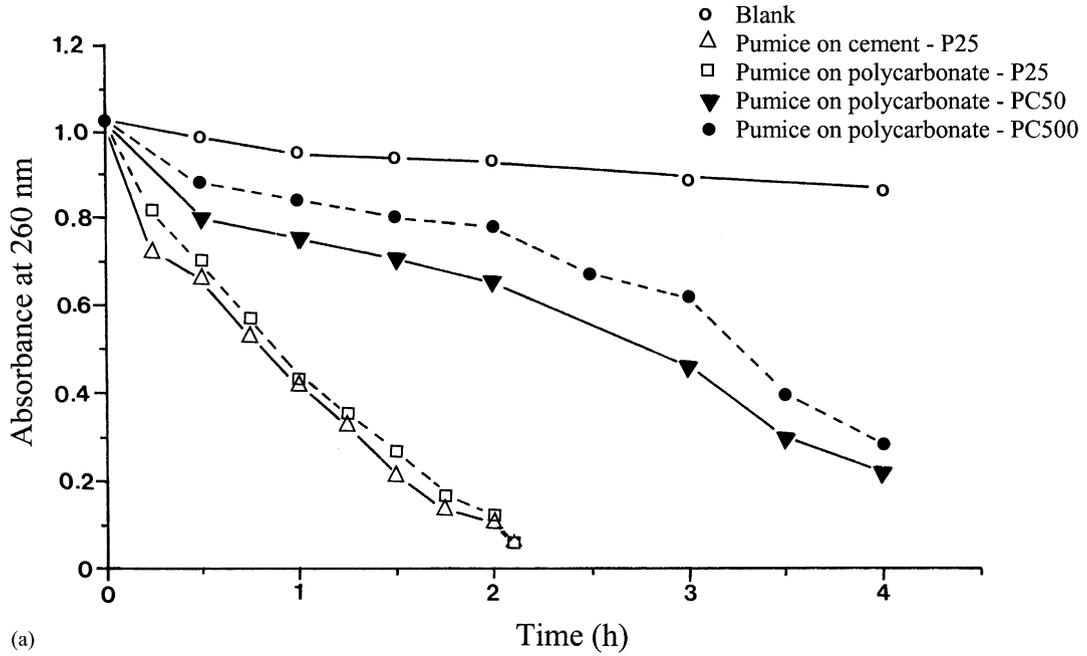


Fig. 5. Photocatalytic treatment of real wastewaters collected after biological treatment: (a) exposed to sunlight (bright sun in April); (b) exposed to UV light 300–450 nm; (c) evolution of TOC (sunlight).

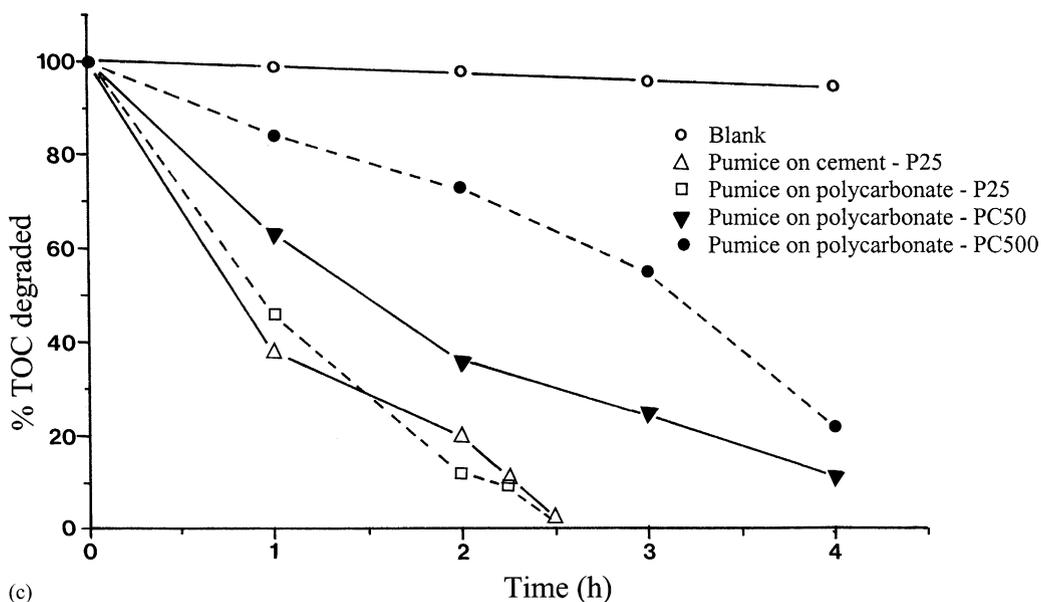


Fig. 5. (Continued)

was approximately 50% less rapid than the first time. The experiment was continued for 1 week. The efficiency decreased again.

This phenomenon was previously reported by Brezová et al. in the case of TiO_2 on glass fibres [6]. It is a general problem also observed with TiO_2 on other

supports as well as with suspended TiO_2 . Actually, it was reported by Al-Sayyed et al. [11] that after 10 experiments the rate of photocatalytic degradation of 4-chlorophenol with suspended TiO_2 is approximately 50% of the initial rate. This decline was attributed to the inhibiting effect of chloride ions released, but it is

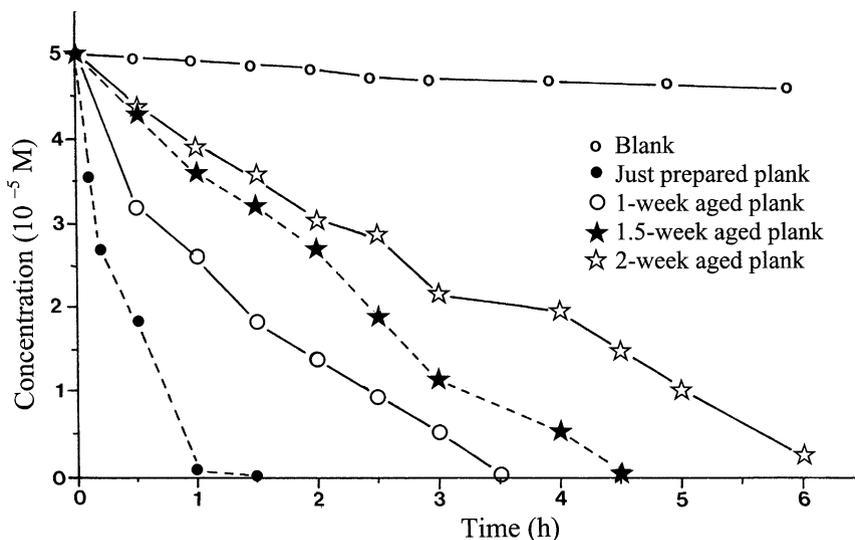


Fig. 6. Influence of long term use on the efficiency of TiO_2 immobilized on pumice stone. Kinetics of disappearance of AO-7 (5×10^{-5} M) with slanting plank just prepared and used during several days with a dye solution of 10^{-3} M.

not necessarily the only reason. Brezová et al., who used phenol as the substrate, have observed that the photocatalytic properties of TiO₂ on glass fibres can be regenerated by heating and they concluded that it is due to the accumulation of products on the surface. In the case of pumice stone, the decrease in efficiency after a long use may be attributed either to the elimination of some particles of titania or to a chemical damage on the surface of the catalyst. To precise the explanation of this ageing effect it will be useful to compare it with the evolution of titania on organic fibres, since the same phenomenon can be expected. Such a study is in progress, but it is long.

4. Conclusion

Immobilization of TiO₂ on pumice stone is an easy and efficient method to obtain photocatalytic reactions without the problem of filtration. The fact that pumice stone is soft and only available as pellets can be eliminated by using thin-film fixed bed reactor with pellets fixed on a slanting plank. It can be used with any commercial grade of titania.

The initial efficiency is higher than with other supports. It decreases slowly with irradiation time and the decrease becomes significant after several days of use. Such phenomenon of ageing is a general problem also observed with suspended TiO₂. It is important for long term application of photocatalysis to depollute wastewaters.

With 3-NBSA and with AO-7 as substrates titania P25 is more efficient than Millennium PCs 50 and 500.

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