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Solar photocatalytic degradation of 4-chlorophenol using the synergistic effect between titania and activated carbon in aqueous suspension

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Abstract

The photocatalytic degradation of 4-chlorophenol, chosen as an aromatic model pollutant, has been performed in contact with a suspended mixture of titania and of activated carbon (AC). Non-additive adsorption capacities were observed when the two solids were mixed. This was ascribed to a strong interaction between both solids. A synergy effect was observed with an increase of the first order rate constant by a factor of 2.4. As for neat titania, the same main intermediate products (hydroquinone and benzoquinone) were found but in much smaller quantities and during a much smaller lifetime. The synergy effect was ascribed to an extended adsorption of 4-chlorophenol on AC followed by a transfer to titania where it is photocatalytically degraded. When extrapolating these experiments by a volume factor of 12 500 to the solar pilot plant at PSA, an identical synergy factor of 2.4 was found, thus confirming the transpositivity of laboratory experiments to large solar set-ups. The synergy effect was not destroyed when re-using the double phase photocatalyst. This combined photocatalytic system may appear as a new performing one, more efficient with a shorter time necessary for decontaminating diluted used waters, which could be of interest in producing drinking water in dry sunny areas.

Keywords: Photocatalysis; 4-chlorophenol degradation; Adsorption capacity; Water decontamination; Synergy effect; Activated carbon; Solar photocatalysis

1. Introduction

Heterogeneous photocatalysis has recently emerged as an efficient method for purifying water and air [1–5] in most of the cases encountered. More than 1700 references have been recently collected on this discipline [6].

The aim of the present study was to confirm, in solar application and in a large scale, the synergistic effect obtained with powdered titania and powdered activated carbon maintained in an aqueous suspended mixture. This was first observed in laboratory experiments on the photocatalytic degradation of phenol [7]. Adding AC to titania induced a strong beneficial effect because of the high adsorption capacity of AC with respect to organic molecules. To better put in evidence the synergistic effect between both solid phases without inducing uncontrolled doping or contamina-

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tion during preparation, we chose a mechanical mixture, which enabled one to preserve the respective initial surface state of each solid constituent. The new test reaction chosen was the photocatalytic degradation of 4-chlorophenol (4-CP), which is a well known example of aromatic pollutant removal [8–26].

2. Experimental

2.1. Materials

4-Chlorophenol, hydroquinone, *para*-benzoquinone, 4-chlorocathecol and 4-chlororesorcinol, which corresponded to the initial pollutant and to the main possible intermediate compounds, respectively, were purchased from Aldrich, with the highest purity grade and used as received. The photocatalyst was TiO_2 Degussa P-25, mainly anatase (ca. 70%) under the shape of non-porous polyhedral particles of ca. 30 nm mean size with a surface area of 50 m^2/g. The same high purity activated carbon (Merck, ref. 102186, <1% ash), already used by some of us for supporting hydrodesulfurization [27] and hydrogenation [28] catalysts was employed. It has a total BET surface area of 775 m^2/g. The mean pore diameter is close to 8 Å (measured by the Horrwarth–Kawazoe method) and the particle size is around 60 μm.

2.2. Laboratory photoreactor and artificial light source

The batch photoreactor was a cylindrical flask made of Pyrex of ca. 100 ml with a bottom optical window of ca. 4 cm diameter and was open to air. Irradiation was provided by a high pressure mercury lamp (Philips HPK 125W) and was filtered by a circulating-water cell (thickness 2.2 cm) equipped with a 340 nm cut-off filter (Corning 0.52). The water cell was used to remove all the IR beams, thus preventing any heating of the suspension, especially in the presence of black activated carbon. The cut-off filter, although decreasing the overall UV-light power available, enables one to eliminate any photochemical side reaction.

2.3. Analysis

Millipore disks (0.45 μm) were used to remove particulate matter before HPLC analysis. Although non-agglomerated solid particles may pass through these membranes, our experience showed that the performance of the chromatographic column was not impaired for a long period of use. The HPLC system comprised a LDC/Milton Roy Constametric 3200 isocratic pump and a Waters 486 tuneable absorbance detector (Millipore) adjusted at 270 nm for the detection of phenol and of the main intermediate products. A reverse-phase column (length, 250 mm; internal diameter, 4.6 mm; particle diameter, 5 μm) ODS2-Spherisorb (Chrompack) was used. The mobile phase was composed of acetonitrile and deionized doubly distilled water. The v/v ratio CH_3CN/H_2O was 10/90 and the flow rate was 1 ml/min.

2.4. Procedure

In an ordinary photocatalytic test performed at room temperature (20°C), 50 mg TiO_2 and 10 mg AC were added under stirring in 20 ml of a millimolar solution of 4-chlorophenol (94 ppm) and maintained in the dark during 1 h to reach a complete adsorption at equilibrium. At time $t = 0$, a screen was removed from the window of the water cell located in front of the preheated lamp. Samples of the suspension (0.2 ml) were removed at regular intervals for analysis. The quantity of 50 mg of titania was chosen since in our conditions there is a full absorption of the UV light entering the photoreactor. The quantity of 10 mg AC was chosen to ensure a good adsorption of phenol related to the high surface area of AC without disturbing the UV absorption by titania nor 4-CP adsorption on it. The oxidation involved oxygen from the air dissolved at saturation ($\leq$1.4 mmol/l).

2.5. Pilot solar photoreactor at PSA

The compound parabolic collector (CPC) modules were selected for the present water detoxification study since it has been shown that they provide a better solar efficiency than parabolic concentrators because they use both direct and diffuse UV-light [29,30]. The present configuration of CPCs solar reactor settled at Plataforma Solar de Almería (PSA), Spain, consists of six modules connected in series (Fig. 1(a)). Their total reflective surface is 8.9 m^2. Each CPC module purchased from Industrial Solar Technology, Denver,

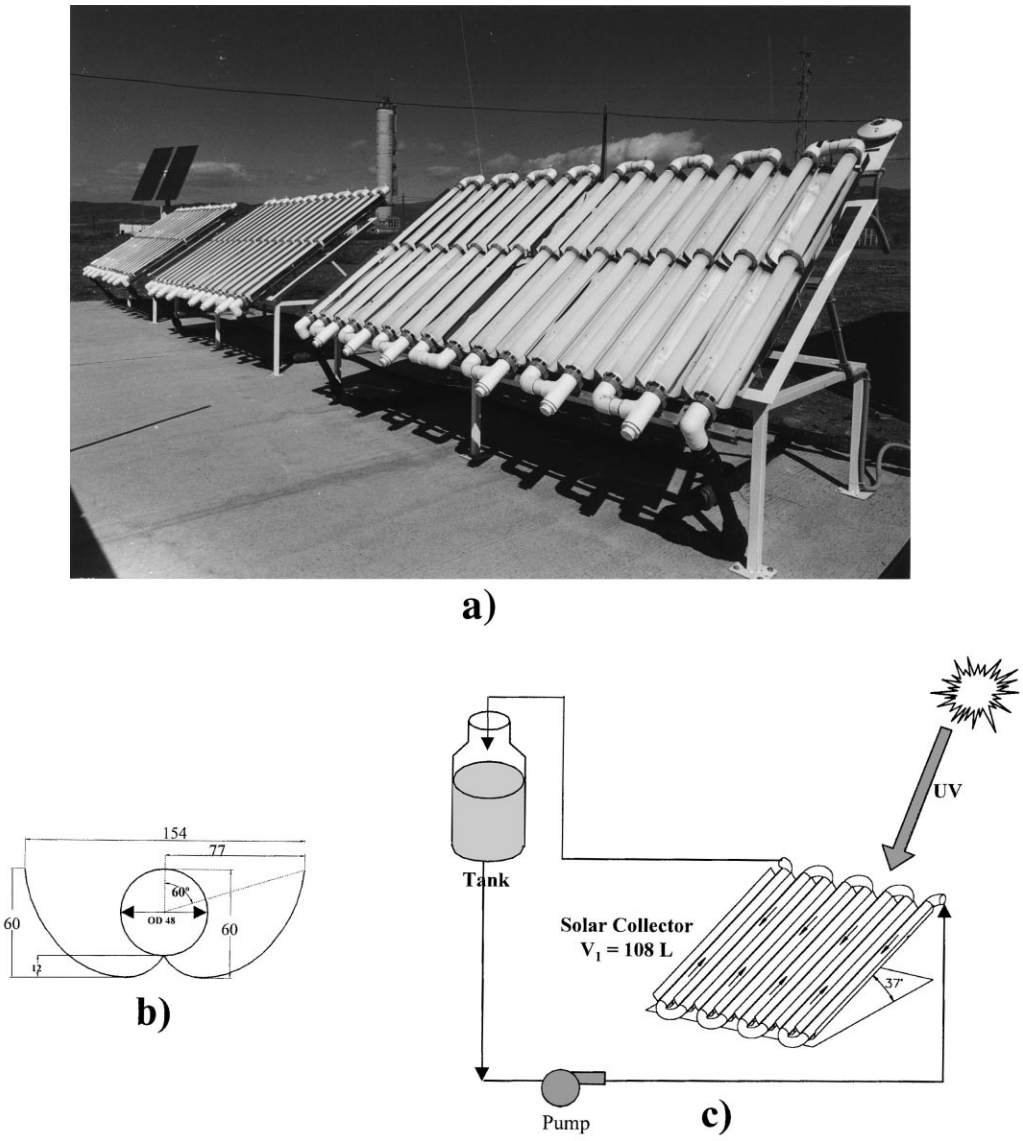

Fig. 1. (a) Photo of the solar collectors, (b) schematic of the CPC and (c) drawing of the solar pilot reactor at PSA.

is 1.22 m wide and 1.22 m long (Fig. 1). It consists of eight parallel CPC reflectors (152 mm wide) with UV-transparent tubular receivers (i.d. 48 mm, Fig. 1(b)), made of fluoropolymer because this material is chemically inert and has excellent UV stability and transmisivity. Two modules are coupled as a collector which is mounted on a fixed platform inclined at 37° corresponding to the latitude of PSA in Almería. This provides optimised performances for a fixed solar system. The three sun-light collectors consisting of two CPC modules were mounted in series

At the beginning of all the experiments, the sun-light collectors were put in the dark by covering them with a canvas sheet, whereas the chemical compound to be destroyed was added to the tank and progressively dissolved by vigorous stirring induced by a high circulation flow-rate (3.5 m^3/h). This was continued until reaching a constant concentra-

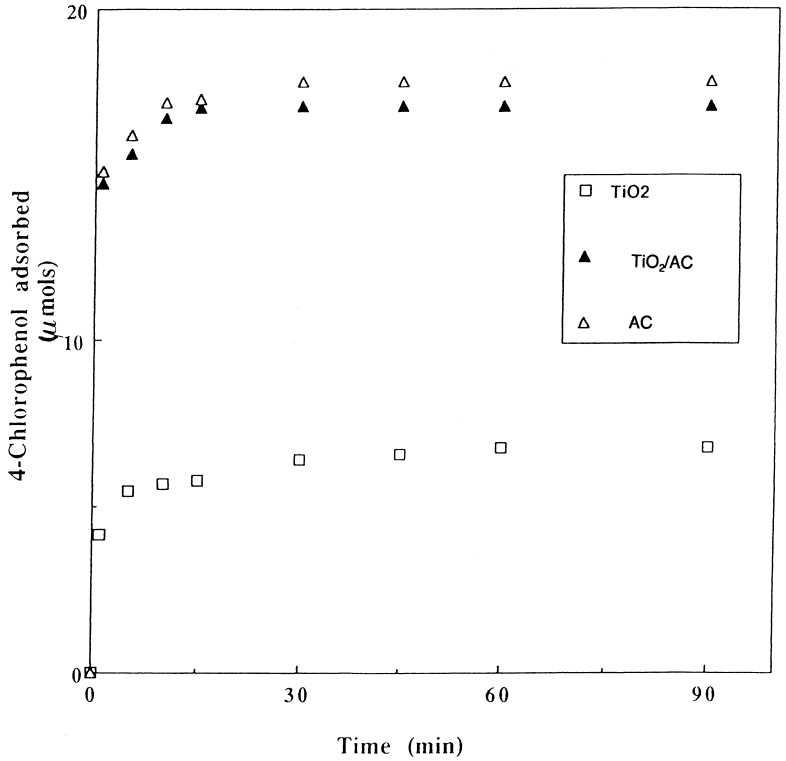

Fig. 2. Kinetics of adsorption of 4-chlorophenol in the dark for $C_0 = 10^{-3}$ mol/l. AC (10 mg), TiO_2 (50 mg) and TiO_2–AC (50/10).

tion throughout the system. Titania (Degussa P-25) was subsequently added with a total concentration of 0.2 g/l, corresponding to the optimised threshold obtained for CPC reactors [30]. The suspension was then agitated in the dark for 1 h to let the adsorption of the pollutant be achieved. The canvas sheets covering the collectors were removed a time $t = 0$. Samples were collected at regular intervals. Kinetics were followed as a function of the residence time. According to the procedure described above, the actual time of reaction corresponds to the residence time t_R. At any flow rate, t_R is proportional to the actual time and to the ratio of the illuminated volume ($V_1 = 108$ l) to the total volume ($V_T = 247$ l).

In such conditions, the CPC sun reactor can be considered as a perfectly agitated slurry batch reactor (Fig. 1(c)). The high flow rate (3.5 m^3/h) provides (i) a good homogeneous suspension of TiO_2, (ii) a satisfactory homogeneity of the concentration throughout all the volume, (iii) a good saturation of water in oxygen from the air estimated to be 6–7 mg O_2/l in summer time (it can increase to 9 mg O_2/l in winter time) and (iv) an oxygen content high enough to provide an optimum conversion of the reactant in one pass in the CPC photoreactor.

3. Results and discussion

3.1. Results obtained in laboratory experiments

3.1.1. Adsorption of 4-chlorophenol

4-Chlorophenol adsorption has been performed at 20°C on neat titania Degussa P25 (50 mg), on activated carbon AC (10 mg) and on a suspended mixture of them with the same respective masses. The kinetics of adsorption in the dark are given in Fig. 2. It can be observed that most of adsorption occurred within 15 min. The adsorption isotherms $n_{ads} = f(C_{eq})$ were determined assuming a conventional Langmuir isotherm model with a surface coverage θ varying as:

$$\theta = (n_{ads}/n_T) = [K_{ads}C/(1 + K_{ads}C)] \quad (1)$$

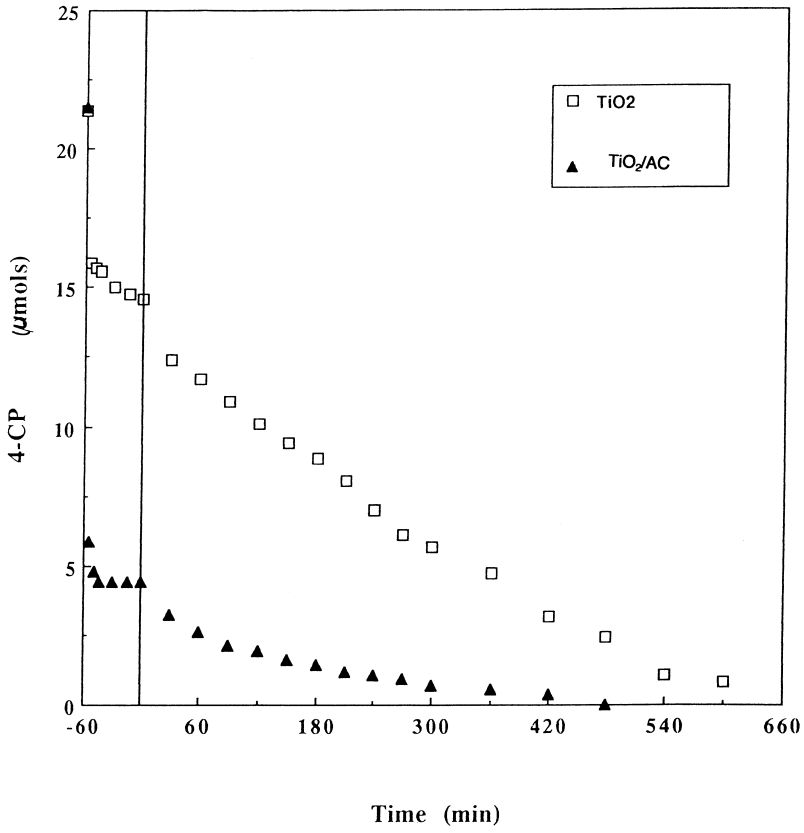

Fig. 3. Kinetics of 4-chlorophenol disappearance in the presence of illuminated TiO_2 and TiO_2–AC. The vertical line at time $t = 0$ separates the dark period from the UV-irradiated one.

In Fig. 2, the amount of 4-chlorophenol adsorbed on TiO_2–AC is slightly but significantly smaller than on pure AC. Similarly, the total numbers of adsorption sites follow the same trend. There is no additivity of the adsorption capacities of both solids when they are mixed together, at least for $C < 10^{-3}$ mol/l. This difference can be ascribed to a strong interaction between titania particles and AC, which creates an intimate interface non-accessible to 4-CP molecules from the solutions.

3.1.2. Kinetics of the photocatalytic disappearance of 4-chlorophenol

All the results are presented in Fig. 3. A period of adsorption in the dark of 60 min has been chosen from the above results of adsorption. The direct photolysis without solids could be neglected as well as the decomposition of 4-chlorophenol in the presence of UV-irradiated AC. Pure titania gives a complete disappearance of 4-chlorophenol in more than 12 h of UV-irradiation. By contrast, the irradiated mechanical mixture TiO_2–AC totally eliminates 4-chlorophenol from the solution within 7 h. The kinetic curves in Fig. 3 are of the apparent first order as confirmed by the linear transforms $\ln(n_0/n) = f(t)$ of Fig. 4, giving apparent rate constants respectively equal to:

$$TiO_2 : \; k_{app} = 2.7 \times 10^{-3}\,\mathrm{min}^{-1}$$

$$TiO_2 - AC : \; k_{app} = 6.4 \times 10^{-3}\,\mathrm{min}^{-1}$$

Although the reaction rate is higher for TiO_2 than for TiO_2–AC because of a higher concentration at time $t_{UV} = 0$, the photocatalytic activity of the TiO_2–AC system determined from the apparent rate constant is higher than that of neat TiO_2. The addition of 10 mg AC to 50 mg TiO_2 obviously creates a kinetic syn-

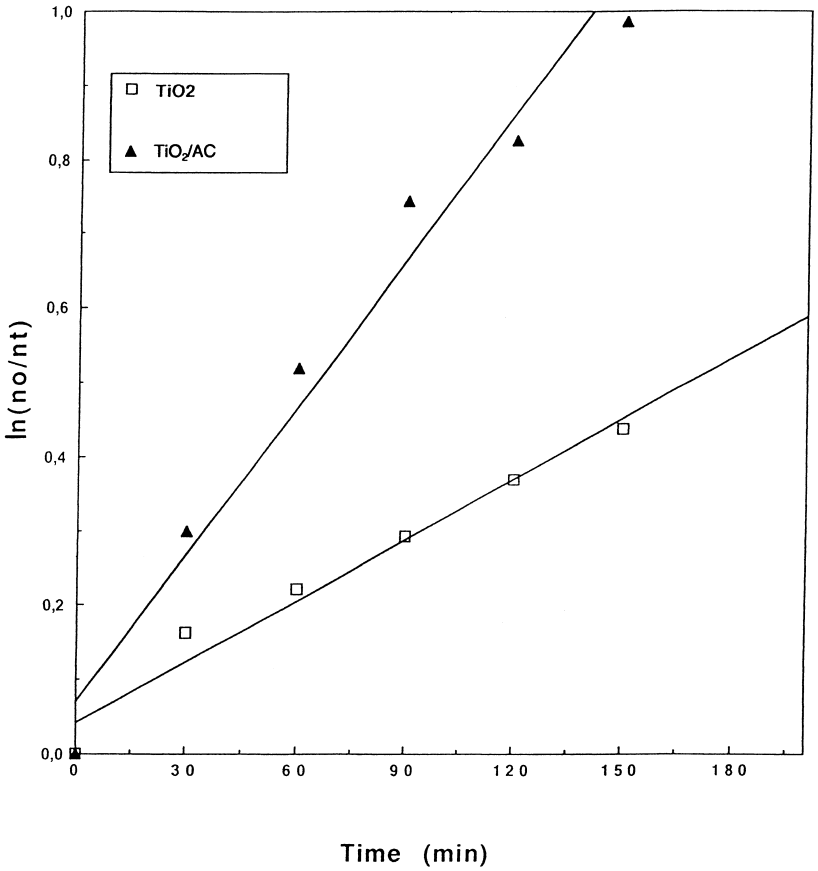

Fig. 4. Linear transform $\ln(n_0/n) = f(t)$ of the kinetic curves of 4-CP disappearance for TiO_2 and TiO_2–AC from Fig. 3.

ergy effect in 4-chlorophenol disappearance with an increase of the rate constant by a factor of 2.4. *The apparent rate constant has been chosen as the basic kinetic parameter, since it is independent of the concentration for the system under investigation*. It enables one to determine a photocatalytic activity independent of the previous adsorption period in the dark and of the concentration of 4-chlorophenol remaining in the solution, which is strongly influenced by the presence of AC.

The increase in activity cannot be ascribed to an increase of temperature induced by the presence of black AC. It was measured that adding 10 mg AC to a UV-illuminated suspension of titania increased the temperature by only 1°C. Since the activation energy of the reaction is of the order of 5 kJ/mol, the corresponding increase of photoactivity is quite negligible and much smaller than the error limit.

3.1.3. Kinetics of appearance and disappearance of intermediate products

As expected, hydroquinone was the main intermediate product observed on both systems, benzoquinone being present as traces. 4-Chlororesorcinol was also detected in small quantities but only with neat TiO_2 and not with AC–TiO_2. The beneficial synergistic effect due to the addition of AC to titania also intervenes in the decreased release of intermediate products in the solution.

3.2. 4-Chlorophenol degradation in the CPC pilot reactor at PSA

3.2.1. Synergy effect

The above experimental results have been transposed to the CPC pilot photoreactor at PSA, using a total volume of 247 l, which represents an extrapola-

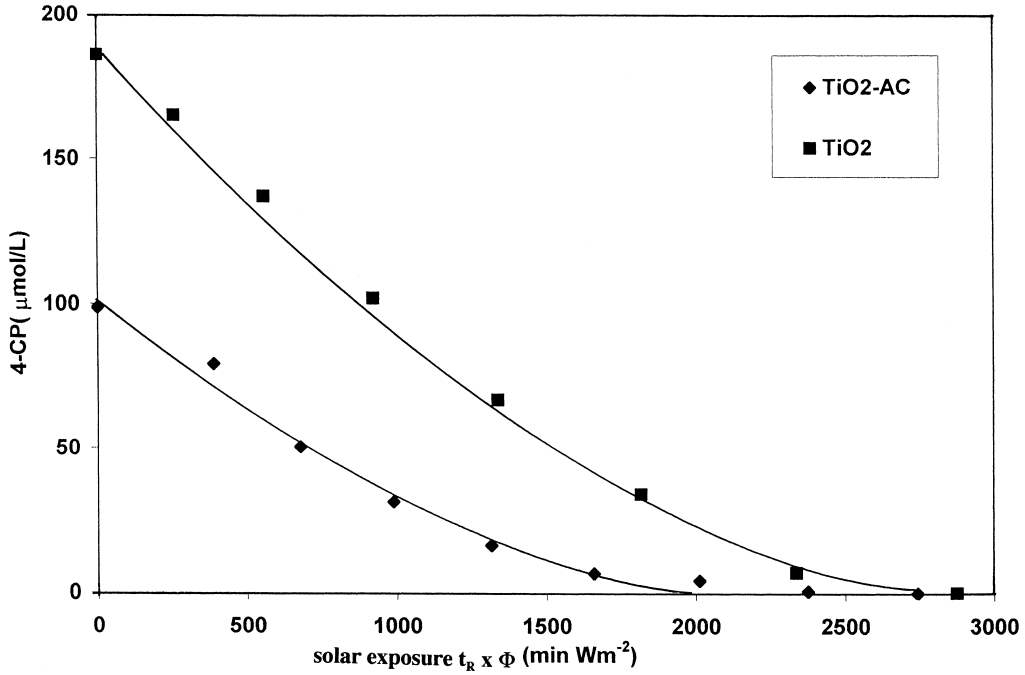

Fig. 5. Kinetic disappearance of 4-CP in contact with TiO_2 and TiO_2–AC as a function of the solar exposure (in min W/m^2).

tion factor of 12 500. The titania concentration was chosen equal to 0.2 g/l, corresponding to the minimum optimal concentration of Degussa P-25. The mass ratio AC/TiO_2 was kept equal to 1/5, and the initial concentration of 4-CP chosen equal to 20 ppm (1.55×10^{-4} mol/l). The disappearance of 4-CP is given in Fig. 5. It has not been plotted as a function of the residence time t_R corresponding to the time really spent in the CPC collector ($t_R = t\ (V_1/V_T)$), but as a function of the instantaneous exposure ($t_R \times \Phi$), in order to correct any possible variations of the radiant flux induced by the earth rotation during the experiment and by the possible occurrence of clouds in the sky.

It is confirmed (i) that before time $t_{UV} = 0$, the AC–TiO_2 mixture has adsorbed much more 4-CP in the dark than titania alone and (ii) that a 4-CP-free water has been obtained with a solar exposure of ca. 2000 min W/m^2 instead of ca. 3000. As in Ref. [7] for phenol or as in section 1.2, a more quantitative estimation of the synergy effect can be obtained by comparing the apparent first order reaction rate, which is independent of the concentration. Fig. 6 indicates that the synergy factor ($R = k_{app}$(AC–TiO_2)/k_{app}(TiO_2) is quite equal to that found in laboratory experiments: $R = 2.4$. This synergy effect is responsible for a lower content of intermediates in the solution and for a shorter solar exposure necessary to reach a total TOC disappearance.

3.2.2. Influence of the initial concentration

By contrast with laboratory experiments, some limitations in the synergy effect appeared when increasing $[4\text{-CP}]_0$ to 50 and to 132 ppm. For $C_0 = 50$ ppm, there was a slight increase of the rate of 4-CP disappearance (Fig. 7) and no effect on TOC disappearance. For $C_0 = 132$ ppm, a light retarding effect was observed as well for 4-CP as for TOC disappearance. This could be interpreted by the smaller optimal concentrations of titania and of AC (0.2 and 0.04 g/l, respectively) in the CPC reactor which are 12.5 times lower than those used in laboratory experiments. Since the synergy effect is based on the titania–AC physical interaction, a relatively higher pollutant concentration (132 ppm) would increase the adsorption of 4-CP on AC, detrimentally to the titania–AC interaction and to the consequent interface created. The slight decrease

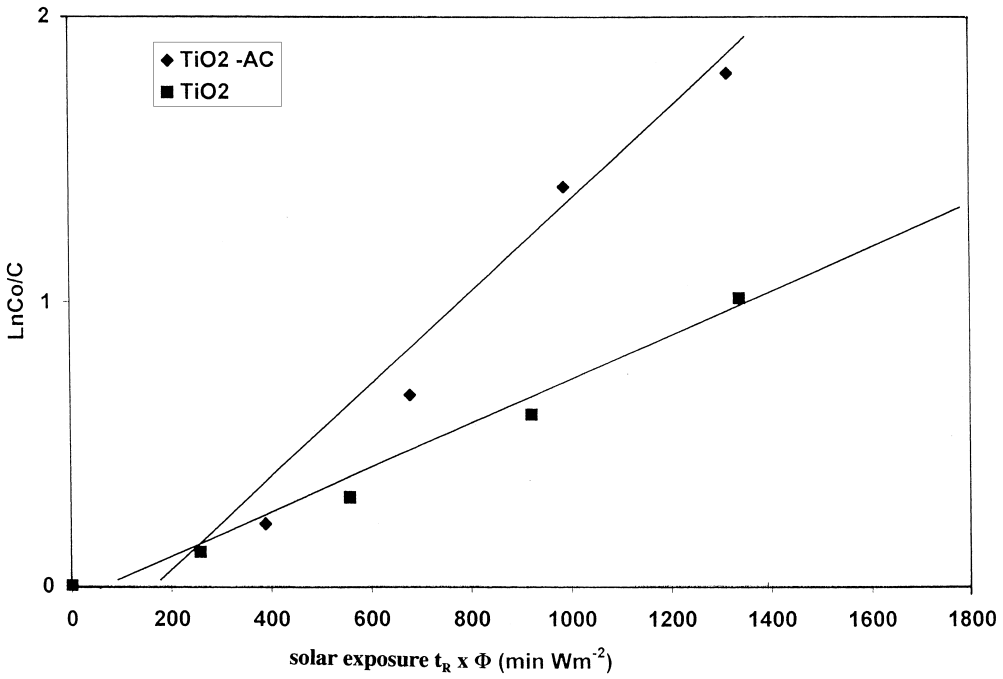

Fig. 6. Linear transforms $\ln(n_0/n) = f$(solar exposure) of the curves of Fig. 5.

in activity observed has to be mainly ascribed to the screening effect of black AC in the suspension. For $C_0 = 50$ ppm, the synergy effect just compensates the screening effect. As a consequence, the concentration of titania and of AC have to be adapted to the level of the initial concentration of the pollutant.

3.2.3. Re-use of the AC–TiO_2 biphasic photocatalyst

To simulate the recycling of the AC–TiO_2 biphasic photocatalyst and to check the stability of the synergy effect, some 4-CP was added several times (see arrows in Fig. 8), once it had disappeared from the solution at the end of the preceding sequence. It can be noted that 4-CP disappeared with the same kinetics in all the sequences. The initial C_0 in the first sequence was lower because of a large initial adsorption of 4-CP on a clean surface. For the other sequences, C_0 was higher because of a lower adsorption of 4-CP due to the competition of some remaining intermediate products resulting from the preceding sequence. Similarly for TOC (Fig. 9), the parallel decreasing straight lines indicate that the rate of TOC disappearance remained constant.

These results demonstrate that the AC–TiO_2 suspended catalytic mixture can be recycled without loosing the beneficial synergy effect observed during the first sequence. In addition, this confirms the self-cleaning character of AC–TiO_2, which is able, under illumination, to degrade the pollutant and its metabolites co-adsorbed on AC as previously shown for phenol [7].

4. Conclusions

It has been shown that the addition of a commercial activated carbon to titania under UV-irradiation could induce a substantial synergy effect by a factor of 2.4 in the photoefficiency of the photocatalyst. It has been explained by an important adsorption of 4-CP on AC followed by a mass transfer to photoactive titania. This transfer occurred mainly via a spillover of 4-CP through the contact surface between AC and TiO_2. This interface is spontaneously created by a mere mixture of both phases in suspension. The simple mixture of the two solids has permitted to avoid a preparation

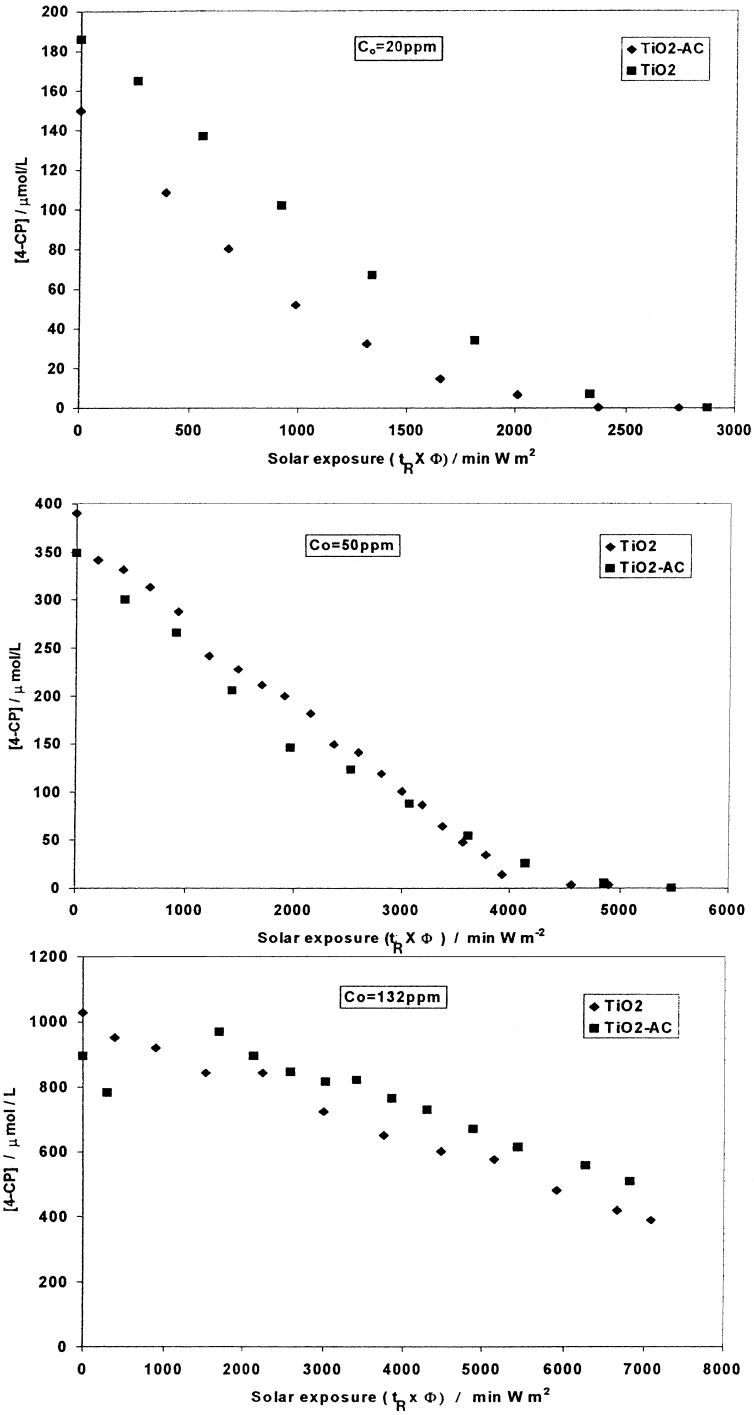

Fig. 7. Kinetics of 4-CP disappearance for three different initial concentrations.

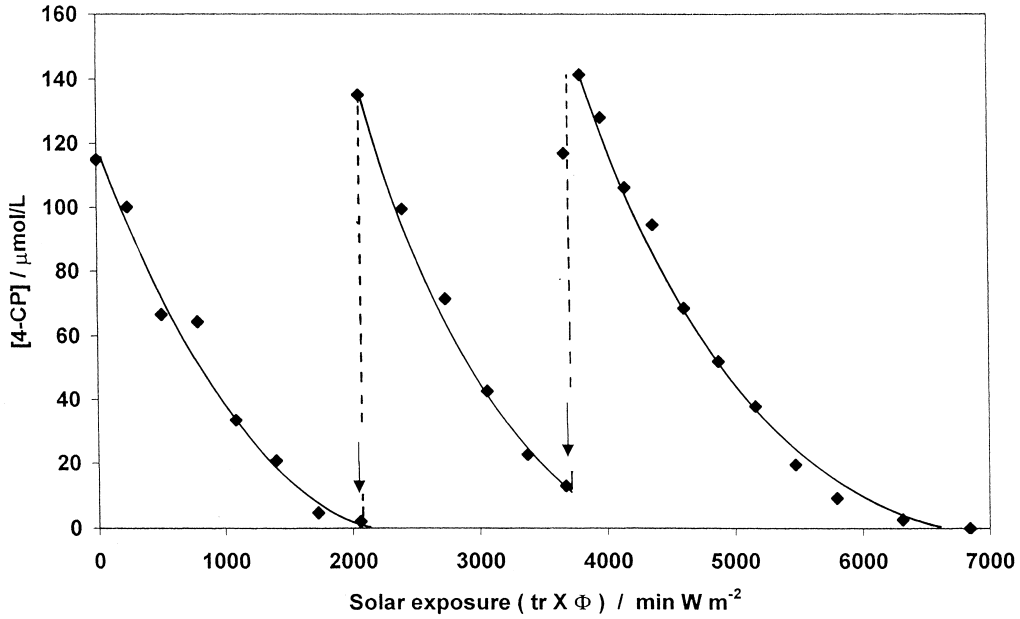

Fig. 8. 4-CP disappearance during sequences of re-use of TiO_2–AC.

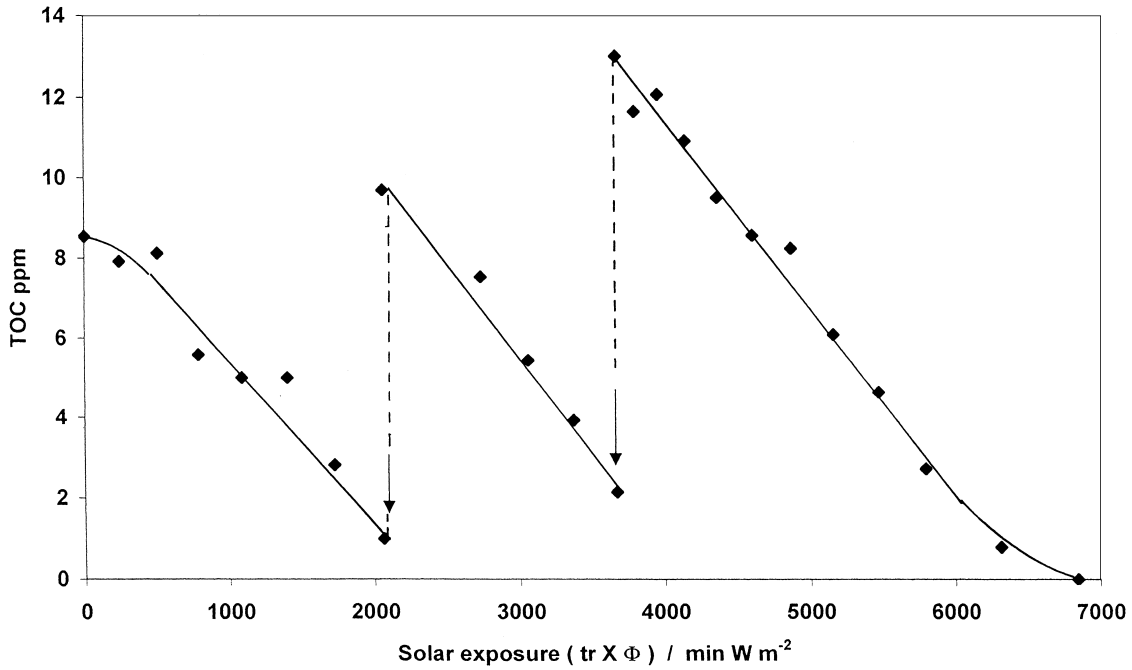

Fig. 9. TOC disappearance during sequences of re-use of TiO_2–AC.

procedure which would have modified the surface of both constituents and prevented a direct comparison from their initial surface state.

The synergy effect, previously established for phenol with $R = 2.5$, has not only been confirmed for 4-CP but could also be extrapolated to a large solar pilot plant scale, working in the near UV-fringe of sun light. It enables one to accelerate the conversion rates, especially in very diluted aqueous solutions and to substantially shorten the treatment duration necessary to produce clean water. From a practical point of view, such a system would be particularly efficient for the detoxification of large volumes of diluted aqueous solutions and for the production of drinking water in sunny arid places.

Acknowledgements

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