

# EFICIENCIA SOLAR DE UN NUEVO FOTO-CATALIZADOR TiO<sub>2</sub> DEPOSITADO SOBRE UN PAPEL FOTO-INERTE PARA LA DEGRADACIÓN TOTAL DE VARIOS PLAGUICIDAS Y COLORANTES

## SOLAR EFFICIENCY OF A NEW TITANIA PHOTOCATALYST DEPOSITED ON PHOTO-INERT PAPER SUPPORT APPLIED TO THE TOTAL DEGRADATION OF VARIOUS POLLUTANTS (PESTICIDES, DYES)

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### ABSTRACT

*A specially designed titania photocatalyst was prepared by coating Ahlstrom non-woven paper, used as a flexible photocatalytic support, with Millennium PC500 anatase. At the same time, a new solar photoreactor (STEP) was designed based on the multi-step cascade falling-film principle to ensure good exposure to sunlight and good oxygenation of the effluent to be treated. Several types of reactants were treated: 4-chlorophenol as a model organic pollutant; formetanate, a widely used pesticide in horticulture; a mixture of pesticides used in vineyards; and Indigo Carmine and Congo Red, which are complex multifunctional dye molecules. Each reaction was performed simultaneously in a solar CPC slurry photoreactor and in the STEP photoreactor under identical solar exposure to better evaluate and validate the results obtained. The STEP solar reactor was found to be as efficient as the CPC one for 4-chlorophenol and formetanate total degradation.*

*Keywords.* - Pesticide, Degradation, Photocatalyst.

### RESUMEN

*Un diseño especial de un fotocatalizador de TiO<sub>2</sub> fue depositado sobre un papel foto inerte. Al mismo tiempo un nuevo fotoreactor solar (STEP) fue diseñado en base a una cascada multipaso, generando buenos resultados a la exposición de la luz solar con buena oxigenación del efluente que se trató. Se utilizaron como reactivos a tratar: 4-clorofenol como un contaminante orgánico, formetano ampliamente usado como pesticida en horticultura, y una mezcla de pesticidas usadas en viñedos; así mismo el índigo carmín y congo red como complejos multifuncional de colorantes. Cada reacción fue realizada en un reactor STEP con agitación y exposición solar CPC simultáneamente para tener una mejor evaluación de los resultados obtenidos. El reactor solar STEP fue muy eficiente como el CPC, para el 4-clorofenol y formetano se obtuvo una degradación total.*

*Palabras clave.* - Plaguicidas, Degradación, Fotocatalizador.

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## INTRODUCTION

Heterogeneous photocatalysis is considered as one of the new "Advanced Oxidation Technologies" (AOT) for air and water purification treatment. Several books and reviews have recently been devoted to this problem [1-8]. A recent review reported more than 1500 references on the subject [9]. Owing to various European Research Programs including SOLWATER and AQUACAT Projects, we have intensively collaborated with the Plataforma Solar de Almería [PSA] whose photocatalytic pilot plant is unique in Europe [10]. Removal of several organic pollutants has been successfully tested at the PSA: phenol [11], 2,4-dichlorophenol [12], pentachlorophenol [13,14], atrazine [15], dichloroacetic acid [16] and other commercial pesticides [17-21]. In a previous study [21], it was demonstrated that the kinetic results obtained with micro-photoreactors at laboratory scale could be extrapolated to pilot photoreactors having capacities of several hundred litres by using a circulating suspension of titania. The variation in photo-efficiency under high solar flux, as well as possible thermal effects of solar light, has also been studied. In two other studies performed at the PSA, photoactivity of several new industrial anatase titania samples [Millennium Inorganic Chemicals] have been tested [21, 22]. However, in all the previous studies performed at PSA, the suspension of photocatalyst employed has required a final tedious filtration. Therefore, to eliminate this drawback, we have tested in the present study, the performance of titania coated on an Ahlstrom non-woven paper and compared it with that of a suspension of the same titania powder in slurry in the degradation of three types of pollutants: (i) 4-chlorophenol (4-CP), (ii) several pesticides (formetanate, a mixture of different pesticides used in vineyards and two dyes: indigo carmine and Congo red).

## EXPERIMENTAL

### Materials and reagents

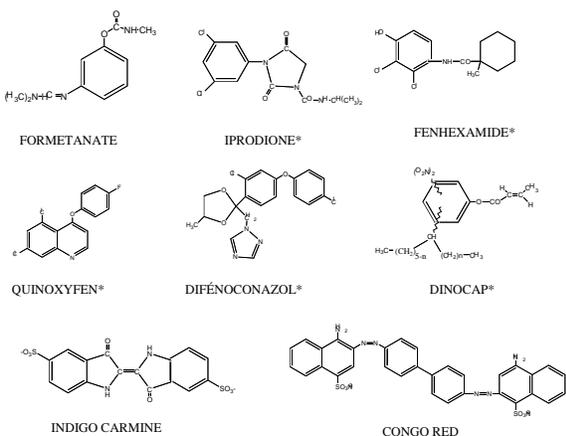
**Chemicals.**- 4 chlorophenol purchased from Aldrich was used as received. Technical-grade formetanate hydrochloride (92.4% purity) was supplied by Argos Shering AgrEvo, S.A.

(Barcelona, Spain) and analytical-standard (Pestanal<sup>®</sup>) formetanate hydrochloride was purchased from Riedel-deHaën (Seelze, Germany). The commercial formulation was AgrEvo Dicarzol<sup>®</sup> (Formetanate 50% w/w). The mixture of pesticides was provided by "Domaine Latour" at Aloxe-Corton (Burgundy, France). Indigo Carmine and Congo Red were supplied by Merck and used as received (40% pure Congo red and >80% pure Indigo Carmine). The respective chemical formulae of pesticides and dyes are given in Figure 1.

**Photocatalysts.**- The powdered photocatalysts were titania Degussa P25 (anatase/rutile = 3:1; surface area = 50 m<sup>2</sup>.g<sup>-1</sup>, non-porous particles, mean size = 30 nm) and PC500 by Millennium Inorganic Chemicals (anatase: > 99% ; surface area > 250 m<sup>2</sup>.g<sup>-1</sup>, crystallites mean size = 5-10 nm). Titania PC500 was coated on non-woven paper (natural and synthetic fibres, 2 mm thick) using a silica-based inorganic binder. A 1.36-m<sup>2</sup> sheet of the non-woven paper on which the titania photocatalyst had been deposited was placed on the 21 steps of the STEP photoreactor.

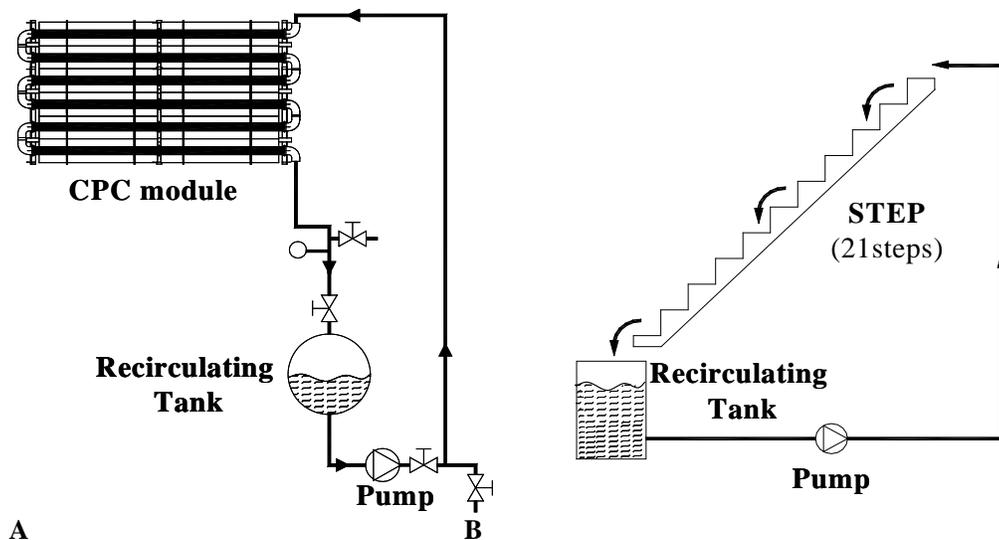
### Illumination procedure and photoreactors

All the experiments were performed in Almería (latitude 37°N, longitude 2.4°W) under natural sunlight in two photoreactors, a compound parabolic collector (CPC) photoreactor working with titania slurries and the STEP photoreactor using TiO<sub>2</sub>-coated paper. Both photoreactors operated simultaneously with the same contaminants at the same time and under identical radiant solar flux.



**Fig. 1** Developed formulae of pesticides and dyes degraded.

**2.2.1 CPC Photoreactor .-** The CPC pilot plant (Fig. 2a) is made up of several 1-m<sup>2</sup> collectors, one tank and one pump. Each collector consists of eight Pyrex tubes connected in series and mounted on a fixed platform tilted 37° (local latitude).



**Fig. 2** Diagrams of the two pilot photoreactors used in the experiment performed in presence of (A) TiO<sub>2</sub> powder (photoreactor CPC) and (B) coated titania (photoreactor STEP).

**STEP Photoreactor.-** The STEP solar reactor (Figure 2b) consists of a rectangular (2 m x 0.5 m = 1 m<sup>2</sup>) 70-mm-high stainless-steel staircase vessel having 21 steps. The photocatalyst-support sheet had a total area of 1.36 m<sup>2</sup>. The photoreactor was covered by a Pyrex glass sheet to limit water

Evaporation ( $\lambda \geq 290$  nm). The photoreactor, with a solar radiation-collecting surface of 1 m<sup>2</sup>, is mounted on a fixed rack inclined at an angle equal to the local latitude (37° for Almería). At the beginning of the experiment, 25 L of distilled water containing the selected organic compounds

Either one or two collectors (i.e., 1 m<sup>2</sup> or 2 m<sup>2</sup>) were used, depending on the objective of the experiment (see Results and Discussion). The water flows at 20 L.min<sup>-1</sup> directly from one module to another and finally into a tank. The total volume (V<sub>T</sub>) of the photoreactor (35 L) is considered in two parts: the 22 L total irradiated volume (in Pyrex tubes) (V<sub>i</sub>) and the dead photoreactor volume (tank + connecting tubing). At the beginning of the experiments while collectors were kept covered, all the chemicals were added to the tank and mixed by recirculating the water to constant concentration throughout the system. Then the covers were removed from the collectors and samples were collected at predetermined times (t). A more detailed description of this recirculating photoreactor has been previously published. During experiments, the temperature of the effluent was in the range of 35-40°C, i.e. close to the optimum value for photocatalysis [1].

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was circulated in the dark at  $7.5 \text{ L}\cdot\text{min}^{-1}$  to reach the same constant concentration as in the CPC photoreactor. Then the cover was removed and samples were collected at the same times as those in the CPC photoreactor.

### Evaluation of solar UV radiation

A UV radiometer (KIPP & ZONEN, model CUV3) with typical sensitivity of  $264 \mu\text{volts W}^{-1} \text{ m}^2$  mounted on a platform tilted  $37^\circ\text{N}$  (the same angle as the CPCs), provides data in terms of incident radiant flux and gives an idea of the UV solar energy reaching any surface in the same position with respect to the sun. With eq. 1, combination of the data from several experiments performed at different times and their comparison with other experiments is possible.

(1)

where  $t_n$  is the experimental time for each sample,  $UV_{G,n}$  the average incident radiant flux  $UV_G$  during  $t_n$ ,  $A$  represents the collector surface,  $V_{TOT}$  the total plant volume and  $Q_n$  is the accumulated energy ( $\text{kJ L}^{-1}$ ) incident on the photoreactor per unit of volume of aqueous sample taken at  $t_n$ . Consequently, when  $Q$  is used, the reaction rate ( $r_Q$ ) is expressed in terms of mg of degraded pollutant per kJoule of UV energy reaching the collector surface. Such a presentation enables one to compare results from different experiments, at different periods or seasons of the year and with different types of weather.

### Analyses

Formetanate and 4-chlorophenol were analysed using reverse-phase liquid chromatography (at  $0.5 \text{ mL}/\text{min}$ ) equipped with UV detection (Hewlett-Packard, series 1100) using a C-18 column (LUNA 5-micron C18,  $3 \times 150 \text{ mm}$  from Phenomenex).

The mobile-phase composition and wavelength were  $\text{K}_2\text{HPO}_4$  ( $18.4 \text{ mM}$  in water,  $\text{pH}=8.9$ )/ACN at 80/20 ratio at  $252 \text{ nm}$  (formetanate) and water/methanol at 60/40 ratio at  $228 \text{ nm}$  (4-chlorophenol). Under these conditions, the detection limit of formetanate is  $0.02 \text{ mg}/\text{L}$  and the quantification limit is  $0.05 \text{ mg}/\text{L}$  ( $\text{RSD}<5\%$ ).

The dye concentrations were determined using a UV-visible spectrophotometer (UNICAM, model UV-2) set at  $\lambda = 610 \text{ nm}$  for indigo carmine and at  $\lambda = 510 \text{ nm}$  for Congo red. Total Organic Carbon (TOC) was analysed by direct injection of the filtered samples into a Shimadzu-5050A TOC analyser calibrated with standard solutions of potassium hydrogen-phthalate. Under these conditions, the detection limit of the TOC analyser is  $0.1 \text{ mg}/\text{L}$  and the quantification limit is  $0.5 \text{ mg}/\text{L}$  ( $\text{RSD}<5\%$ ).

Analyses of ions were performed with Dionex DX-120 ion chromatograph equipped with an AS 14 column. The eluent was  $\text{NaHCO}_3$   $1 \text{ mM}/\text{Na}_2\text{CO}_3$   $3.5 \text{ mM}$ . The IC detection limit for chloride, nitrate and sulphate is  $0.05 \text{ mg}/\text{L}$  and the quantification limit is  $0.2 \text{ mg}/\text{L}$  ( $\text{RSD}<5\%$ ).

## RESULTS AND DISCUSSION

### Degradation of formetanate in CPC and STEP photoreactors

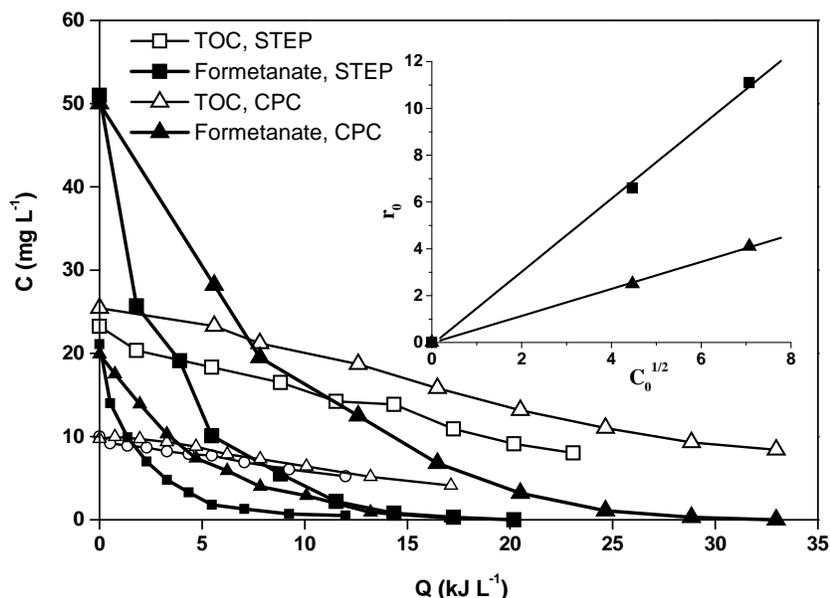
Formetanate is a common insecticide used in horticulture that has already been detected in groundwater in the province of Almería. Its formula is given in Figure 1. Figure 3 shows that whatever the initial concentration of formetanate, coated PC-500  $\text{TiO}_2$  is more efficient than a suspension of the same catalyst in the disappearance of formetanate, while the TOC disappearance rate is quite similar. It has been calculated that the initial degradation rate is proportional to the square root of the initial formetanate concentration in presence of either  $\text{TiO}_2$  in suspension or of  $\text{TiO}_2$ -coated paper. This is illustrated by the two linear transforms in the inset of Figure 3. This result is in agreement with previous results obtained at laboratory scale which implies that two sites are involved in the adsorption of one molecule of formetanate (dissociative adsorption) and that the presence of the binder does not modify the dissociative mode of adsorption.

In addition to active matter, commercial pesticides also contain organic and mineral additives. These additives could have a detrimental effect on catalyst efficiency because they would be adsorbed on the surface and/or compete for the

reaction with the OH° radicals. Moreover, significant differences might be obtained when natural water is used instead of distilled water. Consequently raw water was used in several tests to simulate real conditions.

The most important characteristics of this water were: conductivity = 0.85 mS, (CO<sub>3</sub><sup>2-</sup>+HCO<sub>3</sub><sup>-</sup>) = 49 mg/L (as carbon), pH = 7.7, Cl<sup>-</sup> = 110 mg/L

and SO<sub>4</sub><sup>2-</sup> = 80 mg/L. Experiments with pure formetanate in distilled water and commercial formetanate in tap water were performed in the STEP photoreactor. No substantial differences were observed. In conclusion, the photocatalytic efficiency of titania-coated non-woven paper for the removal under real conditions of commercial formetanate is confirmed.



**Fig. 3** Disappearance of formetanate and TOC in CPC and STEP photoreactors as a function of accumulated energy during the photocatalytic degradation of formetanate at two different initial concentrations (20 and 50 mg/L). In the inset is shown the linear transform  $r_0=f(C_0^{1/2})$  of the  $1/2$  order rate of disappearance of formetanate.

### Degradation in CPC and STEP photoreactors of a mixture of various pesticides

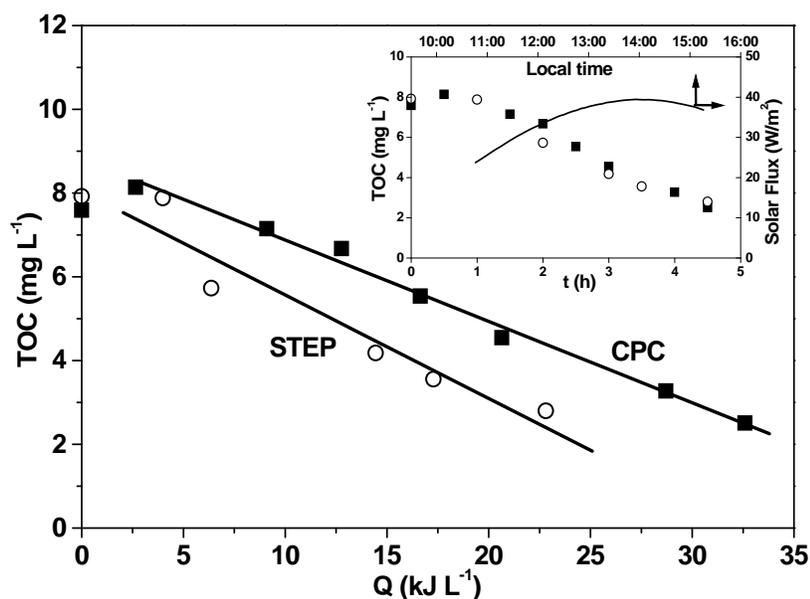
Aqueous effluents from rinsing agricultural equipment (tractors, nebulizers,...) used for spraying pesticides on grapevines in Burgundy (Domaine Latour) were collected and treated in both solar photoreactors. The developed formulae of the active agents are shown in Figure 1. The commercial products were selected to better represent the real world. They were used without purification, i.e., all impurities and additives contributed to the amount of total organic carbon (TOC). Since hydroxyl radicals react non-selectively, numerous intermediates are formed en route to complete mineralization at different concentrations.

In Figure 4, both curves have a sigma shape with an induction period corresponding to around 5 kJ L<sup>-1</sup>. This induction period is due to photodegradation of the original molecules into other intermediates (metabolites) preceding final mineralisation into CO<sub>2</sub>. Since the reaction is not expected to follow simple models like first or zero order kinetics, overall reaction rate constants cannot be calculated. The complexity of the results is caused by the fact that the TOC is an overall parameter including several products that undergo subsequent oxidative reactions. To compare the catalysts, the linear parts in Figure 4 were considered as the kinetic curves. They exhibit apparent zero order rate constants, which are equal to 0.25 mg kJ<sup>-1</sup> and 0.19 mg kJ<sup>-1</sup> for STEP and

CPC, respectively. The efficiencies of both systems are very similar, (that of STEP being slightly better).

This demonstrates that a photoreactor using a catalyst-coated paper as a fixed bed can be as efficient as a slurry one. In Figure 4, it is clearly shown that both photoreactors are working equivalently under the same radiant solar flux. In

the inset in Figure 4, it can be observed that a short period of time (less than 5 hours) is needed for achieving mineralisation of 80% of the initial pesticide mixture. In addition to the simplicity of the two installations necessary for treating this type of agricultural wastewaters, it should be noted that the STEP photoreactor has the additional advantage of avoiding a final filtration to separate and reuse titania.



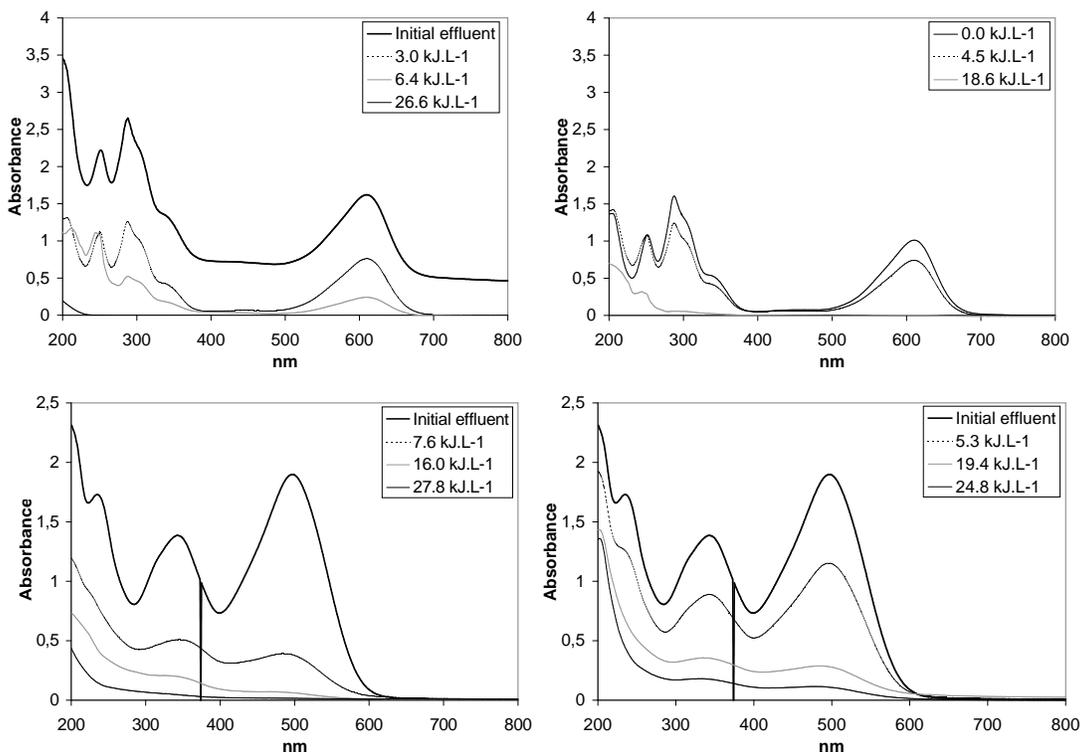
**Fig. 4** Pesticides mixture degradation as a function of the total energy collected per liter of solution. In the inset are shown the temporal variations of the overall solar UV-flux and of TOC concentration as function of the local time.

#### Degradation of dyes in the CPC and STEP photoreactors

The release of colored wastewaters into the ecosystem is a dramatic source of aesthetic pollution, eutrophication and perturbation of the aquatic life. These are frequent problems in Latin American countries where solar energy is abundant.

Since both photoreactors tested in this work are solar driven, two dyes, Congo Red (CR) and Indigo Carmine (IC), were also used as model compounds.

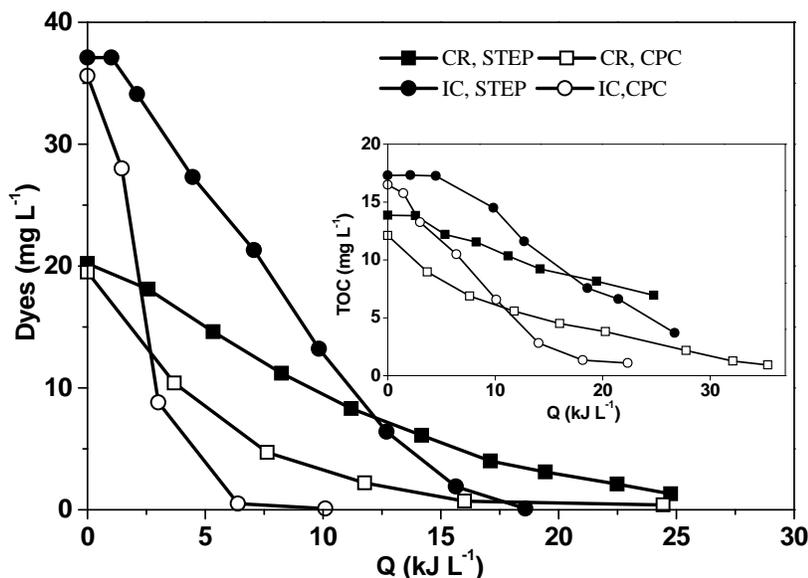
Their structures are given in Figure 1. The degradation process was studied by following the decoloration of dyes, the mineralization of organic carbon and the quantification of evolved sulfate and nitrate ions resulting from S and N atoms. The changes in absorbance of both dyes between 200 and 800 nm for different total solar energies collected are shown in Figure 5. The kinetics of disappearance in dye is presented in Figure 6, whereas the concomitant decrease in TOC is given in the insert. The solar experiments were continued until 25 kJ of UV energy per litre of solution was accumulated.



**Fig. 5** Temporal variations of two dyes UV-absorbance at different accumulated UV-energies in STEP or in CPC photoreactors.

From Figure 6, it can be seen that the STEP photoreactor is less efficient than the CPC. In particular, even though all indigo carmine has disappeared, TOC has not reached total disappearance, in agreement with the detection of aromatic residues. For Congo red, which is known as a very resistant dye, at  $Q = 25$  kJ/L, all the dye had not yet disappeared and the fixed bed of titanium remained pale red. However, it recovered its original white appearance when the solar treatment was continued. Therefore, even if the STEP photoreactor is less efficient than the CPC, total detoxification of the water could nevertheless also be achieved.

Concerning the heteroatoms present in the dye molecules, total mineralisation of sulfur to sulfate was 100% for both dyes in both photoreactors while selectivity in nitrate was less than 1%. This is in agreement with laboratory photocatalytic studies. In the case of indigo carmine, nitrogen was first converted into ammonium ions, and then into nitrate. By contrast, in the case of Congo red, azo groups were selectively transformed into gaseous nitrogen. The slow changes in TOC at the beginning of degradation in the presence of TiO<sub>2</sub>-coated paper correspond to the slow formation and degradation of hydroxylated compounds which are considered as the main primary intermediates formed. It should be mentioned that both dye molecules are negatively charged in aqueous solutions and that the pH of water during the phototreatment maintained itself around neutrality, possibly owing to the simultaneous release of sulfate and ammonia. Moreover, at pH = 6.7, the surface of TiO<sub>2</sub> is also neutral. Under these conditions, the adsorption of the dyes on TiO<sub>2</sub> is not so difficult. But, when TiO<sub>2</sub> is coated, the surface of the SiO<sub>2</sub> binder is negatively charged, since the point of zero charge (PZC) of SiO<sub>2</sub> is close to 2. Therefore, dye adsorption is decreased, which is detrimental to its photocatalytic degradation.



**Fig. 6** Disappearance of Congo Red (CR) and of Indigo Carmine (IC) as a function of accumulated energy in both photoreactors. The simultaneous changes in TOC are described in the insert.

## CONCLUSIONS

It has been demonstrated that the tedious final filtration of titania in slurries can be avoided by using a new deposited photocatalytic material, Millennium PC500 titania coated on Ahlstrom non-woven paper. The STEP solar photoreactor, working with such coated material, was found to be as efficient as the CPC one working with slurries of the same titania catalyst in formetanate degradation and in detoxification of waters contaminated by pesticides (usually at low-medium concentrations, but highly toxic) under identical solar exposure. For dye decolorisation and degradation, the STEP photoreactor was, however, found to be less efficient. The lower efficiency of Millennium titania coated on Ahlstrom non-woven paper in the degradation of dyes seems to be related to the presence of the silica binder, whose PZC value is detrimental to anionic compound adsorption.

The main conclusion is that titania can be used successfully when deposited on Ahlstrom papers. The same fixed photocatalyst are being used in the prototypes elaborated for both SOLWATER and AQUACAT European Projects. Later, this type of photocatalytic coated material could be usefully applied in the future potabilization of water in remote sunny areas.

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