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2,4,6-Triphenylthiapyrylium cation as homogeneous solar photocatalyst

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Abstract

Triphenylthiapyrylium cation (TPTP$^+$) has been studied as solar photocatalyst and compared with other organic dyes (triphenylpyrylium, acridine yellow, methylene blue, rosolic acid and alcian blue) using ferulic acid as model pollutant. The best results were obtained with TPTP$^+$ (ca. 85% elimination), although important photodegradation was also achieved with acridine yellow and triphenylpyrylium. Concentrations of TPTP$^+$ in the range 10–30 mg/l had only a moderate effect on the reaction rate; on the other hand, the concentration of ferulic acid had a remarkable influence on the pseudo-first order rate constant, for which higher values were measured in diluted solutions of the substrate. The results from photophysical studies based on fluorescence quenching and laser flash photolysis were compatible with an electron transfer mechanism. Although the process is thermodynamically feasible from the first singlet excited state, triplet involvement cannot be ruled out at the present stage. The studies were extended to detoxification of Sevnol, a commercial pesticide, based on carbaryl as active ingredient. Total removal of carbaryl was accomplished, although mineralization was only 30%. However, activated sludge respirometry showed that elimination of carbaryl resulted in a complete detoxification of the solution and a significant enhancement of the biodegradability.

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Keywords: Thiapyrylium; Solar photocatalysis; Electron transfer; Ferulic acid; Carbaryl

1. Introduction

Solar photocatalysis is an emerging method for decontamination of industrial effluents [1], which involves "in situ" generation of highly reactive species, able to oxidise organic matter [2,3] upon solar irradiation of the catalyst; this treatment can be considered a "green process" [4] as it is carried out under mild conditions, no hazardous chemicals are added, and the energy consumption is rather low.

A considerable amount of work has been published dealing with the photo-oxidation of industrial toxic compounds [5–7], mostly employing titanium dioxide and iron salts as solar photocatalysts. However, organic dyes can also play this role, and hence their use in wastewater treatment deserves further research [8–10]. In general, dyes are expected to absorb more efficiently sunlight, as their spectra show important bands not only in the UVA but also in the visible range. However, their use is not free from disadvantages, such as their difficult recovery after the reaction or their possible toxicity. For this reason, homogeneous catalysis can be considered as a preliminary stage; it is useful to proof the concept and to perform mechanistic studies in order to understand the process. For practical applications, a logic step forward would be heterogenisation by adsorbing the dye onto a solid support [11,12].

Dyes are usually able to oxidise organic matter through two different mechanisms: (a) energy transfer to form singlet oxygen as the oxidising species, or (b) direct electron transfer between the photocatalyst and the substrate [9]. An example of predominating electron transfer mechanism is found in the case of 2,4,6-triphenylpyrylium cation (TPP$^+$) [13]. This species is able to absorb efficiently radiation with wavelengths below 450 nm. Upon excitation, TPP$^+$ is able to withdraw one electron from the substrate. The generated pyranyl radical can be re-oxidised to TPP$^+$ in the presence of oxygen [14], which is generally the electron sink (Eqs. (1) and (2)).

$$\mathrm{TPP}^+ \xrightarrow{h\nu} (\mathrm{TPP}^+)^* \tag{1}$$

$$(\mathrm{TPP}^+)^* + \mathrm{S} \rightarrow \mathrm{TPP} + \mathrm{S}^+ \xrightarrow{\mathrm{O}_2} \text{oxidation products} + \mathrm{TPP}^+ \tag{2}$$

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Pyrylium salts have been tested in homogeneous phase as solar photocatalysts and found to be rather promising, as elimination of several phenolic pollutants has been achieved [9,14–16]. In addition to this, TPP^+ supported onto silica gel [11] and zeolites [12] also shows a clear photocatalytic power and enhanced stability [17].

In view of the satisfactory results previously obtained with TPP^+, it appeared interesting to study the photocatalytic properties of other organic dyes. In particular, 2,4,6-triphenylthiapyrylium cation ($TPTP^+$) is a related aromatic heterocycle, containing sulphur instead of oxygen and exhibiting similar photophysical behaviour as TPP^+ [18]. Some laboratory experiments have been performed using supported $TPTP^+$ as heterogeneous photocatalyst, and UV radiation as energy source [19–21].

In the present work, the perchlorate salt of $TPTP^+$ has been used as homogeneous solar photocatalyst, and its performance compared with that of other organic dyes using ferulic acid as model compound (see Chart 1 for structures). This phenolic pollutant is usually found in food processing effluents. Photophysical studies have been carried out in order to gain some insight into the mechanism of action of $TPTP^+$. Finally, a practical application of this photocatalytic system is also given using Sevnol^{TM}, a commercial pesticide based on carbaryl as active ingredient. Detoxification of aqueous solutions of this pesticide has been evaluated by means of activated sludge respirometry [22]. Increase in the biodegradability has also been determined using activated sludge [23], as it can be related to the behaviour of the biological reactors of wastewater treatment plants and is a very useful tool to determine the

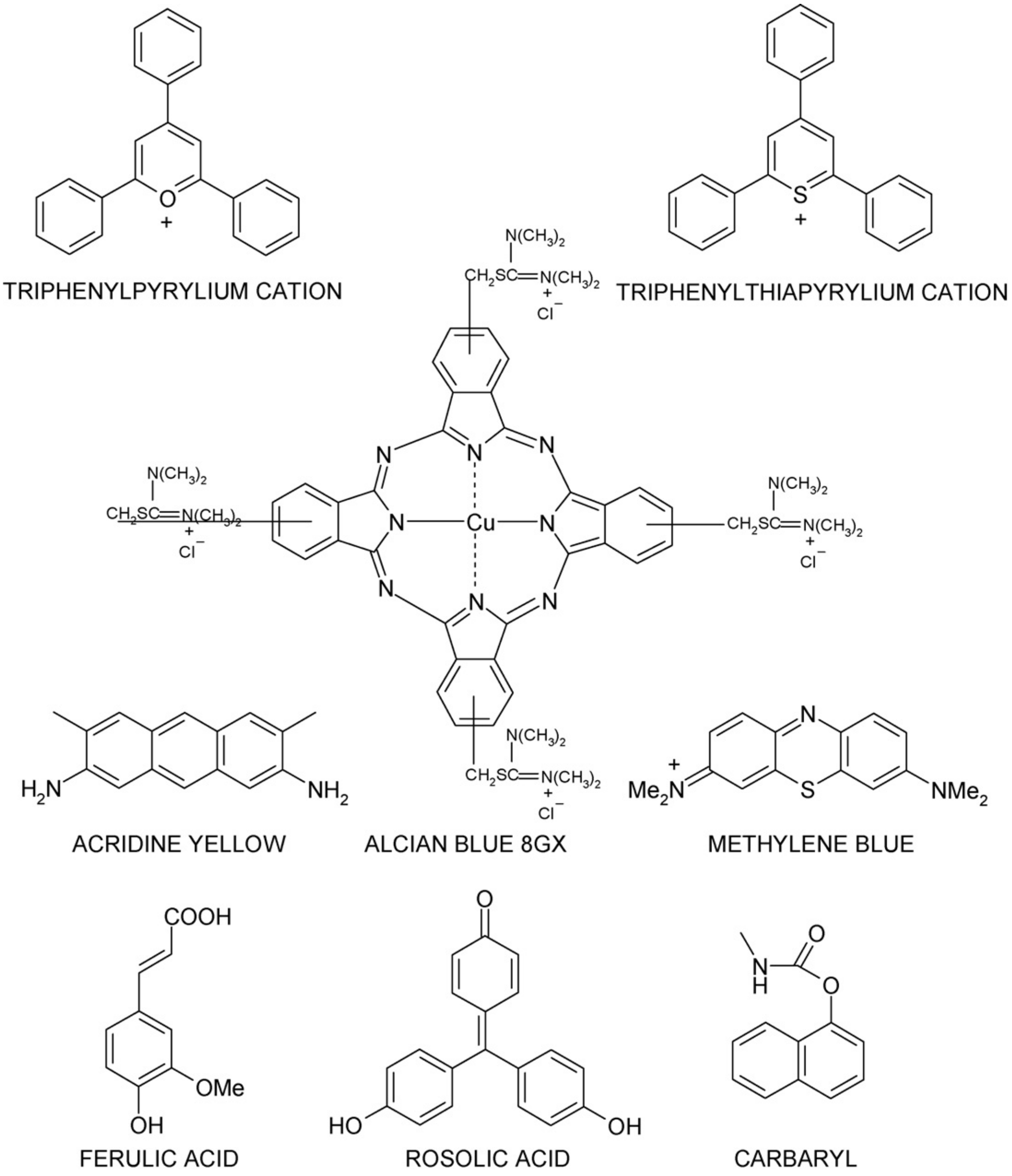

Chart 1. Chemical structures of the photocatalysts and pollutants employed in the work.

feasibility of coupling biological process with photochemical treatments.

2. Experimental

2.1. Reagents

TPP^+ hydrogensulfate, TPP^+ tetrafluoroborate, methylene blue (MB), alcian blue (AB), acridine yellow (AYG) and rosolic acid (RA) were purchased from Aldrich and used without further purification.

Ferulic acid (4-hydroxy-3-methoxycinnamic acid) was purchased from Aldrich and used as received. The pesticide Sevnol^{TM} was obtained from MAFA and contained 85% (w/w) of the active ingredient, carbaryl. All other reagents were purchased from Panreac. Water employed in all the experiments was Milli-Q grade.

The $TPTP^+$ perchlorate was obtained according to the following experimental procedure [24]: 0.17 g of 2,4,6-triphenylpyrylium tetrafluoroborate were dissolved in 8 ml of acetone. Then an aqueous solution of sodium sulphide (10%, w/w) was added until the mixture turned red, and the solution was acidified with perchloric acid (20%, w/w). Upon addition of 8 ml of water a yellow powder precipitated, which corresponds to the $TPTP^+$ salt. The solid was filtered and purified by recrystallisation.

2.2. Reactions

Reactions were performed in open glass vessels. In every batch the vessel was loaded with 250 ml of an aqueous solution of the substrate, whose initial concentration was in the range 0.1–1.5 mM in the case of ferulic acid, and 50 mg/l for carbaryl. The amount of photocatalyst was 10 mg/l, except in those experiments where the effect of TPTP concentration was checked. When necessary, the pH of the solution was adjusted by adding hydrochloric acid. In order to make results as reproducible as possible, sunlight irradiations started at 10:00 a.m. Magnetic stirring was kept all along the reaction time, and water was added periodically in order to compensate for the evaporation loss. Samples were also irradiated by means of a solar simulator (Oriel Instruments, Model 81160 equipped with a 300 W xenon lamp), following otherwise the procedure described above for solar reaction.

2.3. Analysis

Concentration of ferulic acid was determined by liquid chromatography. Samples were taken from the reaction mixture, filtered through glass fibre and injected into the HPLC (Perkin Elmer Autosystem XL equipped with a diode-array detector and an autosampler). A LiChrosphere 100 RP-18 column was employed, and a gradient of a 0.01 M aqueous solution of sulfuric acid and methanol was used for elution (1 ml/min flow rate). Detection was based on the absorption at 210 and 280 nm. In the case of carbaryl, the eluent was an isocratic mixture of methanol (48%) and water (52%), and detection was fixed at 280 nm.

Total organic carbon (TOC) in the treated solutions was determined by means of the Shimadzu model TOC-V CSH, provided with an autosampler. This device was also employed to determine total nitrogen according to the chemiluminescence method.

2.4. Biological assays

Respirometric assays were carried out using an activated sludge respirometer BM3-LAB (Neurtek) equipped with an oxygen sensor (WTW-Cell Ox). Oxygen uptake rate (OUR) was obtained from the difference in the concentration of oxygen in the activated sludge when it was pumped to the oxygen sensor through two pathways of different length [23].

In the OUR inhibition experiments, 1 g of solid sodium acetate was added to 500 ml of the activated sludge so that they achieved their maximum oxygen uptake rate (OUR_{max}). Then, 250 ml of the aqueous solution of the pesticide were added, and the final oxygen consumption (OUR_f) was measured. With these data, the inhibition can be calculated by Eq. (3). However, dilution of the sludge by addition of the liquid sample is responsible of some decrease in the OUR, as determined by blank experiments (inh_B); thus, a corrected inhibition (inh_c) was calculated by means of Eq. (4):

$$\mathrm{inh}\,(\%) = \frac{\mathrm{OUR_{max}} - \mathrm{OUR_f}}{\mathrm{OUR_{max}}} \times 100 \qquad (3)$$

$$\mathrm{inh_c}\,(\%) = \frac{\mathrm{inh} - \mathrm{inh_B}}{100 - \mathrm{inh_B}} \times 100 \qquad (4)$$

For short-term biological oxygen demand (BOD_{st}) determination, the biological reactor was loaded with 1 L of active sludge and 10 ml of effluent. The BOD_{st} value was calculated by integration of the obtained respirometric curve (OUR versus time) after addition of the sample.

2.5. Photophysical measurements

UV/Vis absorption measurements were performed on a Shimadzu UV-2101PC spectrometer. Fluorescence spectra were recorded on a FS900 fluorimeter, and lifetimes were measured with a FL900 setup, both from Edinburgh Instruments. Lifetime measurements are based on single-photon-counting using a hydrogen flashlamp (1.5 ns pulse width) as excitation source. The kinetic traces were fitted by mono-exponential decay functions using a re-convolution procedure to separate from the lamp pulse profile.

Laser flash photolysis studies in the kinetic mode were carried out with a pulsed Nd:YAG SL404G-10 Spectron Laser Systems at the excitation wavelength of 355 nm. The single pulses were ~10 ns duration and the energy was lower than 10 mJ/pulse. The detecting light source was a pulsed Lo255 Oriel xenon lamp. The laser flash photolysis system consisted of the pulsed laser, the Xe lamp, a 77200 Oriel monochromator, an Oriel photomultiplier tube (PMT) system made up of a

77348 side-on PMT tube, 70680 PMT housing and a 70705 PMT power supply. The oscilloscope was a TDS-640A Tektronix. The output signal from the oscilloscope was transferred to a personal computer. All measurements were performed at room temperature in nitrogen-purged solutions for the removal of oxygen. Cuvettes were of 1 cm optical path length, and the absorbance at excitation wavelength was kept at ca. 0.2, in order to avoid non-linear effects like self-absorption or inhomogeneous transient distribution.

3. Results and discussion

A series of six soluble organic dyes, namely 2,4,6-triphenylpyrylium hydrogensulfate, 2,4,6-triphenylthiapyrylium perchlorate, methylene blue, alcian blue, acridine yellow and rosolic acid were tested as homogeneous solar photocatalysts using ferulic acid (0.001 M) as target pollutant (see Chart 1). Results obtained after 2 h irradiation in a solar simulator are shown in Fig. 1; they indicate that only TPTP$^+$ (85% removal) and AYG (83% photo-oxidation) were able to improve the results obtained with TPP$^+$ (59% elimination). The other three dyes, MB, AB and RA were less efficient solar photocatalysts, as the abatement of ferulic acid was in all cases below 20%. In view of the obtained results, a study on the photocatalytic properties of TPTP$^+$ was undertaken. A related study on AYG is currently being performed.

Although 10 mg/l is a usual concentration for organic dyes in homogeneous solution, 20 mg/l and 30 mg/l of TPTP$^+$ were also tested. Experiments were run in a solar simulator, using 0.001 M ferulic acid as substrate. Results shown in Fig. 2 indicate that within this range, TPTP$^+$ concentrations do not play an important role. In all cases less than 20% of the initial amount of ferulic acid remained in the solution; results were fitted to a semi-logarithmic plot and the pseudo first order rate constants were 0.022 min^{-1} for 10 mg/l, 0.029 min^{-1} for 20 mg/l and 0.031 min^{-1} for 30 mg/l. A possible explanation is that, once the dye is able to absorb all the incident photons with a given wavelength, addition of extra catalyst results in no significant improvement of the reaction rate.

The effect of pollutant concentration was also checked in the range 0.1–1.5 mM (Fig. 3). This factor had a clear influence on the reaction rate, as the obtained pseudo-first order *k* values were 0.078 min^{-1} for an initial 0.1 mM concentration of ferulic acid, 0.029 min^{-1} for 0.5 mM, 0.021 min^{-1} for 1 mM and 0.012 min^{-1} for the highest concentration checked, 1.5 mM. Fig. 3, inset, shows the converted mmol of thiapyrylium versus irradiation time; the highest reaction rate was measured for the most concentrated solution, although the lowest *k* was calculated for this reaction. Both observations are not in contradiction, as the first order reaction rate is obtained as the product of the rate constant and the substrate concentration; from this point of view the best results were achieved from 1 mM and 1.5 mM solutions.

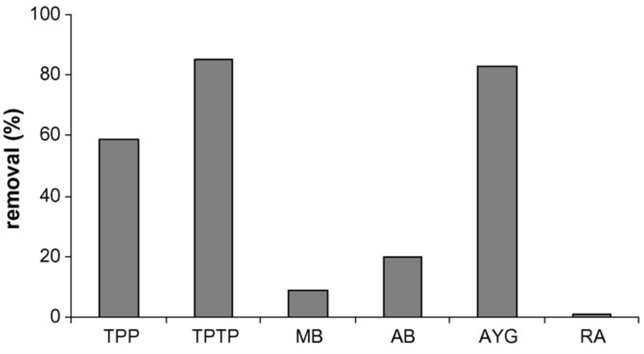

Fig. 1. Solar degradation of ferulic acid (0.001 M) photocatalysed by six different organic dyes (10 mg/l).

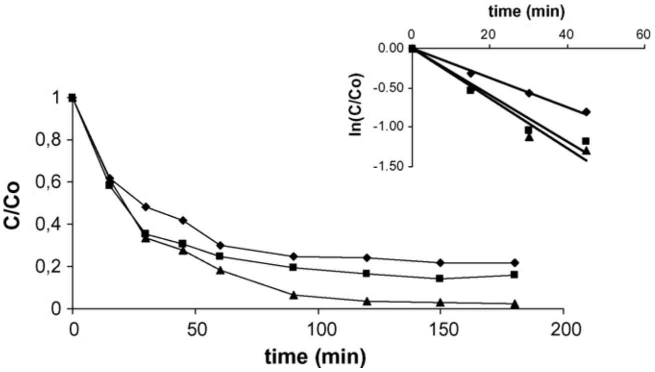

Fig. 2. Plot of the relative concentration of ferulic acid when submitted to solar irradiation in the presence of different amounts of TPTP$^+$ perchlorate: 10 mg/l (◆), 20 mg/l (■) and 30 mg/l (▲). The semi-logarithmic plot is given as an inset.

The possible oxidising effect of the perchlorate ion was ruled out by means of a control experiment, in which irradiation of a ferulic acid solution in the presence of lithium perchlorate did not result in any measurable elimination of the phenolic pollutant.

Some experiments were carried out in order to investigate the mechanism operating with TPTP$^+$. First, the involvement of hydroxyl radical was ruled out by carrying out the reaction in the presence of *t*-butanol, a well known radical scavenger [25]. Irradiation of an aqueous mixture of ferulic acid 1 mM and TPTP$^+$ (10 mg/l) gave essentially the same results without and with *t*-butanol (ca. 1 mM); in both cases elimination of ferulic acid followed a pseudo first order kinetics, and the rate constant was ca. 0.021 min^{-1}.

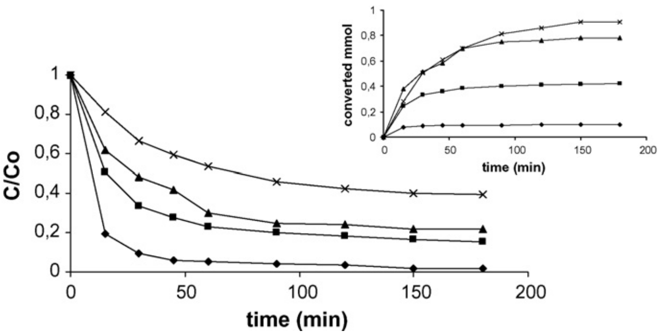

Fig. 3. TPTP$^+$-catalysed (10 mg/l) photodegradation of different concentrations of ferulic acid: 0.1 mM (◆), 0.5 mM (■), 1 mM (▲), 1.5 mM (×). Plot of the relative concentration vs. the irradiation time. In the inset, *Y*-axis represents the converted mmol in each reaction.

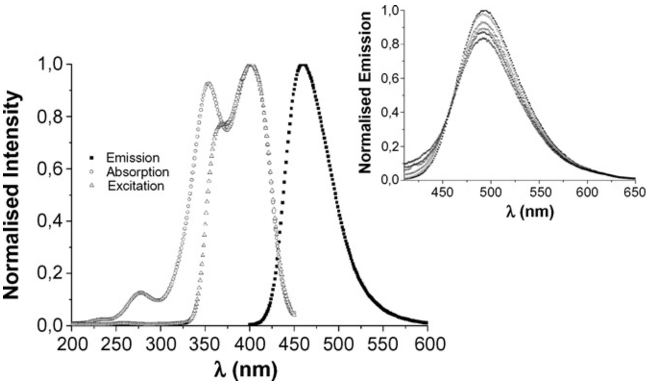

Fig. 4. Emission, absorption and excitation spectra of TPTP$^+$ obtained in aqueous medium. Inset: quenching of the fluorescence emission of TPTP$^+$ by ferulic acid (concentrations in the range 0–5.6 × 10^{-4} M).

In order to gain further insight into the mechanism of TPTP$^+$ photocatalysis, photophysical studies were performed. Fig. 4 shows the absorption, emission and excitation spectra of TPTP$^+$. The absorption spectrum displays two maxima at 354 and 400 nm, with a tail reaching until 450 nm; this indicates that UVA and part of the visible radiation could in principle be employed for exciting this dye; by contrast, titanium dioxide can only absorb the UVA fraction below 385 nm.

The TPTP$^+$ cation shows a strong fluorescence emission in aqueous medium, with a maximum at 470 nm. In the case of the oxygen analogue TPP$^+$, a significant quenching of the fluorescence was observed in the presence of several substrates, including ferulic acid. This behaviour would be compatible with an electron transfer between the photocatalyst and the substrate [9]. Likewise, inset in Fig. 4 shows that the fluorescence of TPTP$^+$ is also efficiently quenched by ferulic acid. The Stern–Volmer equation (Eq. (5)) predicts a linear relationship between the decrease in the fluorescence and the concentration of the substrate, where I_0 and I are the fluorescence intensities in the absence and in the presence of ferulic acid, [Q] is the concentration of ferulic acid and K_{SV} is the Stern–Volmer constant [26]. From the time-resolved fluorescence decay a lifetime of 4.2 ns was found for the first singlet excited state (S_1) of TPTP$^+$ in aqueous medium. Based on these data and applying Eq. (6), the bimolecular quenching rate constant was calculated as $k_q = 2.8 \times 10^8\ M^{-1}\ s^{-1}$. This indicates that a light mediated reaction from the S_1 of TPTP$^+$ to the ground state (S_0) of ferulic acid may indeed occur.

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \tag{5}$$

$$K_{SV} = k_q\tau \tag{6}$$

Nevertheless, the k_q obtained for TPTP$^+$ is clearly lower than that previously measured for quenching of TPP$^+$ with ferulic acid ($1.0 \times 10^{11}\ M^{-1}\ s^{-1}$) although TPP$^+$ was less efficient in the solar photodegradation of the phenolic pollutant. This points to the possibility that the first excited triplet state (T_1) of TPTP$^+$ rather than the singlet, S_1, could be the actual key species involved in the process. To check this point laser flash photolysis experiments were carried out. The transient spectra showed a band attributed to the $T_1 \rightarrow T_n$ absorption (Fig. 5). The decay of this band was recorded in the presence of different concentrations of ferulic acid (Fig. 5, inset); the reduced lifetimes indicated that reaction from the T_1 could actually occur. However, further studies are needed to clarify this point, which are beyond the aim of this paper.

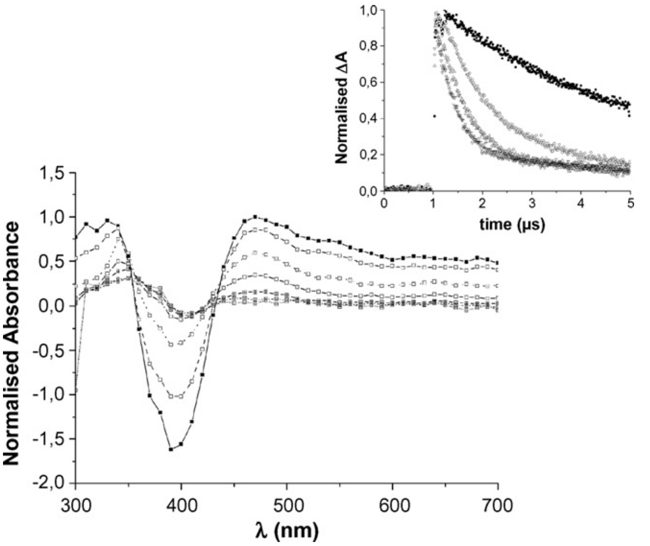

Fig. 5. Transient spectra of TPTP$^+$ obtained by laser flash photolysis, showing a band that can be attributed to $T_1 \rightarrow T_n$ absorption. Inset: decay of the band without and with different concentrations of ferulic acid (in the range 0–1.7 × 10^{-4} M).

The use of a model compound, such as ferulic acid, is very convenient in order to evaluate the efficiency of TPTP$^+$ as solar photocatalyst and also for the elucidation of the reaction mechanism. However, it was also considered interesting to study the behaviour of TPTP$^+$ as photocatalyst for the degradation of the commercial pesticide Sevnol^{TM}, based on carbaryl as active ingredient. Aqueous solutions containing 50 mg/l of carbaryl were irradiated in the presence of TPTP$^+$ (10–30 mg/l). After 2 h of irradiation the elimination of carbaryl was ca. 80%. The results were somewhat better when the reaction was carried out in mildly acidic medium (pH around 3), than when it was driven at neutral pH 6–7. This could be attributed to the different stability of TPTP$^+$ in the two media, due to solvolysis [27].

Using 20 mg/l of photocatalyst at pH 3, the reaction was further investigated to measure other interesting parameters. After 2 h irradiation some TOC decrease was observed, from an initial value of 46 mg/l down to 33 mg/l. This indicates that around 30 % of the organic matter was being mineralised. Total nitrogen was also determined; no variation was observed indicating that no volatile nitrogen-containing species were formed.

As TPTP$^+$ was very efficient to oxidise carbaryl, but it was not able to achieve complete mineralisation, it seems necessary to couple the photocatalytic process with other method able to deal with the remaining organic matter. Biological systems based on activated sludge could be used for this purpose. As matter of fact, much effort is now being devoted to study the feasibility of coupling solar photocatalysis with biological processes to treat highly toxic effluents [28,29].

Activated sludge respirometry was employed to check whether the solar photocatalytic process was able to detoxify the carbaryl solution. This method estimates the toxicity of a pollutant by measuring the decrease in the oxygen uptake rate of the activated sludge upon addition of the toxic species. The first series of assays were devoted to check the toxicity of $TPTP^+$; the results indicated that in the range of concentrations employed in this work (10–30 mg/l) no significant OUR decrease is detectable. Although for technical purposes $TPTP^+$ should advantageously be used as a heterogeneous catalyst, it is always important to make sure that only non-toxic chemicals are used for wastewater detoxification. In addition to this, the photocatalyst should not interfere in the toxicity/biodegradability assays involving Sevnol. Actually, the non-treated Sevnol solution showed a corrected OUR inhibition of 20%, indicating some toxicity towards the activated sludge. On the other hand, assays carried out with the $TPTP^+$ treated effluent proved that a complete detoxification of the mixture was achieved. In addition to this, BOD_{st} was also calculated; although the significance of the numerical value obtained for this parameter should not be overemphasised, it was found to increase from ca. 9 mg O_2/l to 20 mg O_2/l. This indicates that, together with detoxification of the sample, there was also a significant increase in the biodegradability of the effluent.

4. Conclusions

Triphenylthiapyrylium cation has proven to be a very efficient photocatalyst to remove some pollutants from aqueous effluents. It absorbs UVA radiation and a part of the visible light (below 450 nm). It requires only atmospheric oxygen as a reagent and thus it could be considered for a green process. Although photocatalysis with $TPTP^+$ is not able to achieve complete mineralisation of organic matter, detoxification and increased biodegradability of the effluent can be achieved. Hence, coupling $TPTP^+$ photocatalysis with a biological treatment to deal with the remaining organic matter seems feasible.

The mechanism of $TPTP^+$ photocatalysis appears to involve a photochemical electron transfer process. Although the process is thermodynamically feasible from the first singlet excited state, involvement of the triplet excited state seems more likely. Additional experiments are needed to confirm this point.

From the practical point of view, due to the limited stability on $TPTP^+$ in neutral and basic media and to its difficult recovery at the end of the treatment, heterogenisation by adsorption of $TPTP^+$ on a convenient solid support could be appropriate.

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