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Abatement of methidathion and carbaryl from aqueous solutions using organic photocatalysts

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ABSTRACT

Degradation of two pesticides, methidathion and carbaryl, has been studied using organic photocatalysts, namely triphenylpyrylium (TPP^+), triphenylthiapyrylium ($TPTP^+$) and acridine yellow G (AYG). Experiments carried out using a solar simulator showed that methidathion was more easily photo-oxidised than carbaryl, in all cases. TPP^+ and $TPTP^+$ exhibited a better performance than AYG. Detoxification of solutions was related with the primary abatement of the pesticides, as indicated by respirometry studies. Major reaction intermediates were identified by GC–MS, indicating early removal of the carbamate or phosphorated moiety. Photophysical experiments (fluorescence and laser flash photolysis) proved the involvement of an electron-transfer mechanism, most probably from a ground state complex formed between substrate and catalyst.

1. Introduction

Advanced oxidation processes are efficient methods to detoxify industrial effluents, which cannot be treated by conventional means [1]. In particular, the use of sunlight as irradiation source represents an important enhancement in the sustainability of the processes [2].

Solar-driven processes commonly used in wastewater detoxification are the photo-Fenton system, which is based on a combination of iron salts with hydrogen peroxide [3], and heterogeneous photocatalysis with TiO_2 [4,5]. These methods have been shown to be efficient in the elimination of an important number of toxic compounds, such as chlorinated organics, dyes, pesticides, antibiotics or cyanides [6].

These photo-oxidative systems are able to use the UVA fraction of sunlight reaching the Earth's surface; however, visible light is not efficiently employed. For this reason, the search for alternative photoactive compounds displaying strong absorption bands in the visible range of the spectrum is still meaningful. Among the species that might fit these characteristics can be found: (a) organic dyes and aromatic hydrocarbons, (b) porphyrins, phthalocyanines and tetrapyrroles and (c) transition metals complexes such as ruthenium or osmium [7].

Pyrylium and thiapyrylium salts are organic dyes that have been employed as solar photocatalysts [8]. These compounds, upon solar irradiation, become strong oxidising agents, acting *via* an electron-transfer mechanism. A series of papers have been published on the use of 2,4,6-triphenylpyrylium (TPP^+) salts as homogeneous catalysts for the removal of phenolic pollutants [9–12]. In addition, these compounds can be hosted in inorganic materials such as zeolites [13] or sepiolites [14], giving rise to heterogeneous photocatalysts. Triphenylthiapyrylium ($TPTP^+$) salts have also been tested for this purpose with satisfactory results, both in homogeneous [15] and heterogeneous media [16–18]. Acridine yellow G, has also shown to be efficient in the elimination of phenols, even with a better performance than TPP^+ [19].

In previous papers we have established the mechanistic pathway operating in the degradation of cinnamic acids photocatalysed by TPP^+ and $TPTP^+$ [20]. In those particular cases triplet excited states were the species responsible for oxidative electron transfer. Nevertheless, not only the triplet but also the singlet excited state or excited complexes could also play a role in these processes.

Thus, further research in this field is still needed, in order to gain a better understanding of the mechanistic aspects and to explore the applicability of those methods to achieve the detoxification of effluents containing other families of pollutants, such as pesticides [21]. In the present work, two different pesticides, namely methidathion and carbaryl (containing an organothiophosphate and a carbamate moiety, respectively; see Table 1 for structures), have been used as target pollutants.

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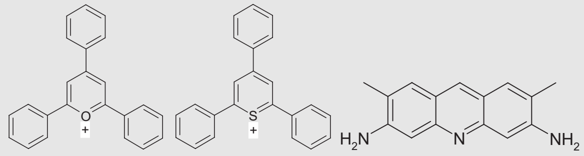
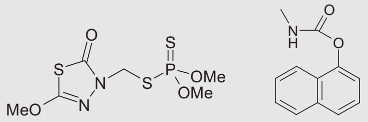
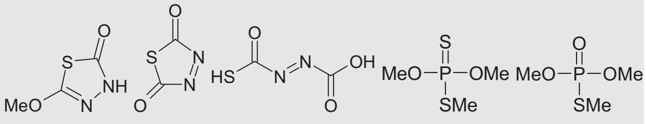
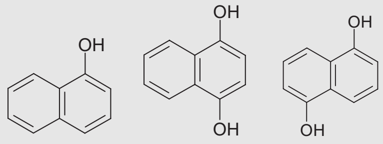
Table 1
Chemical structures of the photocatalysts and pesticides employed in this work. Main intermediates detected are also shown.

Phototocatalysts	 + TPTP$^+$ AYG
Pesticides	 Methidathion Carbaryl
Intermediates derived from methidathion	 A B C D E
Intermediates derived from carbaryl	 F G H

In addition to the study of the catalyst performance in homogeneous and heterogeneous media, different bioassays have been applied in order to evaluate the biocompatibility of the treated effluent. Finally, photophysical experiments have also been carried out to assess the involved mechanism.

2. Experimental

2.1. Reagents

TPP$^+$ hydrogensulfate and TPP$^+$ tetrafluoroborate, as well as acridine yellow G (AYG) were obtained from Aldrich and used without further purification. The TPTP$^+$ perchlorate was synthesised according to the procedure described by Wizinger and Urich [22]: 0.17 g of TPP$^+$ tetrafluoroborate were dissolved in 8 ml of acetone; an aqueous solution of Na_2S (10%, w/w) was added until the mixture turned red, and then the solution was acidified with $HClO_4$ (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.

Supported TPP$^+$ and TPTP$^+$ onto zeolites were obtained following a formal ion exchange method, according to the "camel through the eye of a needle" approach described elsewhere [13,23]. Briefly, Y-zeolite (2.5 g) was suspended in 10 ml of acidified water (HCl, pH approximately 3) and the corresponding amount of TPP$^+$ or TPTP$^+$ was added to obtain a material containing a 6% (w/w) of carbon. The mixture was stirred at 40 °C in the dark for 24 h. Then, it was filtered and the solid was dried for 24 h in an air oven at 105 °C.

The pesticides methidathion and carbaryl were purchased from Aldrich (Pestanal). All other reagents were supplied by Panreac. Water employed in all the experiments was Milli-Q grade.

2.2. Reactions

Homogeneous reactions were performed in open glass vessels, loaded with 250 ml of an aqueous solution of the pesticide (initial concentration 50 mg/l). The amount of photocatalyst was 10 mg/l. The pH of the solution was adjusted to 3 by adding hydrochloric acid, in order to prevent hydrolysis of the catalysts at neutral or basic media [24]. Samples were irradiated by means of a solar simulator (Oriel Instruments, Model 81160 equipped with a 300 W xenon lamp). Magnetic stirring was kept all along the reaction time, and water was added periodically in order to compensate for the evaporation loss. A similar procedure was followed for the heterogeneous reactions; in this case, the amount of suspended solid material was 0.2 g/l, corresponding to 14 mg/l of active compound.

2.3. Analysis

Concentration of the pesticides was determined by liquid chromatography. Samples were taken from the reaction mixture, filtered through polypropylene (0.45 μm) and injected into the HPLC (PerkinElmer Autosystem XL equipped with a diode-array detector and an autosampler). A LiChrosphere 100 RP-18 column was employed, and the eluent was an isocratic mixture of methanol (60%) and sulphuric acid 0.01N (40%). UV-detection was fixed at 215 nm for methidathion and 280 nm for carbaryl.

A GCMS-QP2010S (Shimadzu) gas chromatograph equipped with a quadrupole mass analyser was employed to identify the major intermediates formed along the process. During the analysis, temperature was increased from 60 to 250 °C with a 5 °C/min rate. A Meta X5 Teknokroma column was used. Samples were previously concentrated by solid phase extraction: 100 ml of the aqueous solution were filtered through a LiChrolut EN 200 mg (Merck) cartridge; then organics were recovered with 3 ml of methanol.

Dissolved organic carbon (DOC) in the treated solutions was determined by means of the Shimadzu model TOC-V CSH, provided with an autosampler. This apparatus was also employed to determine carbon in solid samples and it was employed to check the loading of the zeolite-based heterogeneous photocatalysts. Chemical oxygen demand (COD) was determined spectrometrically according to the dichromate method; digestions were performed at 148 °C in a Thermoreaktor TR300 (Merck) and a Spectroquant NOVA 60 (Merck) was used for the photometric determination.

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 [25]. Sodium acetate (1 g) was added to 500 ml of the activated sludge so that the maximum oxygen uptake rate was reached ($\mathrm{OUR_{max}}$). Then, 250 ml of the aqueous solution of the pesticide were added, and the final oxygen consumption ($\mathrm{OUR_f}$) was measured. With these data, the inhibition was calculated by Eq. (1). Dilution of the sludge by addition of the liquid produced some decrease in the OUR ($\mathrm{inh_B}$); thus, a corrected inhibition ($\mathrm{inh_c}$) was calculated by means of Eq. (2):

$$\mathrm{inh}(\%) = \frac{\mathrm{OUR_{max}} - \mathrm{OUR_f}}{\mathrm{OUR_{max}}} \times 100 \qquad (1)$$

$$\mathrm{inh_c}(\%) = \frac{\mathrm{inh} - \mathrm{inh_B}}{100 - \mathrm{inh_B}} \times 100 \qquad (2)$$

Activated sludge was taken from the local wastewater treatment plant from Alcoy (East of Spain). The amount of suspended solids was kept in the range 1500–2000 mg/l, 80% of which were volatile solids.

2.5. Photophysical measurements

UV/vis absorption measurements were performed in acetonitrile on a Shimadzu UV-2101PC spectrometer. Fluorescence spectra were recorded in the same solvent 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 solutions were purged with nitrogen for at least 15 min before the measurements. The absorbance of the solutions at the excitation wavelength (405 nm for $\mathrm{TPP^+}$ and 420 nm for $\mathrm{TPTP^+}$) was kept below 0.1. Cuvettes of 1 cm optical path length were employed, and experiments were performed at room temperature. For the quenching experiments, increasing amounts of methidathion or carbaryl (from 1.7×10^{-4} to 3×10^{-3} M) were added to the corresponding photocatalyst solution in acetonitrile.

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. Cuvettes of 1 cm optical path length were used and all measurements were performed at room temperature in nitrogen-purged solutions for the removal of oxygen. Typically, solutions of $\mathrm{TPP^+}$ or $\mathrm{TPTP^+}$ (7×10^{-5} M) in acetonitrile were used for the quenching experiments and increasing amounts of methidation or carbaryl (from 8.3×10^{-5} to 7.9×10^{-4} M) were added.

3. Results and discussion

3.1. Degradation of methidathion in homogeneous medium

Aqueous solutions of methidathion (50 mg/l) were irradiated in a solar simulator in the presence of 10 mg/l of homogeneous $\mathrm{TPP^+}$, $\mathrm{TPTP^+}$ or AYG. Photocatalyst concentration was chosen to ensure full light absorption at the maxima 404, 405 and 460 nm, respectively [15,19]. Fig. 1 shows that for methidathion the efficiency of the three photocatalysts was $\mathrm{TPTP^+} > \mathrm{TPP^+} \gg \mathrm{AYG}$. Thus, the relative concentration of methidathion *vs.* time was fitted to a semi-logarithmic plot, and the pseudo first order rate constant, *k*, was obtained: the highest value was obtained for $\mathrm{TPTP^+}$ (0.034 $\mathrm{min^{-1}}$) followed by $\mathrm{TPP^+}$ (0.013 $\mathrm{min^{-1}}$), and AYG (0.003 $\mathrm{min^{-1}}$), following the same trends as the percentages of photodegradation. In all cases, acceptable fits were obtained, with *R* values higher than 0.95.

Elimination of the active principles did not result in a significant mineralisation of the organic matter, as indicated by the low DOC decrease (less than 10%) in all cases. This behaviour suggests an efficient transformation of methidathion into less reactive oxidation intermediates. This is in better agreement with an electron-transfer mechanism than with a less selective oxidation by the highly reactive hydroxyl radicals. The latter would be able to react with the oxidation intermediates until formation of $\mathrm{CO_2}$. Nevertheless, important oxidation occurred (COD decrease was 34% for $\mathrm{TPP^+}$ and 38% for $\mathrm{TPTP^+}$).

Extensive oxidation without mineralisation suggests the convenience of investigating the nature of the possible oxidation intermediates, as they might contribute to the toxicity of the resulting solution [26]. A GC–MS analysis was performed to identify the major degradation products. They were found to involve cleavage of the phosphothioester moiety, eventually followed by thiadiazole ring opening and further oxidation (structures A–E in Table 1). Similar pathways have previously been reported for the solar-driven $\mathrm{TiO_2}$-catalysed oxidation of this family of pesticides [27]. In particular, a paper has been recently published by Calza et al. [28] on the $\mathrm{TiO_2}$-degradation of

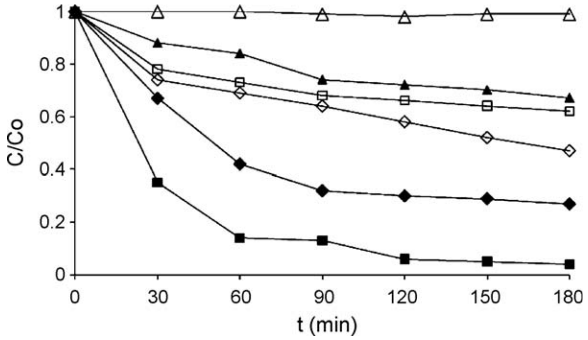


Fig. 1. Plot of the relative concentration of methidathion (C/C_0, where C_0 = 50 mg/l) *vs.* irradiation time in the presence of three different photocatalysts (10 mg/l): $\mathrm{TPP^+}$ (◆), $\mathrm{TPTP^+}$ (■) and AYG (▲). Data obtained for carbaryl under the same conditions are given for all three photocatalysts: $\mathrm{TPP^+}$ (◇), $\mathrm{TPTP^+}$ (□) and AYG (△).

methidathion, where similar intermediates have been detected by LC–MS analysis.

The toxicity of the solutions was estimated by inhibition of the activated sludge respiration. An untreated solution of methidathion (50 mg/l) was able to cause a 47% decrease in oxygen uptake rate of the sludge. After 3 h of treatment samples showed no ($TPTP^+$) or very low (TPP^+) toxicity by comparison with AYG-treated samples (25%). This is in agreement with the efficiency observed in removal of methidathion. A clear relationship between the elimination of phosphorated pesticides and detoxification, according to activated sludge respiration, has already been observed using TiO_2 as catalyst [29,30].

3.2. Degradation of carbaryl in homogeneous medium

Likewise, carbaryl (a carbamate pesticide) was treated with TPP^+, $TPTP^+$ or AYG in homogeneous solution. As shown in Fig. 1 this photocatalytic treatment was less efficient than the corresponding process with methidathion. Best results were achieved in this case by TPP^+, followed by $TPTP^+$. On the other hand, AYG was not able to photo-oxidise significant amounts of carbaryl. Rate constants were also determined (0.003 min^{-1} for TPP^+ and 0.002 min^{-1} for $TPTP^+$) and found to be clearly lower than those measured for methidathion.

Besides, mineralisation was achieved only to a low extent and GC–MS indicated formation of intermediates such as naphthol. Additional hydroxylation can occur at different positions of the naphthalene ring (see structures F–H in Table 1). Again in this case, these products were coincident to those found by Pramauro et al. in the TiO_2 photodegradation of carbaryl driven under UV irradiation [31].

Respirometric assays were also performed. The untreated solution showed some toxicity, decreasing respiration of the activated sludge by 20%. This toxicity was remarkably lower than that of methidathion (47%). The values obtained after the TPP^+ or $TPTP^+$-photocatalysed oxidative process (180 min), were 9% and 14%, respectively, showing marginal detoxification. As expected, no detoxification was found in the AYG driven reaction.

3.3. Degradation of methidathion in heterogeneous medium

As results obtained in homogeneous medium were satisfactory, further experiments were carried out to check the possibility of using supported photocatalysts, as a preliminary step for future technical applications. The main advantages of using heterogeneous photocatalysts are mainly associated with higher stability, easier separation from the reaction mixture, and possibility of recycling [23,32]. For this purpose, TPP^+ and $TPTP^+$ were adsorbed on Y-zeolites, as described in the experimental section. The resulting hybrid material (200 mg/l) was suspended in 250 ml of methidation solution (50 mg/l). Results shown in Fig. 2 indicate that the heterogeneous process also led to efficient degradation of the pesticide; again better results were obtained with $TPTP^+$. Control experiments indicated that removal of methidathion by adsorption was only minor (in the range 10–20%) so the disappearance of the pollutant from the solution was mainly attributable to the photocatalysed oxidation.

Results were fitted to a pseudo first order kinetics; the rate constants were 0.002 min^{-1} for TPP^+ and 0.006 min^{-1} for $TPTP^+$, significantly lower than the corresponding k values in homogeneous medium. This fact was attributed to slower diffusion inside the cavities of Y-zeolite since a similar behaviour was observed when supported TPP^+ was employed to oxidise ferulic acid [23].

Toxicity was determined through inhibition of the respiration of activated sludge; results indicated that important detoxification was achieved. The remaining toxicity was in concordance with the residual amount of methidathion: 28% decrease of sludge respiration was measured after TPP^+ photocatalysis as compared with 16% observed for $TPTP^+$.

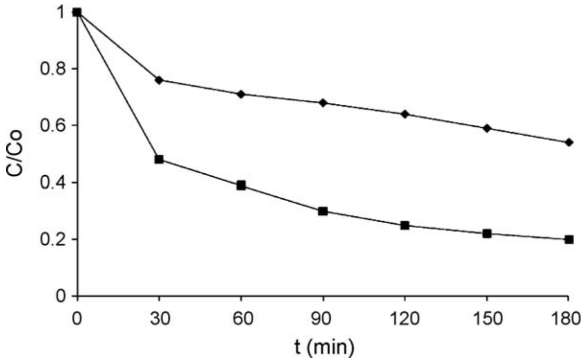


Fig. 2. Plot of the relative concentration of methidathion (C/C_0, where C_0 = 50 mg/l) *vs.* irradiation time in the presence of 2 different heterogeneous photocatalysts (200 mg/l): TPP^+ (◆), $TPTP^+$ (■).

3.4. Photophysical studies

Photophysical experiments were performed to gain some insight into the mechanism operating in the photodegradation of pesticides. For this purpose, only TPP^+ and $TPTP^+$, the most efficient catalysts, were employed.

To investigate the possible participation of singlet excited states into the photodegradation of methidation and carbaryl, static and dynamic quenching experiments of TPP^+ and $TPTP^+$ singlet states by the two contaminants were performed. It is already known that the emission spectra of TPP^+ and $TPTP^+$ in acetonitrile have a maximum at 453 and 458 nm, respectively [10,33]. Thus, when emission spectra of TPP^+ and $TPTP^+$ were recorded in the presence of increasing amounts of pesticides a strong decrease of the fluorescence emission was observed (see Fig. 3 as a representative example). Application of the Stern–Volmer relationships using TPP^+ and $TPTP^+$ singlet state lifetimes [20] allowed us to determine the corresponding quenching rate constants (see Table 2).

The photocatalysts fluorescence quenching was also studied by time-resolved emission spectroscopy. By contrast with the steady-state results, the fluorescence lifetimes of TPP^+ and $TPTP^+$ did not decrease in the presence of methidation or carbaryl, indicating that quenching of singlet excited states is not dynamic in nature. This result, together with the obtained values for the rate constants in the steady-state experiments, higher than the diffusion-controlled rate, exclude the involvement of singlet excited states in the photodegradation of the contaminants and suggests the formation of a non-emissive ground state complex as the responsible for the observed fluorescence quenching (see Scheme 1).

To gain further insight into the reaction mechanism laser flash photolysis experiments were carried out. Thus, after excitation of deaerated TPP^+ or $TPTP^+$ acetonitrile solutions transient spectra characterised by a broad absorption band (between 400 and 800 nm) were observed and attributed to the T-T absorption [20]. Transient spectra of photocatalysts in the presence of methidathion or carbaryl were also recorded (see Fig. 4 for the experiment performed using TPP^+ and methidathion as a representative example).

As it can be seen in Fig. 4, after addition of methidathion (5.4×10^{-4} M) the signal corresponding to the pyranyl radical (λ_{max} at *ca.* 550 nm) was observed [20], proving the photoinduced electron-transfer mechanism. Similar results were observed for $TPTP^+$ and with the other pesticide. No more signals attributable to

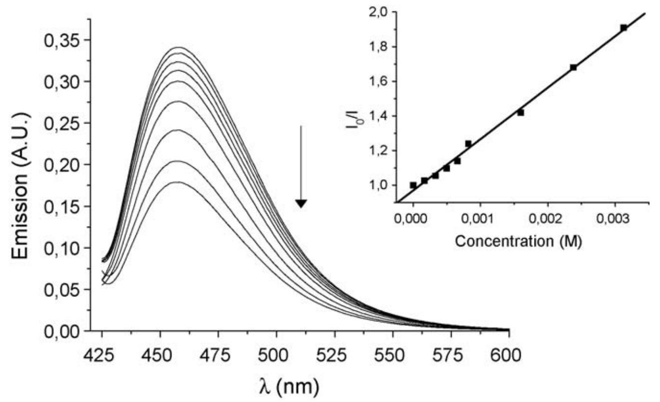
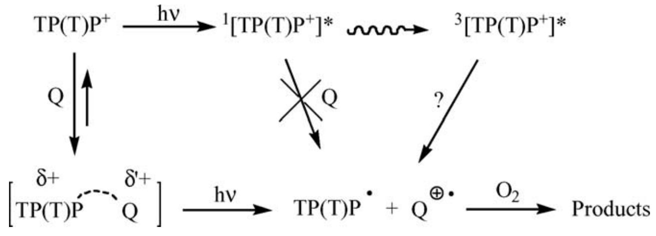


Fig. 3. Fluorescence spectra of TPTP$^+$ in acetonitrile in the presence of increasing concentrations of carbaryl (from the top: 0, 1.66×10^{-4}, 3.31×10^{-4}, 4.95×10^{-4}, 6.58×10^{-4}, 8.20×10^{-4}, 1.6×10^{-3}, 2.38×10^{-3}, 3.12×10^{-3} M). Excitation wavelength: 420 nm. The Stern–Volmer plot is given as an inset.

Table 2
Determined singlet state quenching constants (k_q in $M^{-1}\ s^{-1}$).

Pesticide	TPP$^+$	TPTP$^+$
Methidation	1.3×10^{12}	1.7×10^{11}
Carbaryl	1.4×10^{12}	6.1×10^{10}



Scheme 1. Proposed mechanism for the degradation of methidathion and carbaryl (Q) photocatalysed by TPP$^+$ and TPTP$^+$ (TP(T)P$^+$).

the methidathion or carbaryl radical cations were observed in the available spectral window.

Further experiments were carried out to investigate the participation of the triplet states in the formation of the photocatalysts radicals. Hence, evolution of characteristic triplet (λ_{max} at *ca.* 470 nm) and radical (λ_{max} at *ca.* 550 nm for TPP$^+$) bands, by increasing amounts of contaminants was recorded. Fig. 5A shows that, upon addition of carbaryl, ΔOD after the pulse for trace at 470 nm is decreasing; the opposite is observed for trace at 550 nm (see Fig. 5B). However, decrease of the triplet lifetime by addition of the pesticide was not clearly observed and appearance of signal at 550 is not concomitant with triplet disappearance. Analogous behaviours were observed for TPTP$^+$ and with the other pesticide.

From the above results, contribution of the triplets to the formation of the corresponding radicals cannot be ruled out; however, the fact that the ΔOD for signal due to the pyranyl is higher with higher amounts of contaminant, within the laser pulse, means that the major precursor of this intermediate is not the triplet excited state. Taking into account that the singlet excited states do not lead to reaction, the suggested excited complex appears as the most likely active species responsible for the photoinduced electron transfer (see Scheme 1).

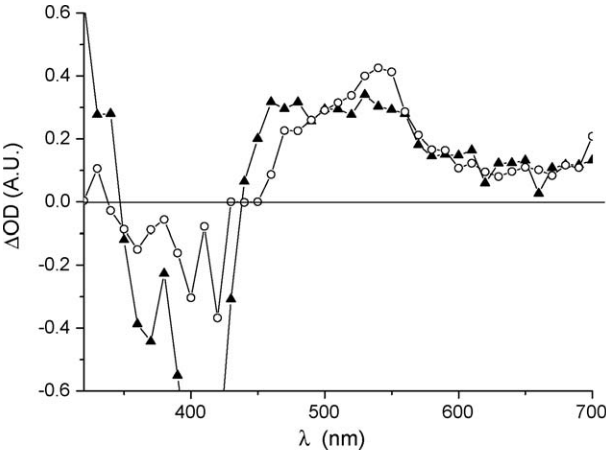


Fig. 4. Transient absorption spectra obtained from laser flash photolysis ($\lambda = 355$ nm) of TPP$^+$ (7×10^{-5} M) in degassed acetonitrile, recorded 1 μs after the laser pulse: (a) in the presence of methidathion (○) and (b) in the absence of methidathion (5.4×10^{-4} M) (▲).

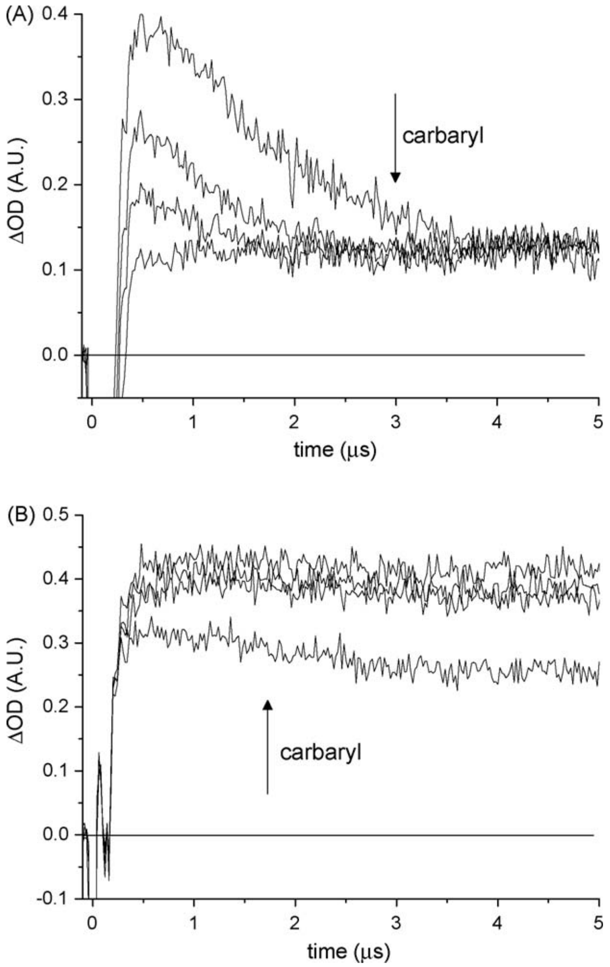


Fig. 5. Laser flash photolysis of TPP$^+$ ($\lambda_{exc} = 355$ nm) upon addition of increasing concentrations of carbaryl: 0, 8.3×10^{-5}, 1.7×10^{-4}, 3.3×10^{-4} M. (A) Transient decay trace monitored at 470 nm; (B) transient decay trace monitored at 550 nm.

4. Conclusions

Homogeneous degradation of methidathion and carbaryl by organic photocatalysts (TPP$^+$ and TPTP$^+$) has been achieved under simulated sunlight irradiation, while AYG was less efficient.

Extensive oxidation without mineralisation (as indicated by DOC and COD measurements) occurred. Nevertheless, respirometry studies indicated that detoxification achieved levels were in good agreement with the observed pesticide removal. Furthermore, heterogenised photocatalysts (TPP^+ and $TPTP^+$ supported onto Y-zeolite) were also able to significantly oxidise methidathion. The efficiency of the hybrid material and the possibility of coupling a biological process after detoxification makes the process technically feasible.

Photophysical experiments suggested the formation of a ground-state complex as the major active species responsible for the photoinduced electron-transfer mechanism, although the contribution of triplet states cannot be disregarded.

Acknowledgements

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References

[1] D. Mantzavinos, E. Psillakis, J. Chem. Technol. Biotechnol. 79 (2004) 431–454.
[2] I. Muñoz, I.J. Peral, J.A. Ayllón, S. Malato, P. Passarinho, X. Doménech, Water Res. 40 (2006) 3533–3540.
[3] J.J. Pignatello, E. Oliveros, A. McKay, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84.
[4] A.G. Agrios, P. Pichat, J. Appl. Electrochem. 35 (2005) 655–663.
[5] U.I. Gaya, A.H. Adbullah, J. Photochem. Photobiol. C 9 (2008) 1–12.
[6] J. Blanco-Gálvez, P. Fernández-Ibáñez, S. Malato-Rodriguez, J. Sol. Energy Eng. 129 (2007) 4–15.
[7] M.C. De Rosa, R.J. Crutchley, Coord. Chem. Rev. 233–234 (2002) 351–371.
[8] M.A. Miranda, H. García, Chem. Rev. 94 (1994) 1063–1089.
[9] A.M. Amat, A. Arques, M.A. Miranda, Appl. Catal. B 23 (1999) 205–214.
[10] M.A. Miranda, F. Galindo, A.M. Amat, A. Arques, Appl. Catal. B 28 (2000) 127–133.
[11] M.A. Miranda, F. Galindo, A.M. Amat, A. Arques, Appl. Catal. B 30 (2001) 437–444.
[12] M.A. Miranda, M.L. Marín, A.M. Amat, A. Arques, S. Seguí, Appl. Catal. B 35 (2002) 167–174.
[13] A.M. Amat, A. Arques, S.H. Bossmann, A.M. Braun, S. Göb, M.A. Miranda, Angew. Chem. Int. Ed. 42 (2003) 1653–1655.
[14] A. Arques, A.M. Amat, L. Santos-Juanes, R. Vercher, M.L. Marin, M.A. Miranda, J. Mol. Catal. A 271 (2007) 221–226.
[15] A. Arques, A.M. Amat, L. Santos-Juanes, R. Vercher, M.L. Marin, M.A. Miranda, Catal. Today 129 (2007) 37–42.
[16] M. Alvaro, E. Carbonell, H. García, Appl. Catal. B 51 (2004) 195–202.
[17] M. Alvaro, E. Carbonell, V. Fornés, H. García, New J. Chem. 28 (2004) 631–639.
[18] M. Alvaro, E. Carbonell, H. García, C. Lamaza, M.N. Pillai, Photochem. Photobiol. 3 (2004) 189–193.
[19] A.M. Amat, A. Arques, F. Galindo, M.A. Miranda, L. Santos-Juanes, R.F. Vercher, R. Vicente, Appl. Catal. B 73 (2007) 51–57.
[20] M.L. Marín, A. Miguel, L. Santos-Juanes, A. Arques, A.M. Amat, M.A. Miranda, Photochem. Photobiol. Sci. 6 (2007) 848–852.
[21] I.K. Konstantinou, T.A. Albanis, Appl. Catal. B 42 (2003) 319–335.
[22] R. Wizinger, P.L. Urich, Helv. Chim. Acta 39 (1956) 207.
[23] A.M. Amat, A. Arques, S.H. Bossmann, A.M. Braun, M.A. Miranda, R.F. Vercher, Catal. Today 101 (2005) 383–388.
[24] M.A. Miranda, A.M. Amat, A. Arques, Catal. Today 76 (2002) 113–119.
[25] A.M. Amat, A. Arques, H. Beneyto, A. García, M.A. Miranda, S. Seguí, Chemosphere 53 (2003) 79–86.
[26] M. Lapertot, S. Ebrahimi, S. Dazio, A. Rubinelli, C. Pulgarin, J. Photochem. Photobiol. A 186 (2007) 34–40.
[27] H.D. Burrows, M.L. Canle, J.A. Santaballa, S. Steenken, J. Photochem. Photobiol. C 67 (2002) 71–108.
[28] P. Calza, C. Massolino, E. Pelizzetti, J. Photochem. Photobiol. A 199 (2008) 42–49.
[29] A. Arques, A.M. Amat, A. García-Ripoll, R. Vicente, J. Hazard. Mater. 146 (2007) 447–452.
[30] A. García-Ripoll, A.M. Amat, A. Arques, R. Vicente, M.F. López, I. Oller, M.I. Maldonado, W. Gernjak, Chemosphere 68 (2007) 293–300, 2007.
[31] E. Pramauro, A. Bianco-Prevot, M. Vicenti, G. Brizzolesi, Environ. Sci. Technol. 31 (1997) 3126–3131.
[32] M.A. Miranda, A. Amat, A. Arques, Catal. Today 76 (2002) 113–119.
[33] F. Morlet-Savary, S. Parret, J.P. Fouassier, K. Inomata, T. Matsumoto, J. Chem. Soc., Faraday Trans. 94 (1998) 745–752.