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Time-resolved kinetic assessment of the role of singlet and triplet excited states in the photocatalytic treatment of pollutants at different concentrations

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Abstract

A kinetic-based rationale to assess the role of each excited species in thermodynamically favored photocatalytic processes at different pollutant concentrations, has been developed and illustrated with new experimental data. Specifically, 2,4,6-triphenylthiapyrylium ($TPTP^+$) salt has been chosen as a representative organic compound capable to act as photocatalyst, and the possible involvement of its excited states in the photodegradation of pollutants commonly found in aqueous ecosystems has been investigated using five chemicals, namely acetaminophen, acetamiprid, caffeine, clofibric acid and carbamazepine. First, steady-state photolysis has been carried out under simulated solar irradiation in the presence of $TPTP^+$, and second, photophysical measurements (fluorescence and laser flash photolysis) have been performed in order to obtain reliable fast kinetic data. Thermodynamic considerations allow ruling out energy transfer processes, while the kinetic results are in good agreement with an electron transfer to the triplet excited state of $TPTP^+$. Hence, the higher the intersystem crossing quantum yield the better. Although quenching of the singlet excited state is also observed, the contribution of this reactive species is only minor, due to its shorter lifetime. In general, the efficiency of a photocatalyst should be enhanced at higher pollutant concentrations, at which the intrinsic decay of the triplet excited state is minimized.

Keywords

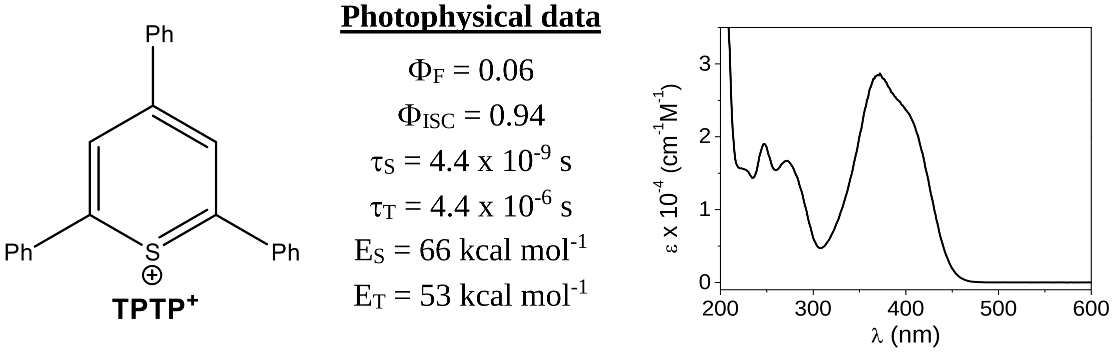
Electron transfer; laser flash photolysis; photo-redox catalysis; singlet excited state; triplet excited state

1. Introduction

Photochemical processes are among the most important abiotic pathways for the removal of pollutants from aqueous ecosystems.[1, 2] These processes can occur upon direct absorption of light by the pollutant (direct photolysis), or indirectly through the formation of highly reactive species that react, in turn, with the pollutant (photocatalyzed degradation). Several species can mediate the indirect mechanisms, among them hydroxyl radicals, singlet oxygen, superoxide anion, inorganic radicals (chloride, sulfate, carbonate), organic radicals (carboxyl, peracyl) or excited states of dissolved or suspended organic substances.[3-7]

An overall analysis of photocatalyzed-redox processes should consider two complementary aspects: the thermodynamic and the kinetic viability of all the competing pathways. More specifically, first thermodynamic estimations based on the redox potentials of the involved species could help to discard those pathways that result highly endergonic. Second, a fast kinetic analysis of the thermodynamically allowed key steps, based on the lifetime of the involved transient species, is necessary to elucidate whether the processes are competitive at that time scale. In this context, a photophysical study seams meaningful, as it allows direct monitoring of reactive species, providing time-resolved data in the micro or nanosecond scale.[8] An overall analysis of the obtained photophysical data would help to elucidate the role of each competitive photoactive species. One more parameter that seems meaningful to evaluate is the efficiency of the photocatalyst *versus* pollutant concentration. In fact, it is generally accepted that below a critical concentration, pollutants behave as recalcitrant.

Such a complete analysis requires a proxy that offers the possibility of monitoring the derived-excited species. For this purpose, a 2,4,6-triphenylthiapyrylium ($TPTP^+$) salt (see Fig. 1 left for the chemical structure) could be a good candidate to study the interaction between excited organic species and pollutants. As regards the thermodynamic aspect, $TPTP^+$ is an extremely good oxidant from its singlet and triplet excited states with $E^*(TPTP^+/TPTP^{\cdot})$ *ca.* 2.5 or 2.0 V *vs* SCE, respectively. Besides, it is able to absorb UV-visible light (Fig. 1 right) and displays appropriate photophysical parameters (Fig. 1 middle): it exhibits a low fluorescence quantum yield (Φ_F) of 0.06, but a high intersystem crossing quantum yield (Φ_{ISC}) of 0.94; it does not sensitize formation of $^1O_2$ nor superoxide anion, and its singlet (τ_S) and triplet lifetimes (τ_T) are of 4.4 ns and 4.4 μs, respectively.[8, 9] Despite its high intersystem crossing quantum yield, $TPTP^+$ has already demonstrated to achieve oxidative photodegradation of pollutants, through its singlet or/and triplet excited states.[10, 11]



Photophysical data

$\Phi_F = 0.06$

$\Phi_{ISC} = 0.94$

$\tau_S = 4.4 \times 10^{-9}$ s

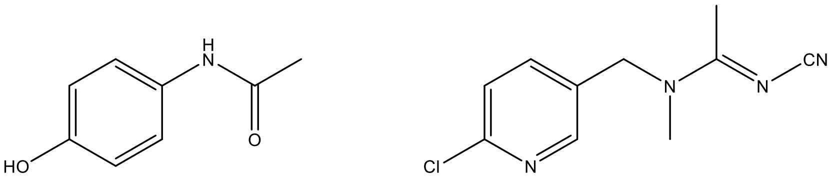
$\tau_T = 4.4 \times 10^{-6}$ s

$E_S = 66$ kcal mol^{-1}

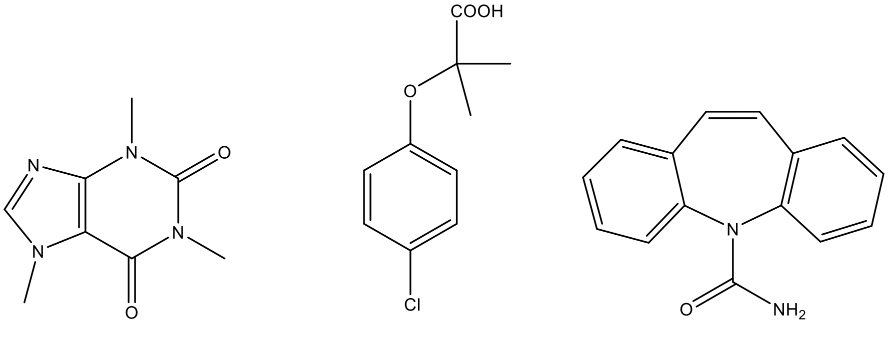
$E_T = 53$ kcal mol^{-1}

Fig. 1. Chemical structure of 2,4,6-triphenylthiapyrylium ($TPTP^+$) salt together with its main photophysical parameters and its UV-visible absorption spectrum.

With this background, the main goal of the present paper is to provide a kinetic-based rationale to assess the role of each excited species in a photocatalytic process at different pollutant concentrations. For this purpose, new experimental data are provided and used to illustrate the concept. Specifically, $TPTP^+$ has been chosen as a representative organic compound capable to act as photocatalyst, and the possible involvement of its excited states in the photodegradation of pollutants commonly found in aqueous ecosystems has been investigated. In this work, five chemicals have been selected for the study, namely acetaminophen (ACF), acetamiprid (ACP), caffeine (CAF), clofibric acid (CLOF) and carbamazepine (CBZ) (Fig. 2). First, steady-state photolysis has been carried out under simulated solar irradiation in the presence of $TPTP^+$; second, photophysical measurements (fluorescence and laser flash photolysis) have been performed in order to obtain reliable fast kinetic data; and third, the role of pollutant concentration on the relative contribution of the different excited states to the overall photocatalytic process has been established.



Acetaminophen (**ACF**) Acetamiprid (**ACP**)



Caffeine (**CAF**) Clofibric acid (**CLOF**) Carbamazepine (**CBZ**)

Fig. 2. Chemical structures of the selected pollutants.

2. Experimental

2.1. Solar simulated reactions

Samples were irradiated by means of a solar simulator (Oriel Instruments, Model 81160) equipped with a 300W Xenon lamp, which closely reproduces the solar spectrum.[10] An aqueous solution (250 mL) of the mixture of the five pollutants (initial concentration: 5 mg L^{-1} each) and $TPTP^{+}$ (10 mg L^{-1}) was introduced in an open Pyrex glass vessel, the pH was adjusted to 3 by dropwise addition of sulfuric acid, and then irradiated. Magnetic stirring was kept all along the reaction time, and water was added periodically to compensate for the evaporation loss.

Aliquots were taken from the reaction mixture, filtered through polypropylene (0.45 μm) and then injected into a liquid chromatograph (Perkin Elmer model Flexar UPLC FX-10) equipped with a UV-vis detector.

2.2. Photophysical instrumentation

Absorption spectra (UV/Vis) were performed on a Shimadzu UV-2101PC spectrometer. Steady-state fluorescence and time-resolved fluorescence experiments were performed in a FS900 fluorometer and a FL900 setup, respectively (Edinburgh Instruments). Lifetime measurements were based on single-photon-counting using a 1.5 ns pulse width hydrogen flash-lamp as excitation source. The kinetic traces were fitted by monoexponential decay functions using a deconvolution procedure to separate them from the lamp pulse profile.

Laser flash photolysis (LFP) experiments were carried out with a pulsed Nd: YAG SL404G-10 Spectron Laser Systems at the excitation wavelength of 355 nm. The energy of the single pulses (~10 ns duration) was lower than 15 mJ $pulse^{-1}$. The laser flash photolysis system consisted of the pulsed laser, a pulsed Lo255 Oriel Xenon lamp, a 77200 Oriel monochromator, an Oriel photomultiplier tube (PMT) housing, a 70705 PMT power supply and a TDS-640A Tektronix oscilloscope.

2.3. Photophysical experiments

Quartz cells of 1 cm optical path length were employed for all photophysical measurements, which were run at room temperature.

For the steady-state and time-resolved fluorescence experiments, increasing concentrations of pollutants (up to 7 x 10^{-3} M in CH_3CN) were added to deaerated acetonitrile solutions of $TPTP^+$ with absorbance at the excitation wavelength (400 nm) lower than 0.1. For the laser flash photolysis experiments, increasing amounts of pollutant (up to 7 x 10^{-5} M) were added to deaerated acetonitrile solutions of $TPTP^+$ (7 x 10^{-5} M). Job's plot experiments were carried out to investigate the stoichiometry of the complex ($TPTP^{\delta+}$--ACP $^{\delta'+}$). The absorbance changes were measured at 404 nm and plotted against the ACP molecular fraction, keeping the total concentration of ACP and $TPTP^+$ at the constant value of 1 x 10^{-5} M.

3. Results and discussion

3.1 Solar simulated photodegradation of the pollutants

It is known that $TPTP^+$ is an extremely good oxidant from its singlet and triplet excited states with $E^*(TPTP^+/TPTP^\cdot)$ *ca.* 2.5 or 2.0 V *vs* SCE, respectively.[9] Thus, on the basis of the reported redox data for the pollutants[12-15] the photooxidation processes are thermodynamically favoured in all cases.

Therefore, an aqueous solution containing the five selected pollutants was irradiated with a solar simulator in the presence of $TPTP^+$. The pH of the medium was adjusted to 3 in order to ensure the photostability of this photocatalyst.[16] Fig. 3 shows plots of the relative concentration of each pollutant *vs.* irradiation time: CLOF and ACF showed the highest photodegradation rates, followed by CBZ and CAF, while removal of ACP was negligible under the studied experimental conditions. However, quantitative differences were observed among the selected pollutants: in fact, CLOF was completely removed after only 10 min of irradiation, while *ca.* 60 min were required in the case of ACF. On the other hand, CAF and CBZ were not completely removed within the irradiation time, but percentages of removal after 180 min were *ca.* 50%.

Control experiments performed by direct photolysis (in the absence of $TPTP^+$) showed almost no reaction apart from CLOF that suffered direct photodegradation but to a much lesser extent. Thus, the photocatalytic degradation produced complete abatement of CLOF in 15 min while direct photolysis needed 180 min to provoke 80 % removal (see Fig. S2).

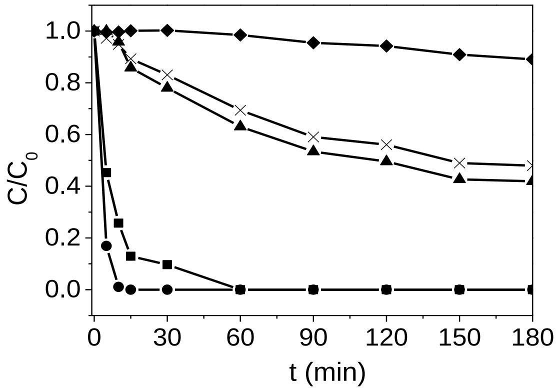


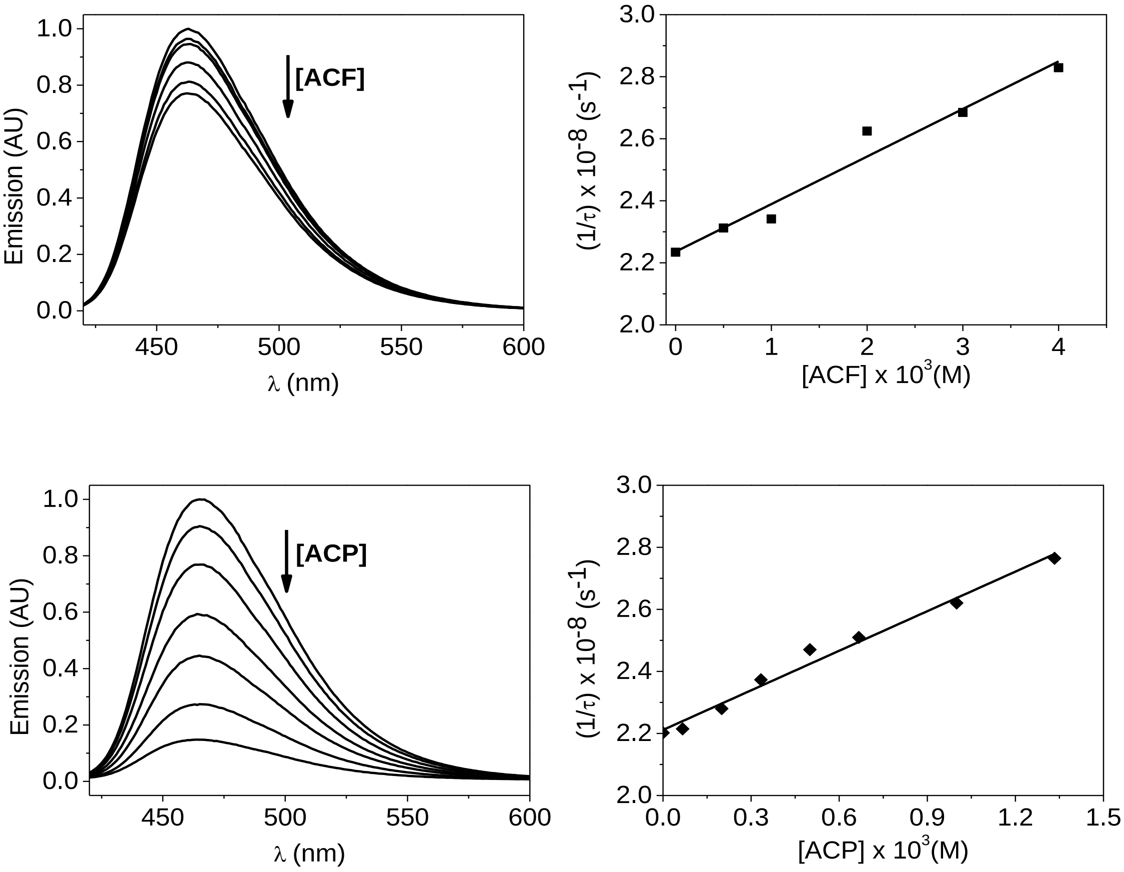
Fig. 3. Plot of the relative concentration of ACF (■), ACP (♦), CAF (×), CLOF (●) and CBZ (▲) at C_o= 5 mg L^{-1} and pH = 3, *vs*. solar simulated irradiation time, in the presence of 10 mg L^{-1} of $TPTP^+$.

3.2. Photophysical studies

$TPTP^+$ is known to act as photocatalyst *via* electron transfer from its singlet or triplet excited states. In fact, examples of photodegradation from the singlet, triplet or even formation of photoactive ground-state complexes can be found for (thia)pyrylium salts.[10, 11, 17-19] Hence, participation of every potential species in the photodegradation has to be determined in each particular case. Thus, systematic photophysical studies were undertaken and the combined results analyzed for each pollutant at different concentrations.

3.2.1. Fluorescence quenching studies

The potential participation of the singlet excited state of $TPTP^+$ was investigated by means of steady-state and time-resolved experiments. In fact, a decrease in the emission intensity and singlet lifetime of $^1(TPTP^+)^*$ in deaerated acetonitrile was observed in all cases upon addition of increasing concentration of every pollutant (Fig. 4). The corresponding quenching rate constants were determined applying the Stern-Volmer relationship, between $1/\tau$ and pollutant concentration. The obtained values (Table 1) confirmed the dynamic involvement of the singlet excited state in all cases, with values close to the diffusion limit.[20]



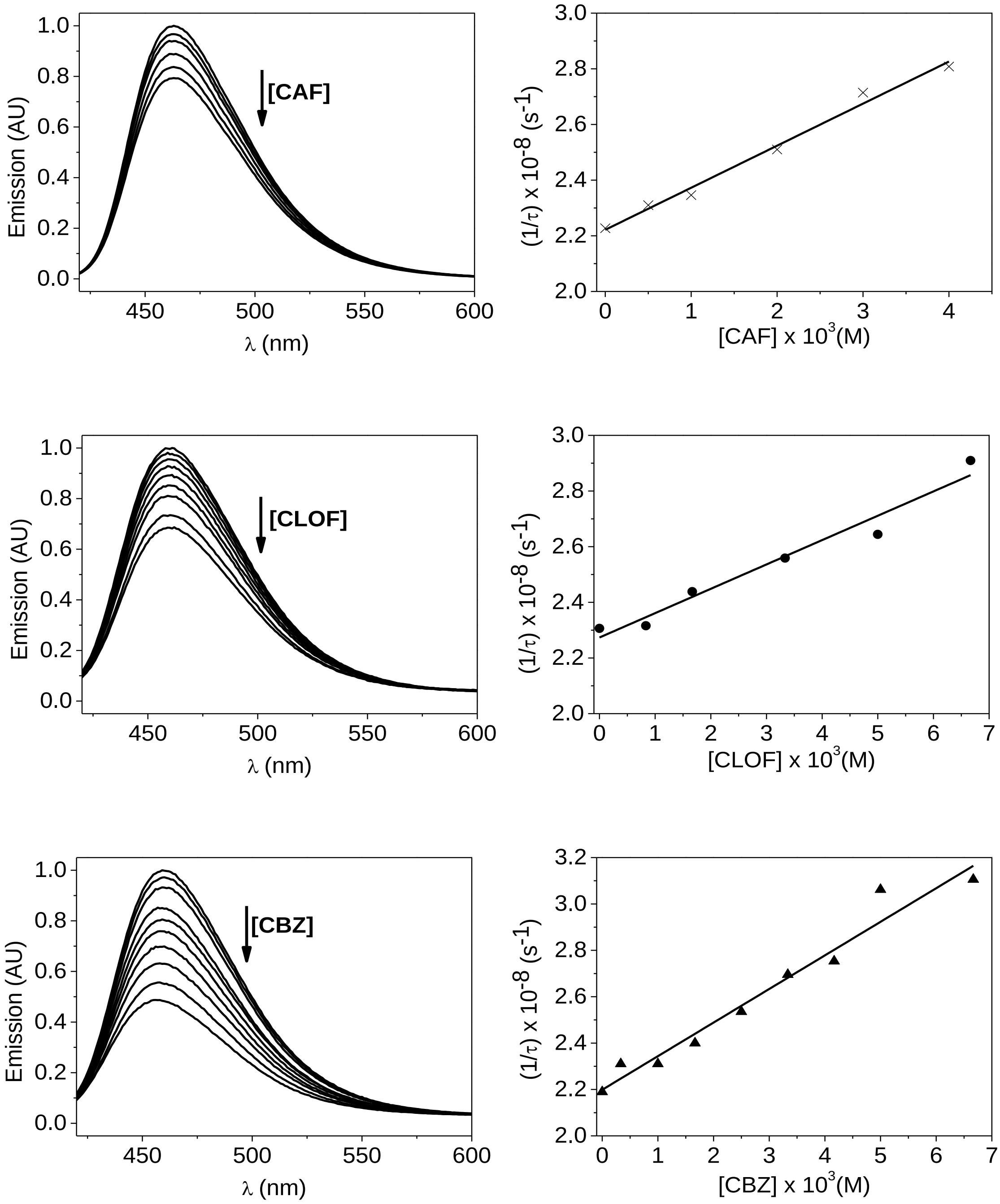


Fig. 4. Left column: Steady-state $^1(TPTP^+)^*$ fluorescence quenchings; Right column: Stern-Volmer plots obtained from time-resolved experiments; all upon increasing pollutant concentration (up to 7 x 10^{-3} M) in CH_3CN (λ_{exc} = 400 nm).

Moreover, it is worth to note that in the case of ACP, when the steady-state emission of $^1(TPTP^+)^*$ was recorded upon increasing [ACP], the Stern-Volmer relationship revealed a different behavior (see Supporting Information), clearly deviated from a linear one, and pointing to the formation of a non-emissive ground state complex. The stoichiometry of the purported complex between $TPTP^+$ and ACP ($TPTP^{\delta+}$--$ACP^{\delta'+}$) was determined from a Job's plot experiment,[21, 22] and subsequent K value determination was achieved on the basis of the Benesi-Hildebrand relationship (K=503 M^{-1}) (see Supplementary Material).[23, 24] Formation of ground-state complexes can have a huge influence on the photocatalytic degradation of a contaminant, since pre-association could result in an "intramolecular-like" reaction proceeding at much higher rate (not-controlled by diffusion) and therefore offering a much more competitive degradation pathway.

3.2.2. Transient absorption spectroscopy

The involvement of the triplet excited state of $TPTP^+$ was investigated on the basis of laser flash photolysis (LFP) experiments. Thus, deaerated acetonitrile solutions of $TPTP^+$ were submitted to laser flash excitation (355 nm) and its triplet lifetime was monitored at 620 nm. A decrease in the lifetime was clearly observed in all cases (Fig. 5). The corresponding quenching constants, determined from the Stern-Volmer linear relationships, are shown in Table 1.

Table 1. Rate constant values (k_{qS} and k_{qT}) for the quenching of $^1(TPTP^+)^*$ and $^3(TPTP^+)^*$ by the pollutants determined from time-resolved fluorescence quenching and laser flash photolysis experiments.

POLLUTANT	**k_{qS} x 10^{-10} ($M^{-1}s^{-1}$)**	**k_{qT} x 10^{-8} ($M^{-1}s^{-1}$)**
	$^1(TPTP^+)^*$	**$^3(TPTP^+)^*$**
ACF	1.5	110
ACP	4.4	6.8
CAF	1.5	98
CLOF	0.8	84
CBZ	1.5	81

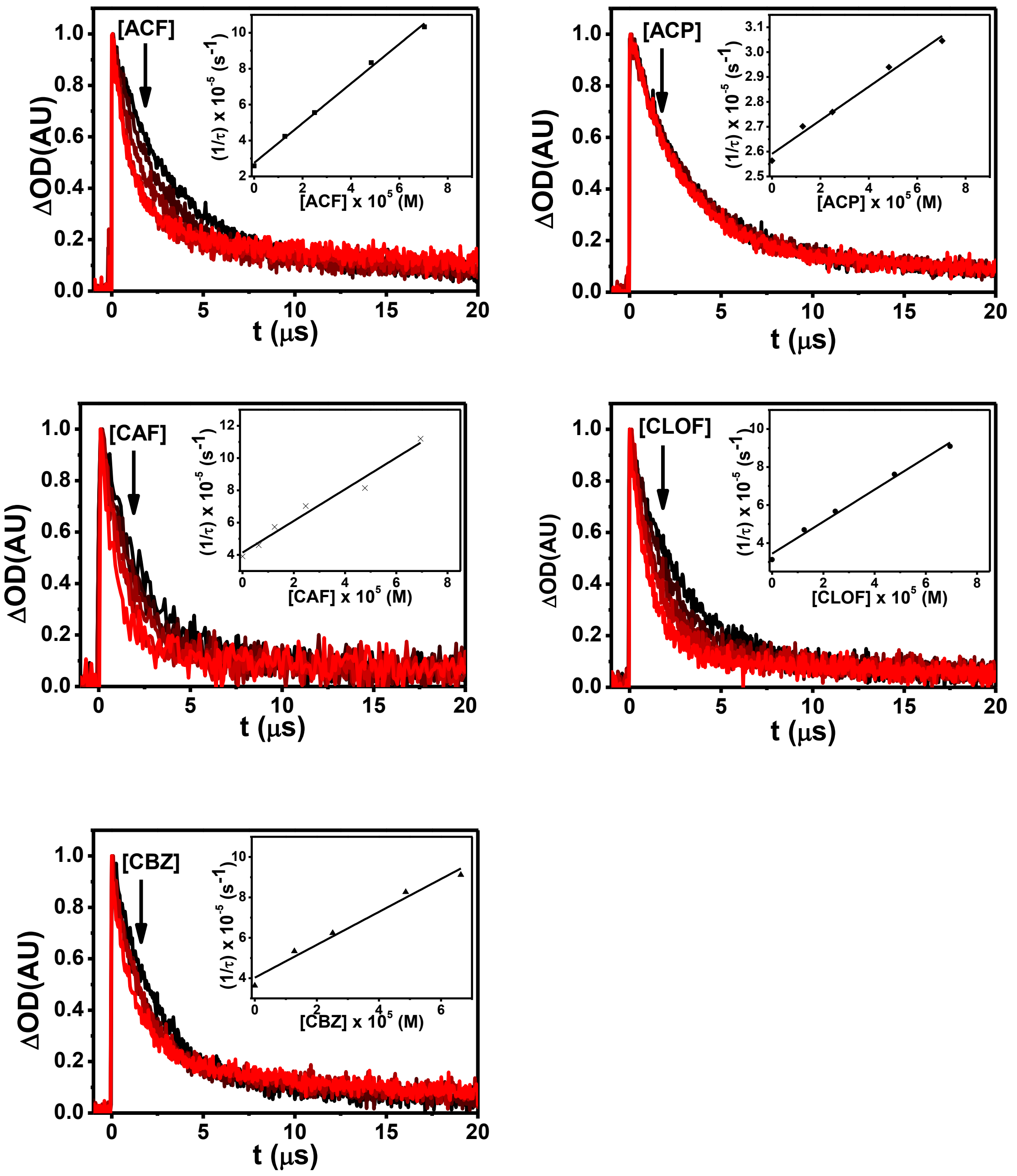
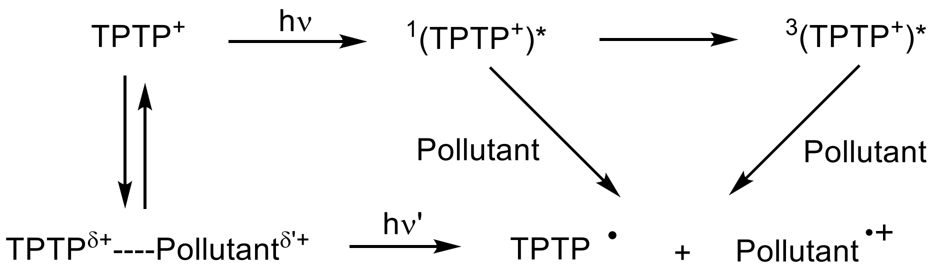


Fig. 5. Normalized kinetic traces obtained upon LFP excitation (355 nm) of deaerated acetonitrile solutions (7 x 10^{-5} M) of $TPTP^+$ upon increasing pollutant concentrations. Insets: Corresponding Stern-Volmer plots.

3.3. Mechanistic proposal

Quenching of the excited states of $TPTP^+$ could, in principle, be due to an energy transfer mechanism or a photoinduced electron transfer one. The former was ruled out on the basis of the UV-visible spectra of the photocatalyst and pollutants (Fig.1 right and Fig. S1); while TPTP$^+$ absorbs up to 450 nm, the pollutants absorb at much shorter wavelength, all below 320 nm. Therefore, much more energetic excited states in the case of the pollutants were inferred (both singlets and triplets). As a result, the energy transfer from TPTP$^+$ will be thermodynamically disfavored in all cases. Moreover, using CAF as example, the quenching of the triplet excited state of TPTP$^+$ was performed in an additional solvent of lower relative permittivity to support the electron transfer process. Specifically, tetrahydrofuran ($\varepsilon = 7.58$) was selected and compared to the result obtained in acetonitrile ($\varepsilon = 35.94$). The obtained quenching constants were 6.0×10^8 $M^{-1}s^{-1}$ and 9.8×10^9 $M^{-1}s^{-1}$ in tetrahydrofuran and acetonitrile, respectively; thus supporting the photoxidation occurring through an electron transfer process (see Figure Sx in the Supplementary Material). Therefore, the above detailed photophysical results allowed us to postulate the following overall electron transfer mechanistic pathway to explain the observed photodegradation of ACF, ACP, CAF, CLOF and CBZ in the presence of TPTP$^+$ (Scheme 1). In all cases quenching of the singlet and triplet excited states of TPTP$^+$ was observed, while formation of complexes has only been demonstrated in the case of ACP.



Scheme 1. Overall mechanistic pathways to explain photodegradation of pollutants by oxidative e$^-$ transfer to TPTP$^+$.

3.4. Relative contribution of the involved excited species at different pollutant concentrations

The relative contribution of a photocatalyst-derived reactive species, singlet or triplet excited states, or photoactive ground-state complex can be evaluated on the basis of the following equations. In addition, the efficiency in the use of a photocatalyst to perform the photodegradation of the pollutants can be determined upon pollutant concentration.

If part of the photocatalyst (P) in its ground state is forming a complex with the pollutant (Q), the percentage of photocatalyst involved in it (for 1:1 stoichiometry) is shown in eq.4:

$$K = \frac{\left[P^{\delta+}\cdots Q^{\delta'+}\right]}{([P]-[P^{\delta+}\cdots Q^{\delta'+}])([Q]-[P^{\delta+}\cdots Q^{\delta'+}])}\ (eq.1)$$

Assuming that:

$$\left[P^{\delta+}\cdots Q^{\delta'+}\right] \ll [P]\ and\ \left[P^{\delta+}\cdots Q^{\delta'+}\right] \ll [Q] (eq.2)$$

$$\left[P^{\delta+}\cdots Q^{\delta'+}\right] \cong\ K \times [P] \times [Q] (eq.3)$$

$$\left[P^{\delta+}\cdots Q^{\delta'+}\right](\%) \cong K \times [Q] \times 100\ (eq.4)$$

Therefore, the percentage of photocatalyst able to reach the singlet excited state comes from equation 5:

$$^{1}(P)^{*}\ formation\ (\%) =\ 100 - \left[P^{\delta+}\cdots Q^{\delta'+}\right](\%) \approx 100 - K \times Q \times 100 = (1 - K \times Q) \times 100\ (eq.5)$$

The processes that can occur to the photocatalyst from its singlet excited state include emission(Φ_F/τ_S), intersystem crossing (Φ_{ISC}/τ_S) and quenching by the pollutant $\left(k_{qs}[Q]\right)$, according to equation 6:

$$\sum Processes\ from\ {}^{1}(P)^{*} = \frac{\Phi_F}{\tau_S} + \frac{\Phi_{ISC}}{\tau_S} + k_{qs}[Q]\ (eq. 6)$$

In addition, the part of the photocatalyst that reaches the triplet excited state can be deactivated following two additional pathways: intrinsic decay $(1/\tau_T)$ and quenching by the pollutant $\left(k_{qT}[Q]\right)$ as shown in equation 7:

$$\sum Processes\ from\ {}^{3}(P)^{*} = \frac{1}{\tau_T} + k_{qT}[Q]\ (eq. 7)$$

Using the above defined equations, the percentage of photocatalyst that is used in the quenching of the pollutants can be determined from eq. 8 (if it occurs from the singlet) and eq. 11 (if it occurs from the triplet); therefore, the relative contribution of the singlet and triplet excited states in the quenching can be compared among them and also evaluated against the intrinsic decay of the triplet (eq. 12):

$$Quenching\ of\ {}^{1}(P)^{*}\ (\%) = {}^{1}(P)^{*}\ formation(\%) \times \frac{k_{qs}[Q]}{\frac{\Phi_F}{\tau_S} + \frac{\Phi_{ISC}}{\tau_S} + k_{qs}[Q]}\quad (eq. 8)$$

$$Quenching\ of\ {}^{3}(P)^{*}\ (\%) = {}^{3}(P)^{*}\ formation\ (\%) \times \frac{k_{qT}[Q]}{\frac{1}{\tau_T} + k_{qT}[Q]}\quad (eq. 9)$$

$${}^{3}(P)^{*}\ formation(\%) = {}^{1}(P)^{*}\ formation\ (\%) \times \frac{\frac{\Phi_{ISC}}{\tau_S}}{\frac{\Phi_F}{\tau_S} + \frac{\Phi_{ISC}}{\tau_S} + k_{qs}[Q]}\ (eq. 10)$$

$$Quenching\ of\ {}^{3}(P)^{*}\ (\%) = {}^{1}(P)^{*}\ formation\ (\%) \times \frac{\frac{\Phi_{ISC}}{\tau_S}}{\frac{\Phi_F}{\tau_S} + \frac{\Phi_{ISC}}{\tau_S} + k_{qs}[Q]} \times \frac{k_{qT}[Q]}{\frac{1}{\tau_T} + k_{qT}[Q]}\quad (eq. 11)$$

$$Deactivation\ of\ {}^{3}(P)^{*}\ (\%) = {}^{1}(P)^{*}\ formation\ (\%) \times \frac{\frac{\Phi_{ISC}}{\tau_S}}{\frac{\Phi_F}{\tau_S} + \frac{\Phi_{ISC}}{\tau_S} + k_{qs}[Q]} \times \frac{\frac{1}{\tau_T}}{\frac{1}{\tau_T} + k_{qT}[Q]}\quad (eq. 12)$$

As it can be seen from the above equations, the relative contribution of the different deactivation channels of the photocatalyst depends on its intrinsic properties, on the experimentally determined quenching constants and on the quencher (pollutant) concentration.

In this particular example, only formation of photoactive ground-state complex, singlet and triplet excited states are considered. Then, from the experimentally obtained quenching rate constants for the pollutants (Table 1) and using the intrinsic data of the photocatalyst (Fig. 1 middle), [8] the determined relative contribution of every pathway is shown in Table 2.

Table 2. Relative contributions of the ground-state complex formation, singlet and triplet quenchings and intrinsic singlet and triplet deactivation in the photocatalytic degradation of the pollutants using TPTP$^+$.

[Q] (M)	Pollutant	Complex formation (%)	Quenching of ^{1}(TPTP)* (%)	^{1}(TPTP)* intrinsic decay (%)	Quenching of ^{3}(TPTP)* (%)	^{3}(TPTP)* intrinsic decay (%)
10^{-3}	ACF	-	3.2	5.8	89.2	1.8
	ACP	50.6	1.6	2.9	33.7	11.3
	CAF	-	3.2	5.8	89.0	2.1
	CLOF	-	3.2	5.8	88.6	2.5
	CBZ	-	3.2	5.8	88.6	2.4
10^{-5}	ACF	-	<0.1	6.0	30.7	63.2
	ACP	0.5	<0.1	6.0	2.7	90.8
	CAF	-	<0.1	6.0	28.3	65.7
	CLOF	-	<0.1	6.0	24.8	69.2
	CBZ	-	<0.1	6.0	25.4	68.6

As it can be seen from Table 2, when quenching of singlet and triplet occurs, the relative contribution of the singlet is negligible compared to that of the triplet, in agreement with the general fact that the shorter the lifetime of the excited species, the more difficult to be quenched. Therefore, since quenching of the triplet is more efficient than quenching of the singlet, we could state that the higher the intersystem crossing quantum yield, the better. In addition, the values obtained for the quenching constants of the triplet are in good agreement with the photodegradation extent (Fig. 3) except from the case of CLOF in which oxidation is even faster than predicted by the photophysical experiments.

Moreover, regarding the efficiency of the photocatalyst *versus* pollutant concentration, one can imagine how efficient the excited photocatalyst can be in the source of disposed wastewater, when the concentration of the pollutants is still high (for instance in the order of 10^{-3} M). This situation could be compared to another one in which the photocatalyst is applied later on in the wastewater stream when the pollutants are much more diluted (for instance 10^{-5} M). From the data shown in Table 2, as the pollutant concentration decreases, the relative contribution of the excited species decreases in favor of the intrinsic decay of the excited state. This means that the higher the concentration of the pollutants, the more efficient the photocatalyst is. In other words, the energy employed in activating the photocatalyst is better invested when the concentration of the pollutants is still high.

4. Conclusions

The results obtained using $TPTP^+$ as proxy for the photocatalytic oxidation of pollutants, allow stating that the ideal photocatalyst should be the one that offers the following features: i) it absorbs in the visible region; ii) its redox potential from the excited state is appropriate; iii) it has a high intersystem crossing quantum yield; and iv) its triplet lifetime is long enough. In addition, one can envisage two different scenarios to treat an industrial effluent: i) as soon as the wastewater is generated, when the concentration of the pollutants is the highest, or ii) conversely, when the effluent reaches an open area, thus, the concentration of the pollutant has decreased. In the former, the efficiency of a photocatalytic treatment will be the best; while in the latter, although the efficiency of the triplets acting as photocatalyst is low, natural sunlight could become an inexpensive illumination source (Fig. 6).

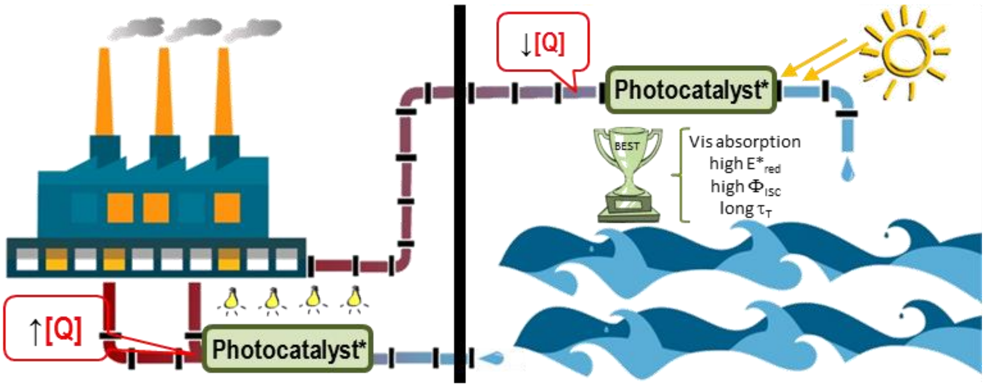


Fig. 6. Two different scenarios to treat wastewater effluents.

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