



# Photocatalytic Treatment of Cork Wastewater Pollutants. Degradation of Gallic Acid and Trichloroanisole using Triphenyl(thia)pyrylium salts



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## ABSTRACT

The photocatalytic degradation of two typical pollutants present at the wastewaters of cork industry, namely gallic acid (GA) and 2,4,6-trichloroanisole (TCA) has been investigated using triphenylpyrylium (TPP<sup>+</sup>) and triphenylthiapyrylium (TPTP<sup>+</sup>) salts as organic photocatalysts. Fast removal of GA and slow but efficient degradation of the reluctant TCA were observed. The role of the transient species involved in the photodegradation has been investigated by means of photophysical experiments. Participation of singlet excited states was safely disregarded since lifetimes of both photocatalysts remained invariable upon addition of GA or TCA. Formation of photoactive ground state complexes was observed, and the complexation constants were estimated as  $K_{\text{TPP-GA}} = 468.4 \text{ M}^{-1}$ ,  $K_{\text{TPP-TCA}} = 528.0 \text{ M}^{-1}$  and  $K_{\text{TPTP-TCA}} = 657.1 \text{ M}^{-1}$ . Moreover participation of the triplet excited states in the electron transfer oxidation of GA was very efficient, while no reaction occurred from the triplet excited states in the case of TCA. In addition, thermodynamic calculations support the participation of the triplet excited state in the case of GA, while the lack of triplet quenching in the case of TCA is associated with a thermodynamically disfavored process. Overall, photophysical experiments indicate that for GA, oxidative electron transfer occurs mainly from the triplet excited state with marginal contribution of the ground state complexes, while for TCA formation of ground state complexes constitutes the only mechanistic pathway.

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## 1. Introduction

Water is an essential resource to life on Earth; thus, protecting the quality of water resources is doubtlessly one of the greatest challenges of sustainable development [1]. Moreover, to address the higher demand of good quality water availability by the increasing population, decontamination of wastewaters derived from the industrial activities is currently a subject of active research [2].

The elevate production of wine in Spain involves a parallel cork stoppers industry to guarantee the proper conservation of the product until consumption. However, the industrial production of cork stoppers includes a post-harvesting treatment of raw material with water at high temperatures to improve plastic properties. This results in a dark complex liquor containing not only suspended solids but also a high level of organic matter [3], in which phenolic and polyphenolic compounds are among the most representative pollutants [4,5]. This effluent exhibits low biodegradability,

thus, reducing the effectiveness of conventional biological treatments [6–8]. Nevertheless, advanced oxidation processes (AOPs) are promising alternatives that have demonstrated high efficiency for removal of reluctant organic contaminants [9].

The use of organic photocatalysis as appropriate AOPs to oxidize pesticides [10,11], or emerging pollutants, [12–15] such as drugs in wastewaters effluents, has been widely reported. Organic photocatalysts exhibit absorption bands in the UV–visible region that can be excited to generate transient species that are able to interact with the pollutants [2]. Moreover, detection of these transient excited states or reactive intermediates by time-resolved techniques (emission, transient absorption spectroscopy, etc.) provides a powerful tool to investigate the involved reaction mechanisms. In this context, triphenylpyrylium (TPP<sup>+</sup>) and triphenylthiapyrylium (TPTP<sup>+</sup>) salts have been employed [10,15–18] due to their capability to produce photocatalytic degradation of pollutants *via* oxidative electron transfer [19].

With this background, the aim of this work is to investigate the photocatalytic degradation of two typical pollutants present at the wastewaters of cork industry, namely gallic acid (GA) and 2,4,6-trichloroanisole (TCA) (see Fig. 1), using TPP<sup>+</sup> and TPTP<sup>+</sup> as organic photocatalyst. Different mechanisms will be postulated to explain

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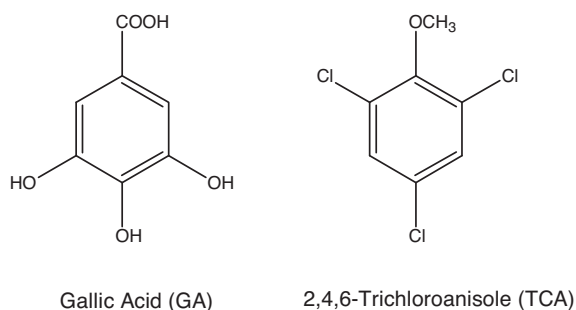


Fig. 1. Chemical structures of the selected cork wastewater pollutants.

the photodegradation of each pollutant on the basis of the transient species involved.

## 2. Experimental

### 2.1. Reagents

Gallic acid (GA), 2,4,6-trichloroanisole (TCA), 2,4,6-triphenylpyrylium (TPP<sup>+</sup>) tetrafluoroborate salt, 2-nitrobenzoic acid, pentadecane and acetonitrile were obtained from Aldrich.

2,4,6-Triphenylthiapyrylium (TPTP<sup>+</sup>) perchlorate was obtained from TPP<sup>+</sup> as described previously [20]. Briefly, a solution of TPP<sup>+</sup> (0.50 g) in acetone (23.6 mL) was treated with aqueous sodium sulphide (10% w/w, 1.97 mL) until the mixture turned red-coloured. Then, perchloric acid (20% w/w, 5.9 mL) and water (23.6 mL) were added to precipitate the TPTP<sup>+</sup> salt as a yellow powder. Then, the solid was filtered, washed with water and purified by re-precipitation from acetone-ether.

### 2.2. Photochemical reactions

Photochemical reactions were performed in Pyrex glass vessels with magnetic stirring using a Luzchem photoreactor (model LZC-4 V). Unless otherwise stated, vessels were loaded with 100 mL of acetonitrile solutions of the pollutants GA or TCA (5 mg/L) and photocatalysts TPP<sup>+</sup> or TPTP<sup>+</sup> (10 mg/L). The pollutant:photocatalyst molar ratio (1:1) was chosen to optimize the absorption of photons and reduce irradiation times. Internal standards, 2-nitrobenzoic acid or pentadecane (5 mg/L), were added to monitor photodegradation of GA or TCA, respectively. Irradiations were performed under N<sub>2</sub> or air as indicated.

Aliquots were taken at different irradiation times, and the removal of GA or TCA was monitored by HPLC or GC, respectively. The HPLC was a Varian 240 model with quaternary pump 9012Q, photodiode detector DAD 9065 and wavelength detection from 200 to 360 nm. A Mediterranean Sea 18 column (25 mm × 0.46 mm, 5 μm particle size) was employed. The mobile phase was an isocratic mixture of water pH 3 (50%) and acetonitrile (50%) at the flow rate of 0.7 mL/min; the detection wavelength was fixed at 275 nm. UPLC-MS-MS was performed on an ACQUITY UPLC system (Waters Corp.) with a conditioned autosampler at 4 °C. The separation was carried out on an ACQUITY UPLC BEH C18 column (50 mm × 2.1 mm i.d., 1.7 μm). The Waters ACQUITY<sup>TM</sup> XevoQToF Spectrometer (Waters Corp.) was connected to the UPLC system via an electrospray ionization (ESI) interface. The ESI source was operated in negative ionization mode with the capillary voltage at 3.0 kV. The GC equipment was a Bruker instrument 430-GC equipped with a ZB50 (30 m × 0.25 mm × 0.5 μm) column with stationary phase of 5% of alternated phenylmethyl silicone. The GC-MS analyses were carried out in an Agilent 6890N equipped with a HP-5MS (30 m × 0.25 mm × 0.5 mm) column and a 5973 network mass selective detector.

### 2.3. Photophysical instrumentation

Quartz cells of 1 cm optical path length were employed for all photophysical measurements, which were run at room temperature under air (steady-state and time-resolved fluorescence) or nitrogen (laser flash photolysis).

Absorption spectra (UV/Vis) were performed on a Shimadzu UV-2101PC spectrometer. Steady-state fluorescence spectra were recorded on a FS900 fluorometer, and time-resolved fluorescence experiments were measured in a FL900 setup, both from Edinburgh Instruments. Lifetime measurements were based on single-photon-counting using a hydrogen flash-lamp (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 them from the lamp pulse profile.

Laser flash photolysis (LFP) studies 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 15 mJ pulse<sup>-1</sup>. 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 77,200 Oriel monochromator, an Oriel photomultiplier tube (PMT) housing and a 70,705 PMT power supply. The oscilloscope was a TDS-640A Tektronix. The output signal from the oscilloscope was transferred to a personal computer.

### 2.4. Photophysical experiments

For the steady-state and time-resolved fluorescence experiments, increasing concentrations of pollutants (up to  $1.6 \times 10^{-3}$  M or  $1.1 \times 10^{-3}$  M for GA or TCA, respectively) were added to solutions of TPP<sup>+</sup> or TPTP<sup>+</sup> (with absorbance 0.1 at the irradiation wavelength of 410 nm and 365 nm for TPP<sup>+</sup> and TPTP<sup>+</sup>, respectively).

Job's plot experiments were performed to investigate the stoichiometry of the [Photocatalyst<sup>δ+</sup> - Q<sup>δ+</sup>] complexes. The absorbance changes were measured at 406 nm and plotted against the pollutant molecular fraction, keeping constant the total concentration of pollutant and photocatalyst ( $1 \times 10^{-5}$  M).

For the laser flash photolysis experiments, increasing amounts of pollutant (up to  $7 \times 10^{-5}$  M for GA and TCA) were added to solutions of  $7 \times 10^{-5}$  M of TPP<sup>+</sup> or TPTP<sup>+</sup>, under N<sub>2</sub> atmosphere.

## 3. Results and discussion

### 3.1. Photochemical degradation

The efficiency of the homogeneous photocatalysts TP(T)<sup>P+</sup>, acting usually via electron transfer mechanism [19], in the degradation of GA and TCA was evaluated in organic media under N<sub>2</sub> and air, using lamps centred at 420 nm to ensure selective excitation of TP(T)<sup>P+</sup>. For consistency, the same solvent was used for the photodegradation studies and for the mechanistic experiments (see Sections 3.2–3.5). Hence, in order to avoid possible interferences from aggregation phenomena and hydrolysis of the photocatalyst, acetonitrile was selected as the solvent of choice. From the data shown in Fig. 2A and B complete removal of GA was observed in less than one hour, while TCA was more reluctant to degradation; in fact 90% of TCA removal was only found after 50 hours using TPTP<sup>+</sup> under air. Moreover, in the case of TCA, where long irradiation times were needed, the reaction rate decreased considerably after 10 h. This effect, due to the partial solvolysis of the central heterocyclic ring of the photocatalysts, has been observed previously and could eventually be circumvented upon adsorption onto inorganic supports [17]. Photodegradation of pollutants was more efficient under air using either TPP<sup>+</sup> or TPTP<sup>+</sup>; however, while TPP<sup>+</sup>

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