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Stability and performance of silica gel-supported triphenylpyrylium cation as heterogeneous photocatalyst

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Abstract

Pyrylium salts are known to be good photocatalysts in aqueous solutions, able to achieve the photodegradation of several phenolic pollutants. Nevertheless, they exhibit a limited stability in these media. The rate of the hydrolytic reaction depends on the pH of the solution, the intensity of irradiation and the pyrylium concentration. Silica gel plates have been employed as inorganic support of the pyrylium cation in order to improve its stability and performance as a heterogeneous catalyst. The resulting material has been tested using ferulic acid as a model compound. Important degradation yields have been achieved (up to 80% after 6 h of solar irradiation). The catalyst is stable under these conditions and can be easily recovered for further use.

Keywords: Pyrylium salts; Photocatalyst; Phenolic pollutants; Heterogeneous catalysis; Ferulic acid; Solar irradiation

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1. Introduction

The use of photocatalysts based on pyrylium salts for treatment of reluctant pollutants [1–8] has proved to be a potential alternative to other oxidative methods used in detoxification of wastewaters [9–13]. In this type of application, oxygen is used as the oxidising agent and solar light as the energy source.

The reaction mechanism involves electron transfer from the pollutant to the excited state of the photocatalyst as a key step (see Scheme 1) [14]. In particular, 2,4,6-triphenylpyrylium cation has two important absorption bands in the UV-Vis region of the solar spectrum (maxima at 350 and 400 nm); upon acceptance of an electron from the pollutant, it gives rise to the pyranyl radical and the corresponding radical cation of the donor. Trapping of this intermediate by molecular oxygen leads to oxidation/fragmentation products until mineralisation is finally achieved.

A major drawback of this methodology is the fact that pyrylium cations show a limited stability in aqueous media; only at acidic pH they are stable enough as to be used as catalysts. Moreover, a series of factors such as the pyrylium concentration and the presence or absence of light might have some influence on the stability of these cations. Hence, in this paper we have studied the effect of pH, concentration of the catalyst and light intensity on the stability of 2,4,6-triphenylpyrylium cation.

A possible improvement of the process could be the use of pyrylium adsorbed on inorganic supports such as silica gel, zeolites, clays, etc. [15,16]. This

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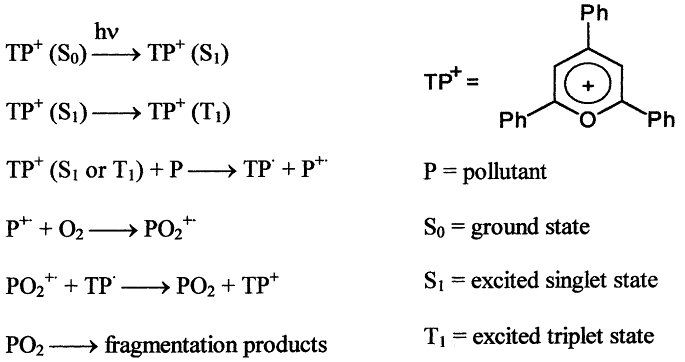


Scheme 1. Reaction mechanism for the oxidation of pollutants photocatalysed by pyrylium salts.

could allow an easy removal (and recovery) of the photocatalyst, which constitutes a major problem in decontamination processes. As a preliminary study, we have used commercial silica gel plates as support and studied their efficiency in the photodegradation of ferulic acid (4-hydroxy-3-methoxycinnamic acid) a model pollutant found in olive oil mill wastewaters [17,18].

2. Experimental

2.1. Reagents

2,4,6-Triphenylpyrylium hydrogensulphate (>98%, Art. No. 29626-0) and ferulic acid (97%, predominantly *trans*, Art. No. 10301-2) were supplied by Aldrich (Steinheim, Germany). Hydrochloric acid, sulphuric acid, nitric acid and acetic acid were purchased from Panreac (Barcelona, Spain). All of them were analytical (p.a.) grade. Water employed for the solutions was Milli Q grade.

The heterogeneous photocatalyst was prepared by introducing a standard silica gel plate for thin layer chromatography (Kieselgel 60, Merck, Art. No. 1.05748) into an aqueous solution of pyrylium salt (4–40 mg/l) acidified to $\mathrm{pH} = 1$ with HCl. After equilibration during 1 day in the dark, the plate was air dried with a hair-drier and stored for 24 h in the dark before use. To check longer-term stability, one plate was stored during 1 month under ambient laboratory conditions. After this time, no degradation of the adsorbed pyrylium was observed by UV-Vis reflection spectroscopy.

2.2. Reactions

Degradation of the pyrylium cation in aqueous media was studied both in the dark and under irradiation by means of a solar simulator (Oriel Instruments model 68811) equipped with a polychromatic xenon lamp (300 W). Aqueous solutions (250 ml) of the pyrylium salt (5–30 mg/l) at different pH were magnetically stirred inside a glass vessel. Samples were periodically taken from the solution and the remaining concentration of pyrylium was measured spectrophotometrically at 400 nm. The light intensity was measured by means of a digital light meter (A.W. Sperry Instruments, model SLM-110).

Solutions of ferulic acid (40 ml, 0.001 M) were submitted to solar irradiation in an open vessel in the presence of a silica gel plate containing pyrylium cation. Thus, they were just exposed to atmospheric air without stirring; no extra air or oxygen was bubbled through the solutions. The experiments were run in sunny days of June and July in Valencia. The reactions started at 10:00 h and finished at 16:00 h.

The degradation of ferulic acid was followed by means of HPLC (Perkin Elmer Autosystem XL equipped with a diode-array detector and a Split injector). A C18 column was used, and the flow rate was 1 ml/min. A gradient of a 0.01 M aqueous solution of sulphuric acid and methanol was used as eluent. Detection was based on the absorption at 280 nm.

The reflection spectra of pyrylium cation supported on the silica gel plates was obtained by means of a Minolta CM 3600d spectrophotometer, able to measure the reflected light in the visible range.

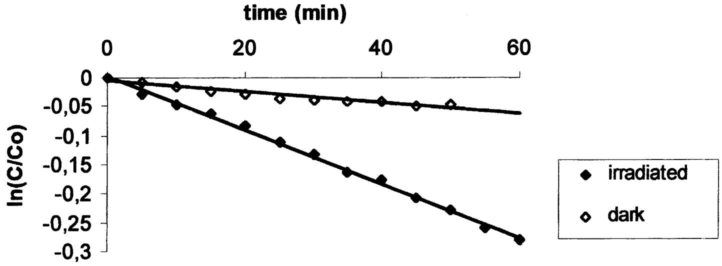


Fig. 1. First order kinetics plot obtained for the degradation of pyrylium cation (10 mg/l) at a pH = 3.5.

3. Results and discussion

3.1. Stability of the pyrylium cation in aqueous solution

The kinetics of degradation of 2,4,6-triphenylpyrylium cation in aqueous media was followed both in dark and under irradiation with a solar simulator (adjusted to an output of 300 W, approximately 1150 lx of intensity). As can be seen in Fig. 1 for a typical case, a linear relationship was observed between ln(C/C_0) and time, where C and C_0 are the instantaneous and initial concentrations of pyrylium. From the slopes of the straight lines, the first order rate constants (k) were obtained.

First of all, the effect of pH was studied. For this purpose, the concentration of pyrylium salt was fixed at 10 mg/l and the solution was acidified with hydrochloric acid to obtain different pH values. The kinetic constants (k) were obtained for every pH with and without irradiation. The values are shown in Fig. 2. At pH lower than 3, k was very low and the pyrylium cation was stable; however, when the pH values were higher than 3, a sharp increase of k was observed. Thus, OH^- anions mediate solvolysis of the pyrylium ring, as shown in the reaction mechanism (Scheme 2) where hydroxyl anions are consumed [19].

Figs. 1 and 2 show that the reaction rates were always higher in the irradiated samples. In order to check the effect of irradiation, five solutions of pyrylium salt of the same concentration (10 mg/l, pH = 3.3) were irradiated with different light intensities (by changing the potency of the solar simulator form 200 to 500 W). The k values were calculated for every experiment. As shown in Fig. 3, there was also a clear relationship between the degradation rates and the intensity. Thus, hydrolytic degradation of 2,4,6-triphenylpyrylium cation appears to be enhanced in the excited states.

The effect of the initial concentration of pyrylium was also checked; the results are shown in Fig. 4a. The hydrolytic reaction was faster when more diluted concentrations were used. The absorption spectra of the different solutions are shown in Fig. 4b.

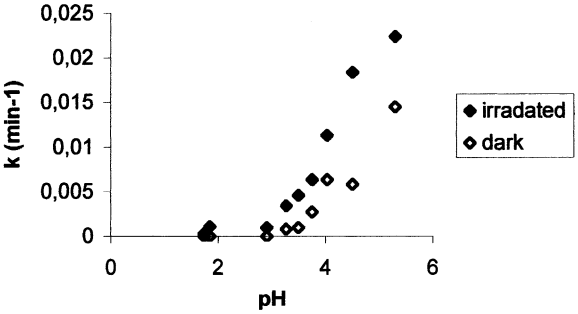
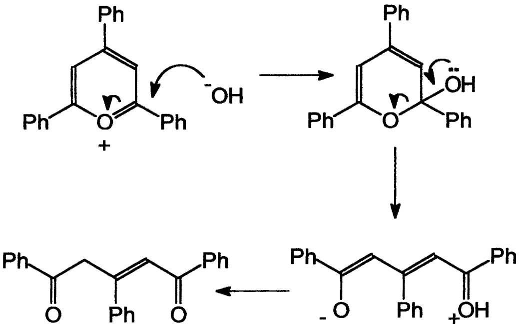


Fig. 2. Plot of the k values obtained for 2,4,6-triphenylpyrylium cation degradation at different pH.



Scheme 2. Hydrolysis of triphenylpyrylium cation.

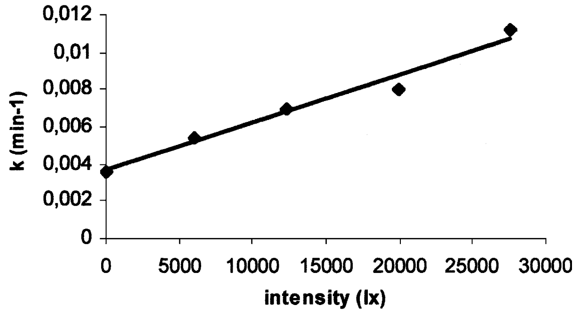


Fig. 3. Plot of the k values obtained for 2,4,6-triphenylpyrylium cation degradation using different intensities of irradiation.

Finally, in order to test a possible effect of the counter-anion the solutions were acidified using hydrochloric acid, sulphuric acid, nitric acid and acetic acid. The obtained data, both in the dark and upon irradiation (Fig. 5), show that no significant effect is associated with the use of different acids.

3.2. Pyrylium cation supported on silica gel

In view of the limited stability of the pyrylium cation in aqueous solutions, the possibility of preparing heterogeneous catalysts with improved properties appeared interesting. Among the different inorganic supports, silica gel has been chosen for a preliminary study in the present work.

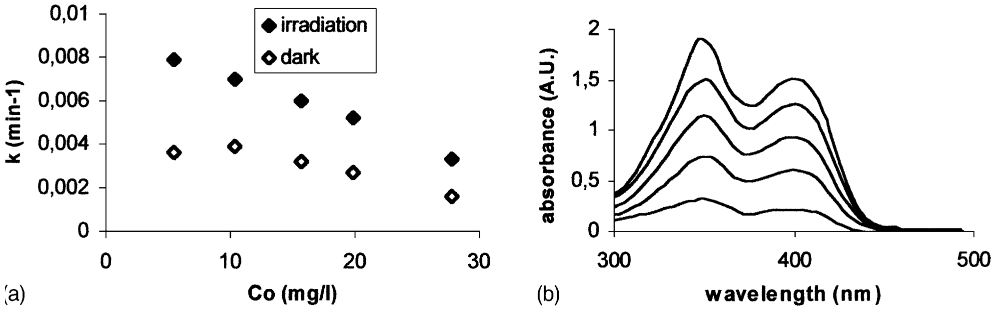


Fig. 4. (a) Plot of the k values obtained for 2,4,6-triphenylpyrylium cation degradation with different initial concentrations of the pyrylium cation in the dark and under irradiation; (b) absorption spectra of the employed solutions (5, 10, 15, 20, and 25 mg/l).

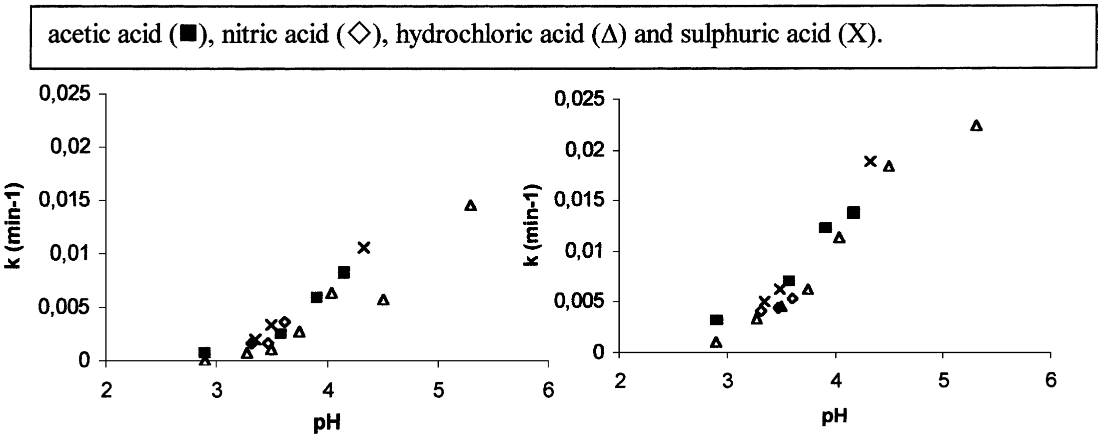


Fig. 5. Plot of the k values obtained for 2,4,6-triphenylpyrylium cation degradation in the dark (a) and irradiated (b) in the presence of different acids: acetic acid (■), nitric acid (◇), hydrochloric acid (△) and sulphuric acid (×).

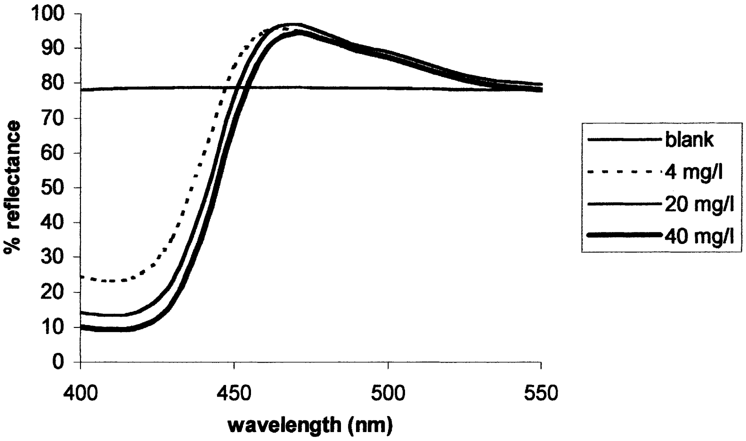


Fig. 6. Reflection spectra of three silica gel plates supporting the pyrylium cation. Plates were prepared by submersion in different aqueous solutions of pyrylium salt. The reference spectrum (a plate without pyrylium cation) is the horizontal line at approximately 80% reflection.

The catalyst was prepared by submerging a commercial silica gel plate inside a vessel containing 200 ml of acidified (pH = 1) aqueous solution of pyrylium salt (40, 20 or 4 mg/l) at room temperature. After 1 day in the dark, the plate was taken out of the solution and dried. The obtained silica gel showed a yellow colour characteristic of the pyrylium cation. The reflection spectra of the plates in the visible range can be seen in Fig. 6, where the typical band of the pyrylium cation at 400 nm, along with a weaker fluorescence emission with maximum around 465 nm, are observed.

To determine the amount of adsorbed pyrylium, the absorbance of the solutions was measured before and after introducing the silica gel plates. From the difference between these two data, it can be calculated that 120, 100 and 80 mg/m^2 were adsorbed when the plates were submerged inside the 40, 20 and 4 mg/l solutions, respectively.

Next, the stability of the heterogeneous catalysts under the irradiation conditions was determined. For this purpose, a pyrylium-containing plate was submitted to solar irradiation for 1 day. The reflection spectra before and after the irradiation were completely coincident (Fig. 7). Then, the plate was submerged into acidulated water (pH = 3) and irradiated for another day. Again the spectrum was similar to the initial one. These results clearly point to an improved stability of

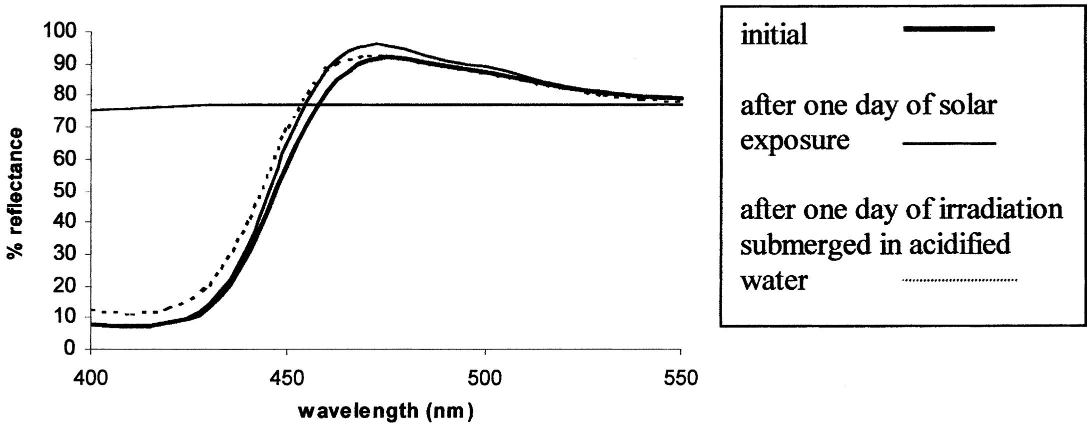


Fig. 7. Stability of the pyrylium cation when supported onto silica gel; reflection spectra.

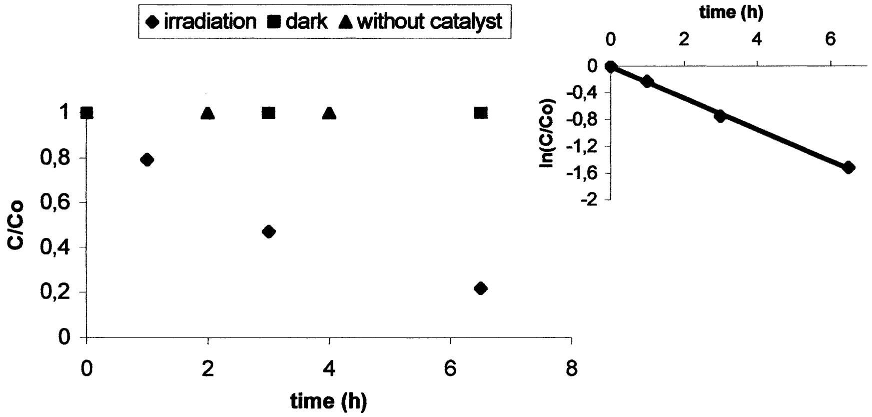


Fig. 8. Degradation of ferulic acid catalysed by pyrylium cation supported on silica gel. First order kinetics fitting is shown in the inset (no reaction occurred in absence of photocatalyst).

the adsorbed pyrylium and to a very low diffusion of the supported catalyst to the aqueous phase.

Finally, the catalytic activity was tested using ferulic acid as substrate. A silica gel plate containing 120 mg/m^2 of pyrylium was placed in the bottom of an open vessel, charged with 40 ml of a 0.001 M solution of ferulic acid and submitted to solar exposure. The relative concentration of ferulic acid vs. time is shown in Fig. 8. The kinetics was clearly first order; there was no decrease in the k value (0.236 h^{-1}) with the time, by contrast with previous observations on the corresponding homogeneous process [2,3]. Moreover, important degradation yields of ferulic acid were achieved (ca. 80% after 6 h). Thus, the use of the heterogeneous pyrylium-based catalyst is clearly advantageous. Similar experiments were performed with silica gel plates containing 100 and 80 mg/m^2 of pyrylium; the obtained rate constants were 0.199 and 0.120 h^{-1}, respectively.

Blank experiments showed that no significant degradation of ferulic acid occurs with the pyrylium-containing silica gel plates in the dark, nor with pyrylium-free silica gel plates upon irradiation. So, degradation of ferulic acid is due to the photocatalytic effect of the adsorbed pyrylium cation.

4. Conclusions

Adsorption of 2,4,6-triphenylpyrylium cation onto silica gel is convenient, because it allows an easy removal (and recovery) of the photocatalyst for further use. It also results in an improved stability of this cation towards hydrolytic ring opening. The pyrylium-containing silica gel performs well as a heterogeneous photocatalyst for the degradation of ferulic acid, a model pollutant for olive oil wastewaters.

Acknowledgements

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