

Sepiolites as supporting material for organic sensitizers employed in heterogeneous solar photocatalysis

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Abstract

Triphenylpyrylium cation (TPP⁺) was supported onto sepiolites to be used as heterogeneous solar photocatalyst. The procedure to prepare this material was a formal ion exchange process: the desired amount of TPP⁺ was added to an aqueous suspension of the sepiolite and stirred in the dark for 24 h. Then the mixture was filtered and the solid dried in an oven at 105 °C. Infrared and UV–vis spectroscopy indicated the presence of TPP⁺ in the new material; solid TOC analysis showed that the process was quantitative, allowing easy control of the sepiolite loading. Diffractograms indicated that no significant modification of the sepiolite structure occurred. Despite the low ion-exchange ability of this clay, important loadings were accomplished, most probably due to the removal of some Mg²⁺ in acidic medium; this was demonstrated by the presence of magnesium cation in the filtered aqueous fraction obtained in the synthetic process. Finally, the efficiency of the pyrylium-loaded sepiolite was tested using ferulic acid as target pollutant; results were very satisfactory, and important percentages of photo-oxidation were achieved.

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1. Introduction

In recent years, photochemical processes for decontamination of wastewaters have provided a possible alternative to classical treatments, in particular for those effluents, which are refractory to biological treatments [1]. Some of the employed photochemical processes can be carried out by means of UV-A or visible light; thus, sunlight could be used instead of lamps [2].

Pyrylium salts have proved to work as solar photocatalysts in wastewater treatment. In particular, 2,4,6-triphenylpyrylium cation (TPP⁺) is able to absorb the fraction of sunlight with wavelength below 450 nm; upon light excitation, it becomes a strong oxidizing agent [3]. Consequently, this oxidation method might be advantageous because solar light is the energy source

and oxygen the only oxidising agent. Different phenolic pollutants have been treated by means of homogeneous TPP⁺ as solar photocatalyst, and results have been promising [4–7]. However, for technical purposes, supporting pyrylium cation onto a solid material seems very convenient, as the catalyst could be recovered and used in successive processes [8].

In preliminary experiments, silica gel plates were tested as solid supports for TPP⁺ and improved efficiency and stability of the photocatalyst were achieved [8]. Also Y-zeolites have been used to host the pyrylium cation [9,10]. The zeolite-based heterogeneous photocatalysts have proved to be able to degrade some contaminants, using either UV lamps [11–13] or real sunlight [14].

In this paper, sepiolites have been employed as inorganic supports to host 2,4,6-triphenylpyrylium cation. They are naturally occurring magnesium silicates [15], which have found industrial application as adsorbents [16–18], supports for microorganisms [19,20] or catalysts [21]. Their molecular formula is Si₁₂Mg₈O₃₀(OH)₄(OH₂)₄·8H₂O; they exhibit a layered structure with linear channels with 3.6 Å × 10.6 Å dimensions.

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In addition to the economical advantage of using very cheap naturally occurring clay, this type of support could also be advantageous over zeolites because of its hydrophilic character, due to the higher amount of silanol groups and to its more open structure allowing easier diffusion of the pollutant.

2. Methods

2.1. Reagents

The 2,4,6-triphenylpyrylium salts, hydrogensulfate and tetrafluoroborate, were supplied by Aldrich and used without further purification. Ferulic acid and titanium dioxide (anatase) were also obtained from Aldrich. Hydrochloric acid was purchased from Panreac.

A high purity sepiolite (pansil) was employed. It was supplied by Tolsa S.A. and used as received. However, being a natural material, some impurities were present: Al_2O_3 (2.4%), CaO (0.5%), Fe_2O_3 (0.9%), Na_2O (0.1%), K_2O (0.5%). The particle size was smaller than 5 μm .

2.2. Preparation of the catalyst

The material containing 3% of carbon was prepared in the following way: hydrochloric acid was added to 40 ml of water until the pH was adjusted to 2. Then, 10 g of sepiolite and 0.54 g of 2,4,6-triphenylpyrylium hydrogensulfate were added to the solution. The suspension was stirred in the dark during 1 day at 40 °C. Then, it was filtered and the solid product washed with 40 ml of water acidified with HCl (pH = 2). Finally, it was dried in an oven at 100 °C overnight. Batches of catalyst containing different loadings were synthesised following the same procedure, but involving the adequate sepiolite/pyrylium salt ratio.

The 2,4,6-triphenylpyrylium tetrafluoroborate salt can also be used as starting material to synthesise the same heterogeneous catalyst. This is convenient for practical reasons as the tetrafluoroborate salt is cheaper and more easily available than the hydrogensulfate.

2.3. Photochemical reactions

The reactor employed in the solar experiments was a glass open vessel with a capacity of 250 ml. For every reaction, it was loaded with 250 ml of a 0.001 M solution of ferulic acid and the corresponding amount of catalyst (between 0.1 and 0.4 g/l). The pH of the liquid phase was 3.5. The mixture was submitted to solar exposure. In order to make the experiments as reproducible as possible, they started at 10 a.m. and were only performed on spring sunny days. Water was periodically added to compensate for the evaporation losses. No extra air was bubbled into the solution.

In order to rule out the possible interference of direct photolysis, ferulic acid (250 ml, 0.001 M) was submitted to solar irradiation, in the absence of pyrylium salt. Dark experiments were also run with both, sepiolite and pyrylium-doped sepiolite. Also the mixture of ferulic acid and sepiolite was irradiated.

2.4. Analysis

Elemental analysis has been used to determine the quantity of pyrylium adsorbed onto the sepiolite; analyses were performed using a combustion Perkin-Elmer analyser. Diffuse reflectance in the ultraviolet–visible region was performed in a Cary 5 Varian equipped with a Praying Mantis cell from Harrick. The infrared spectra in the region of framework vibrations were recorded in a Nicolet 710 FTIR spectrometer using the KBr pellet technique. The differential scanning calorimetry (DSC) analyses were performed in a Mettler Toledo 821 cell.

Ion chromatography was used to analyse the filtered phase obtained in the synthesis of the catalyst. A cationic column (Lichrosil IC CA 2) was used, and a 0.003 M solution of phosphoric acid was employed as eluent, with a flow rate of 1 ml/min.

In order to follow the photocatalytic reaction, samples were periodically taken from the reactor. They were filtered, and the concentration of ferulic acid was followed by means of HPLC (Perkin-Elmer Autosystem XL equipped with a diode-array detector and a Split injector). The column employed was a C18 one, and the flow rate was 1 ml/min. A gradient of an aqueous solution of sulfuric acid (0.01 M) and methanol was used as eluent.

3. Results and discussion

3.1. Synthesis and characterisation of the catalyst

The method previously employed for zeolites [10] was used in this case, with sepiolite as support. In a preliminary experiment, a batch was prepared employing 2.5 g of sepiolite and 0.27 g of pyrylium hydrogensulfate (ca. 6% of carbon, w/w). Elemental analysis indicated that the actual amount of carbon in the obtained solid was 6.8%, thus, nearly all the organic matter involved in the process was incorporated to the sepiolite.

The obtained material was characterised to confirm the presence of TPP^+ . Fig. 1 shows the infrared spectrum of the solid. The typical bands of TPP^+ between 1550 and 1650 cm^{-1} were found, together with a very broad one, with maximum at 1670 cm^{-1} , which can be attributed to sepiolite. Also the diffuse reflectance spectrum in the UV–vis range of the solid was nearly coincident with that of triphenylpyrylium in solution, with maxima at 350–360 nm and 400–420 nm.

The pyrylium/sepiolite ratio was varied in order to prepare heterogeneous photocatalysts containing different TPP^+ loading. Results shown in Table 1 indicate that the actual percentage of carbon was in all cases close to the expected one. This indicates that the employed approach allowed controlling the loading of the heterogeneous photocatalyst in the tested range.

Table 1 also shows that the amount of sulfur detected in the solid material was in all cases negligible. These results could be explained by the existence of an ion exchange mechanism, in which the positive charge of the TPP^+ is equilibrated by the negative charges of the sepiolite (sep). As a consequence, an equivalent amount of inorganic cations (M^+) should be removed from the sepiolite and released to the aqueous phase, where they should be found together with the hydrogensulfate

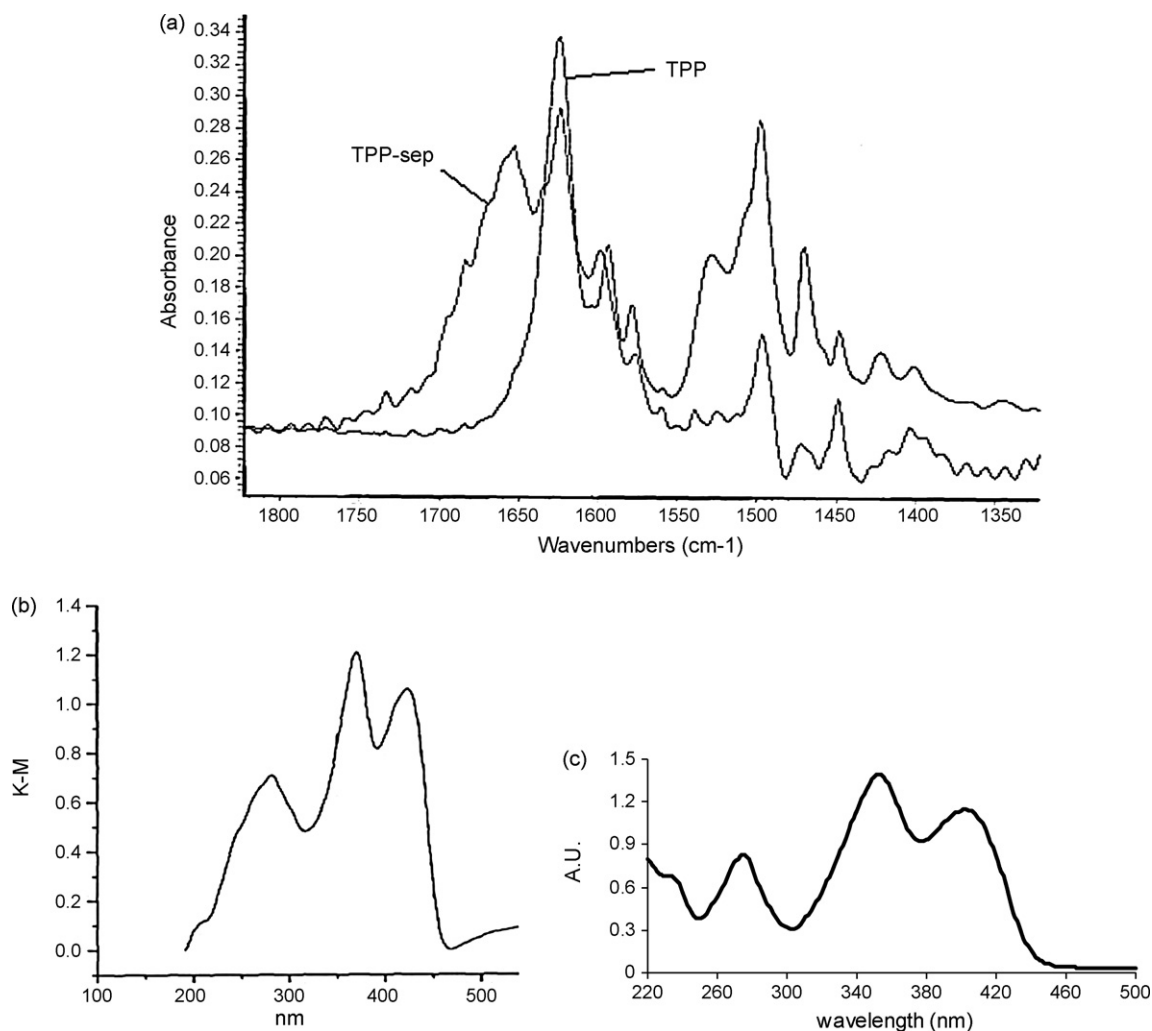
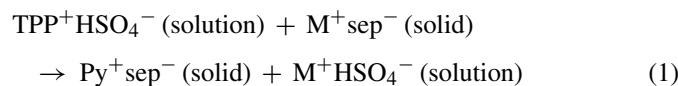


Fig. 1. (a). Infrared spectra of pure triphenylpyrylium hydrogensulfate and triphenylpyrylium supported onto sepiolites. (b) Diffuse reflectance spectrum of triphenylpyrylium cation supported onto sepiolites. (c) Absorption spectrum of 2,4,6-triphenylpyrylium hydrogensulfate in aqueous solution.

anion (Eq. (1)):



However, sepiolites are known to have only a moderate ion exchange capacity, in the range of 10–15 mEq. per 100 mg of clay. Ion chromatography analysis of the aqueous phase obtained from selected batches (3%, 9% and 15% of carbon) indicated the presence of Mg^{2+} , together with some Na^+ and Ca^{2+} ; quan-

titative data are shown in Table 2. The equivalents of inorganic cations found in the aqueous phase were roughly coincident with those of pyrylium salts employed in the process, in agreement with the ion exchange process. These results suggest partial attack to the sepiolite structure, at least in the case of higher loadings, most likely to the relatively accessible Mg^{2+} located in the mouth of the channels. This behaviour has already been observed by other authors and is described in literature [15]. Finally, the presence of sodium and calcium cations is attributable to the impurities of the natural sepiolite; they are more easily leached than the magnesium ions. As a matter of fact, these cations were found in higher proportion in the aqueous phase from less loaded sepiolites, while magnesium was the predominating exchanged ion, in the batches leading to more loaded materials.

It is unlikely that the pyrylium cation was located inside the zeolitic channels of the sepiolite, as water is usually the only species found inside these cavities. Thus, it seems more reasonable that the ion exchange process occurs in the mouths of the channels. There, the magnesium ions do not complete their octahedral coordination, and thus they are more easily removed. This is in agreement with the fact that, even in the batch con-

Table 1
Elemental analysis of pyrylium-doped sepiolite prepared with different pyrylium/sepiolite ratios

Sample	Expected carbon (%)	Actual carbon (%)	Sulfur (%)
A	0	0.5	0.0
B	3	3.8	0.0
C	6	6.8	0.0
D	9	10.0	0.1
E	15	15.6	0.1
F	20	21.2	0.1

Table 2
Quantitative analysis of the filtered water obtained in the preparation of different batches of photocatalyst

Batch (% of C)	Ca ²⁺ (mmol)	Mg ²⁺ (mmol)	Na ⁺ (mmol)	Total (mEq.)	Pyrylium (mEq.)
3	0.072	0.026	0.058	0.254	0.272
9	0.190	0.173	0.075	0.801	0.813
15	0.254	0.320	0.167	1.315	1.360

Equivalents of cations in the solutions are compared with the theoretical amount that should be exchanged by the pyrylium cation.

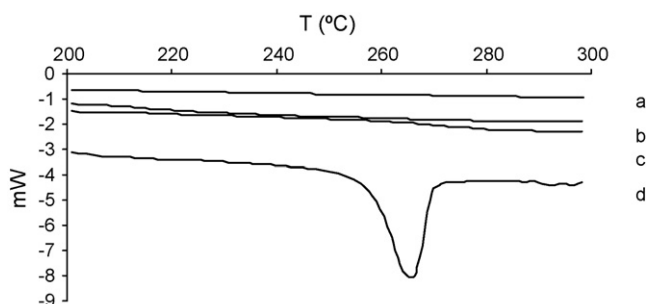


Fig. 2. DSC analysis of sepiolite loaded with pyrylium cation: (a) 3% of carbon; (b) 15% of carbon; (c) unloaded sepiolite; and (d) 2,4,6-triphenylpyrylium hydrogensulfate salt.

taining 15% organic loading, only 0.5% of the total magnesium is removed. Accordingly, X-ray diffractograms do not suggest any significant change in the sepiolite structure after the ion-exchange process.

Additional support for the ion exchange mechanism was obtained from thermal analysis (Fig. 2). Thus, a sharp peak corresponding to an endothermic process was observed at 265 °C in the DSC analysis of 2,4,6-triphenylpyrylium hydrogensulfate; this can be associated with the melting point of this salt, and expectedly was absent in the sepiolite before treatment. Remarkably, when two different batches of pyrylium doped-sepiolite (3% and 15% of carbon loading) were also submitted to DSC analysis, the endothermic process was not found, indicating that the Py⁺ is no longer in the form of hydrogen sulphate salt.

Desorption of the pyrylium cation from the sepiolite upon repeated washing with water was found to be negligible: filtration through cellulose (0.45 μm) of the suspensions gave a consistently colourless liquid, where no pyrylium was detected by spectrophotometric analysis or by TOC measurements.

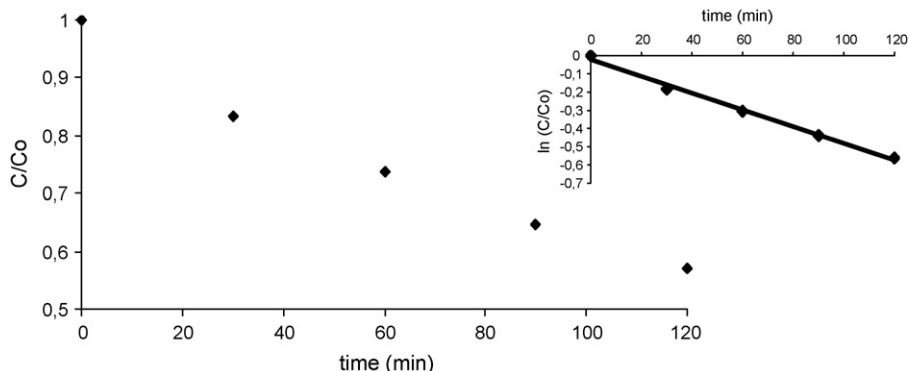


Fig. 3. Photodegradation of ferulic acid catalysed by pyrylium-containing sepiolite. Plot of the relative concentration of ferulic acid (C/C_0) vs. time. The logarithmic plot is shown as an insert.

Table 3
Elemental analysis of pyrylium-doped sepiolite prepared using different pyrylium salts and procedures

Counter-anion	pH (acid)	Expected carbon (%)	Actual carbon (%)
HSO ₄ ⁻	2 (HCl)	6	7.3
BF ₄ ⁻	2 (HCl)	6	7.3
BF ₄ ⁻	2 (H ₂ SO ₄)	6	7.8
BF ₄ ⁻	0 (H ₂ SO ₄)	6	7.6

In preliminary experiments, it was considered convenient to employ 2,4,6-triphenylpyrylium hydrogensulfate as starting material because of two reasons: (a) its solubility in water and (b) the presence of sulfur allowed its tracking during the process. Nevertheless, for technical reasons, it seems more advisable to check the tetrafluoroborate salt, a cheaper and more easily available compound, although less soluble in aqueous media. Hence, an attempt was made to prepare a material containing a 6% of carbon with pyrylium tetrafluoroborate as source. The reaction was carried out in three different aqueous acidic media: (a) hydrochloric acid at pH 2; (b) sulfuric acid at pH = 2; and (c) sulfuric acid at pH < 1. After drying the filtered solid, all three materials were submitted to elemental analysis, and the carbon content (Table 3) matched the expectations; thus, the catalyst could also be prepared using this alternative procedure.

3.2. Performance of the photocatalyst

The photocatalyst was tested using ferulic acid (4-hydroxy-3-methoxycinnamic acid) as a target pollutant. For instance, a 6% pyrylium-loaded sepiolite (0.2 g/l) was added to a solution of ferulic acid (250 ml, 0.001 M) and submitted to sunlight. Under these conditions, an important percentage of photodegradation (43%) was achieved after only 2 h of irradiation (Fig. 3): the lin-

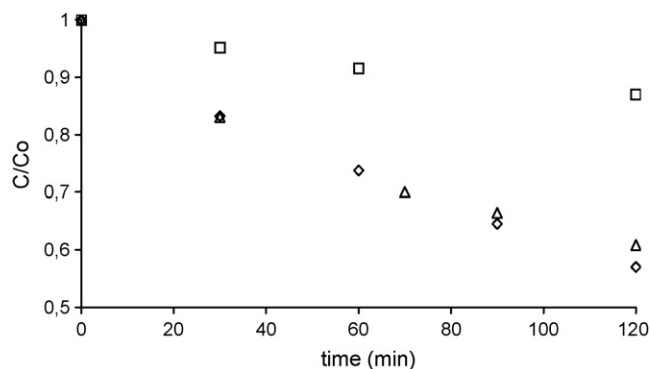


Fig. 4. Photodegradation of ferulic acid catalysed by pyrylium-containing sepiolite obtained from the tetrafluoroborate (Δ) and the hydrogensulfate salt (\diamond). Comparison with titanium dioxide (anatase) (\square). The amount of photocatalyst was 0.2 g/l in all cases.

ear plot of the logarithm of the relative concentration of substrate versus time indicated that the disappearance of the pollutant followed a pseudo-first order kinetics.

In order to confirm that sepiolite-supported TPP⁺ was the actual photocatalyst, different controls were run. Thus, a solution of ferulic acid was stirred in the dark in the presence of the pyrylium loaded sepiolite; as no significant variation in the concentration of the substrate was detected, important adsorption of ferulic acid onto the sepiolite as the reason for its disappearance from the solution was ruled out. Non-loaded sepiolite was found to be able to achieve some degradation of ferulic acid upon solar irradiation; however, results were clearly worse than those obtained with the TPP⁺ loaded material.

The performance of the photocatalyst synthesised using as starting reagent the tetrafluoroborate or hydrogensulfate salts of triphenylpyrylium were compared. As expected, the obtained results were coincident in both cases. Finally, titanium dioxide was also used as solar photocatalyst (Fig. 4). The pseudo-first order rate constant obtained with 0.2 g/l of TiO₂ (0.0010 min⁻¹) was around four times lower than the one achieved with the same amount of pyrylium-loaded sepiolite (0.0046 min⁻¹). This confirms that the use of pyrylium-supporting materials could be an alternative to the widely used titanium dioxide for solar photodegradation of some organic pollutants.

In order to study the effect of the amount of photocatalyst on the reaction rate, ferulic acid (250 ml, 0.001 M) was irradiated in parallel experiments with 0.1, 0.2, 0.3 and 0.4 g/l of catalyst. From the rate constants it became clear that the optimum performance was achieved using 0.2 g/l of catalyst (Fig. 5). The observed plateau-like behaviour is well known when working with heterogeneous photocatalysts and has been explained elsewhere [13]. Briefly, it is due to shadowing of parts of the solution when the concentration of the solid material is too high (as photons become the limiting reagent) and also to light scattering.

Finally, the effect of the loading was also tested. For this purpose, solar photodegradation of ferulic acid (250 ml of a 0.001 M solution) was studied in parallel reactions employing differently loaded sepiolite. In all cases, the amount of solid was 0.2 g/l. The pseudo-first order rate constant was calculated; results shown in Fig. 6 indicate that the k value increased with loading up to reach

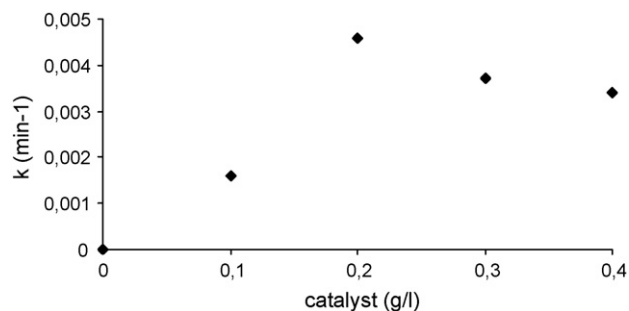


Fig. 5. Plot of the rate constant (k) for the solar photodegradation of ferulic acid against the amounts of photocatalyst.

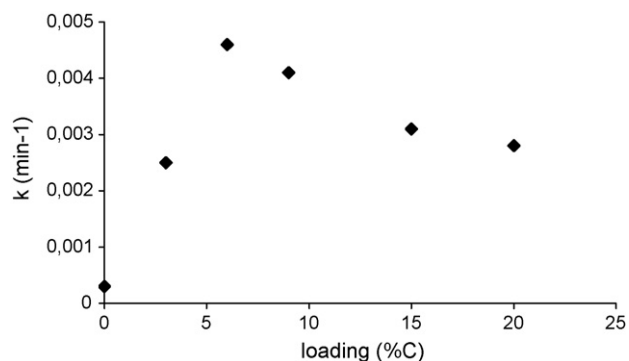


Fig. 6. Plot of the rate constant (k) for the solar photodegradation of ferulic acid catalysed by differently-loaded batches of TPP⁺ supported onto sepiolite.

an optimum for the material containing a 6% of carbon; then, additional loading did not result in increased reaction rates, but rather the k values progressively decreased. This behaviour can be attributed to two different factors: (a) the above mentioned TPP⁺ concentration effect, with photons becoming the limiting reagent and (b) the presence of important amounts of organic matter which increases the hydrophobicity of the solid material, as well as the particles size, as a consequence of aggregation.

4. Conclusion

Sepiolite appears to be a convenient support for pyrylium salts, to be employed as heterogeneous solar photocatalyst. A simple method, based on formal ion exchange, has been used to achieve an efficient support of TPP⁺ onto the sepiolite structure, allowing an easy control of the loading level. Promising results have been obtained testing the performance of the new material with ferulic acid as target pollutant. The best results are obtained with 0.2 g/l of the 6%-loaded heterogeneous photocatalyst.

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