# Concentrating versus non-concentrating reactors for solar photocatalytic degradation of *p*-nitrotoluene-*o*-sulfonic acid

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**Abstract** The photocatalytic oxidation of the non-biodegradable *p*-nitrotoluene-*o*-sulfonic acid (*p*-NTS) in homogeneous (photo-Fenton reactions) and heterogeneous (with $TiO_2$) solutions has been studied at a pilot-scale under solar irradiation at the Plataforma Solar de Almeria (PSA). In this study two different reactors were tested: a medium concentrating radiation system (Heliomans, HM) and a non-concentrating radiation system (CPC). Their advantages and disadvantages for *p*-NTS degradation have been compared and discussed. The degradation rates obtained in the CPC collector are around three times more efficient than in the HM collectors. However, in both systems, 100% of the initial concentration of *p*-NTS was removed. Kinetic experiments were performed in both systems using $TiO_2$ suspensions. During the photodegradation, the disappearance of *p*-NTS was followed by HPLC, the mineralization of the solution by the TOC technique, the evolution of $NO_3^-$, $NO_2^-$, and $SO_4^-$ concentration by ionic chromatography, the toxicity by the standard Microtox® test, and the biodegradability by $BOD_5$ and COD measurements. The obtained results demonstrated the utility of the heterogeneous catalysis (using $TiO_2$ as catalyst) as a pretreatment method that can be followed by a biological process.

**Keywords** Photocatalysis; photochemical treatment; photo-Fenton reaction; *p*-nitrotoluene-*o*-sulfonic acid; solar collectors; solar detoxification; titanium dioxide

## Introduction

The *p*-NTS is considered a non-biodegradable compound having nitro and sulfate groups as electron-withdrawing groups. It is used by chemical industries in the manufacture of dyes, surfactants, brighteners, and is often found in effluents of these industries. The non-biodegradability of *p*-NTS has been proved by the Zahn–Wellens biodegradability test and in a fixed bed reactor under theoretically favorable conditions as the presence of co-substrates and adapted bacteria. Advanced oxidation processes (AOPs) have been proposed (Ollis and Al-Ekabi, 1993) in recent years as an attractive alternative for the treatment of contaminated ground, surface, and wastewater containing non-biodegradable organic pollutants. The most commonly used AOPs utilized $H_2O_2$, $O_3$ or $O_2$ as oxidant. Among AOPs, the combined systems $UV/TiO_2/H_2O_2$ and $UV/Fe_3^+/H_2O_2$ (photo-Fenton) are considered as the most promising for the remediation of contaminated waters. A wide range of applications has been reported for different compounds using these systems (Bahnemann *et al*., 1994; Ribordy *et al*., 1997; Huston and Pignatello, 1999). The *p*-NTS photo-degradation mediated by $TiO_2/H_2O_2$ and $UV/Fe_3^+$ in batch systems using artificial sunlight has been reported in published works of our laboratory (Minsker *et al*., 1994; Bandara *et al*., 1997; Pulgarin *et al*., 1999). To our knowledge, besides these mentioned works, only two other papers about *p*-NTS have been reported (Hao and Phull, 1993; Phull and Hao, 1993). In these publications, the wet air oxidation of *p*-NTS and its reaction pathways are discussed.

In the present paper we report the photocatalytic destruction of *p*-NTS at the largest solar system in Europe, the Plataforma Solar de Almeria (PSA), in Spain. The biodegradability

of the initial solution of *p*-NTS is demonstrated. The efficacy of the solar photocatalytic treatment of *p*-NTS in homogeneous (photo-Fenton system) and heterogeneous solution (using $TiO_2$ as catalyst), and the influence of the $H_2O_2$ as an electron acceptor in the heterogeneous system is studied. Two different reactors were used in this work: a medium concentrating radiation system (Helioman-type, HM) and a low concentrating radiation system (Compound Parabolic Collectors, CPC). We compare here the efficiencies of these two reactors by studying the degradation of *p*-NTS.

## Materials and methods

### Reagents

All chemical products were used as received. *p*-NTS was provided by Ciba (Monthey, Switzerland). The chemical structure of this compound is given in Figure l. $FeCl_3.6H_2O$ and $H_2O_2$ (30% w/w) analysis grade (p.a.) were Fluka. $TiO_2$ was a Degussa P-25 (mainly anatase, surface area 50 $m^2/g$).

### Photoreactors and procedures

Solar-driven experiments were carried out at the Plataforma Solar de Almeria (PSA), in southern Spain, an ideal place for installing solar plants, as more than 300 days per year can be expected to be sunny, with an average of 3,000 sunny hours per year. Two different reactors at the PSA were used: a medium concentrating radiation system (Helioman-type, HM) and a low concentrating radiation system (Compound Parabolic Collectors, CPC). In both cases, a slurry of *p*-NTS solution and catalyst was prepared in the reservoir tanks and fed into the photoreactor. Figure 2 shows photographs of the two photoreactors. Two sensors for UVlight measurements were used, one for global UV, installed on a 37° fixed-angle platform (KIPP&ZONEN, model CUV3), and the other for direct UV (International Light-ESD 400), mounted on a sun-tracking platform. Global and direct UV irradiances were measured during all the experiments, permitting the evaluation of incident radiation dependant on the hour of the day, cloudiness, atmospheric turbulences, and other environmental variations.
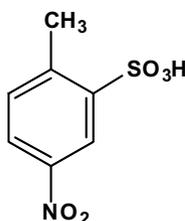


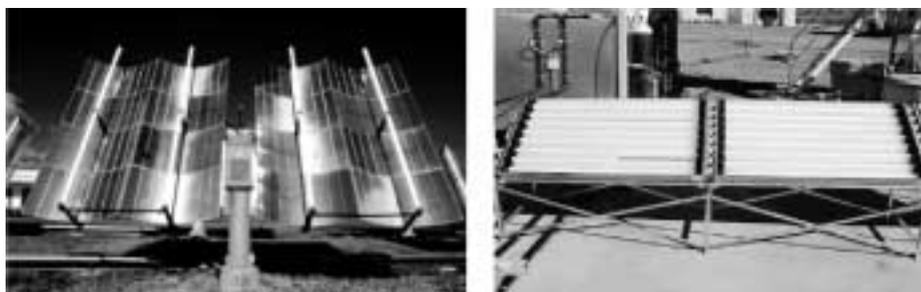**Figure 1**  Chemical structure of *p*-NTS



**Figure 2**  View of the two photoreactors used at the PSA: (a) Helioman-type collectors (HM); and (b) Compound Parabolic Collectors (CPC)

*Helioman-type collectors*. The HM collector (Figure 2a) consists of a turret on which a platform supporting four parabolic trough collectors with an absorber tube in the focus has been placed. The platform is moved by two motors controlled by a two-axis (azimuth and elevation) tracking system. The tracking system consists of a photoelectric cell keeping the aperture plane perpendicular to the solar rays, which are reflected onto the focus (absorber), through which circulates the water to be treated.

*Compound parabolic collectors*. The CPC collector (Figure 2b) has three modules (collector surface, 3.08 m$^2$, photoreactor volume 22 L, and total reactor volume 39 L). One module consists of eight tubes. The three modules of the reactor are mounted on a fixed platform inclined 37° (local latitude). The three modules are connected in series and the water flows direct from one to the other and finally to a tank. A centrifugal pump then returns the water to the collectors. At the beginning of the experiments, with the collectors covered, all the chemicals are added to the tank and mixed until constant concentration is achieved throughout the system. Then the cover is removed and samples are collected at predetermined times ($t$).

### Chemical and biological analysis

Total organic carbon (TOC) was measured directly in slurries by using a Heraeus-Fass Electric TOC-2001 (UV-peroxy-disulphate method). Calibration was achieved by using standards of potassium phthalate. High performance liquid chromatography (HPLC) was carried out in a Hewlett-Packard model 1050 equipped with a UV-detector and a RP-18 column (Lichrocart, 5 mm inside diameter, 150 mm long). The eluent was a methanol/water mixture (50/50 v/v). This technique is able to measure the *p*-NTS concentration during the degradation process. The consumption of $H_2O_2$ during the reaction was followed by the Merckoquant® test for peroxides and by titrating the samples with potassium permanganate in acid medium. Analysis of ions was performed with a Dionex DX-120 ionic chromatograph equipped with an Ion Pac column; aqueous solutions of $NaHCO_3$ (1 mM) and $Na_2CO_3$ (3.5 mM) were used as eluent.

Biological Oxygen Demand ($BOD_5$) analysis was made by means of a Hg free WTW 2000 Oxytop unit thermostatted at 20°C. Chemical oxygen demand (COD) was carried out via a Hach-2000 spectrophotometer using dichromate solution as the oxidant in strong acid media. The Zahn–Wellens biodegradability test was used with bacterial concentration of 1 g/L. The sludge was aerated for a 24 hours and subsequently centrifuged. A fixed bed reactor (FBR) was also used to test the biodegradability of the initial solution. It consisted in a column of 1 L of water capacity containing biolite colonized by activated sludge from a municipal wastewater treatment plant. Other details for the FBR operation have been reported elsewhere (Seignez *et al*., 1993). During the photochemical pre-treatment, the toxicity was assessed using the Microtox® technique. The bioluminescence of the bacteria *Vibrio fischeri* in the presence of *p*-NTS was followed as a function of photochemical pre-treatment time. The toxicity of the sample was determined by measuring the EC50, the effective concentration at which 50% of the light is lost.

### Results and discussion

#### Biodegradability of initial *p*-NTS solution

From the Zahn–Wellens biodegradability test, it has been shown that the *p*-NTS can not be biologically degraded in the test conditions, since the TOC remains at its initial level as shown in Figure 3. This test is carried out under conditions that are similar to those of a wastewater treatment plant using activated sludge. The TOC concentration does not change during the experiment, even when continuing this test during a long period of time
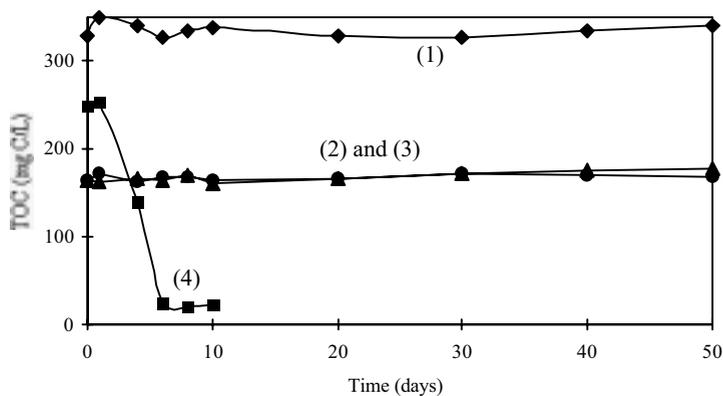
**Figure 3** Evolution of TOC as a function of time for the Zahn–Wellens biodegradability test of *p*-NTS solution: (1) non-adapted biomass; (2) non-adapted biomass and lower concentration of *p*-NTS; (3) adapted biomass; (4) control with diethyleneglycol

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(50 days). This indicates that bacteria cannot adapt to degrade this compound. Two types of inoculum were tested. Samples 1 and 2 contained activated sludge from an urban waste-water treatment. Sample 3 contained activated sludge, which had previously been in contact with *p*-NTS during 35 days. Two concentrations were tested in order to discover if a toxicity effect is present. A parallel control experiment using diethyleneglycol (0.5 g/L) was carried out to test if the sludge was otherwise active. The diethyleneglycol was in fact degraded as much as 98% in six days.

A supplementary test to measure the biodegradation of *p*-NTS was carried out in batch mode with a fixed bed reactor. Even under theoretically favorable conditions, the presence of co-substrates and adapted bacteria, as well as a strict control of pH, temperature, and aeration, this test confirms that *p*-NTS is nonbiodegradable in the tested conditions. Three methods were used to follow this test: (a) respirometric measurements with an $O_2$ probe in both the inlet and outlet of the FBR, (b) determination of *p*-NTS concentration by HPLC, and (c) measurements of TOC as a function of time.

### Kinetics of the photocatalytic disappearance of p-NTS in different advanced oxidation processes

Using the CPC photoreactor, different experiments were carried out in order to compare the efficacy of the solar photocatalytic treatment of *p*-NTS in homogeneous (photo-Fenton system) and heterogeneous (using $TiO_2$ as catalyst) solution. Figure 4 shows the evolution of *p*-NTS when a solution of this compound (0.5 mM) is reacted using direct sunlight in different degradation systems: $UV/TiO_2$, $UV/TiO_2/H_2O_2$, and $UV/Fe^{3+}/H_2O_2$. It has not been plotted as a function of the residence time corresponding to the time spent in the CPC reactor, but as a function of the accumulated amount of energy per unit of volume (kJ/L), in order to correct any possible variations of the radiant flux. The accumulated energy ($Q_{UV,n}$) on the reactor, for each sample taken during the experiment, was calculated as follows:

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \, \overline{UV}_{G,n} \, \frac{A_{CPC}}{V_{TOT}} \tag{1}$$

where $\Delta t_n = t_n - t_{n-1}$, $t_n$ is the experimental time for each sample, $\overline{UV}_{G,n}$ is the average $UV_G$ during $\Delta t_n$, $A_{CPC} = 3.08$ m$^2$, and $V_{TOT} = 39$ L. For the HM reactor, $A_{HM} = 29$ m$^2$, and $V_{TOT} = 260$ L.

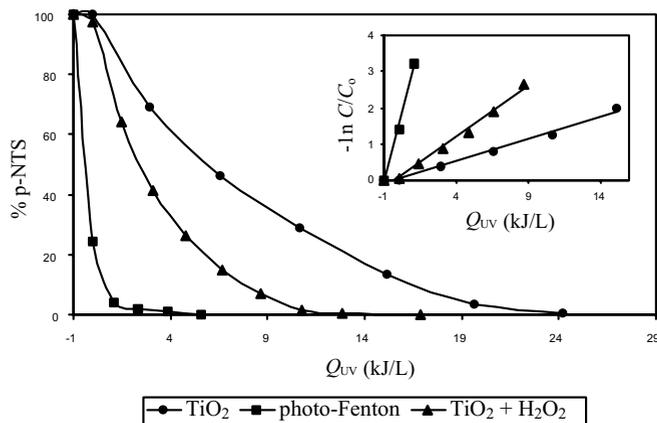The kinetic curves in Figure 4 are of apparent first-order as confirmed by the linear

**Figure 4** Evolution of p-NTS in different degradation systems as a function of accumulated energy. p-NTS (0.5 mM); $H_2O_2$ (25.0 mM); $Fe^{3+}$ (1.0 mM); $TiO_2$ (0.2 g/L). The inset represents the linear transformation $-\ln (C/C_o) = f(Q_{UV})$

transforms shown in the inset of the figure. The apparent first-order rate constants are presented in Table 1.

As can be observed, the p-NTS degradation rate in the photo-Fenton system is higher than in the heterogeneous reactions. To explain these results, the different absorption capabilities of both $Fe^{3+}$ and $TiO_2$ catalyst have to be taken into account. The $TiO_2$ absorbs in the UV light with a wavelength between 300–400 nm (7% of the solar irradiation) and the Fenton system presents a light sensitivity to a wavelength up to 600 nm (35% of the solar irradiation). Furthermore, in homogenous solution the depth of light penetration is high and the contact between pollutant and oxidizing agent is closed.

In both homogenous and heterogeneous process, the $^{\bullet}OH$ radicals are mainly responsible for the organic pollutant oxidation. In the key reaction of the photo-Fenton process $Fe^{2+}$ ions are oxidized by $H_2O_2$ while one equivalent $^{\bullet}OH$ is produced. The obtained $Fe^{3+}$ act as the light absorbing species that produces another radical while the initial $Fe^{2+}$ is regenerated:

$$Fe^{3+} + H_2O + hv \rightarrow {}^{\bullet}OH + H^+ + Fe^{2+} \tag{2}$$

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + {}^-OH + Fe^{3+} \tag{3}$$

In the case of heterogeneous photocatalysis, it is known that the addition of $H_2O_2$ enhances the photodegradation rate. As shown in Table 1, the $k_{app}$ for the abatement of p-NTS in the $UV/TiO_2/H_2O_2$ system is two times higher than the observed $k_{app}$ of the $UV/TiO_2$ system. For this last system, the generation of $^{\bullet}OH$ is done by oxidation process that involves electron donors ($H_2O$ and $^-OH$) and a less efficient electron acceptor than $H_2O_2$, such as $O_2$. The $H_2O_2$ is considered as an efficient electron scavenger, which react with electrons of the conduction band of the $TiO_2$ to generate additional $^{\bullet}OH$ radical by the following equation:

**Table 1** Apparent rate constants ($k_{app}$) for the abatement of p-NTS in different degradation systems

| Degradation system | $UV/TiO_2$ | $UV/TiO_2/H_2O_2$ | $UV/Fe^{3+}/H_2O_2$ |
|---|---|---|---|
| $K_{app}$ (L/kJ) | 0.13 | 0.28 | 1.57 |

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + {}^-OH + {}^\bullet OH \tag{4}$$

Even if the photo-Fenton reaction is the most efficient process for the $p$-NTS degradation, both homogeneous and heterogeneous photocatalysis are considered as suitable methods to reach the complete mineralization of this solution. We are interested in the study of the applicability of the heterogeneous catalysis for the $p$-NTS degradation due to the possibility of separating the $TiO_2$ from the treated water, which is very important when an industrial application is contemplated (clean treated water could be drained away and TiO2 reused again). Recently, a fast $TiO_2$ sedimentation procedure has been patented by the PSA (Blanco *et al.*, 1999).

From the experimental point of view, the slowness of the heterogeneous degradation process facilitates the access to information about the degradation fate of $p$-NTS and the comparison of the efficiencies of both HM and CPC solar reactors.

### Comparison between Heliomans and CPC reactors

This part of the paper is focused on the efficiency comparison of the two types of solar collectors (HM and CPC) using the degradation rate of $p$-NTS in heterogeneous catalysis as the experimental parameter. Figure 5 shows the linear transformation $-\ln(C/C_o) = f(Q_{UV})$ of the kinetic curves of $p$-NTS disappearance in the two studied reactors. In both cases, the kinetics of $p$-NTS degradation are of apparent first-order, with a rate constant ($k_{app}$) equal to 0.128 and 0.045 for the CPC and HM reactors, respectively.

Previous research at the PSA indicates that the degradation rates obtained in the CPC collectors are around three times more efficient than the parabolic collectors (Blanco *et al.*, 1996) We have found the same ratio in our experiments. As shown in Figure 5 the degradation rate of $p$-NTS is also three times higher in the CPC reactor than in the HM reactor (the ratio $k_{app}$ CPC/$k_{app}$ HM is 2.84). One of the factors to take into account to explain the differences in these degradation rates is that the non-concentrating collectors are able to capture the diffuse UV sunlight, as well as the direct light (the diffuse component can make up 50% of the total available UV light, even on a clear day). In contrast, a concentrating design such as the HM reactor, benefit only from the direct UV radiation (the direct component of global UV-sunlight could be negligible on a cloudy day) (Bockelmann *et al.*, 1995; Malato *et al.*, 1996; Malato *et al.*, 1997). In the experiment in Figure 5 the average global radiation (used by the CPC) and direct radiation (used by the HM) were of 23.9 and 15.4 W/m$^2$ respectively. The characteristics of both reactors and their performances are summarized in Table 2.

As shown in Table 2, the primary degradation efficiency expressed as percentage of $p$-NTS removed was 100% in both reactors. At the time when the total disappearance of $p$-NTS is observed, the reached mineralisation was of 55% and 73% in the HM and CPC reactors, respectively. This is an indication that the kinetics of the formation and the degradation of intermediates, resulting from the phototreatment, depend on the reactor used in the degradation experiment.

### Photocatalytic degradation of p-NTS in aqueous TiO$_2$ suspension

The degradation of $p$-NTS without addition of $H_2O_2$ is presented in Figure 6. The data corresponds to a one-day test run using a CPC reactor. 3.9 g of $p$-NTS were added to the total volume of water of 39 L (100 mg/L $p$-NTS corresponding to a TOC of 38.7 mgC/L and a sulfate content of 44.3 mg/L). Figure 6a shows the disappearance of $p$-NTS as well as the evolution of $NO_3^-$, $NO_2^-$, and $SO_4^=$ during the photodegradation as a function of the accumulated energy. The evolution of TOC and toxicity is shown in Figure 6b.
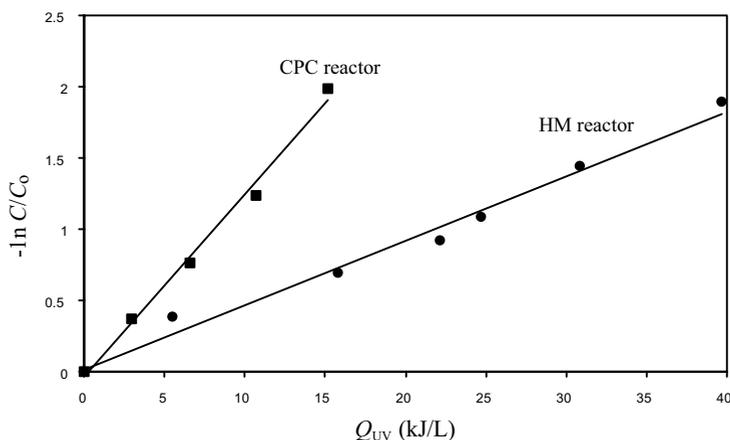
**Figure 5** Linear transformation $-\ln(C/C_o) = f(Q_{UV})$ of the kinetic curves of $p$-NTS disappearance in CPC and HM reactors. $p$-NTS (0.5 mM) and $TiO_2$ (0.2 g/L)

**Table 2** Characteristics of both HM and CPC reactors and their performances for the $p$-NTS degradation

|  | HM reactor | CPC reactor |
| --- | --- | --- |
| Photoreactor volume (L) | 41 | 22 |
| Total reactor volume (L) | 260 | 39 |
| Collector surface (m) | 29 | 3.08 |
| Residence time, $t_R$, (h)[a] | 1.5 | 1.7 |
| Duration of the experiment, $t$ (h) | 9 | 3 |
| Average global UV radiation (w/m²) | – | 23.9 |
| Average direct UV radiation (w/m²) | 15.4 | – |
| Accumulated energy per volume of reactor (kJ/L)[b] | 66.0 | 24.2 |
| $p$-NTS removed (primary degradation, %) | 100 | 100 |
| TOC removed (mineralization, %)[c] | 55 | 73 |

[a] The $t_R$ is derived from the duration of the experiment ($t$) by: $t_R = t \times V_i/V_T$, where $V_T$ is the total volume of the reactor and $V_i$ is the illuminated volume of the photoreactor.
[b] Amount of energy accumulated required for the total degradation of $p$-NTS.
[c] These values correspond to the moment when the total disappearance of $p$-NTS is reached.

Figure 6a shows that in the presence of solar light and $TiO_2$, $p$-NTS is completely degraded in about 3 hours of residence time (corresponding to 24 kJ per litre under normal operating conditions). Analysis of ions in solution shows that $SO_4$ is generated in the stoichiometric value (about 44 mg $SO_4^-$/L, corresponding to 100% in the figure) after about 3 hours of residence time, indicating the absence of sulfo-compounds in solution. As shown in the figure, the formation of $SO_4^=$ goes together with the abatement of $p$-NTS.

The total mineralization of the solution is confirmed by the TOC results. Toxicity tests were performed to ascertain the average toxicity of the $p$-NTS and of the solution resulting from its phototreatment. The decrease on the toxicity (expressed as 1/EC50) shown in Figure 6b exhibits the same shape as the kinetics of the solution mineralization (TOC results), indicating that no more toxic species are formed during the photodegradation process.

Concerning the biodegradability of the treated solution, the ratio $BOD_5$/COD (representative of the biodegradability) was found to be 0.0 without phototreatment. It increases up to 0.37 after the heterogeneous treatment (as a reference, this parameter for municipal wastewater is around 0.4). In our previous researches on photodegradation of $p$-NTS by photo-Fenton reaction (Pulgarin *et al.*, 1999) at laboratory scale, a similar decrease on the
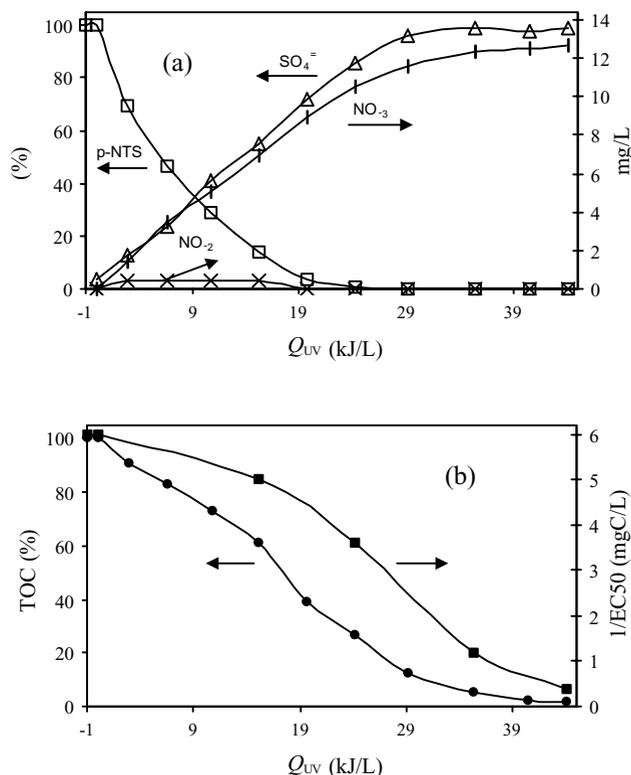
**Figure 6** Degradation of *p*-NTS (0.5 mM) in a CPC reactor with 0.2 g/L of TiO$_2$: (a) evolution of *p*-NTS, NO$_3^-$, NO$_2^-$, and SO$_4^=$; (b) evolution of TOC and toxicity (expressed as 1/EC50) during the phototreatment as a function of accumulated energy

toxicity and an increase on the biodegradability was observed and a photochemical-biological coupled flow reactor could be used for the complete mineralization of *p*-NTS. Therefore, the experimental results presented here, clearly demonstrate that the heterogeneous catalysis (using TiO$_2$ as catalyst) is a promising pretreatment method that can be followed by a biological treatment.

## Conclusions

The non-biodegradability of *p*-NTS was proved by the Zahn–Wellens biodegradability test and in a fixed bed reactor under theoretically favorable conditions such as the presence of co-substrates and adapted bacteria. The efficacy of the solar photocatalytic treatment of *p*-NTS under direct sunlight in different degradation systems: UV/TiO$_2$, UV/TiO$_2$/H$_2$O$_2$, and UV/Fe$^{3+}$/H$_2$O$_2$ was studied and compared. Even if the photo-Fenton reaction is the most efficient process for the *p*-NTS degradation, both homogeneous and heterogeneous photocatalysis are considered as suitable methods to reach the complete mineralization of this solution.

Our experiments concerning the solar photocatalytic degradation of *p*-NTS using different types of reactor performed at the PSA have clearly demonstrated the practical applicability and effectiveness of these systems. However, as the CPC collectors benefit from direct and diffuse UV radiation, the degradation rates obtained using these collectors are around three times higher than those of the HM collectors. This fact, together with low manufacturing and installation costs, and easy maintenance and operation of the CPC

collectors compared with the HM reactors, allows us to infer that the CPCs are the best known way to use the solar technology.

This study demonstrates the utility of the heterogeneous catalysis (using $TiO_2$ as catalyst) as a pretreatment method that can be followed by a biological treatment. Further investigations are needed concerning the biological treatment of the solution resulting from the treatment of *p*-NTS at pilot scale. After that, a coupled photochemical (with $TiO_2$) biological system could be envisaged to complete the mineralization of *p*-NTS solutions.

## Acknowledgements

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