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# Solar photocatalytic degradation of dichloroacetic acid with silica-supported titania at pilot-plant scale

Javier Marugán [a,1], Jose Aguado [a], Wolfgang Gernjak [b], Sixto Malato [b,*]

[a] Department of Chemical and Environmental Technology, ESCET, Universidad Rey Juan Carlos, C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain
[b] Plataforma Solar de Almería, CIEMAT, Carretera Senés km 4, 04200 Tabernas, Almería, Spain

## Abstract

A multivariate analysis using experimental design techniques was performed to determine the effect of iron, hydrogen peroxide and titanium dioxide in the solar photodegradation of dichloroacetic acid in a combined $TiO_2$/photo-Fenton process. The study was carried out at pilot-plant scale, using $TiO_2$ supported on silica as the heterogeneous photocatalyst to facilitate separation of the solids after the reaction, and iron concentrations of less than 3 mg $L^{-1}$ to avoid removal of iron from the effluent. The results show that iron is the most important factor influencing the reaction rate, which suggests that in strongly acidic solutions, the Fenton mechanism controls the process even at such low iron concentrations. Under these conditions, the expected synergism between $TiO_2$ and iron degradation pathways seems to be negligible compared to the antagonistic effect between hydrogen peroxide and $TiO_2$, which reduces the activity of the combined system. However, in the absence of hydrogen peroxide, the activity achieved by the combined Fe/$TiO_2$ system is similar to that of the photo-Fenton process, with the advantage that $H_2O_2$ is replaced by a reusable $TiO_2$-based catalytic material. Consequently, the analysis of pilot-plant operation economics took not only the degradation rate, but also the cost of chemicals into account.

*Keywords:* Photocatalysis; Photo-Fenton; Supported titania; Dichloroacetic acid; Experimental design; Optimization; Economic analysis

## 1. Introduction

The use of photochemical technologies has been shown to be a promising alternative for the detoxification of industrial effluents [1–3], especially from the environmental point of view [4]. Solar-driven advanced oxidation technologies such as semiconductor photocatalysis and photo-Fenton processes have demonstrated their suitability for the disposal of toxic and non-biodegradable pollutants resistant to conventional biological treatments [5–9].

One of these resistant chemicals is dichloroacetic acid (DCA), a widely used industrial pollutant also identified as an intermediate in the biological degradation pathway of many chlorinated hydrocarbons, and as one of the potentially carcinogenic disinfection by-products (DBP) formed in chlorination of water with traces of natural organic matter [10]. Since the early work of Ollis et al. [11], DCA has been used as the model pollutant by many research groups for the study of fundamental photocatalytic mechanisms [12], the influence of operating variables on solar photocatalytic processes [13,14], for kinetic modelling and photoreactor design [15], to compare the activity of new $TiO_2$ photocatalysts [16,17], and also to assess the activity of supported $TiO_2$ [18–20]. The use of supported titania has been shown to be a satisfactory way of recovering the catalyst after the reaction [21], one of the main problems hindering commercial application of $TiO_2$ photocatalysis in aqueous systems.

A previous work has studied Fe/$TiO_2$/pH interaction in the solar photodegradation of a model pesticide using $TiO_2$ supported on silica in the presence of excessive $H_2O_2$ [22]. Results showed that simultaneous semiconductor and photo-Fenton photocatalytic mechanisms were present. The reaction rates observed were controlled mainly by the iron chemistry, and pH was clearly the most influential variable, the reaction rate being fastest at acidic pH, as expected for a Fenton mechanism. However, at higher pH, the presence of $TiO_2$/$SiO_2$ photocatalysts produces a synergistic combination of the two degradation mechanisms, reducing the required amount of iron to below discharge limits.

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[*] Corresponding author. Tel.: +34 950 387 940; fax: +34 950 365 015.
*E-mail addresses:* javier.marugan@urjc.es (J. Marugán), sixto.malato@psa.es (S. Malato).
[1] Tel.: +34 91 664 7466; Fax: +34 91 488 7068.

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This work focuses on the study of $TiO_2/H_2O_2$/Fe interaction in the solar photodegradation of DCA when $Fe/H_2O_2$ and silica-supported titania are used simultaneously in a pilot plant. Nogueira et al. [14] have reported on a small-scale multivariate analysis of the combined $TiO_2$/photo-Fenton process using powdered Degussa P25 $TiO_2$ and iron concentrations up to 60 mg $L^{-1}$. The purpose of the this study was to asses the activity and the synergies of the combined $TiO_2/H_2O_2$/Fe system at pilot-plant scale using $SiO_2$-supported $TiO_2$ photocatalysts to improve recovery of the solids after the reaction and iron concentrations of less than 3 mg $L^{-1}$ to avoid iron removal. Experiments at acidic pH to maximize photo-Fenton efficiency and a multivariate analysis were performed to find out the effects of the three selected variables. Concentrations of $TiO_2/SiO_2$, iron and hydrogen peroxide were studied at five different levels (−1.68, −1, 0, +1 and +1.68), using a statistical approach to find the response surface of the photodegradation reaction rate. This method enables the influence of each variable to be determined along with any possible synergistic or antagonistic effects. The mathematical model obtained makes it possible to optimize pilot-plant operating conditions, minimizing the number of experiments required for process scale-up.

## 2. Experimental

### 2.1. Materials

Titanium dioxide was incorporated into a commercial porous silica (INEOS ES70Y, $S_{BET} = 257$ $m^2$ $g^{-1}$) using a sol–gel method. The synthesized photocatalyst consists of large approximately 50–70 μm silica particles with $TiO_2$ nanocrystals with a mean size of 7.2 nm homogeneously distributed over the $SiO_2$ surface. Further information on laboratory-scale synthesis, characterization and photocatalytic activity is available in a previous work [23].

Iron sulphate ($FeSO_4{\cdot}7H_2O$) and reagent-grade hydrogen peroxide (30 wt% aqueous solution) were used as the Fenton catalyst. No pH adjustment was required, as experiments were carried out at the natural acid pH of 5.0 mM dichloroacetic acid (DCA) reacting solution (~2.4). Demineralised water came from the Plataforma Solar de Almería (PSA) distillation plant (conductivity < 10 μS $cm^{-1}$, $Cl^- = 0.2$–0.3 mg $L^{-1}$, $NO_3^- =$ 0.5 mg $L^{-1}$ and organic carbon < 0.5 mg $L^{-1}$).

### 2.2. Solar photodegradation experiments

Photocatalytic reactions were carried out under solar irradiation in compound parabolic collectors (CPC) at the Plataforma Solar de Almería (latitude 37°N, longitude 2.4°W). The twin pilot-plant systems each have a total volume of 35 L and 3.09 $m^2$ of irradiated surface. The 22 L irradiated aqueous suspension inside the solar collectors is recirculated through the system by a pump connected to a holding tank. A schematic of the experimental set-up can be found elsewhere [24]. At the beginning of the experiment, with collectors covered, all the chemicals and the $TiO_2/SiO_2$ material are added to the tank and mixed until constant concentration is achieved throughout the system. Usually 15 min are enough to assure the complete mixture of the reactor volume and then the photodegradation reaction is begun by removing the collector cover.

Samples were taken at preset time intervals and filtered through Millex-GN 0.2 μm syringe filters prior to analysis. Mineralization of DCA was monitored by measuring the total organic carbon (TOC) concentration remaining in the clear solution, using a Shimadzu 5050A TOC analyser calibrated with hydrogen potassium phthalate standard solutions. According to the accepted DCA photocatalytic degradation mechanism [11,16], TOC analysis provides information on the remaining amount of reagent due to the absence of any stable intermediates during the total mineralization process. In addition, chloride formation was measured by ion chromatography (IC) using a Dionex-600 (anions column IonPac AS14) with NaOH as the eluent. The mass balance between DCA degradation measured by TOC and the stoichiometric chloride formation detected by IC was achieved in all the experiments.

$H_2O_2$ concentration was monitored by iodometric titration, and dissolved iron concentration was determined by its colorimetric reaction with 1,10-phenanthroline after reduction of the iron(III) ions with ascorbic acid.

Solar ultraviolet radiation was measured by a global UV radiometer (KIPP & ZONEN, model CUV3) mounted on a south-facing platform tilted 37° (the same angle and orientation as the CPCs), which provides data in terms of incident $W_{UV}$ $m^{-2}$, $UV_G$. As the irradiation conditions change during the experiments, to compare the results, the concentration profiles refer to the accumulated energy, $Q_{UV,n}$ (kJ $L^{-1}$), calculated as follows

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

where $t_n$ is the experimental time for each sample, $\overline{UV}_{G,n}$ the average $UV_G$ during $\Delta t_n$, $A_{CPC}$ the collector surface (3.09 $m^2$) and $V_{TOT}$ is the total plant volume (35 L).

A multivariate analysis of the influence of iron, $TiO_2$ and $H_2O_2$ concentrations on the photodegradation rate has been carried out, following a statistical approach based on a factorial design of experiments. It consisted of (i) eight experiments carried out at the −1/+1 levels of the three variables, (ii) three experiments at the centre point of the experimental domain (level 0 of the three factors) to determine the experimental error and check the linearity of results, and (iii) six experiments at the so-called star points where two variables are at the centre value and the third is set at two additional levels (−1.68/+1.68) above and below the maximum and minimum of the factorial design. These points are located on the axes of the coded variables at the same distance from the centre point as the factorial design experiments, defining a spherical experimental domain in which the same experimental error can be assumed. Table 1 summarizes the values and levels of the variables used to find a quadratic model by the response surface methodology [25]. Notice that the values of the factors were chosen in such a way that pure ($Fe/H_2O_2$) ($Fe/TiO_2$), and ($TiO_2/H_2O_2$) experiments were conducted at three of the star points.