Photocatalytic treatment of water containing imazalil using an immobilized TiO$_2$ photoreactor

Dunia E. Santiago*, M.R. Espino-Estévez, Gabriel V. González, J. Araña, O. González-Díaz, J.M. Doña-Rodríguez*

Grupo de Fotocatálisis y Espectroscopía Aplicada al Medioambiente-FEAM (Unidad Asociada al ICMSE, Centro Mixto C.S.I.C.-USE), CIDIA-Dpto. de Química, Edificio Polivalente I del Parque Científico Tecnológico, Universidad de Las Palmas De Gran Canaria, Campus Universitario de Tafira, 35017 Las Palmas, Spain

ABSTRACT

In this study, the photoactivity of commercial and lab-made TiO$_2$ when immobilized on different supports, namely borosilicate glass, alumina foam and refractory brick, was examined for the removal of the fungicide imazalil from different water matrices. Alumina foam provided the largest exposed photocatalyst surface but degradation kinetics were not significantly improved by the use of this material.

TiO$_2$ coatings were also subjected to thermal treatment at 450 °C to improve adhesion to the support and exhibited higher photocatalytic mineralization, at levels comparable to the conventional suspended system.

However, successive photocatalyst reuse led to its deactivation. Different regeneration methods were studied for the TiO$_2$ films and it was concluded that deionized water washes were the most effective regeneration procedure.

Finally, a typical industrial wastewater containing imazalil was successfully treated using TiO$_2$ supported on borosilicate glass under solar irradiation.

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1. Introduction

Imazalil is a fungicide that is widely applied in fruit and vegetable packing industries to combat a variety of fungal diseases. Its range of application is broader than that of other fungicides and it is active against strains that are resistant to other pesticides [1]. As the disposal of water contaminated with toxic substances like imazalil into sewage systems can have a severe environmental impact, various regulations have been introduced to control fungicide MCLs (maximum contaminant levels) in wastewater. In this respect, Council Directive 98/83/EC on the quality of water intended for human consumption states that total pesticide concentration cannot be higher than 0.05 mg L^{-1}.

Due to its low biodegradability, conventional wastewater treatment plants are unable to eliminate substances like imazalil. Adsorption methods and advanced oxidation processes have been reported as alternatives for its removal from deionized water solutions [2–6], but very few studies have focused on the elimination of this fungicide from real wastewaters [7–9]. In this respect,

heterogeneous TiO$_2$ photocatalysis has been reported as a possible technique for the degradation and mineralization of imazalil in industrial wastewater [9].

Given the expense involved in separation of nano-sized TiO$_2$ particles from treated water and the difficulties faced in terms of photocatalyst reuse, there has been growing interest in immobilization of the photocatalyst on inert solid supports [10]. However, supported TiO$_2$ has been mainly reported for the treatment of emerging pollutants or low pollutant concentrations [11–13]. This is because when the catalyst is immobilized, there is an inherent decrease in the surface area available for reaction and thus reaction rates are lower [14]. Different porous supports have been studied to try to mitigate this problem [15–18], although the support may introduce interfering species into the photocatalytic system [16].

Among the immobilization techniques available, dip-coating is a very simple procedure which offers several advantages over others, including its low cost and high film uniformity [19,20].

The purpose of this work was to study the performance of TiO$_2$ immobilized on different supports in the degradation and mineralization of 50 mg L^{-1} imazalil using deionized water (DW) and a simulated/synthetic wastewater (SW). Photocatalyst stability was evaluated using the material under the same operating conditions

* Corresponding authors. Tel.: +34 928457301.
E-mail address: dsantiago@proyinves.ulpgc.es (D.E. Santiago).

over several consecutive cycles. Finally, lab-scale studies were compared with solar experiments.

2. Experimental

2.1. Reagents/chemicals

The commercial imazalil Fruitgard-IS-7.5 was used for this study. pH was adjusted with diluted H_2SO_4 and NaOH aqueous solutions. Sodium chloride (NaCl), aluminium sulphate ($Al_2(SO_4)_3 \cdot 18H_2O$) and calcium hydroxide ($Ca(OH)_2$) from Panreac were used as PRS reagents for SW preparation. Ethanol ($\geq 99.5\%$) from Panreac was employed as TiO_2 dispersant agent for the immobilization procedure.

2.2. Preparation of the TiO_2 films

The general procedure applied is described elsewhere [11]. In brief, immobilization of the TiO_2 powder was carried out by dip-coating procedure using a KSV-DC Dip-Coater (KSV Instruments). The inert support was submerged in a TiO_2-ethanol suspension for 2 min and then withdrawn from the suspension for 4 min to dry the surface and thereby ensure correct fixation of the catalyst. This procedure or cycle was repeated 80 times. Suspensions of $2\,g\,L^{-1}$ and $4\,g\,L^{-1}$ were used for the commercial and lab-made catalysts, respectively. In addition, 0.2 mL of a 0.1 M HNO_3 aqueous solution was added to the lab-made photocatalyst suspensions to enhance particle disaggregation. The mass of deposited TiO_2 was measured using an analytical balance (A&D HR-200 with $1\,mg \pm 0.1\,mg$ precision).

Three types of support were considered in this study, borosilicate glass, refractory brick and alumina foam. Each support had a total covered surface area of approximately $110\,cm^2$.

All the coatings were thermally treated at $105\,°C$ for 2 h. These were named D105. A series of thermally treated coatings were subjected to further heat treatment at $450\,°C$ for 2 h to increase adherence of the catalysts to the support [11]. These were named D450.

Adherence of the coatings was evaluated by vigorous washing with deionized water. Catalyst detachment was determined by turbidity measurements. For this purpose, a turbidity vs. catalyst concentration calibration curve was used.

2.3. Photocatalytic experiments

2.3.1. Laboratory scale

Adsorption and degradation tests were conducted in a 300 mL photoreactor with recirculation. The reactor consisted of two concentric cylindrical tubes, with the photocatalyst fixed to the outer surface of the inner tube. The TiO_2 fixation procedure followed that described in Section 2.2.

Two sets of Solarium Philips HB175 lamps equipped with four 15 W Philips CLEO fluorescent tubes with emission spectrum from 300 to 400 nm (maximum around 365 nm) (9 mW) were employed as UV light source. Before irradiation was initiated, the imazalil solution was pumped through the reactor for 15 min in the dark to reach the adsorption–desorption quasi-equilibrium. The pump used for recirculation purposes was a Resun SP-500 with a $90\,L\,h^{-1}$ flow rate. Adsorption equilibrium experiments were performed at ambient temperature ($22 \pm 1\,°C$).

Blank experiments were carried out with the photocatalyst in suspension for comparison purposes. For this, degradation tests were performed in the same recirculation reactors, filled with 300 mL of the pollutant aqueous solution and $1\,g\,L^{-1}$ of

photocatalyst. The samples were filtered using $0.45\,\mu m$ syringe filters before analysis.

2.3.2. Solar experiments

For solar experiments, the 300 mL photoreactor was exposed to natural sunlight.

Solar ultraviolet radiation was measured with a UV-A radiometer (Acadus 85-PLS). This radiometer includes an LS-3200 integrator to provide the accumulated energy $E(t)$ received by the total irradiated surface area of the photoreactor (in W h). The relationship between the experiment duration time (t), the total volume of the reactor (V), the average instantaneous irradiance flux (UV), the collector surface area (A) and the accumulated energy $E(t)$ is:

$$E(t) = E(t_0) + \Delta t \bar{U} V \left(\frac{A}{V} \right)$$

A statistical treatment was performed on the data presented in this work. The standard errors were calculated using 95% confidence limits.

2.4. FTIR studies

For the FTIR (Fourier Transform Infrared) determinations, a FTIR Thermo Scientific Nicolet iS10 spectrometer was used at intervals of $4000–1000\,cm^{-1}$. The catalyst films were placed between two CaF_2 windows.

The ammonia/catalyst surface interaction was studied to determine the presence and modification of Lewis or Brönsted acid centres. The experimental procedure followed a similar method to that described in [21]. The system consisted of a vessel containing a 25 wt.% ammonia solution which was continuously air-bubbled at a flow rate of $150\,mL\,min^{-1}$. The resulting air containing ammonia was introduced into a 15 cm long, 4 mm diameter cylindrical glass reactor containing the catalyst for its adsorption and the photocatalyst was then placed between the two CaF_2 windows for the FTIR measurements.

2.5. Analytical determinations

Concentrations of imazalil at different reaction times were HPLC-measured using a Supelco Discovery C18 column ($25\,cm \times 4.6\,mm$ ID, $5\,\mu m$ particles) and an acetonitrile-10 mM KH_2PO_4 solution (45:55) with $100\,mg\,L^{-1}$ of sodium 1-octanesulfonate as mobile phase (adjusted to pH 3 with phosphoric acid), using a UV detector ($\lambda = 225\,nm$). Quantification was performed using the least-squares fit method. The detection and quantification limits for imazalil were $0.05\,mg\,L^{-1}$ and $0.15\,mg\,L^{-1}$, respectively. The adjusted R^2 was 0.998.

Total organic carbon (TOC) was measured using a Shimadzu TOC-L analyser. Turbidity was measured with a Velp Scientifica TB1 portable turbidimeter. BET surface area measurements were carried out by N_2 adsorption at 77 K using a Micromeritics Gemini instrument.

Diffuse reflectance spectra were recorded for all samples on a Varian Cary 5 spectrophotometer and the Kubelka–Munk function, $F(R_\infty)$, was applied to obtain the band-gaps.

X-ray diffraction (XRD) patterns were obtained by using a Siemens D-500 difractometer (Cu $K_{\alpha,\lambda} = 1.5432\,Å$). Crystallite sizes in the different phases were estimated from the line broadening of the corresponding X-ray diffraction peaks by using the Scherrer equation.

Scanning electron microscopic (SEM) analyses were performed on a JSM-5400 Jeol apparatus equipped with an X-ray dispersive energy (EDX) analyzer.