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Photocatalyzed degradation of flumequine by doped TiO_2 and simulated solar light

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Abstract

Titanium dioxide was obtained in its pure form (TiO_2) and in the presence of urea (u-TiO_2) and thiourea (t-TiO_2) using the sol–gel technique. The obtained powders were characterized by BET surface area analysis, Infrared Spectroscopy, Diffuse Reflectance Spectroscopy and the Rietveld refinement of XRD measurements. All the prepared catalysts show high anatase content (>99%). The *a* and *b*-cell parameters of anatase increase in the order TiO_2 < u-TiO_2 < t-TiO_2, while the *c*-parameter presents the opposite trend. Because of the interplay in cell dimensions, the cell grows thicker and shorter when prepared in the presence of urea and thiourea, respectively. The cell volume decreases in the order t-TiO_2 > u-TiO_2 > TiO_2. The photocatalytic activities of the samples were determined on flumequine under solar-simulated irradiation. The most active catalysts were u-TiO_2 and t-TiO_2, reaching values over 90% of flumequine degradation after 15 min irradiation, compared with values of 55% for the pure TiO_2 catalyst. Changing simultaneously the catalyst amount (t-TiO_2) and pH, multivariate analysis using the response surface methodology was used to determine the roughly optimal conditions for flumequine degradation. The optimized conditions found were pH below 7 and a catalyst amount of $1.6\,g\,L^{-1}$.

Keywords: Antibiotic; Flumequine; Photocatalysis; Sol–gel; Doped titanium dioxide

1. Introduction

Antibiotics have been designed to reduce diseases, positively impacting on the quality of life and saving many human lives since their introduction. However, when antibiotics are released into the environment with little control, they can become a tremendous problem due to their side effects on natural biota and the development of new resistant bacteria that could result in severe consequences to public health. Antibiotics cannot be naturally degraded and conventional secondary effluent treatments cannot be considered, limiting the possibilities to eliminate them from the environment.

Advanced Oxidation Processes (AOPs) have been proposed as a valuable method to degrade refractory organic compounds due to the uniqueness of hydroxyl radicals to drive organic matter oxidation rendering high reaction rates and low selectivity. Among the AOPs, the photocatalytic method is currently mentioned as one of the most studied technologies. The process presents recognized advantages, such as the low price and chemical stability of the more used catalyst (TiO_2) and the possibility to combine the process with biological decontamination methods [1]. The possibility of using solar light to produce low molecular weight and biodegradable compounds has been mentioned [2]. Among the drawbacks of photocatalysis for industrial applications commonly mentioned are the design of adequate reactors for efficient utilization of photons, catalyst immobilization to avoid the filtration step, and the low absorption of light in the visible region.

The large band gap of TiO_2 (3.2 eV) is the main hindrance to a better utilization of the small UV fraction of the solar light (2–3%). To extend the catalysts' visible light absorption, Ohno et al. [3–6] recently suggested the modification of titania by doping the catalyst with non-metallic atoms, such as nitrogen and sulphur. They suggested that sulphur could be incorporated as a

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cation replacing Ti ions in the TiO_2 structure. It has also been reported that the photocatalytic activity of TiO_2 in the visible region could be enhanced by nitrogen doped into the TiO_2 lattice [7]. On the other hand, Umebayashi et al. [8] have recently synthesized S-doped TiO_2 with good performance in the visible-light region for methylene blue degradation. They suggest that sulphur anions replace the oxygen atom in the TiO_2 lattice.

The aim of this paper is to determine the photocatalytic activity on the degradation of flumequine while irradiated with simulated solar light of two TiO_2 samples obtained by sol–gel technique in the presence of urea and thiourea. For comparison, pure TiO_2 was also studied. Flumequine, a quinolone structure, is a broad spectrum antibiotic widely used in salmon farms. The obtained data are correlated with the catalysts' structural parameters such as cell size and band gap determinations.

2. Methods

2.1. Catalyst preparation

The catalysts were prepared by the sol–gel technique according to the methodology proposed by Ohno et al. [6]. An ethanolic solution of titanium tetraisopropoxide (0.35 mol L^{-1}) was stirred during 2 h followed by ethanol evaporation at reduced pressure. The obtained gel was calcinated at 500 °C during 3 h. The doped titania samples were obtained by adding urea or thiourea (1:2 molar ratios) to the ethanolic solution. The catalysts were named u-TiO_2 and t-TiO_2, respectively. The samples were sonicated during 20 min and magnetically stirred for 2 h in water (100 mL per 0.5 g catalyst). Before direct use in catalysis, the solids were centrifuged, washed with 1 L of distilled water, and dried.

2.2. Photocatalytic reactions

The photocatalytic activity of the TiO_2 powders was evaluated by measuring the decomposition rate of the antibiotic flumequine in aqueous solution (20 ppm, SIGMA). The reaction was monitored in a Shimadzu 1603 spectrophotometer by measuring the absorption at 248 nm. To prevent possible interferences by formed intermediates, the reaction was also followed by HPLC analysis using a Merck–Hitachi instrument equipped with a LichroCART 250-4 RP-18 column. Acetonitrile/water/methanol (30/55/15) was used as eluent at 3.5 mL min^{-1}. The same results were obtained by both techniques. Irradiation was performed on 60-mL volume solution in a Pyrex reactor with a Suntest XLS^+ (Atlas, USA) using irradiance of 500 W m^{-2}.

2.3. Analytical methods

X-ray diffraction patterns were recorded in a Siemens D5000 diffractometer using a Cu Kα radiation. Generator settings were 40 kV, 30 mA. Divergence scattered and receiving slits were 1 mm, 1 mm and 0.2 mm, respectively. A curved graphite monochromator was used. Data were collected in the 2θ range: 22.0–135.995°, with a scanning step of 0.035° and a counting time of 15 s per point. The step width assured a minimum of about 12 intensity points for the narrower peaks. The data were analyzed using the GSAS system [9]. Starting unit-cell parameters and atomic coordinates for anatase and rutile were taken from the literature [10,11]. Peak profiles were fitted using the Thompson–Cox–Hastings pseudo-Voigt function [12]. Mean coherence paths (MCPs) dimensions were calculated taking into account the instrument broadening function, determined using NIST SRM 660 lanthanum hexaboride (LaB_6) standard.

Diffuse reflectance spectra of the sol–gel powders (TiO_2, u-TiO_2 and t-TiO_2) were recorded in a Shimadzu UVPC 3101 spectrophotometer equipped with an integration sphere. The powder samples were directly placed into a cylindrical sample port holder (3 cm diameter, 1 mm deep).

IR spectra were obtained with a FTIR Nicolet 510 P spectrophotometer, using KBr pellets. The pellet concentration was approximately 1% weight.

The Brunauer–Emmett–Teller (BET) surface area of the powders was determined by nitrogen adsorption in a Micromeritics Gemini 2370 instrument. Approximately 0.2 g of sample were degassed at 350 °C for 3 h prior to nitrogen adsorption measurements. The BET area was determined using the adsorption data in the relative pressure (P/P_o) range of 0.005–0.99.

For multivariate analysis, a response surface methodology (RSM) was used as previously described for photocatalytic processes [13,14]. This model is based on a central composite circumscribed design made of a factorial design and star points. The data was analyzed using the Modde 7.0 software. The variable values were coded and normalized in unitary values, −1 and +1, for TiO_2 amount and pH, ranging between 0.85 and 2.15 g L^{-1}, and 7 and 8.2, respectively. From these ranges, the central point (coded 0) was set and determined in triplicate. The star points were distributed at a distance of $n^{1/2}$ from the central point, where n is the number of variables. The response factor was flumequine degradation after 15 min irradiation. The experimental design with the codified and non-codified values is shown in Table 4.

A second-order function that described the system's behaviour was determined by a multiple regression. The optimized values of the analyzed variables were obtained using the Modde 7.0 software. The statistical validation was performed by an ANOVA test with a 95% of confidence.

3. Results and discussion

The crystalline forms of the three catalysts were determined using X-ray diffraction analysis (Fig. 1), and the data was simulated using the Rietveld method [15]. The reliability factors Rwp, R_B and GofF, which describe the goodness of the fittings, are in the range of 8.03–8.94, 1.99–3.67 and 1.11–1.26, respectively (Table 1) and are considered satisfactory.

A comparison of the XRD patterns shows that the peak positions are nearly the same for all the catalysts. The diagrams correspond to anatase phase. Rutile phase was not observed in the samples.

The doped sample, t-TiO_2, shows broader peaks than those of pure and u-doped TiO_2 (Fig. 1, inset). Ohno et al. found