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ScienceDirect
Journal of Hazardous Materials 158 (2008) 460–464
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Oxolinic acid photo-oxidation using immobilized TiO_2

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Received 7 December 2007; received in revised form 24 January 2008; accepted 25 January 2008
Available online 19 February 2008

Abstract

This work studied the photocatalysed oxidation of the antibiotic oxolinic acid (OA) in an annular reactor operated with immobilized TiO_2 on sintered glass cylinders (SGC). Experiments were carried out in 1 l solution of OA (18 mg l^{-1}) at pH 9 with oxygen bubbling. Irradiation was performed with black light (36 W). The reaction was monitored by COD, TOC and average oxidation state (AOS) calculations. The antibacterial activity of intermediates was followed using the inhibition halo technique on *Escherichia coli* cultures. The initial antibiotic concentration decreases in one order of magnitude after 60 min irradiation, and was completely eliminated at 100 min reaction. The TOC was reduced in 54% and the AOS reach values around +3 indicating the formation of low molecular weight carboxylic acids. The oxidation reaction fit well with the Langmuir–Hinshelwood kinetic model indicating the dependence of reaction rate with initial adsorption step. The antibacterial activity of the solution decreases with antibiotic removal, demonstrating that intermediates do not present antibiotic activity.

Keywords: Antibiotic; Immobilized TiO_2; Oxolinic acid; Photocatalysis

1. Introduction

The increasing consumption of antibiotics by humans and their excessive application in food production could transform the native flora of soils and waters into sources of antibiotic-resistant bacteria. Considering that isolated ecological communities do not exist, the high possibility that this resistance be transferred to nearby humans poses a serious risk for public health [1].

Oxolinic acid (OA) is a widely used antibiotic in the industrial aquiculture and poultry and bovine production. It has been monitored in agriculture soils, lake sediments, and in aquatic environments near fishing farms [2]. Antibacterial activity half-life of the OA in marine sediments surpasses 150 days [3]. Additionally, the quinolone structure of the OA has been reported as potentially genotoxic, which could provoke harmful effects on the environment [4].

Due to their antibacterial activity, waters containing antibiotics commonly used in animal and human health (antibiotics included) are refractory to natural biological degradation or conventional wastewater treatments. The great concern is that waters contaminated with antibiotics can reach waters used for human consumption or municipal water treatment facilities [5,6]. Several alternatives to destroy these kinds of compounds have been considered in recent studies in the literature. These include reverse osmosis, adsorption on activated carbons or advanced oxidation technologies, such as Fenton reaction, ozonation and peroxidation combined with UV light [7–9].

Heterogeneous photocatalysis using a semiconductor (mainly TiO_2) have earned an important place among the advanced oxidation technologies due to the stability of the catalyst in the entire pH range, the absence of residuals after the treatment, and the possible use of solar light as light source. This heterogeneous system has been recently proposed as an alternative treatment for antibiotics, such as tetracycline and flumequine, where mechanistic aspects as well as the use of immobilized catalyst were discussed [10–12]. The photocatalysis is initiated with the formation of charge-carrier pairs (e^-, h^+) resulting from photon absorption by the catalyst. The photon must have an energy equal or larger than the catalyst's band gap (3.2 eV, $\lambda < 385$ nm). After that, the charge-carriers

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doi:10.1016/j.jhazmat.2008.01.117

can migrate to the catalyst's surface, recombining or reacting with adsorbed species on the surface. Detailed aspects regarding the mechanism have been amply discussed in the literature [13–15]. In summary, it is has been proposed that conduction band electrons can reduce molecular oxygen, forming superoxide anion. Simultaneously, holes oxidize adsorbed molecules of hydroxide anions or water molecules generating hydroxyl radicals. Furthermore, these holes are able to directly oxidize the organic matter by electron abstraction. In spite of the great number of papers published on photocatalysis, there are still some uncertainties in relation with the primary mechanisms involved [16]. A first source of debate comes from whether delocalized (free), photogenerated valence band holes (h_f^+) react directly with the organic substrate via a direct transfer (DT) mechanism [17], or rather photo-oxidation occurs via an indirect transfer (IT) mechanism with intervention of photogenerated $OH^\bullet$ radicals (surface-trapped holes, h_s^+) [18].

The photocatalytic process can proceed using the catalyst in suspension or immobilized on inert surfaces. The use of a catalyst coated on porous materials avoids the catalyst-recovery step after the reaction, resulting in energy and cost savings [19]. To develop an approach to apply this technology, several immobilization methodologies have been proposed and new reactors have been designed. Immobilization techniques, such as dip coating, spray coating, sputtering, sol–gel-related methods and electrophoretic deposition have been investigated [19,20]. Moreover, different support materials, including glass beads, glass tubes, fiberglass, quartz, stainless steel, aluminum, activated carbon, and silica have been assayed [19,20].

In the present work, a sinterized glass bed was used as support for titania Degussa P-25. The support material, in the form of cylinders, was placed surrounding a black lamp in a reactor setup described in a recent report [11]. Oxolinic acid was used as a target compound, following its oxidation profile by spectrophotometric analyses, COD and TOC determinations and average oxidation state calculations. The antibacterial activity was determined applying the inhibition halo methodology on *Escherichia coli* cultures.

2. Experimental

2.1. General procedure of photocatalytic reactions

The laboratory-scale annular reactor shown in Fig. 1 was used in all the photocatalytic experiments. The reactor's lamp was completely encircled in its internal length (75 cm) by TiO_2-impregnated SGC. Altogether, 13 cylinders were placed around the lamp with a total of 8.97 g of titania distributed more or less uniformly on the total of the cylinders. A black light lamp (360 nm, 36 W) was used in the experiments. The solution of oxolinic acid (7×10^{-5} mol l^{-1}, 18 ppm), adjusted to pH 9, was impelled through the reactor by a peristaltic pump operated at 155 ml min^{-1}. The pH of the solution was chosen due to the low solubility of the antibiotic at neutral or acidic pH. The solution was recirculated in the dark during 30 min before the lamp was turned on. All the photocatalytic experiments were performed with direct oxygen bubbling in the solution and under magnetic stirring in the vessel outside of the reactor. Samples of irradiated solutions were taken at different intervals for analysis and bacteriological measurements.

2.2. Materials and methods

Titanium dioxide Degussa P-25 with a surface area 50 m^2 g^{-1} (size ∼20–30 nm) was used as provided. Oxolinic acid was purchased from Sigma and used without any further purification. The oxolinic acid degradation was monitored at 341 nm by spectrophotometric analysis using a Shimadzu UV-1603 instrument. TOC analyses were carried out in a Shimadzu 5000 A instrument. The chemical oxygen demand was determined using a commercial kit (HACH) in a Digital Reactor Block 200 (HACH).

To determine the antibacterial activity of irradiated OA samples, tripticase agar plates were seeded with a 10^5 CFU ml^{-1} suspension of *E. coli* (ATCC 6317). The plates were loaded, in small holes made in the agar, with 100 μl of irradiated samples and incubated for 24 h at 37 °C. The inhibition halo formed around the spot was measured in mm and compared to the calibration curve made with the pure solutions of antibiotic and

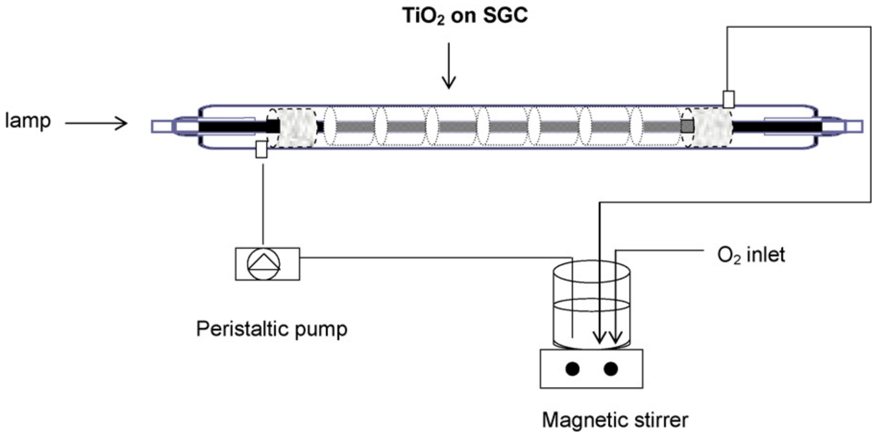

Fig. 1. Schematic representation of the experimental setup for photocatalytic reactions.