



Simulated solar-light assisted photocatalytic ozonation of metoprolol over titania-coated magnetic activated carbon

Ana Rey^{a,*}, Diego H. Quiñones^a, Pedro M. Álvarez^a, Fernando J. Beltrán^a, Pawel K. Plucinski^b

^a Departamento de Ingeniería Química y Química Física, Universidad de Extremadura, Avenida de Elvas S/N, 06006 Badajoz, Spain

^b Department of Chemical Engineering, University of Bath, BA2 7AY Bath, United Kingdom

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ABSTRACT

A magnetically separable photocatalyst consisting of magnetic porous activated carbon with attached anatase TiO₂ particles has been prepared and tested for the degradation of metoprolol (MTP) in aqueous solution. The synthesized photocatalyst (TiFeC) was characterized by nitrogen adsorption, XRD, FTIR, SEM, EDX and SQUID magnetometer. The obtained catalyst with a TiO₂ composition of 61 wt.% (mostly anatase) had moderate surface area (BET surface of 331 m² g⁻¹) and volume of micropores and exhibited magnetic properties with saturation magnetization of 1.6 emu g⁻¹ and neither remanent magnetization nor coercivity. The photocatalytic activity of TiFeC samples was tested by degrading MTP by simulated solar photocatalytic ozonation. The results were compared to those obtained with a commercial titania (Degussa P25) and by photolytic ozonation (i.e., absence of catalyst). Complete MTP removal and more than 60% TOC conversion were achieved after 3 h of photocatalytic ozonation of an aqueous solution containing as much as 50 mg L⁻¹ MTP initial concentration. The reusability and stability of the catalyst were tested through a series of five photocatalytic ozonation experiments. Minor amounts of iron and titanium were leached out from the catalyst and the catalytic activity decreased to a very low extent with the reuse of the catalyst.

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1. Introduction

Solar photocatalytic detoxification of water and wastewater is an emerging area of research and commercial development as it may be considered as one of the most cost effective treatment technologies in regions of high incoming solar radiation [1,2]. Solar photocatalytic detoxification is a relatively new clean technology to remove toxic and persistent pollutants in water and wastewater by focusing sunlight onto a reactor through which the contaminated water is flowing in the presence of a catalyst. Among candidates for solar photocatalysis, TiO₂ in the form of anatase is the most suitable material for industrial use at present because it is a non-toxic material with high chemical stability, low cost and high oxidation power. It is a semiconductor with a band gap of about 3.2 eV allowing absorption of UV light with wavelengths below 387.5 nm (about 5% of solar spectrum) to generate electron–hole pairs (e⁻/h⁺) on the catalyst surface. Electron–hole pairs, in turn, trigger a series of reactions generating free-radicals (mainly hydroxyl radicals, HO•), which are very efficient non-selective oxidizers of water pollutants, both chemical compounds and microorganisms

(disinfection). Solar TiO₂ photocatalysis is receiving great attention for water and wastewater remediation and it has been extensively investigated for the removal of organic recalcitrant pollutants as for example, pharmaceuticals [3–6], dyes [7] or pesticides [8] as well as to inactivate pathogenic microorganisms such as *Escherichia coli* [9].

Given the concern over the risk posed by the presence of pharmaceutical compounds in water bodies, and hence the possible impacts on public health and aquatic ecosystems a great deal of research is being carried out on technologies for the removal of these compounds [10–12]. In general, pharmaceutical compounds are hardly biodegradable so they are not eliminated by conventional treatment at wastewater treatment plants (WWTPs) and, as a consequence, they are frequently reported to be present in WWTP effluents at ng L⁻¹ and even μg L⁻¹ concentration levels [13]. Although solar TiO₂ photocatalysis has been found effective for the removal of different pharmaceutical compounds from aqueous solution, to achieve complete mineralization long reaction times are needed because of the formation of a number of intermediates which, frequently, are hard to degrade [2].

In this work, with the aim of enhancing process performance regarding mineralization rate of complex organic molecules such those of pharmaceutical compounds, solar photocatalytic ozonation has been applied. Photocatalytic ozonation, which is the

* Corresponding author. Tel.: +34 924289385; fax: +34 924289385.

E-mail address: anarey@unex.es (A. Rey).

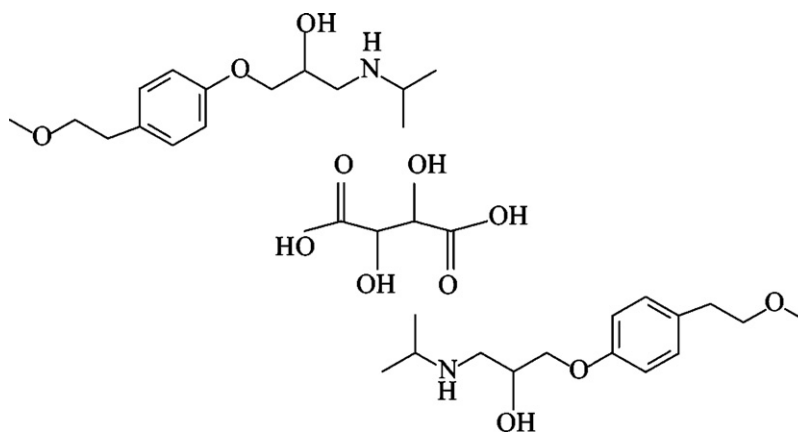


Fig. 1. Molecular structure of metoprolol tartrate.

combination of TiO_2 photocatalysis and ozonation, is a promising advanced oxidation technology capable of producing much larger number of hydroxyl radicals than single ozonation or TiO_2 photocatalysis. In the combined process, the recombination of electron–hole pairs on the TiO_2 surface is reduced with respect to single TiO_2 photocatalysis as electrons are captured by ozone generating a new via of hydroxyl radicals formation and, therefore, increasing the oxidation rate [14,15]. Most of the photocatalytic ozonation studies conducted to date make use of TiO_2 suspensions and UV lamps from low to high pressure [16–18]. In spite of the great degradation rates found for the studied pollutants, two drawbacks of the process can be considered: (1) the use of UV lamps as a source of radiation can make the process expensive for commercial applications; (2) the separation of TiO_2 catalyst in suspension after the reaction is a major obstacle. To overcome these problems, in this work simulated solar radiation has been used as UV light source and a TiO_2 magnetic activated carbon photocatalyst has been synthesized and applied. Literature reports on the preparation of various types of magnetic TiO_2 photocatalysts, which can be easily recovered by the application of an external magnetic field [19–23]. Among them, TiO_2 magnetic activated carbon catalysts have shown a high activity in the photodegradation of phenol and dyes [24,25], but no study has been found on their use in photocatalytic ozonation process.

In this work, we have prepared and characterized a TiO_2 magnetic activated carbon catalyst with enhanced photocatalytic activity to mineralize complex organic pollutants in water such as the pharmaceutical compound metoprolol tartrate (MTP). MTP (see Fig. 1 for structure) is a β -blocker used for several cardiovascular diseases which has been frequently detected in surface waters and effluents from sewage treatment plants [26,27]. The TiO_2 magnetic activated carbon catalyst has been tested in both solar photocatalysis and solar photocatalytic ozonation and compared with the efficiency of commercial TiO_2 powder (Degussa P25), which is a standard material in the field of photocatalytic reactions.

2. Experimental

2.1. Preparation of catalyst

First, a magnetically separable activated carbon (FeC) was prepared following the method reported by Fuertes and Tartaj [28]. In a typical preparation, 10 g of a meso-microporous activated carbon (Darco 12-20, Sigma–Aldrich) were impregnated with 8.7 mL of ferric nitrate (923 g L^{-1}) in ethanol solution to obtain about 12 wt% Fe in the final product. Once the solution was adsorbed onto the activated carbon, the sample was dried at 90°C for 2 h. After that, it was

impregnated with 150 mmol of ethylene glycol. The impregnated activated carbon was then transferred into an oven where it was heated in nitrogen at 350°C for 2 h. After cooling to room temperature in nitrogen, the magnetic activated carbon sample was milled into powder ($d_p < 125 \mu\text{m}$).

Titania coated magnetic activated carbon (TiFeC) was prepared by the sol–gel method reported by Ao et al. [24]. First, 25.5 mL of titanium (IV) butoxide (97%, Aldrich) were diluted with 8.2 mL of isopropanol (>99%, Aldrich), and the mixture was added dropwise to 205 mL of distilled water at pH 2 (adjusted with HNO_3 65%, Pan-reac) under vigorous stirring. The solution was kept under stirring and refluxed at 75°C for 24 h and, thereafter, transferred to a rotary evaporator where excess alcohol was removed by heating at 80°C under vacuum, thus obtaining a titania sol. Finally, 3 g of the prepared magnetic activated carbon (FeC) were dispersed in the titania sol and subjected to ultrasonic treatment for 1 h. After evaporation to dryness under vacuum at 80°C on a rotary evaporator, the residue sample was repeatedly washed with distilled water until no total organic carbon (TOC) was detected in the supernatant and then separated from the liquid fraction by an external magnet to select only the magnetic particles. The TiFeC catalyst thus prepared was dried at 100°C overnight.

2.2. Catalyst characterization

Surface areas and pore structure of the activated carbon used as support (AC), the magnetic activated carbon (FeC) and the TiFeC catalyst were obtained from nitrogen adsorption–desorption isotherms at -196°C acquired with a Autosorb 1 apparatus (Quantachrome). Before measurements, the samples were outgassed at 250°C for 12 h under high vacuum ($<10^{-4}$ Pa). The isotherms were analyzed by BET equation and t -plot to obtain BET and external surface areas, respectively. X-ray diffraction (XRD) patterns were collected with a Bruker D8 Advance XRD diffractometer with a $\text{CuK}\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$). The data were collected from $2\theta = 20^\circ$ to 70° at a scan rate of $0.02^\circ \text{ s}^{-1}$ and 1 s per point. FTIR spectra were obtained on a Nicolet iS10 spectrometer using KBr wafers containing about 0.01 g sample. Data were acquired in the wavelength range $400\text{--}4000 \text{ cm}^{-1}$ using 32 scans with a resolution of 4 cm^{-1} . The morphology of catalyst particles was characterized by scanning electron microscopy (SEM) using a Hitachi S-4800 apparatus working at 20–30 kV accelerating voltage and 500–2000 magnification. In addition, the catalyst was examined by means of energy dispersive X-ray (EDX) analysis to determine the distribution of Ti and Fe in the particles. For that purpose, a SSD detector XFlash 5010 (Bruker), working at 5 kV accelerating voltage and 500–2000 magnification was used. The iron content of the TiFeC catalyst was

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