



Boron doped TiO₂ catalysts for photocatalytic ozonation of aqueous mixtures of common pesticides: Diuron, o-phenylphenol, MCPA and terbuthylazine



D.H. Quiñones^a, A. Rey^{a,*}, P.M. Álvarez^a, F.J. Beltrán^a, G. Li Puma^b

^a Dpto. Ingeniería Química y Química Física, Universidad de Extremadura, Avda. Elvas s/n, 06006 Badajoz, Spain

^b Environmental Nanocatalysis and Photoreaction Engineering, Department of Chemical Engineering, Loughborough University, LE11 3TU Loughborough, United Kingdom

ARTICLE INFO

Article history:

Received 11 July 2014

Received in revised form 10 October 2014

Accepted 12 October 2014

Available online 18 October 2014

Keywords:

Photocatalytic ozonation

Boron doped TiO₂

Boron leaching

Pesticides

Solar light

ABSTRACT

TiO₂ and B-doped TiO₂ catalysts were synthesized using a sol–gel procedure. The photocatalysts were characterized by ICP-EOS, N₂ adsorption–desorption, XRD, XPS, and DR-UV-Vis spectroscopy. Four recalcitrant pesticides (diuron, o-phenylphenol, 2-methyl-4-chlorophenoxyacetic acid (MCPA) and terbuthylazine) were subjected to degradation by ozonation, photolytic ozonation, photocatalysis and photocatalytic ozonation using the prepared catalysts under simulated solar irradiation in a laboratory scale system. The B-doped TiO₂ catalysts, with 0.5–0.8 wt.% of interstitial boron, were more active than bare TiO₂ for the removal and mineralization of the target compounds. The combination of ozonation and photocatalysis led to faster mineralization rates than the treatment methods considered individually and allowed the complete removal of the pesticides below the regulatory standards. The B-doped catalyst was stable and maintained 75% mineralization after three consecutive runs.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Water pollution and scarcity is a global concern. Agriculture is the industrial activity that has the major impact on aquatic ecosystems, due to the large volumes of water consumed (70% of the world accessible freshwater [1]) and the high content of organic substances (pesticides and fertilizers) which are dispersed in aqueous environments by runoff or leaching. Many pollutants found in water ecosystems are recalcitrant to some degree to biological and physicochemical processes that are conventionally used in wastewater treatment plants. In the last decades, Advanced Oxidation Processes (AOPs) have been pointed out as effective alternatives to deal with this kind of contaminants. These technologies can generate non-selective, highly reactive and short-life oxidizing species, which in turn can completely degrade organic pollutants through oxidation reactions [2].

Photocatalysis is one of the most successfully and extensively studied AOP. It involves the excitation of a semiconductor through the absorption of photons having energy greater than its band gap. This excitation promotes an electron from the valence to the conduction band, which triggers a series of oxidation–reduction

reactions involving the excited electron and the generated hole at the valence band [2]. Recently, solar-driven TiO₂ photocatalytic oxidation has attracted considerable attention in water treatment applications. It offers the possibility of using solar energy to activate the semiconductor. However, due to the TiO₂ wide band gap (3.2 eV) its photoactivity is limited to ultraviolet irradiation ($\lambda < 380$ nm) and thus less than 5% of the solar spectrum can be exploited [3]. In general, doping TiO₂ appears to be an effective way to overcome this limitation, since the photoactivity of the doped semiconductor may be extended to the visible-light region [4,5]. Boron doping constitute a way to accomplish it, since O atoms in the TiO₂ lattice can be substituted by B atoms mixing the p orbital of B with O 2p orbitals, narrowing the band gap and thus shifting the optical response into the visible range [5]. On the other hand, boron can also be located in interstitial positions of the TiO₂ lattice leading to the partial reduction of Ti(IV) to Ti(III), which could act as an electron trap enhancing the photocatalytic activity of TiO₂ [5,6].

Another way to improve the performance of TiO₂ photocatalytic systems is its simultaneous application with other AOPs, such as ozonation. The combined application of ozone and TiO₂ photocatalysis, known as photocatalytic ozonation, leads to a synergistic effect due to enhanced production of reactive oxygen species (ROS) such as hydroxyl radicals in comparison with the application of either single ozonation or single TiO₂ photocatalysis [7,8].

* Corresponding author. Tel.: +34 924289383; fax: +34 924289385.
E-mail address: anarey@unex.es (A. Rey).

In this study, the degradation of four herbicides and pesticides: diuron (DIU), o-phenylphenol (OPP), 2-methyl-4-chlorophenoxyacetic acid (MCPA) and terbuthylazine (TBA), commonly found in water ecosystems, has been studied. Their molecular structures can be found in Table S1 of the supplementary material. The degradation methods used were photocatalysis, ozonation, photolytic ozonation, and photocatalytic ozonation. Different boron doped TiO₂ photocatalysts (B-TiO₂) were synthesized and used in the photocatalytic treatments.

2. Experimental

2.1. Catalysts preparation

The synthesis of TiO₂ and B-TiO₂ catalysts was carried out following a sol-gel procedure previously reported [9]. Initially, a precursor solution was prepared by diluting the required amount of boric acid (Fisher Scientific) in 10 mL anhydrous ethanol (Panreac, 99.5%), then adding 4.26 mL tert-butyl titanate (Sigma-Aldrich, 97%), adjusting the pH to 3–4 with glacial acetic acid (Merck) and stirring for 30 min. After that, 20 mL ethanol were added to the precursor solution and the stirring was kept for two more hours. Ammonia aqueous solution (Fisher Scientific, 35%) was then added dropwise to reach pH 9. Afterward 10 mL ethanol was added and stirring was kept for another 30 min. The suspension was centrifuged and washed with ethanol three times. The resulting solid was dried at 60 °C overnight, manually grinded and finally calcined at 500 °C for 30 min. Catalysts with 3, 6, 9 and 12 wt.% of B were prepared. The nomenclature and some parameters of the catalysts are shown in Table 1. A fraction of catalysts with 6 and 12 wt.% of B were washed with ultrapure water to analyze the effect of B leaching.

2.2. Characterization of the catalysts

The characterization of the catalysts was carried out by inductively coupled plasma optical spectroscopy, N₂ adsorption-desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and DR-UV-Vis spectroscopy.

Total B content of the catalysts was analyzed by inductively coupled plasma with an ICP-OES Optima 3300DV (Perkin-Elmer) after acidic microwave digestion of the samples.

BET surface area and pore structure of catalysts were determined from their nitrogen adsorption-desorption isotherms obtained at –196 °C using an Autosorb 1 apparatus (Quantachrome). Prior to analysis the samples were outgassed at 250 °C for 12 h under high vacuum (<10^{–4} Pa).

The crystalline structure was analyzed by X-ray diffraction (XRD) using a Bruker D8 Advance XRD diffractometer with a CuKα radiation (λ = 0.1541 nm). The data were collected from 2θ = 20° to 80° at a scan rate of 0.02 s^{–1} and 1 s per point.

XPS spectra were obtained with a Kα Thermo Scientific apparatus with an AlKα (hν = 1486.68 eV) X-ray source using a voltage of

12 kV under vacuum (2 × 10^{–7} mbar). Binding energies were calibrated relative to the C1s peak at 284.6 eV.

Diffuse reflectance UV-Vis spectroscopy (DR-UV-Vis) measurements, useful for the determination of the semiconductor band gap, were performed with an UV-Vis-NIR Cary 5000 spectrophotometer (Varian-Agilent Technologies) equipped with an integrating sphere device.

Transmitted photon flux through a catalyst suspension was analyzed by actinometrical measurements following the method proposed by Loddo et al. in [10], using the solar simulator described below with 250 mL of actinometrical solution and 250 mL of catalyst suspension at 0.33 g L^{–1}. Incident radiation flux was determined with ultrapure water replacing the catalyst suspension and was found to be 8.96 × 10^{–4} einstein min^{–1}.

2.3. Photocatalytic activity measurements

Photocatalytic experiments were carried out in a laboratory-scale system consisting of a 250 mL pyrex made 3-neck round-bottom flask (8.8 cm outer diameter) provided with a gas inlet, a gas outlet and a liquid sampling port. The reactor was placed in the chamber of a commercial solar simulator (Suntest CPS, Atlas) equipped with a 1500 W air-cooled Xe lamp with emission restricted to wavelengths over 300 nm (quartz and glass cut-off filters). The emission spectrum of the solar simulator can be seen in Fig. S1 of the supplementary material. The irradiation intensity was kept at 550 W m^{–2} and the temperature of the system was maintained between 25 and 40 °C throughout the experiments. If required, a laboratory ozone generator (Anseros Ozomat Com AD-02) was used to produce a gaseous ozone-oxygen stream that was fed to the reactor.

In a typical photocatalytic ozonation experiment, the reactor was first loaded with 250 mL of an aqueous solution containing 5 mg L^{–1} initial concentration of each pesticide (in a mixture). Then, the catalyst was added at a concentration of 0.33 g L^{–1} and the suspension was stirred in the darkness for 30 min (dark adsorption stage). Then, the lamp was switched on and, simultaneously, a mixture of ozone-oxygen (5 mg L^{–1} ozone concentration) was fed to the reactor at a flow rate of 10 L h^{–1}. The irradiation time for each experiment was 2 h. Samples were withdrawn from the reactor at intervals and filtered through a 0.2 μm PET membrane to remove the photocatalyst particles.

Photolysis experiments (i.e., absence of catalyst and ozone), adsorption (i.e., absence of radiation and ozone), ozonation alone (i.e., absence of radiation and catalyst), and photolytic ozonation (i.e., absence of catalyst) were also carried out for comparative purposes.

Pesticides concentrations were analyzed by HPLC (Hewlett Packard) provided with a Kromasil C18 column (5 μm, 150 mm long, 4 mm diameter, Teknokroma). As mobile phase a mixture of acetonitrile (solvent A) and 0.1% (v/v) phosphoric acid solution (solvent B) was used at 1 mL min^{–1}. Initially the mobile phase composition was varied from 40 to 25% solvent A in 12.5 min, then

Table 1
Nomenclature and some properties of the B-TiO₂ catalysts.

Catalyst	B (wt.%)	d _A (nm)	S _{BET} (m ² g ^{–1})	V _P (cm ³ g ^{–1})	(B/Ti) _{ICP} (at./at.)	(B/Ti) _{XPS} (at./at.)	E _g (eV)
TiO ₂	n.d.	16.8	68.3	0.102	0	0	3.07
3B-TiO ₂	0.91	9.9	121.3	0.209	0.068	0.469	3.12
6B-TiO ₂	1.06	9.2	120.1	0.147	0.079	0.531	3.03
9B-TiO ₂	1.81	7.6	122.4	0.163	0.137	0.541	3.05
12B-TiO ₂	3.55	7.5	125.5	0.180	0.273	0.693	3.01
6B-TiO ₂ -w	0.42	9.8	n.m.	n.m.	0.031	0.018	n.m.
12B-TiO ₂ -w	0.49	7.9	n.m.	n.m.	0.036	0.029	n.m.

n.d.: not detected, n.m.: not measured.

Download English Version:

<https://daneshyari.com/en/article/44945>

Download Persian Version:

<https://daneshyari.com/article/44945>

[Daneshyari.com](https://daneshyari.com)