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Photocatalytic degradation of endocrine disruptor compounds under simulated solar light

Vanessa Maroga Mboula [a,*], Valérie Héquet [a], Yves Andrès [a], Luisa Maria Pastrana-Martínez [c], José Miguel Doña-Rodríguez [b], Adrián M.T. Silva [c], Polycarpos Falaras [d]

[a] LUNAM Université, Ecole des Mines de Nantes, CNRS, GEPEA, UMR 6144, 4 rue Alfred Kastler, 44307 Nantes cedex 03, France

[b] FEAM-Departamento de Química, Universidad de Las Palmas de Gran Canaria, Edificio Central del Parque Científico-Tecnológico de la ULPGC, Campus Universitario de Tafira, 35017 Las Palmas, Spain

[c] LCM – Laboratory of Catalysis and Materials – Associate Laboratory LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[d] Institute of Physical Chemistry, NCSR Demokritos, 153 10 Aghia Paraskevi Attikis, Athens, Greece

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ABSTRACT

Nanostructured titanium materials with high UV-visible activity were synthesized in the collaborative project Clean Water FP7. In this study, the efficiency of some of these catalysts to degrade endocrine disruptor compounds, using bisphenol A as the model compound, was evaluated. Titanium dioxide P25 (AEROXIDE® TiO_2, Evonik Degussa) was used as the reference. The photocatalytic degradation was carried out under the UV part of a simulated solar light (280–400 nm) and under the full spectrum of a simulated solar light (200 nm-30 μm). Catalytic efficiency was assessed using several indicators such as the conversion yield, the mineralization yield, by-product formation and the endocrine disruption effect of by-products. The new synthesized catalysts exhibited a significant degradation of bisphenol A, with the so-called ECT-1023t being the most efficient. The intermediates formed during photocatalytic degradation experiments with ECT-1023t as catalyst were monitored and identified. The estrogenic effect of the intermediates was also evaluated *in vivo* using a ChgH-GFP transgenic medaka line. The results obtained show that the formation of intermediates is related to the nature of the catalyst and depends on the experimental conditions. Moreover, under simulated UV, in contrast with the results obtained using P25, the by-products formed with ECT-1023t as catalyst do not present an estrogenic effect.

1. Introduction

During recent decades, bisphenol A (BPA) has gained attention and become a public concern since it was recognized as causing an endocrine disruption effect (Staples et al., 1998; Birkett and Lester, 2003). Bisphenol A is a chemical compound widely used as a raw material to manufacture chemical products such as polycarbonate plastics and epoxy resins. It is released into the environment during manufacturing processes and by leaching from final products (Staples et al.,

* Corresponding author. Tel.: +33 (0) 251858253.
E-mail addresses: vanessa.maroga-mboula@mines-nantes.fr, marogavs@yahoo.fr (V. Maroga Mboula).
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2000). Numerous studies have reported the occurrence of BPA in the environmental matrices (Fromme et al., 2002; Céspedes et al., 2005) and in waste water treatment effluent because it is not completely removed during conventional treatments (Oulton et al., 2010; Rodil et al., 2012). Hence, to reduce its ubiquity in environmental matrices, it is necessary to develop sustainable treatment technologies to tackle this issue.

Advanced oxidation processes (AOPs) have proved to be a good alternative for the removal of recalcitrant compounds and the most popular AOPs studied are heterogeneous photocatalysis with semiconductors, ozonation and the photo-Fenton process (Klavarioti et al., 2009). Heterogeneous photocatalysis and the photo-Fenton process are of special interest since sunlight can be used as the irradiation source (Malato et al., 2009) while among the catalysts used in heterogeneous photocatalysis, TiO_2 has been gaining attention for its strong photoinduced oxidation power (Kaneko and Okura, 2002).

However, one disadvantage of TiO_2 is that it can only absorb UV light and this makes up only 3–5% of solar light. Hence, many studies have been done to extend its photoactivity from UV into the visible light range in order to enable practical applications using solar energy (Byrne et al., 2011). The strategies most employed are doping TiO_2-based materials with transition metals and with non-metallic elements (Rehman et al., 2009).

Alternatively, when TiO_2-based materials are not doped, the key to using solar light efficiently is to have a catalyst with a higher photocatalytic activity. Some studies have shown that catalysts of high efficiency can be synthesized and obtained when some parameters such as crystal phases, particle size, surface area, particle morphology, distribution of hydroxyl groups, and charge separation are taken into account and optimized (Ambrus et al., 2008; Fujishima et al., 2008). Increasing the surface area and charge separation can be achieved by anchoring TiO_2 particles onto substrates with a large surface area, such as mesoporous structures, zeolites or carbon-based materials where the graphene based composites look very promising. The combination of TiO_2 and graphene oxide could enhance the photodegradation of organic contaminants due to an improvement in electron transport, which prevents the recombination of charge, and to the adsorption capacity of organic contaminants on graphene oxide-TiO_2 (Nguyen-Phan et al., 2011).

In this context, innovative nanostructured UV-visible photocatalysts were synthesized within the collaborative project Clean Water FP7. These catalysts were tested for the degradation of several micropollutants. Previous results are presented elsewhere (Arana et al., 2010; Kontos et al., 2008; Pastrana-Martínez et al., 2012a; 2012b). The objective of the present work is to evaluate the photocatalytic activity of the catalysts, synthesized during the Clean Water project, toward the degradation of an endocrine disruptor compound, bisphenol A, under both the UV part and the full spectrum of a simulated solar light. In this study, the photocatalytic activity of the catalysts is described not only with parameters like kinetic constant, conversion and mineralization percentages but also in terms of reactionnel intermediates and potential endocrine disruption effect of the treated solution.

In literature, the estrogenic effect of BPA intermediates is often measured using the Yeast Estrogen Screen (Chiang et al., 2004; Neamtu and Frimmel, 2006; Frontistis et al., 2011). This test, done *in vitro*, is able to detect estrogen agonists. However, the endocrine disruptor compounds do not only act as agonists of estrogen, they may also inhibit enzymatic catalysis reactions. In this case, only *in vivo* analysis could provide a full spectrum of the disruption caused by these compounds in organisms. Thus, to identify a broad range of endocrine disruptor compounds, it is better to carry out estrogenic tests *in vivo* which enable the detection of estrogen agonists and antagonists, aromatizable androgens, activators and inhibitors of enzymatic catalysis reactions. In our study, to assess the estrogenic effect of intermediates formed during the photocatalytic degradation of BPA, a ChgH-GFP transgenic medaka line, was used. To our knowledge, this is the first study using this kind of test to detect the estrogenic effect of intermediates formed during an advanced oxidation process.

2. Materials and methods

2.1. Materials

Bisphenol A (BPA), hydroxyacetophenone and isopropyl phenol were purchased from Sigma Aldrich. Titanium dioxide (AEROXIDE® TiO_2 P25, S_{BET} = 50 m^2/g) was obtained from Evonik Degussa GmbH (Frankfurt, Germany). Analytic reagents were obtained from Merck. Tree catalysts in powder form have been received from project partners: Non-doped TiO_2 (ECT-1023t, S_{BET} = 18.3 m^2/g), nitrogen-doped TiO_2 (N–TiO_2, S_{BET} = 141 m^2/g) and graphene oxide TiO_2 (GO-TiO_2, S_{BET} = 110 m^2/g). ECT-1023t was synthesized by means of a sol-gel method in which aggregates have been selected before thermal treatment (Arana et al., 2010); N–TiO_2 was synthesized as the hydrolysis condensation product of tetrabutyl titanate reaction with urea (Kontos et al., 2008) and GO-TiO_2 (graphene oxide content of 4.0 wt. %) was prepared by liquid phase deposition followed by post-thermal reduction at 200 °C (Pastrana-Martínez et al., 2012a).

2.2. Photocatalytic experiment

Photocatalytic experiments were carried out in a cylindrical reactor irradiated on the top with a solar simulator (Newport, USA), equipped with a Xenon arc lamp of 450 W (Fig. 1). A quartz cover was placed on top of the glass reactor to minimize water loss due to evaporation. At the beam output, an AM 1.5 filter was placed to obtain a solar-like spectrum and, by using dichroic mirrors, a proper working wavelength range was selected. To conduct experiments, two wavelength ranges were chosen: 280–400 nm (UV) and 200 nm-30 μm (UV-visible). The intensity of light in different conditions (UV or UV-visible) was measured using a RAMSES-ARC-Hyperspectral UV-VIS Radiance Sensor-320–950 nm and a radiometer VLX-3W.The volume of the reactor was 1 L. Catalyst load (P25, ECT-1023t, N–TiO_2 and GO-TiO_2) and initial BPA concentration was 40 mg/L and 2 mg/L, respectively. During irradiation, the solution was shaken and continuously bubbled with air (~20% of O_2) in order to maintain the solution in excess of O_2. Aliquots were taken every ten minutes to determine the BPA residual