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Bisphenol A removal from wastewater using self-organized TIO$_2$ nanotubular array electrodes

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ABSTRACT

Photoelectrocatalytic oxidation of 0.1 mM of Bisphenol A (BPA) leads to 100% of degradation monitored by liquid chromatography with diode array optical detection (limit 1 μg L^{-1}) and 100% TOC removal. Optimum performance was obtained using TiO$_2$ nanotubular array (NTA) electrodes, grown by anodization of Ti foil in 0.25 wt.% NH$_4$F and a mixture of glycerol and water (ratio 90:10 vol.%) using an applied voltage of 20 V for 50 h. The effects of supporting electrolyte, pH, applied bias potential and BPA concentration were evaluated as to their effect on the BPA degradation kinetics and the best condition was found to be 0.1 M Na$_2$SO$_4$ at pH 6 as supporting electrolyte and applied bias potential of +1.5 V vs. Ag/AgCl under UV irradiation. Our findings indicate that TiO$_2$ NTAs prepared by anodization are versatile and efficient photocatalysts for the degradation of endocrine disruptors.

1. Introduction

Bisphenol A (BPA), 2,2-bis-(4-hydroxyphenyl)propane or 4,4-isopropylidenediphenol, is an estrogen mimic that induces hormonal response even at low dose exposures and can promote imbalance in the endocrine system. This chemical has been commercialized for more than 50 years as an important monomer precursor for the production of various polycarbonate, polysulphone plastics and epoxy resins (Alexander et al., 1988). It can be found in natural water as a consequence of untreated industrial effluent and it is very dangerous in the aquatic ecosystem due to role as an estrogen receptor agonist. Therefore, regulatory laws have limited its presence in surface waters to limits around 1.0–15.0 μg mL^{-1} (Ahel et al., 1994; Blackburn and Waldock, 1995; Rosenfeldt and Linden, 2004).

Various chemical and physical treatment processes are currently proposed for BPA removal. Most conventional methods for the removal of this pollutant such as adsorption on activated carbon, ultrafiltration, and reverse osmosis are non-destructive and merely transfer pollutant from one phase to the other (Gupta et al., 2004; Jain et al., 2004). Biodegradation has also been tested (Lobos et al., 1992; Spivack et al., 1994; Ike et al., 2000; Ronen and Abeliovich, 2000; Kang and Kondo, 2002; Kang et al., 2004; Sasaki et al., 2005; Yamanaka et al., 2008) but the method is slow and low BPA degradation activities of most strains are insufficient to permit their use as a practical BPA removal system.

Ozonation (Lee et al., 2003; Alum et al., 2004; Lenz et al., 2004; Irmak et al., 2005; Kamiya et al., 2005) and photo-Fenton (Gözmen et al., 2003; Katsumata et al., 2004; Ioan et al., 2007) have been investigated, but the relative inefficiency to remove Bisphenol A down to permitted limits has limited their applicability. Alternative methods based on heterogeneous photocatalysis, which rely on the generation of hydroxyl radicals for environmental remediation, have been employed for the treatment of BPA in wastewaters (Terzian et al., 1991; Linsebigler et al., 1995; Hofmann et al., 1995; Ohko et al., 2001; Zhang et al., 2003; Chiang et al., 2004; Kaneco et al., 2004; Lee et al., 2004; Coleman et al., 2005; Xie and Li, 2006). The results are satisfactory but the method requires at least 4 h to remove a maximum of 95% of Bisphenol A. Taking into account that this kind of endocrine disruptor can be harmful even at very low concentration the demand for efficient methods able to remove traces of such compounds remain a challenge.

An attractive strategy to increase the photocatalytic efficiency consists of introducing a reverse bias potential to the anode coated by the photocatalyst. Examples of such photoelectrocatalytic oxidation of organic dyes are available (Byrne et al., 2002; Waldner and Krýsa, 2005). To increase this efficiency several authors have used photoelectrocatalysis on anodically grown self-organized TiO$_2$ nanotubes (Zwilling et al., 1999; Krýsa et al., 2005; Xie, 2006; Macak et al., 2007a,b; Osugi et al., 2008). These nanotubes can be prepared by anodic oxidation of Ti substrate (essentially in any form, e.g., as sheet, foil, wire, etc.) in fluoride containing

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electrolytes (Zwilling et al., 1999) and while growing they remain attached on the substrate. By tailoring the electrochemical conditions, nanotube layers with thickness in the range of few hundreds of nm up to few hundreds of mm can be synthesized using this electrochemical approach (Zlamal et al., 2007). The diameter of the nanotubes can be varied in the range of 20–300 nm (Zlamal et al., 2007). The large surface area of the nanotubular array (NTA) structure and the vectorial charge transport can enhance the efficiency of light energy conversion and maximize the number of photogenerated electron–hole pairs. Therefore, higher photoelectrocatalytic efficiency has been observed (Osugi et al., 2008; Ghicov and Schmuki, 2009).

In this work, we report the photoelectrocatalytic degradation of BPA using self-organized TiO_2 NTA electrodes made by anodization. The Bisphenol A degradation kinetics parameters have been evaluated through spectrophotometry (UV–Vis), liquid chromatography with diode array optical detection (HPLC–DAD) techniques and total organic carbon (TOC) removal to assess the effectiveness of this remediation approach.

2. Experimental

2.1. Preparation of TiO_2 NTA electrode

Titanium foil (Goodfellow Cambridge Ltd., 0.5 mm thick, 99.6%) was used as the substrate for growth of the oxide NTAs. Strips (5 cm × 5 cm) were cut and mechanically polished using abrasive papers of successively finer roughness (400, 600 and 1200 grit). After, the Ti surfaces were polished, they were cleaned in three 15 min steps in ultrasonicated acetone, ethanol and finally ultrapure water before drying in flowing N_2 stream. The cleaned strips were used immediately. Anodization was performed in a two-electrode cell configuration with the treated Ti sheet serving as anode and a platinum (Pt) foil as cathode, and both were placed in a solution of 0.25 wt.% NH_4F and a mixture of glycerol and water (ratio 90:10 vol.%). The anodization was performed at a constant voltage of 20 V for 50 h. The freshly generated TiO_2 NTA electrode was then rinsed with distilled water and dried in air. Finally, the photoelectrode was fired at 450 °C during 30 min in a muffle oven of controlled temperature.

2.2. Apparatus and procedure

The photoelectrocatalytic oxidation experiments were performed in a 250 mL photoelectrochemical reactor equipped with water refrigeration using an ultra-thermosthatic bath (Nova Técnica, Brazil). The cell was equipped with a working electrode, an auxiliary electrode, Pt gauze, and Ag/AgCl (KCl, 3 M) reference electrode. The photoactive area of the TiO_2 NTA anode was 25 cm^2 and it was illuminated with UV light source (315–400 nm) using a 125 W Philips medium pressure mercury lamp ($I = 9.23\ W\ m^{-2}$) without the glass, inserted in a quartz bulb. The BPA aqueous solution was placed in the reactor and the photoelectrochemical process was carried out by bubbling compressed air. An Autolab PGSTAT-300 potentiostat/galvanostat (Eco Chemie) controlled by General Purpose Electrochemical System (GPES) software (Eco Chemie) was used to bias the photoanode in the photoelectrocatalytic oxidation experiments.

The concentration of the BPA (Aldrich) in the solution was monitored by measuring the absorbance of samples of the BPA solution at controlled time using a Hewlett Packard 8453 spectrophotometer operating from 190 to 1000 nm in a quartz cell. Total organic carbon was monitored using a total organic carbon analyzer (Shimadzu 5050A).

A Shimadzu Model 10AVP high performance liquid chromatograph (HPLC) equipped with a photodiode array detector and a SIL-10ADVP auto sampler was used for chromatographic analysis of the treated samples. The separation column used was ODS (250 × 4.6 mm, 5 μm) and the mobile phase (acetonitrile/water (50:50 v/v) flowing at 0.8 mL min^{-1} was used to separate and identify products and intermediates of the BPA oxidation. All chemical reagents were HPLC grade. Elution was monitored in the UV portion of the spectrum and quantifications were performed with the UV detector operating at 227 nm.

All pH measurements were carried out using a combined glass electrode (Orion, Thermo Electron Corporation) connected to a digital pH meter (Orion, Thermo Electron Corporation). The de-ionized water was purified with a Milli-Q system (Model Simplicity 185, Millipore).

3. Results and discussion

3.1. Characteristics of the photoanode

Fig. 1a shows SEM images of the TiO_2 NTA film, where uniform nanotube growth over the entire substrate can be observed. The average pore diameter from the images is 150 nm with a standard deviation of 10 nm (Macak et al., 2007a; Osugi et al., 2008). The XRD patterns of the TiO_2 NTAs prepared as listed in the experimental section after being annealed at 450 °C under ambient air for 30 min is shown in Fig. 1b. For comparison, the pattern of pure titanium metal is also presented. The diffraction peaks at about 2θ in 25.5°, 37.3°, 38.1°, 48.2°, 54.2° and 55.2° can be indexed to the (1 0 1), (1 0 3), (0 0 4), (2 0 0), (1 0 5), and (2 1 1) crystal faces of anatase TiO_2 on the NTA electrode, respectively. Taking into consideration that this crystalline phase presents higher photoactivity than rutile form, it is reasonable to indicate that the electrode was successfully prepared.

The photoactivity was evaluated recording photocurrents for TiO_2 NTA electrodes under UV irradiation in 0.1 M Na_2SO_4 by recording linear scan voltammograms at 10 mV s^{-1}, as shown in Fig. 2. Typically, under UV irradiation, an n-type semiconductor electrode such as TiO_2 produces a high anodic photocurrent (curve II) at potentials positive to the flat band potential, which is not observed in the dark (curve I). In the same figure, it is also shown the effect of BPA addition increasing from 1.0×10^{-6} to 1.0×10^{-4} M (curves (II–V)).

The flat band potential (E_{fb}) for the nanotube TiO_2 in sulfate was calculated using the Butler equation (Butler, 1977): $I_{ph}^2 = (2q\varepsilon\varepsilon_0 I_0^2\alpha^2/N_d)\ (E\text{–}E_{fb})$; where I_{ph} = photocurrent density, q = electron charge, ε = dielectric constant, ε_0 = permittivity of free space, I_0 = photon flux, α = absorption coefficient, N_d = effective density of states at the conduction band edge, E = bias potential and E_{fb} = flat band potential. A plot of the square of the photocurrent vs. potential produces a straight line with intercept at E_{fb}. Fig. 2b shows the plot obtained for TiO_2 nanotubular array electrode in 0.1 M Na_2SO_4, whose intercept indicates a constant value at E_{fb} = 0.168 V vs. SCE.

It is well known that the shape of the photocurrent voltammograms reflects the balance between the recombination of electron–hole pairs and substrate photooxidation (Zanoni et al., 2003; Rajeshwar et al., 2008). By applying an anodic bias potential to a working electrode, we provide a potential gradient within the photocatalyst film to efficiently force the electrons to arrive at the counter electrode and leave photogenerated holes to react with H_2O/OH^- to give rise to $OH^\cdot$ radicals. However, the higher photocurrent observed in presence of Bisphenol A could be indicative that adsorbed Bisphenol A could be more effective due to direct capture of the photogenerated holes (Rajeshwar et al., 2008). This pathway should be thermodynamically feasible because the redox