

Electrochemical enhancement of solar photocatalysis: Degradation of endocrine disruptor bisphenol-A on Ti/TiO₂ films

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Introduction

Bisphenol-A (BPA) has been widely used as raw material in the manufacture of numerous chemical products, such as polycarbonate plastics and epoxy resins. Because of its wide usage and its endocrine disruption effects, BPA has been regarded as a representative material among endocrine disruptors and causes reproductive damage to aquatic organisms.

In recent years, there have been intensive efforts towards the development of efficient technologies for the removal of persistent xenobiotics from aqueous matrices. In this perspective, advanced oxidation processes are likely to play a key role and several recent studies have dealt with BPA degradation by ozonation [1], ultrasound irradiation [2], dark- [3] and photo-Fenton [4] oxidation, electrochemical oxidation [5], as well as various hybrid processes [6]. The scope of this work was to investigate BPA degradation by solar photoelectrocatalysis on Ti/TiO₂ films and compare its efficiency with photocatalysis (PC) and electrochemical oxidation (EO). **The effect of various operating conditions such as applied current, BPA concentration, catalyst loading, solution pH and the water matrix on kinetics has been examined.**

Experimental

Photoelectrochemical experiments were performed using a solar simulator (Oriel, model 96000) equipped with a 150 W xenon, ozone free lamp in an open cylindrical pyrex cell at ambient conditions under continuous stirring. Current in the range 0.02-0.32 mA/cm² was applied using a galvanostat with the Ti/TiO₂ film operating as the anode, while a zirconium plate was used as the cathode. In a typical experiment, the appropriate amount of BPA was dissolved in ultrapure water and the resulting solution (in the range 120-820 µg/L BPA) was added 5 mM HClO₄ as the supporting electrolyte; sixty mL were then introduced in the reaction vessel and left for 20 min in the dark to equilibrate prior to applying solar irradiation and/or current. To assess the effect of water matrix, experiments were also conducted with BPA spiked in the treated effluent (TE) taken from the municipal wastewater treatment plant of Chania, W. Crete, Greece. The effluent had 8.4 mg/L of dissolved organic carbon, while its pH and conductivity was about 8

and 0.81 mS/cm, respectively.

Analysis of remaining BPA in solution has been achieved with the use of HPLC.

The catalyst, consisting of 75:25 anatase:rutile, was prepared by a sol-gel method and characterized by cyclic voltammetry, X-ray diffraction and scanning electron microscopy.

Results/Discussion

The degradation of bisphenol-A, an emerging aqueous phase pollutant, has been investigated by means of solar irradiation over fixed Ti/TiO₂ catalysts enhanced by the simultaneous application of an electric field. Experiments were conducted to assess the effect of applied current (0.02-0.32 mA/cm²), TiO₂ loading (1.3-9.2 mg), BPA concentration (120-820 µg/L), initial solution pH (1 and 7.5) and the aqueous matrix (pure water and treated effluent) on BPA photoelectrocatalytic degradation. The reaction was favored at anodic currents up to 0.04 mA/cm² and lower substrate concentrations, but it was hindered by the presence of dissolved species in treated effluents. Moreover, a pseudo-first order kinetic model could fit the experimental data well with the apparent reaction constant taking values between 2.9 and 32.4 10⁻³/min. The degradation of BPA by pure photocatalysis or electrochemical oxidation alone was also studied leading to partial substrate removal. In all cases, the contribution of applied potential to photocatalytic degradation was synergistic with the photocatalytic efficiency increasing between 24% and 97% possibly due to a more efficient separation and utilization of the photogenerated charge carriers.

References.

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