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Solar photocatalytic decomposition of ethyl paraben in zinc oxide suspensions

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ABSTRACT

The photocatalytic degradation of ethyl paraben (EP) in zinc oxide (ZnO) suspensions under simulated solar radiation was investigated. The effect of EP concentration (500–1500 $\mu\text{g/L}$), ZnO concentration (100–500 mg/L), reaction time (3–9 min), initial pH (3–9), light intensity ($7.3 \cdot 10^{-7}$ – $1.1 \cdot 10^{-6}$ einstein/(L.s)) and the water matrix (0–10 mg/L of humic acid) on degradation was evaluated implementing a factorial design methodology. Of the six variables tested, EP concentration, ZnO concentration, reaction time and the water matrix were found to be statistically significant variables, and also important was the second order interaction of EP concentration with reaction time. With the exception of the water matrix, all other effects were positive with respect to the concentration of EP removed.

Experiments at increased EP concentration (20 mg/L) were performed to identify transformation products (TPs) and assess the extent of mineralization. LC-TOF-MS analysis revealed the formation of seven early-stage TPs through hydroxylation and dealkylation reactions and a plausible reaction pathway was proposed. Besides the identified TPs, other unidentified TPs were also formed as has been verified measuring the extent of mineralization and performing a carbon balance in the liquid phase. EP at 20 mg/L exhibited mild estrogenic activity, which was partially removed upon oxidation. The stability of ZnO was evaluated measuring the extent of zinc leaching, which was just 1.5%; moreover, ZnO was found to be more active than reference P25 TiO₂ for EP degradation and mineralization.

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1. Introduction

Semiconductor photocatalysis induced by solar light has recently been regarded as a sustainable technology for water/wastewater treatment, with emphasis on the removal of priority micro-contaminants of emerging concern [1]. There is little doubt that TiO₂ has attracted significant interest due to its potential use in a variety of photo-induced processes, although its efficiency for solar-driven applications is limited; this is due to its relatively large band gap energy (3.0–3.3 eV) [2], i.e. it can only absorb UV photons, which account for less than 5% of the total solar radiation that reaches the earth's surface. Yet, titania is by far the most extensively investigated photocatalyst due to

its relatively high quantum yield, low cost, elevated stability and availability.

This said, other semiconductors have also been tested for photocatalytic water remediation; of these, ZnO, whose band gap energy and photocatalytic mechanism are similar to that of TiO₂ [3], exhibits most of titania's beneficial features possibly with the exception of stability due to photo-corrosion [4]. In several cases, ZnO has shown comparable or even better performance than TiO₂ for the degradation of various contaminants [5–10].

Parabens, esters of 4-hydroxybenzoic acid with an alkyl (from ethyl to butyl) or benzyl group, have been employed for about a century as preservatives in foodstuff, cosmetics and pharmaceuticals and personal care products. Despite their wide usage, they have only recently been considered as potentially harmful micro-contaminants due to their (i) continuous release in aquatic environments and detection at ng/L to $\mu\text{g/L}$ levels [11], (ii) ecotoxicity to various microorganisms [12], and (iii) mild estrogenicity [13]. In light of this, it is not surprising that the advanced oxidation

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of parabens has received little attention and this is particularly true for photocatalytic processes. Velegraki et al. [14] studied the degradation of methyl paraben in P25 TiO₂ suspensions elucidating the effect of various conditions on kinetics, transformation products and ecotoxicity, while Atheba et al. [15] employed immobilized TiO₂ for the degradation of butyl paraben. Our group recently investigated the photocatalytic degradation of ethyl paraben in N-doped TiO₂ suspensions, emphasizing on the effect of annealing temperature during catalyst synthesis, as well as various operating conditions (i.e. catalyst and paraben concentration, pH, water quality) on kinetics [16].

In this work, the photocatalytic degradation of ethyl paraben (EP) by simulated solar radiation and in the presence of ZnO was investigated. The effect of various operating conditions (i.e. EP and ZnO concentration, reaction time, initial solution pH, water matrix and radiation intensity) was evaluated implementing a factorial design approach. Moreover, major transformation products (TPs) were identified, based on which a reaction pathway is proposed. The extent of mineralization, as well as ZnO stability and estrogenicity were also assessed. To the best of our knowledge, this is the first report on parabens degradation by the proposed photocatalytic system.

2. Materials and methods

2.1. Materials

Zinc oxide was supplied by Alfa Aesar (CAS no: 1314-13-2, specific surface area 4 m²/g, primary particle size 33 nm), while Degussa (now Aeroxide) P25 TiO₂ by Sigma-Aldrich (CAS no: 13463-67-7, specific surface area 42 m²/g, primary particle size 23 nm). Ethyl paraben (EP) (HO–C₆H₄–CO–O–CH₂CH₃, CAS no: 120-47-8) was supplied by Sigma-Aldrich and used as received. Two water matrices were employed, i.e. ultrapure water (UPW, pH=6.5) taken from a water purification system (EASYPureRF-Barnstead/ThermoFisher, USA), and humic acid (HA) (Sigma-Aldrich, CAS no: 1415-93-6) added in UPW at 10 mg/L. Sulfuric acid or sodium hydroxide was used, as needed, to adjust the initial solution pH of about 6 to acidic or alkaline conditions.

2.2. Photocatalytic experiments

Slurry photocatalytic experiments were conducted in an open-to-air, glass, cylindrical vessel containing 120 mL of the reaction mixture under magnetic stirring at ambient conditions. Prior to irradiation, the suspension was left for 15 min in the dark to equilibrate. The vessel was irradiated from the top using a solar simulator (Oriel, model LCS-100) equipped with a 100 W xenon, ozone-free lamp and an Air Mass 1.5 Global Filter cutting radiation <280 nm. The spectral output of the lamp was from 200 nm to approximately 2400 nm and the simulated radiation contained about 5% UV-A and 0.1% UV-B, according to the data provided by the manufacturer. The incident radiation intensity in the UV region of the electromagnetic spectrum was measured using ferrioxalate as the chemical actinometer [17] and it was found to be 7.3 10⁻⁷ and 1.1 10⁻⁶ einstein/(L.s) when the distance between the lamp and the vessel was 20 and 16 cm, respectively.

2.3. Analytical methods

2.3.1. Concentration of ethyl paraben, total organic carbon (TOC), leached zinc and estrogenicity

EP concentration was followed by high performance liquid chromatography (HPLC: Alliance 2695, Waters) according to the protocols described in Ref. [16].

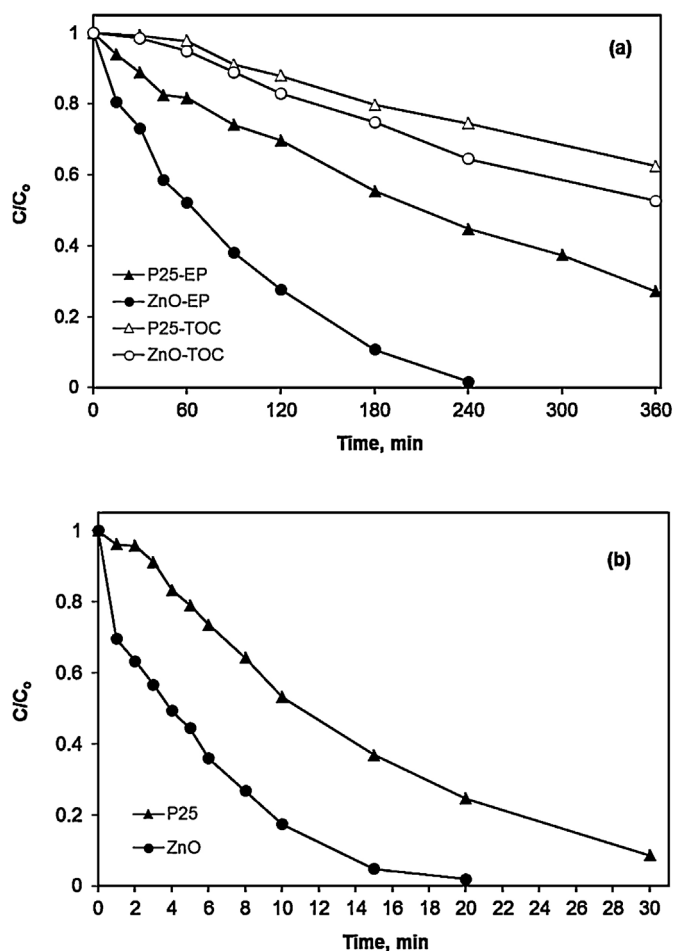


Fig. 1. Comparison between ZnO and P25 TiO₂ for the degradation and mineralization of EP. (a) 20 mg/L EP and 1 g/L photocatalyst; (b) 1 mg/L EP and 250 mg/L photocatalyst. Other conditions: UPW, inherent pH, 1.1 10⁻⁶ einstein/(L.s).

Total organic carbon (TOC) was measured with an Aurora 1030 W analyzer.

The concentration of zinc dissolved in the liquid phase was determined by atomic absorption using a Perkin-Elmer AAS-800 spectrophotometer.

The yeast estrogen screening (YES) assay using the yeast *Saccharomyces cerevisiae* was carried out to assess the estrogenicity of EP before and after photocatalytic treatment according to the procedures described in reference [13].

2.3.2. Identification of TPs

Identification and quantification of TPs was carried out on a Dionex Ultra-HPLC system (Thermo Scientific) incorporated to a microTOF Focus II-time of flight mass spectrometer from Brüker Daltonics (Germany). Before analysis, the samples were pre-concentrated by means of solid-phase extraction, as reported previously [16]. Methyl paraben (MP), 4-hydroxybenzoic acid (4-HBA), 2,4-dihydroxybenzoic acid (2,4-DHB) and 3,4-dihydroxybenzoic acid (3,4-DHB), which are commercially available in reference standards, were quantified by calibration curves. The semi-quantification of the hydroxyl-TPs was based on the assumption that they have quite similar ionization efficiency to the parent compound, EP, and consequently similar response to the employed instrumentation. An AcclaimTM RSLC 120 C18 column, 100 mm × 2.1 mm, 2.2 μm particle size (Thermo Scientific), thermostated at 30 °C and protected by a column guard by Waters was used. Chromatographic separation was conducted using a gra-

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