



Kinetics of the photosensitized degradation of benzyl 4-hydroxybenzoate in homogeneous aqueous solution under visible-light irradiation

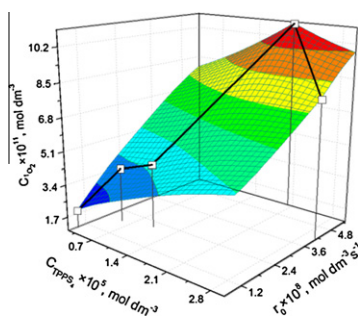
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HIGHLIGHTS

- ▶ Singlet oxygen plays a significant role in photodegradation of benzylparaben (BeP).
- ▶ The formation of a supra-molecular complexes BeP–TPPS₄ were found.
- ▶ The quenching rate constants of singlet oxygen by BeP were determined.
- ▶ The kinetic model has a good agreement with the experimental data at pH 7 and 10.8.

GRAPHICAL ABSTRACT



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ABSTRACT

The photosensitized oxidation of benzyl 4-hydroxybenzoate (benzylparaben, BeP), the endocrine disrupting compound, in homogenous aqueous solution of 4,4',4'',4'''-(porphine-5,10,15,20-tetrayl)tetrakis(benzenesulphonic acid) (TPPS₄) as photosensitizer was examined. A xenon lamp simulating solar radiation was used as a light source. The influence of pH of the reaction mixture, oxygen content and initial concentrations of photosensitizer and BeP on the reaction rate was studied. The major role of singlet oxygen in BeP degradation was proved by the experiments performed in the presence of hydroxyl radicals scavengers and singlet oxygen quenchers. The rate constants of singlet oxygen quenching by BeP in D₂O buffer (pD 7, 9 and 10.8) were determined. Based on the kinetic model, the rate constants of singlet oxygen quenching and reaction with BeP as well as the rate constant of excited photosensitizer quenching by BeP were determined.

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1. Introduction

In recent years pharmaceutical and personal care products (PPCPs) have been detected in diverse environments: sewage effluents, surface, ground and drinking water [1,2]. PPCPs are classified as emerging pollutants of increasing concern due to hazardous impacts on human health and aqueous environment [3,4]. Hydroxybenzoates (parabens, alkyl esters of p-hydroxybenzoic acid) have been manufactured in industry since the 1920s and are used as preservatives in foodstuffs, pharmaceuticals, cosmetics and

personal care products [5]. The aqueous concentration of parabens are in the range 0.01–1 μg dm⁻³, e.g. benzyl 4-hydroxybenzoate (BeP) was detected at concentration 1 μg dm⁻³ in the effluent in Swedish WWTP_s [6] or in Denmark at 0.012 μg dm⁻³ [7]. Many of the endocrine disrupting compounds (EDCs) can cause an estrogenic response at very low concentrations (ppb to ppt) [8]. The estrogenic effects of parabens were extensively investigated [9,10], also the correlation between breast tumors and the use of cosmetics containing parabens have been reported [11]. Therefore parabens are known to be EDCs. The toxicity and estrogenicity tests examined by Bazin and co-workers [3] have shown that benzylparaben is the most toxic and estrogenic compounds of five investigated parabens. Considering the results obtained with

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