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Sonochemical degradation of ethyl paraben in environmental samples: Statistically important parameters determining kinetics, by-products and pathways

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ABSTRACT

The sonochemical degradation of ethyl paraben (EP), a representative of the parabens family, was investigated. Experiments were conducted at constant ultrasound frequency of 20 kHz and liquid bulk temperature of 30 °C in the following range of experimental conditions: EP concentration 250–1250 μg/L, ultrasound (US) density 20–60 W/L, reaction time up to 120 min, initial pH 3–8 and sodium persulfate 0–100 mg/L, either in ultrapure water or secondary treated wastewater.

A factorial design methodology was adopted to elucidate the statistically important effects and their interactions and a full empirical model comprising seventeen terms was originally developed. Omitting several terms of lower significance, a reduced model that can reliably simulate the process was finally proposed; this includes EP concentration, reaction time, power density and initial pH, as well as the interactions (EP concentration) × (US density), (EP concentration) × (pH_o) and (EP concentration) × (time).

Experiments at an increased EP concentration of 3.5 mg/L were also performed to identify degradation by-products. LC–TOF–MS analysis revealed that EP sonochemical degradation occurs through dealkylation of the ethyl chain to form methyl paraben, while successive hydroxylation of the aromatic ring yields 4-hydroxybenzoic, 2,4-dihydroxybenzoic and 3,4-dihydroxybenzoic acids. By-products are less toxic to bacterium *V. fischeri* than the parent compound.

1. Introduction

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 [1]. Several studies published at the turn of the millennium suggested possible estrogenic activity [2,3] and carcinogenic potential [4]. In this respect and although parabens were generally considered harmless to human beings for a long time, several concerns have been raised over the past twenty years about parabens safety with emphasis given on their endocrine disrupting potential [5].

Monitoring campaigns in wastewater treatment plants (WWTPs) in Europe, North America and Japan showed influent concentrations at the ng/L level, although in certain cases these reached the μg/L level [5]. Parabens are not adsorbed in the sludge and mostly remain in the liquid phase where they can be degraded relatively easily but not completely [6]; therefore, WWTPs are considered the major point source of parabens in the environment due to their incomplete removal [5]. Consequently, parabens re-enter the aquatic environment and they are typically found at the ng/L level [1].

Unlike other emerging micro-pollutants, the advanced oxidation of parabens has received considerably less attention possibly due to the facts that (i) suitable detection techniques were only developed in the past 10–15 years [1], and (ii) their adverse effects to living organisms are still arguable. Steter et al. [7] studied the electrochemical oxidation of methyl paraben on boron-doped diamond, while Hernandez-Leal et al. [8] studied the removal of four parabens with C1–C4 alkyl groups by ozonation or activated carbon adsorption in various water matrices. Dobrin et al. [9]

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proposed a hybrid system coupling non-thermal plasma and ozonation to degrade methyl paraben and concluded that the integrated process was more effective than the individual ones in terms of mineralization. Furthermore, several photochemical [10] and TiO_2-based photocatalytic processes [11–13] have also been tested to degrade various parabens.

In recent years, ultrasound irradiation has been widely employed to degrade successfully various micro-pollutants including endocrine disrupting compounds (EDCs) such as bisphenol A [14,15], estrogens [16,17], 4-cumylphenol [18] and phthalates [19]. Nevertheless, the literature on the sonochemical degradation of parabens is very limited consisting only of a couple of recent studies. Sasi et al. [20] investigated the high frequency (200–1000 kHz) sonochemical degradation of methyl paraben with emphasis on the effect of operating variables and the water matrix, while Daghrir et al. [21] reported that the sonochemical degradation of butyl paraben at 518 kHz was enhanced when the system was simultaneously irradiated by UV-C light.

The purpose of this work was to study the low frequency (20 kHz) sonochemical degradation of ethyl paraben (EP) and evaluate the statistically significant parameters that may determine degradation rates implementing a factorial design methodology. Six parameters were tested, namely EP concentration, ultrasound power, reaction time, water matrix, initial pH and the addition of sodium persulfate. Early-stage transformation by-products were also identified and a plausible reaction network was suggested.

2. Materials and methods

2.1. Materials

Ethyl paraben (EP) ($HO–C_6H_4–CO–O–CH_2CH_3$, CAS no: 120-47-8) and sodium persulfate (SPS) ($Na_2S_2O_8$, 99+%, CAS number 7775-27-1) were 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/Thermolyne, USA), and secondary treated wastewater (WW) taken from the university campus treatment plant (pH = 8, COD = 21 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. Ultrasound irradiation

A Branson 450 horn-type digital sonifier operating at a fixed frequency of 20 kHz was employed. Reactions took place in a cylindrical, double-walled, Pyrex vessel, which was open to the atmosphere. Ultrasound irradiation was emitted through a 1 cm in diameter titanium tip which was positioned in the middle of the vessel at a distance of 3 cm from the bottom. The working volume was 0.12 L and the bulk temperature was kept constant at 30 °C with a temperature control unit. The maximum nominal power output of the sonifier was 450 W and the actual energy transmitted to the liquid phase was determined calorimetrically; experiments were performed at actual power densities of 20 and 60 W/L.

2.3. Chromatographic techniques

High performance liquid chromatography (HPLC: Alliance 2695, Waters) was employed to monitor the concentration of EP. Separation was achieved on a Kinetex XB-C18 100A column (2.6 μm, 2.1 mm × 50 mm) and a 0.5 μm inline filter (KrudKatcher Ultra) both purchased from Phenomenex. The mobile phase consisting of 75:25 water:acetonitrile eluted isocratically at 0.35 mL/min and 45 °C, while the injection volume was 40 μL. Detection was achieved through a photodiode array detector (Waters 2996 PDA detector, detection λ = 254 nm).

The evolution of sulfate ions during the process was followed by a Dionex ICS-1500 instrument equipped with an ASRS Ultra II conductivity detector and IonPac AS9-HC anionic column. The mobile phase was an aqueous sodium carbonate (9 mM) solution at a flow rate of 1 mL/min, while the injection volume was 25 μL.

LC–TOF–MS (liquid chromatography-time of flight mass spectrometry) system was applied for the identification of transformation by-products (TBPs) of EP. Prior to analysis, 2 mL of treated solutions were extracted by means of a solid-phase extraction (SPE), reported in our previous work [12], using Oasis HLB (divinyl benzene/N-vinylpyrrolidone copolymer) cartridges (60 mg, 3 mL) from Waters (Mildford, MA, USA). The LC system consisted of an Ultra-High Performance LC pump (Dionex Ultimate 3000, Thermo) incorporating a column thermostat and an autosampler interfaced to a Focus microTOF II – time of flight mass spectrometer (Brüker Daltonics, Germany). The MS part was operated using microTOF control (version 2.0) software. The scan range applied in the full-scan mode was m/z 50–500 at a scan rate 1 Hz. The chromatographic separations were run on a C18 Acclaim™ RSLC, 100 mm × 2.1 mm, 2.2 μm particle size (Thermo Fisher Scientific, San Jose, USA) at 30 °C. The injected sample volume was 10 μL. Mobile phases A and B were water with 0.1% formic acid and acetonitrile, respectively at a flow-rate of 0.2 mL/min. Analysis was performed by ESI source in negative ionization mode. A linear gradient progressed from 5% B (initial conditions) to 99.9% A in 12 min (maintained for 2 min), returned to the initial conditions after 1 min and finally re-equilibration time was set at 3 min. The ESI-source parameters were as follows: dry gas flow rate 8 L/min (nitrogen), nebulizer pressure 2.0 bar, capillary voltage at 3200 V, end plate offset at 500 V, collision cell RF 70.0 Vpp, dry temperature at 220 °C. Prior to analysis, the TOF mass analyzer was externally calibrated using sodium formate, in the scan range m/z 50–1000, to ensure mass accuracy with ±5 ppm. Data were acquired with the HyStar 3.2 software and analysed with Data Analysis 4.1 software package. In addition, chemical formula calculator, included in Data Analysis software was used to provide chemical formula and mass accuracy values. The identification of the majority of the TBPs was also verified by comparison of retention time, high resolution mass and MS spectra to the commercially available standards.

2.4. Acute ecotoxicity

The marine bacterium *Vibrio fischeri* was used to assess the acute ecotoxicity of EP prior to and after sonodegradation. Changes in bioluminescence of *V. fischeri* exposed to EP solutions for 15 min were measured using a LUMIStox analyzer (Dr. Lange, Germany) and the results were compared to an aqueous control.

2.5. Yeast estrogen screening (YES)

The YES assay using the yeast *Saccharomyces cerevisiae* was carried out to assess the estrogenicity of EP according to the procedures described in detail elsewhere [22]. In brief, standard solutions and sample extracts were produced in ethanol and 10 μL of dilution series were dispensed into triplicate wells of 96-well microtiter plates. After evaporation to dryness at room temperature, 0.2 mL of growth medium containing the chromogenic substrate chlorophenol red-b-D-galactopyranoside (CPRG) and the yeast cells were added, followed by incubation at 32 °C for 72 h. Each plate contained at least one row of blanks and a standard curve for 17β-estradiol (E2). During the incubation period, the microtiter plates were shaken at 80 rpm for 2 min to mix and disperse the growing cells. The absorbance of the medium