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Photosonochemical degradation of butyl-paraben: Optimization, toxicity and kinetic studies

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HIGHLIGHTS

- The treatment time and calorimetric power greatly affect the oxidation rate of BPB.
- Their contribution for BPB removal is 45.17% and 22.65%, respectively.
- More than 99% of BPB can be removed using the US/UV process.
- 43.3% of TOC removal was achieved and the toxicity on *V. fisheri* was reduced.
- The BPB degradation is well described by the pseudo-first-order kinetic (0.0367 min^{-1}).

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ABSTRACT

The objective of the present work is to evaluate the potential of a photosonolysis process for the degradation of butyl-paraben (BPB). After 120 min of treatment time, high removal of BPB was achieved by the photosonolysis (US/UV) process (88.0 ± 0.65%) compared to the photochemical (UV) and the conventional ultrasonication (US) processes. Several factors such as calorimetric power, treatment time, pH and initial concentration of BPB were investigated. Using a 2^4 factorial matrix, the treatment time and the calorimetric power are the main parameters influencing the degradation rate of BPB. Subsequently, a central composite design methodology has been investigated to determine the optimal experimental parameters for BPB degradation. The US/UV process applied under optimal operating conditions (at a calorimetric power of 40 W during 120 min and under pH 7) is able to oxidize around 99.2 ± 1.4% of BPB and to record 43.3% of mineralization. During the US/UV process, BPB was mainly transformed into 1 hydroxy BPB, dihydroxy BPB, hydroquinone and 4-hydroxybenzoic acid. Microtox biotests (*Vibrio fisheri*) showed that the treated effluent was not toxic. The pseudo-first order kinetic model (k = 0.0367 min^{-1}) described very well the oxidation of BPB.

1. Introduction

In recent years, the occurrence of toxic organic compounds called endocrine-disrupting compounds (EDCs) in water and wastewater and their fate in aquatic environment are becoming major and global public health issues that need urgent action (Esplugas et al., 2007; Lister and Van Der Kraak, 2001). Parabens (ester of p-hydroxybenzoic acid) are antimicrobial agents; antifungicidal agents and antioxidants widely used in the cosmetic, pharmaceutical and food industries (Gryglik et al., 2009; Tay et al., 2010a, 2010b; Nicoli et al., 2008). Recent studies have shown the estrogenic effect of parabens. Particularly, propylparaben (PPB) and butyl-paraben (BPB) adversely affect the secretion of testosterone and the function of the male reproductive system of rats and mice (Gryglik et al., 2009; Nicoli et al., 2008; Terasaka et al., 2006; Bledzka et al., 2009). It has been proved that

Abbreviations: ANOVA, analysis of variance; AOPs, advanced oxidation processes; BPB, butyl-paraben; CCD, central composite design; EDC, endocrine disrupting compound; ESI, electrospray ionization; FD, factorial design; LC/MS/MS, liquid chromatography/mass spectrometer/mass spectrometer; PPB, propylparaben; RNO, p-nitrosodimethylaniline; ROS, reactive oxygen species; RSM, response surface methodology; TOC, total organic carbon; US, ultrasonication; US/UV, photosonolysis process; UV, photochemical process; WWTPs, wastewater treatment plants.

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parabens are able to easily penetrate the skin (Nicoli et al., 2008; Akomeah et al., 2004; Nanayakkara et al., 2005; El Hussein et al., 2007) and to reach unmodified the underlying tissues and the systemic circulation (Nicoli et al., 2008; Soni et al., 2005). Parabens are frequently found in aquatic environment because of their broad applications (Bledzka et al., 2009; Radovan et al., 2008). In Canada, the concentrations of BPB detected in effluent of wastewater treatment plants (WWTPs) are in the range of 0.01–0.26 μg/L (Lee et al., 2005). It has been shown that conventional WWTPs release organic pollutants such as parabens into the aquatic environment (Bledzka et al., 2009; Kasprzyk-Hordern et al., 2008; Gomez et al., 2008). The presence of these pollutants in water has to be taken into account owing to their potential toxicity for humans. Thus, it is of great importance to develop efficient and cost-effective treatment technologies for the removal of such compounds.

Many techniques are used such as adsorption, biosorption, biological oxidation, chemical oxidation, membrane filtration and advanced oxidation processes (AOPs) (Da Pozzo et al., 2005; Esquivel et al., 2009; Gallard and De Laat, 2001; Tahmasseb et al., 2002). Chemical oxidation using several oxidants (H_2O_2, O_3, etc.) rarely leads to a total mineralization of water contaminants. Biological oxidation is considered to be very economical and widely applicable. However, it seems to be inappropriate in many cases. Physicochemical methods such as membrane filtration and adsorption using activated carbon have been applied to remove refractory organic compounds. The main disadvantage of such methods is that they do not destroy them but rather transfer the pollutant from one phase to another (Tahir and Rauf, 2006; Ozcan et al., 2004; Daghrir et al., 2012a, 2012b).

AOPs (O_3/H_2O_2, UV/O_3, etc.) as well as ultrasonication (US), have been identified as a successful alternative for the destruction and mineralization of some recalcitrant organic compounds in water (Naffrechoux et al., 2000; Nagata et al., 2000; Okitsu et al., 2005; Teo et al., 2001). AOPs are characterized by the generation of the hydroxyl radical species (OH•). These radicals are short-lived and highly reactive chemical species which are able to non-selectively oxidize organic pollutants. Since 1990, US process has received considerable interest to destroy organic pollutants present in wastewater (Petrier et al., 1998; Hao et al., 2004; Wang et al., 2007a; Wang et al., 2011; Pang et al., 2011). The advantages of high calorimetric power are safety, cleanness, high penetrability in water medium, high degradation efficiency and energy conservation with limited generation of secondary pollutants (Wang et al., 2007a; Pang et al., 2011; Wang et al., 2007b). Acoustic cavitation derived from the high calorimetric power of a liquid can provide unusual and unique reaction-sites, which are attributed to extremely transient and small cavitation bubbles with high temperatures and high pressures. Many researchers reported that US process was capable of destroying various recalcitrant organic compounds (Lim et al., 2008; Liu et al., 2009; Ku et al., 2005). However, US alone is not generally deemed to be attractive for large-scale application because they require costly equipment and consume a high amount of energy. From this point of view, it can be interesting to develop photosonolysis (US/UV) techniques combining US and photochemical (UV) processes. This approach offers the possibility to enhance the degradation rate of pollutants (Naffrechoux et al., 2000; Shirgaonkar and Pandit, 1998). Coupling US and UV processes promotes the generation of high amounts of free OH• available to react with pollutants. Shirgaonkar and Pandit (1998) reported that the degradation rate of 2,4,6-trichlorophenol could be increased when US process combined with UV is applied, whereas Naffrechoux et al. (2000) observed an important enhancement of the degradation rate of phenol by combining US and UV processes.

The aim of the present study is to evaluate the performance of the US/UV process using ultrasonication and UV irradiations for the efficient treatment of waters contaminated by BPB. To this end, an experimental design methodology (Myers and Montgomery, 2002) was put into place to investigate the influence of the principal experimental parameters (calorimetric power, treatment time, pH and pollutant concentration) on the efficiency of the US/UV process for BPB degradation. A second objective of this study was to use a statistical methodology for a rational analysis of the combination of operational factors that led to the best treatment process. Besides, the specific objectives of the present work consist to study the kinetics of BPB degradation, to propose a mechanism (reaction pathway) for BPB degradation based on the identified by-products and to verify the quality of treated effluent (versus untreated effluents) in terms of toxicological effect.

2. Materials and methods

2.1. Chemicals

Butyl-paraben (butyl-parahydroxybenzoate; $C_{11}H_{14}O_3$) was an analytical grade reagent supplied by Sigma Aldrich (purity >99%). The physico-chemical proprieties of BPB are summarized in Table 1 (Nicoli et al., 2008; Regueiro et al., 2009). BPB stock solution was prepared in deionized water at 100 mg/L and kept at 4 °C. Synthetic solution of BPB was made by diluting the BPB stock solution in deionized water. The initial pH of BPB solution was adjusted using sodium hydroxide (Fisher Scientific).

2.2. Experimental device

The sono-photochemical reactor unit (65 cm (height) × 8 cm (diameter)) used in the present work had 4 L of capacity and was made of Pyrex glass material (Fig. 1). The reactor was equipped with a traducer (a piezoelectric disk having a 4.0 cm diameter) operated at 518 kHz and 10 to 50 W calorimetric power and equipped with a mercury lamp of 6.9 mW/cm^2 photonic power at 254 nm. The lamp is vertically installed in the reactor and was entirely immersed in the aqueous solution.

2.3. Experimental procedure

The assays were carried out under isothermal conditions (20.0 ± 1 °C) using a working volume of 1.0 L. The reactor temperature was held constant using a Polysta cooling/heating recirculator (Cole-Parmer Canada Inc.). Before each assay, the synthetic solution of BPB was prepared in a 2.0 L beaker and was mixed using a Teflon-covered stirring bar installed at the bottom of the beaker. Then, the synthetic BPB solution was transferred into the sono-photochemical reactor unit where the mixing was ensured by the cavitation bubbles. The initial pH of BPB solution (from 5.50 to 11.50) was adjusted using sodium hydroxide (NaOH, 2.5 10^{-3} mol/L). Three different types of treatment were applied for BPB degradation: (i) application of UV alone with the lamp entirely immersed; (ii) application of US alone; and (iii) coupling US and UV with the lamp totally immersed in the liquid. The photochemical degradation of BPB was carried out in the ultrasonication reactor when the power supply of ultrasounds was switched off. During the experiments, the pH was monitored but not controlled. Samples were withdrawn at various time intervals for the analysis of residual concentration of BPB.

Response surface methodology (RSM) was then applied to evaluate and determine the optimum operating conditions using US/UV. RSM is a collection of mathematical and statistical methods for modeling and optimizing and analyzes a treatment process in which the response can be influenced by several variables (Zaroual et al., 2009). Both FD and CCD methodologies are widely used in RSM. FD was used in order to evaluate the main and interaction effects of the factors on the degradation of BPB. Subsequently, CCD was employed to optimize the photosonolysis process in BPB degradation. The variables investigated in our study were: the calorimetric power (X_1), treatment time (X_2), pollutant concentration (X_3) and initial pH (X_4). BPB degradation efficiency was considered as response (Y). The values of different variables were selected based on the preliminary assays. Analysis of variance