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

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H I G H L I G H T S

- 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}).

A R T I C L E I N F O

Keywords:

Photosonolysis

Butyl-paraben

Response surface methodology

Wastewater treatment

A B S T R A C T

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 ($88.0 \pm 0.65\%$) 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 $99.2 \pm 1.4\%$ 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 ($k = 0.0367 \text{ min}^{-1}$) described very well the oxidation of BPB.

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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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

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; Tahmassebi et al., 2002). Chemical oxidation using several oxidants (H₂O₂, O₃, 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 (O₃/H₂O₂, UV/O₃, 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 photolysis (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; C₁₁H₁₄O₃) was an analytical grade reagent supplied by Sigma Aldrich (purity >99%). The physico-chemical properties 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

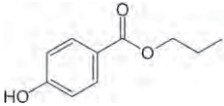
The sono-photochemical reactor unit (65 cm (height) × 8 cm (diameter)) used in the present work had 4 L of capacity and was made of Pyrex glass material (Fig. 1). The reactor was equipped with a transducer (a piezoelectric disk having a 4.0 cm diameter) operated at 518 kHz and 10 to 50 W calorimetric power and equipped with a mercury lamp of 6.9 mW/cm² 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 photolysis process in BPB degradation. The variables investigated in our study were: the calorimetric power (X₁), treatment time (X₂), pollutant concentration (X₃) and initial pH (X₄). BPB degradation efficiency was considered as response (Y). The values of different variables were selected based on the preliminary assays. Analysis of variance

Table 1
Chemical properties of butyl-paraben.

Molecule	CAS number	Molecular formula	Chemical structure	Molecular weight (g/mol)	Solubility (mg/L)	pK _a	Log K _{OW}	Vapor pressure (mm Hg at 25 °C)
BPB	94-26-8	C ₁₁ H ₁₄ O ₃		194.23 ^a	158 ^b	8.47 ^a	3.57 ^b	3.56 10 ⁻⁴

^a Regueiro et al. (2009).

^b Nicoli et al. (2008).

(ANOVA) is a statistical method used to analyze graphical data and to obtain the interactions between the variables and the response. It is an extremely important method in exploratory and confirmatory data analyses. Regression coefficient of linear, quadratic, and interaction involved in the model and their effects were analyzed by ANOVA, all the terms in the model were tested by student's F-test and the significance of the F-values at probability levels ($p \leq 0.05$) was analyzed (Thirugnanasambandham et al., 2014; Prakash Maran et al., 2013). The experimental data were analyzed with statistical analyses such as the determination coefficient (R^2). All the statistical analyses of the experimental data were done with the help of the Design Expert 7.1 program software (Design Expert 7, 2007, Stat-Ease Inc., Minneapolis) and the developed mathematical models were used for the construction of three dimensional (3D) response surface plots in order to predict the relationships between independent and dependent variables.

2.4. Analytical details

2.4.1. Operating parameters and organic measurements

The pH was determined using a pH-meter (Fisher Acumet model 915) equipped with a double-junction Cole-Parmer electrode with an Ag/AgCl reference cell. Total organic carbon (TOC) measurements were performed using a Shimadzu TOC 5000A analyzer (Shimadzu Scientific Instruments Inc.) equipped with an autosampler.

2.4.2. Measurements of BPB concentrations

The progress of BPB degradation in the solution was firstly monitored by the measurements of absorbance using a UV-visible absorption spectrophotometer (UV 0811M136, Varian, Australia). The maximum absorption peak of the BPB solutions was measured at the wavelength

of 256 nm using an optical quartz cell (1 cm). A calibration curve of known BPB concentration versus absorbance was used to calculate the residual BPB concentrations. Likewise, the photolysis degradation of BPB and by-products was monitored and quantified by LC/MS/MS (Thermo TSQ Quantum Access). The chromatographic column used was BetaBasic-C18 (100 mm \times 2.1 mm \times 3 μ m). The isocratic mobile phase was A: 20% H₂O + 0.1% ammonium acetate and B: 80% CH₃OH + 0.1% ammonium acetate at a flow rate of 200 μ L/min. Mass spectral data shown in this study were acquired on an LCQ Duo ion trap tandem mass spectrometer equipped with an electrospray ionization (ESI) source operated in negative ion mode. Nitrogen was used as a sheath and auxiliary gas. Working conditions were as follows: spray voltage was 3000 V and capillary temperature was 390 °C.

2.4.3. Measurements of ROS concentrations

The rate of ROS (reactive oxygen species) production was monitored by absorbance measurements of p-nitrosodimethylaniline (RNO) at 440 nm using an UV-visible absorption spectrophotometer (UV 0811M136, Varian, Australia) (Simonsen et al., 2010). RNO is an organic dye molecule having a strong yellow color in aqueous solution and is easy to detect using UV-visible absorption spectroscopy (Muff et al., 2011). RNO is bleached selectively by oxidation with hydroxyl radicals and does not react with singlet oxygen (¹O₂), superoxide anions (O₂⁻) or other peroxy compounds (Simonsen et al., 2010; Muff et al., 2011). The bleaching rate was monitored by the absorbance measurements. The RNO calibration curve was obtained by plotting the RNO absorbance at 440 nm as a function of RNO concentrations (from 0.0 mg/L to 8 mg/L). The ROS (including OH•, H₂O₂, and O₃) production rate is equal to the RNO disappearance rate. The detail of this analytical method is well described elsewhere (Daghrir et al., 2013).

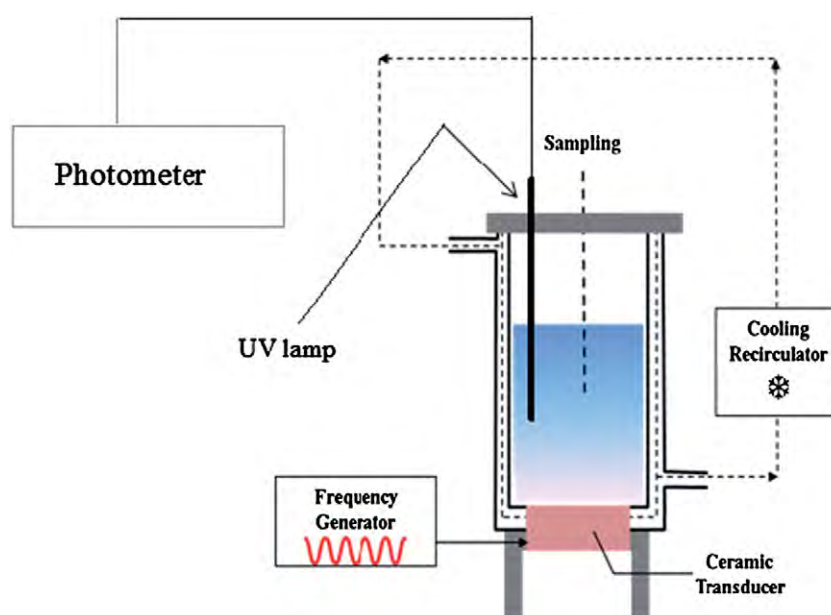


Fig. 1. Schematic view of the sono-photochemical reactor unit.

2.4.4. Aquatic toxicity tests

The quality of treated BPB solution (versus untreated BPB solution) has been evaluated using a biotest in order to determine its toxic effects. Microtox bioassay test was carried out in duplicate by Exova Laboratory (Quebec, Quebec, Canada). Microtox analysis is a standardized toxicity method using the luminescent marine bacteria, *Vibrio fischeri* (Software MTX6, version 6.0, Microbics Corporation). The endpoint of Microtox test is the measurement of bioluminescence reduction. The effects of toxicity were expressed as the percentage of luminescence inhibition at 15 min of exposure.

2.5. Economic aspect

The economic study included energy consumption. The electric cost was estimated at about 0.06 US\$/kWh. The total cost was evaluated in terms of US dollars spent per cubic meter of treated solution (US\$/m³).

3. Results and discussions

3.1. Preliminary investigation of the BPB degradation

Preliminary experiments using direct photolysis (UV alone), ultrasonication (US alone) and photo-sonochemical processes were carried out in order to compare the BPB degradation efficiencies. This set of experiments was conducted by imposing a treatment time of 120 min. As it can be seen from Table 2, the percentage of BPB removal recorded using UV process was 61.3 ± 2.27%, whereas 60.0 ± 3.29% of BPB degradation was recorded using US alone at 40 W of calorimetric power. By comparison, a relatively high percentage of BPB removal (88.0 ± 0.65%) was obtained over 120 min at 40 W of calorimetric power when ultrasonication was combined with UV irradiation. It was advantageous to use the US/UV system (in terms of BPB removal) compared to US or UV applied alone. The UV irradiations absorbed by H₂O molecules induce the appearance of powerful oxidizing species such as H₂O₂ and OH• (Kim and Tanaka, 2009; Heit et al., 1998). Several authors argued that hydroxyl radicals (OH•) can also be formed during direct photolysis using a UV lamp operated at a wavelength of 254 nm (Kim and Tanaka, 2009; Heit et al., 1998; Dagher et al., 2012a, 2012b). The photo-degradation of pollutants (theophylline, diclofenac, clarithromycin, diclofenac) was recorded by Kim and Tanaka (2009) while using a UV lamp at a wavelength of 254 nm. It is worth underlining that, during photolysis the degradation of pollutants can be recorded owing to the transformation induced by bond breaking upon radiation absorption. The degradation percentage of BPB increased when the calorimetric power increased during US process. After 120 min of US treatment, BPB degradation percentage passed from 12.29 ± 1.13% to 60.02 ± 3.29% by increasing the calorimetric power from 10 W to 40 W, respectively. The high acoustic energy applied during the US process ensures the generation of physical and chemical processes (Suri et al., 2007). The physical processes (direct effect) result from the creation of cavitation bubbles, which ensure high mechanical shear stress that is exerted on the pollutant in the solution.

Cavitation bubbles implode generating extreme temperature that could induce pyrolysis of the pollutant (thermal bond breaking at high temperature) (Suri et al., 2007). Besides, the sonochemical degradation of BPB (indirect effect) is caused by the generation of high amounts of ROS such as OH•, which ensure the oxidation of pollutant in the bulk solution (Suri et al., 2007; Behnajady et al., 2008). When ultrasonication treatment was combined with UV irradiation, a higher oxidation percentage of BPB (88.0 ± 0.65%) has been obtained over 120 min at 40 W of calorimetric power. The same trend has been recorded by Wu et al. (2001) and Hamdaoui and Naffrechoux (2008) while applying photolysis process to degrade trichloroacetic acid and 4-chlorophenol, respectively. This enhancement in the BPB degradation by associating ultrasound and UV can be explained by the combination of two oxidation mechanisms: photodecomposition and sono-decomposition. The effect of both UV radiation and ultrasound cavitation on BPB degradation can be explained by the high amount of ROS (OH•, H₂O₂, and O₃) in situ produced, direct photolysis and possibly high thermal degradation. The ROS production rate was estimated to be 17.31 10⁻³ mM h⁻¹. In addition to OH• produced directly by UV and US processes, H₂O₂ produced by ultrasounds could be decomposed into OH• under UV radiation (Hamdaoui and Naffrechoux, 2008). Finally, the US/UV process appears to be much more effective for BPB oxidation than UV and US alone. Thus, US/UV process was selected for the next step of this study dealing with factorial design methodology.

3.2. Effect of the experiment parameters on the BPB degradation using the experimental factorial design methodology

The results presented above allowed us to clearly define the experimental region for RSM to study BPB degradation using the US/UV process. The influence of different variables: calorimetric power (X₁), treatment time (X₂), pH (X₃) and pollutant concentration (X₄) on the BPB removal was investigated using factorial matrix (2^k; k = 4). In this type of design, variables (k) are set at two levels (minimum) and (maximum) normalized as (-1) and (+1). The experiment region investigated for BPB degradation and the experimental results are presented in Table 3. With such a design, it is possible to determine the principle effects of each factor and their interaction (Myers and Montgomery, 2002). The experimental response associated to a 2⁴ factorial design (four variables) is represented by a linear polynomial model with interaction, as follows:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}XX_2 + b_{13}X_1X_3 \quad (1)$$

Where Y represents the experimental response (BPB degradation); b₀ represents the mean value of the experimental responses of the 16 assays; X_i the coded variable (-1 or +1); b_i represents the principal effect of each factor i on the response and b_{ij} represents the interaction effect between factor i and factor j on the response. The coefficients of the model were calculated using the half-difference between the

Table 2
BPB removal under various experimental conditions (volume = 1 L).

Processes	Tests	Parameters						BPB removal (%)
		Calorimetric power (W)	Times (min)	Light intensity (mW/cm ²)	Temperature (°C)	pH	Initial BPB concentrations (mg/L)	
UV	T1	-	120	6.9	20	7	20	61.31 ± 2.27
US	T2	10	120	-	20	7	20	12.29 ± 1.13
	T3	20	120	-	20	7	20	38.50 ± 1.66
	T4	30	120	-	20	7	20	53.83 ± 1.07
	T5	40	120	-	20	7	20	60.02 ± 3.29
	T6	20	120	6.9	20	7	20	71.40 ± 1.67
US/UV	T7	40	120	6.9	20	7	20	87.96 ± 0.65

UV: photochemical; US: ultrasonication; and US/UV: photolysis.

Table 3
Experimental region and experimental results from factorial design matrix (2³).

Coded variables (X _i)	Factor (U _i)	Experimental field				U _{i,0}	ΔU _i		
		Min value (-1)		Max value (+1)					
X ₁	U ₁ : Calorimetric Power (W)	20		40		30	10		
X ₂	U ₂ : Treatment time (min)	60		120		90	30		
X ₃	U ₃ : BPB concentration (mg/L)	7		10		8.5	1.5		
X ₄	U ₄ : pH	10		20		15	5		
Experiment number	Experimental design				Experimental plan				Degradation efficacy (%)
	X ₁	X ₂	X ₃	X ₄	U ₁	U ₂	U ₃	U ₄	
1	-1	-1	-1	-1	20 W	60 min	7	10 mg/L	43.3
2	-1	+1	-1	-1	20 W	120 min	7	10 mg/L	71.3
3	-1	-1	+1	-1	20 W	60 min	7	20 mg/L	28.64
4	-1	+1	+1	-1	20 W	120 min	7	20 mg/L	53.12
5	+1	-1	-1	-1	40 W	60 min	7	10 mg/L	61.45
6	+1	+1	-1	-1	40 W	120 min	7	10 mg/L	87.5
7	+1	-1	+1	-1	40 W	60 min	7	20 mg/L	43.97
8	+1	+1	+1	-1	40 W	120 min	7	20 mg/L	70.15
9	-1	-1	-1	+1	20 W	60 min	10	10 mg/L	26.47
10	-1	+1	-1	+1	20 W	120 min	10	10 mg/L	45.09
11	-1	-1	+1	+1	20 W	60 min	10	20 mg/L	17.41
12	-1	+1	+1	+1	20 W	120 min	10	20 mg/L	37.31
13	+1	-1	-1	+1	40 W	60 min	10	10 mg/L	38.83
14	+1	+1	-1	+1	40 W	120 min	10	10 mg/L	65.04
15	+1	-1	+1	+1	40 W	60 min	10	20 mg/L	33.49
16	+1	+1	+1	+1	40 W	120 min	10	20 mg/L	63.05

mean of the response values when the associated coded variable is at level (+1) and the mean of the response values when the associated coded variable is at level (-1). Design-Expert® Program software (Design Expert 7, Stat-Ease Inc., Minneapolis) was used to calculate the coefficient of the polynomial model.

$$Y = 49.13 + 8.81X_1 + 12.44X_2 - 8.29X_3 - 5.74X_4 + 1.06X_1X_2 + 0.46X_1X_3 + 0.47X_1X_4 - 0.65X_2X_3 + 2.72X_3X_4 \quad (2)$$

The value of the regression coefficient R² was 0.993. The coefficient b₀ = 49.13 represents the average value of the response of 16 assays. From Eq. (2), it can be seen that the treatment time (b₂ = +12.44) greatly influenced the rate of BPB oxidation. The rate of BPB oxidation increases on an average of 24.88% (2 × 12.44) when the treatment time goes from 60 to 120 min. The second most important factor on BPB oxidation is the calorimetric power with a positive effect (b₁ = +8.81). The increase of calorimetric power contributes to enhance the rate of BPB degradation. The rate of BPB oxidation increases on an average of 17.62% (2 × 8.81) when the calorimetric power goes from 20 to 40 W. However, the pH (b₃ = -8.29) and pollutant concentrations (b₄ = -5.74) have a negative effect on the BPB degradation. The rate of BPB oxidation decreased on an average of 11.48% (2 × 5.74) when the

pollutant concentration passed from 10 to 20 mg/L. Among all the interactions, (X₁X₂) and (X₃X₄) have the most important coefficient (b₁₂ = +1.06 and b₃₄ = +2.72, respectively). Pareto analysis can be used to give more significant information to interpret these results (Myers and Montgomery, 2002; Haaland, 1989). The importance of the factors and interactions on BPB degradation has been put into evidence, according to the following relation:

$$P_i = \left(\frac{b_i^2}{\sum b_i^2} \right) * 100 \quad (i \neq 0) \quad (3)$$

where b_i represents the estimation of the principal effect of the factor i. Thus, it is found that the contribution of the treatment time and the calorimetric power on BPB removal is around 45.17% and 22.65%, respectively, whereas that of pH and pollutant concentration account for 20.06% and 9.61%, respectively (Fig. 2). The interpretation of the interaction effects of X₁X₂ and X₃X₄ on BPB degradation can be facilitated by seeing Fig. 3a and b. These figures are obtained as follows: each summit of the square represents a combination of the level of the two factors: pH and pollutant concentration (Fig. 3a). When the pH is fixed at the lowest level (7), the pollutant concentration had a high

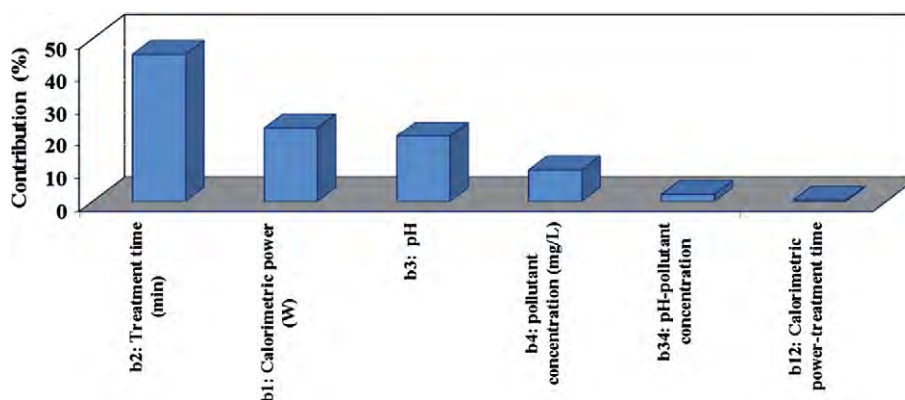


Fig. 2. Graphical Pareto analysis of the effect of calorimetric power, treatment time, pH, and pollutant concentration on BPB degradation.

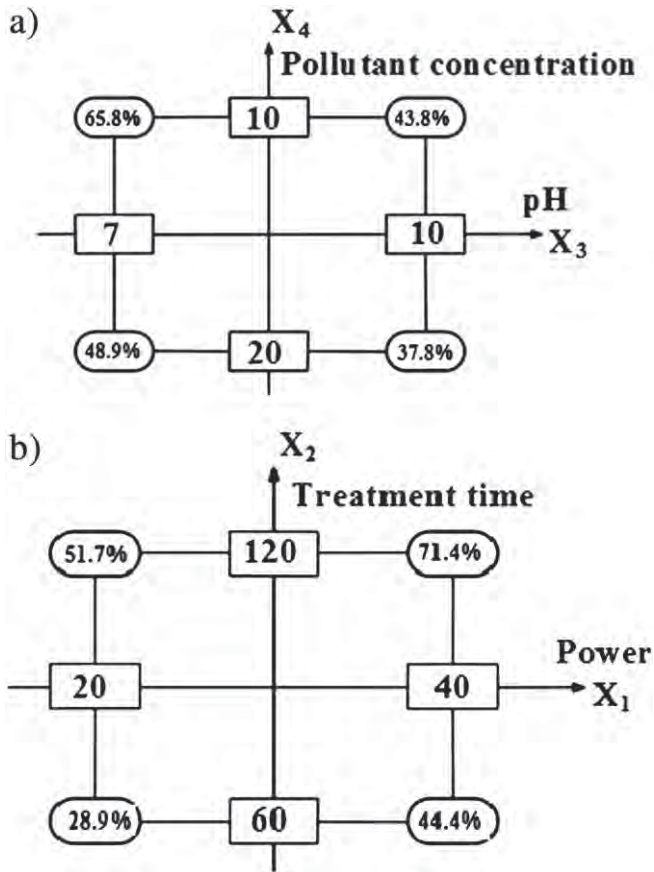


Fig. 3. (a) Interaction X_{34} between pH and pollutant concentration and; and (b) interaction X_{12} between calorimetric power and treatment time.

influence on the response, and the average rate of BPB degradation passed from 48.9% to 65.8% (a reduction gain of 16.9 units). However, if the pH is fixed at the highest level (pH = 10), the average rate of BPB degradation passed from 37.8% to 43.8% when the pollutant concentration passed from 20 mg/L to 10 mg/L. The reduction gain is only 6 units. Thus, pollutant concentration influences the rate of BPB degradation, but it directly depends on the pH. The influence of the initial concentration of pollutant was also put into evidence by Tay et al. (2010a, 2010b) while studying the oxidation of parabens by ozone. The degradation experiments were carried out at different total initial concentrations of paraben (from 250 μ M to 1000 μ M) in 0.67 g/h of O_3 at pH 6.9. The results recorded by Tay et al. (2010a, 2010b) show that the paraben degradation percentage decreased exponentially with the increase of initial concentrations from 250 μ M to 1000 μ M. The decrease in pollutant degradation efficiency while increasing the initial concentration can be attributed to the competition between intermediate products for reacting with hydroxyl radicals (Tay et al., 2010a, 2010b). For higher initial concentrations of pollutant, more degradation products were generated (Tay et al., 2010a, 2010b). Considering now X_1X_2 (X_1 calorimetric power, X_2 treatment time) (Fig. 3b), it can be seen that when the treatment time is fixed at the lowest level (i.e., 60 min is imposed), the calorimetric power has a significant influence on the response, the average rate of BPB degradation increasing from 28.9% to 44.4% (an abatement gain of 15.5 units was recorded). However, if the treatment time is fixed at the highest level (i.e., 120 min is imposed), the average rate of BPB degradation passed from 51.7% to 71.4% depending on power (an abatement gain of 19.7%). Consequently, the treatment time influences the rate of BPB oxidation, but it directly depends on the calorimetric power imposed. In the UV/US process, the treatment time, calorimetric power and direct photolysis influence the removal of

pollutant. The increase of treatment time and calorimetric power enhances the amount of oxidant species (i.e. $OH\cdot$ and H_2O_2) produced in situ and consequently increases the degradation efficiency of pollutant. Finally, the factorial plan design was useful for determining the interactions affecting the response and indicates if the lowest or the highest levels of the factors are favorable or not. However, this type of model cannot be used to predict or to determine the optimization conditions. For this reason, a RSM should be used in a second step to determine the optimal operating conditions for BPB degradation.

3.3. Optimization conditions for BPB degradation using central composite design methodology

One of the advantages of CCD is the possibility to explore the whole of the experimental region. CCD is formed by uniformly distributed points within the space of the coded variable (X_i). The CCD matrix is comprised of a factorial matrix (described above) and 14 additional experiments. The fourteen additional assays consist of six runs required at the center of the experimental region investigated, plus eight other axial runs. For the axial run matrix, α ($\alpha = (N_f)^{1/4} = 2$; N_f is the number of points required for the factorial matrix) has been chosen in order to have iso-variance property (Table 4). For the evaluation of data, the experimental response associated to a CCD matrix was described by a quadratic polynomial model given below:

$$Y = b_0 + \sum_{i=1}^k b_i X_i + \sum_{i=1}^k b_{ii} X_i^2 + \sum_j \sum_{i=2}^k b_{ij} X_i X_j + e_i \quad (4)$$

where Y is the experimental response; X_i and X_j are the independent variables; b_0 is the average of the experimental response; b_i is the estimation of the principal effect of the factor i on the response Y ; b_{ii} is the estimation of the second effect of the factor i on the response Y ; b_{ij} is the estimation of the interaction effect between i and j on the response Y ; and e_i represents the error on the response Y . The coefficients of this model are calculated using the least square method (Myers and Montgomery, 2002):

$$B = (X^T X)^{-1} X^T Y \quad (5)$$

where B represents the vector of estimates of the coefficients; X is the model matrix; and Y is the vector of the experiment results. The experimental values or real variables (U_i) can be calculated from the coded variable X_i using the following equation:

$$X_i = \frac{U_i - U_{i,0}}{\Delta U_i} \quad (6)$$

where $U_{i,0} = (U_{i,max} + U_{i,min})/2$, represents the value of U_i at the center of the experimental field; and $\Delta U_i = (U_{i,max} - U_{i,min})/2$, represents the step of the variation, with $U_{i,max}$ and $U_{i,min}$ which are the maximum and minimum values of the effective variable U_i , respectively. The regression model in terms of coded variables has been expressed by the following second-order polynomial equation:

$$Y = 54.26 + 7.54X_1 + 11.26X_2 - 6.50X_3 - 5.73X_4 + 1.06X_1X_2 \quad (7)$$

where X_i varies from -2 and $+2$ and Y represents the BPB degradation. In terms of actual factors, an empirical relation between the

Table 4

Central composite matrix and experimental results.

Experiment number	Experimental design				Experimental plan				Result, Y degradation efficacy (%)
	X ₁	X ₂	X ₃	X ₄	U ₁	U ₂	U ₃	U ₄	
17	-2	0	0	0	10 W	90 min	8.50	15 mg/L	43.62
18	+2	0	0	0	50 W	90 min	8.50	15 mg/L	63.44
19	0	-2	0	0	30 W	30 min	8.50	15 mg/L	28.18
20	0	+2	0	0	30 W	150 min	8.50	15 mg/L	63.75
21	0	0	-2	0	30 W	90 min	5.50	15 mg/L	60.38
22	0	0	+2	0	30 W	90 min	11.50	15 mg/L	48.70
23	0	0	0	-2	30 W	90 min	8.50	5 mg/L	70.93
24	0	0	0	+2	30 W	90 min	8.50	25 mg/L	48.06
25	0	0	0	0	30 W	90 min	8.50	15 mg/L	54.50
26	0	0	0	0	30 W	90 min	8.50	15 mg/L	54.57
27	0	0	0	0	30 W	90 min	8.50	15 mg/L	54.54
28	0	0	0	0	30 W	90 min	8.50	15 mg/L	53.20
29	0	0	0	0	30 W	90 min	8.50	15 mg/L	55.10
30	0	0	0	0	30 W	90 min	8.50	15 mg/L	55.94

degradation percent of BPB and the variables has been expressed by the following second-order polynomial equation:

$$Y = 61.29 + 0.54U_1 + 0.94U_2 - 4.53U_3 - 5.27U_4 + 0.03U_1U_3 - 0.01U_2U_3 + 0.36U_3U_4 - 0.28U_2^2 \quad (8)$$

where $10\text{ W} \leq U_1 \leq 50\text{ W}$; $30\text{ min} \leq U_2 \leq 150\text{ min}$; $5.50 \leq U_3 \leq 11.50$; and $5\text{ mg/L} \leq U_4 \leq 25\text{ mg/L}$. The coefficients of the polynomial model were calculated using the Design-Expert® Program software.

From these Eqs. ((7) and (8)), it can be seen that the calorimetric power and treatment time have a positive effect on BPB removal, whereas pH and pollutant concentrations have a negative effect on BPB degradation. The predicted contour plot (curve of constant response) is given in Fig. 4. When the BPB concentration was kept constant at 15 mg/L (pollutant concentration at the center of the experimental region investigated), BPB removal efficiency increased with increasing calorimetric power for all treatment times studied. As seen from the contour plot, more than 64% of BPB removal could be recorded at 15 mg/L of initial concentration of BPB while the calorimetric power was higher than 30 W and the treatment time was lower than 120 min. In terms

of optimization, the treatment time has a more significant impact on BPB removal efficiency than the calorimetric power.

Table 5 shows the analysis of variance (ANOVA) of regression parameters of the predicted response surface quadratic model for BPB removal using the US/UV process. As it can be seen from this table, the model F-value of 16.44 and a low probability value ($Pr > F = 0.0001$) indicate that the model is significant for BPB removal. The value of the correlation coefficient ($R^2 = 0.9388$) indicates that only 6.12% of the total variation could not be explained by the empirical model. An agreement between actual and predicted values of BPB degradation is satisfactory and consistent with the quadratic model. According to Joglekar and May (1987), R^2 should be at least 0.80 for a good fit of model. The R^2 value (0.9388) recorded in the present study for BPB removal was higher than 0.80, indicating that the regression model explained the US/UV process well. Besides, the lack of fit F-value of 89.75 and the low probability value ($Pr > F = 0.0001$) indicate that the lack of fit of the model is significant for the removal of BPB by the UV/US process.

The main objective of the optimization is to determine the optimum values for BPB removal using the US/UV process. To rigorously determine the optimal conditions for BPB degradation in terms of cost/effectiveness, the energy consumption during the treatment should be taken into account. The criteria selected for the optimization conditions for BPB degradation by the US/UV process are the following: (i) pollutant

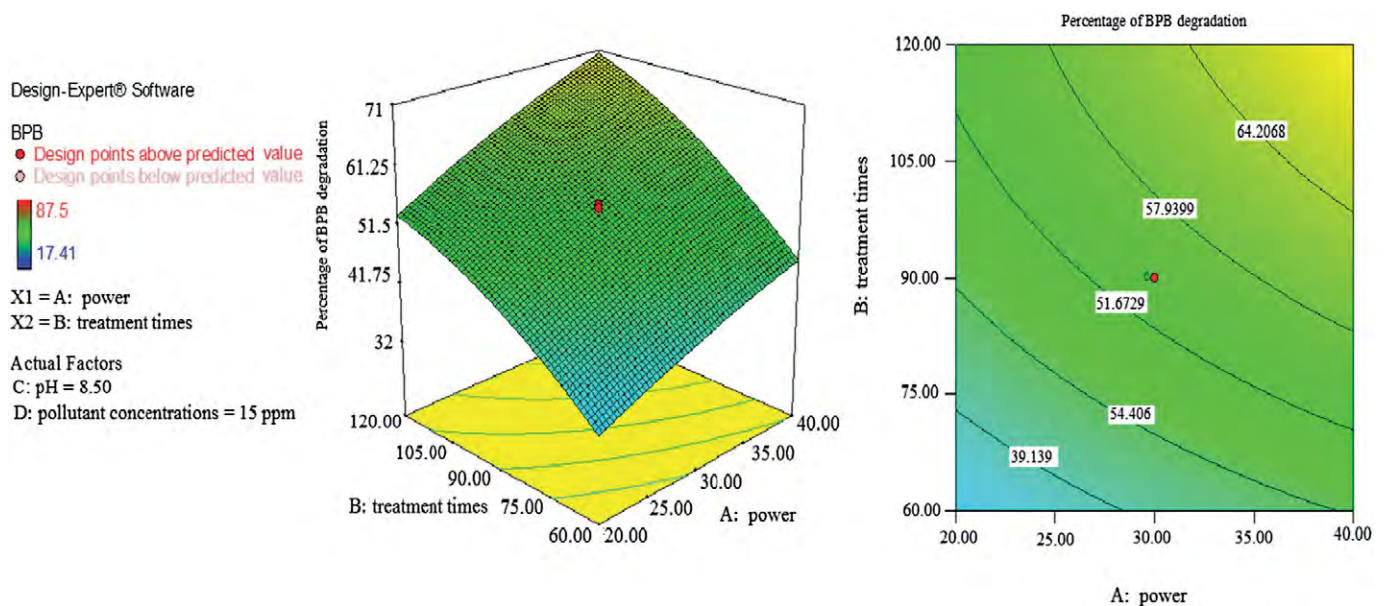


Fig. 4. The effect of calorimetric power (W) and treatment time (min) on BPB removal (pollutant concentration: 15 mg/L). Three-dimensional plot: results obtained from central composite matrix.

Table 5
ANOVA results for BPB degradation.

Source	Analysis of variance				
	d.f. ^a	Sum of square	Mean of square	F-value	Pr > F
Model	14	6614.21	472.44	16.44	<0.0001
Residual	15	431.14	28.74	-	-
Lack of fit	10	428.75	42.88	89.75	<0.0001
Pure error	5	2.39	0.48	-	-

^a Degree of freedom; F: Fisher coefficient; and $R^2 = 0.9388$.

concentration has to be minimized with the highest importance (5/5 weighting factor) and (ii) the energy consumption has to be minimized with lesser importance (4/5 weighting factor) in order to reduce the treatment cost. The different solutions proposed are classified per order of desirability. The desirability value gives information about the adequacy between the solution and the criteria imposed. The optimum operating conditions proposed by the Design Expert Program software are the following: 40 W of calorimetric power imposed during 120 min of treatment time, at pH 7 and at 10 mg/L of initial concentration of BPB. The desirability function value was found as 0.982 for these optimum conditions. The theoretical response proposed by the Design-Expert® Program software for BPB degradation was 85.02%. By

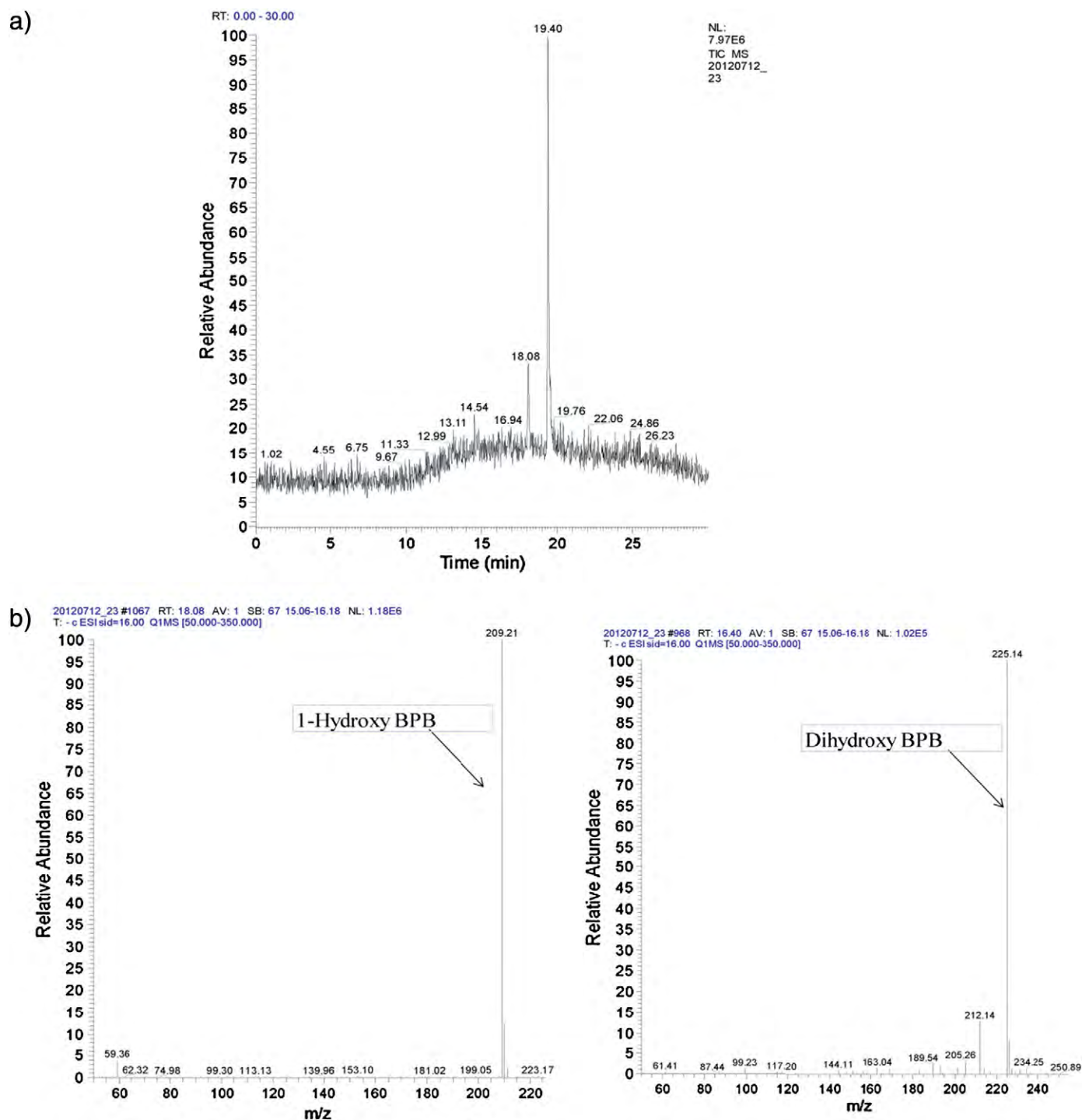


Fig. 5. (a) LC/MS/MS chromatogram presented with (b) individual MS spectra of possible by-products of BPB by US/UV process.

comparison, the average value of the BPB removal measured using UV-vis absorption spectrophotometer is $89.5\% \pm 1.5\%$. This result was recorded at the end of this experiment, and it is found to be very close to the value proposed by the model (85.02% of BPB degradation). Under these optimal conditions, the energy consumption recorded was 80.69 kWh/m^3 .

However, experimental results determined using liquid chromatography-mass spectrometry (LC/MS/MS) show that the removal of BPB is around $99.18 \pm 1.4\%$. A UV-vis absorption spectrophotometer is an indirect analytical method. According to the Beer-Lambert law, the measure of the concentration of species is determined from the measure of absorbance. The presence of interfering substances such as by-products can influence the absorption spectrum and consequently can modify

the results. By comparison, LC/MS/MS analysis is a technique combining simultaneously a powerful physical separation technique and powerful technique of analysis and mass detection. The LC/MS/MS technique has a very high sensitivity and selectivity towards several compounds (Hernández et al., 2007).

3.4. By-product formation and proposed mechanism of BPB degradation

Our objective is to follow the formation of some by-products while treating the synthetic BPB solution using the UV/US process. With LC/MS/MS analysis, two main BPB by-products were identified on the basis of their mass spectra. However, other by-products could exist. The LC/MS/MS chromatogram and the individual MS spectra of possible

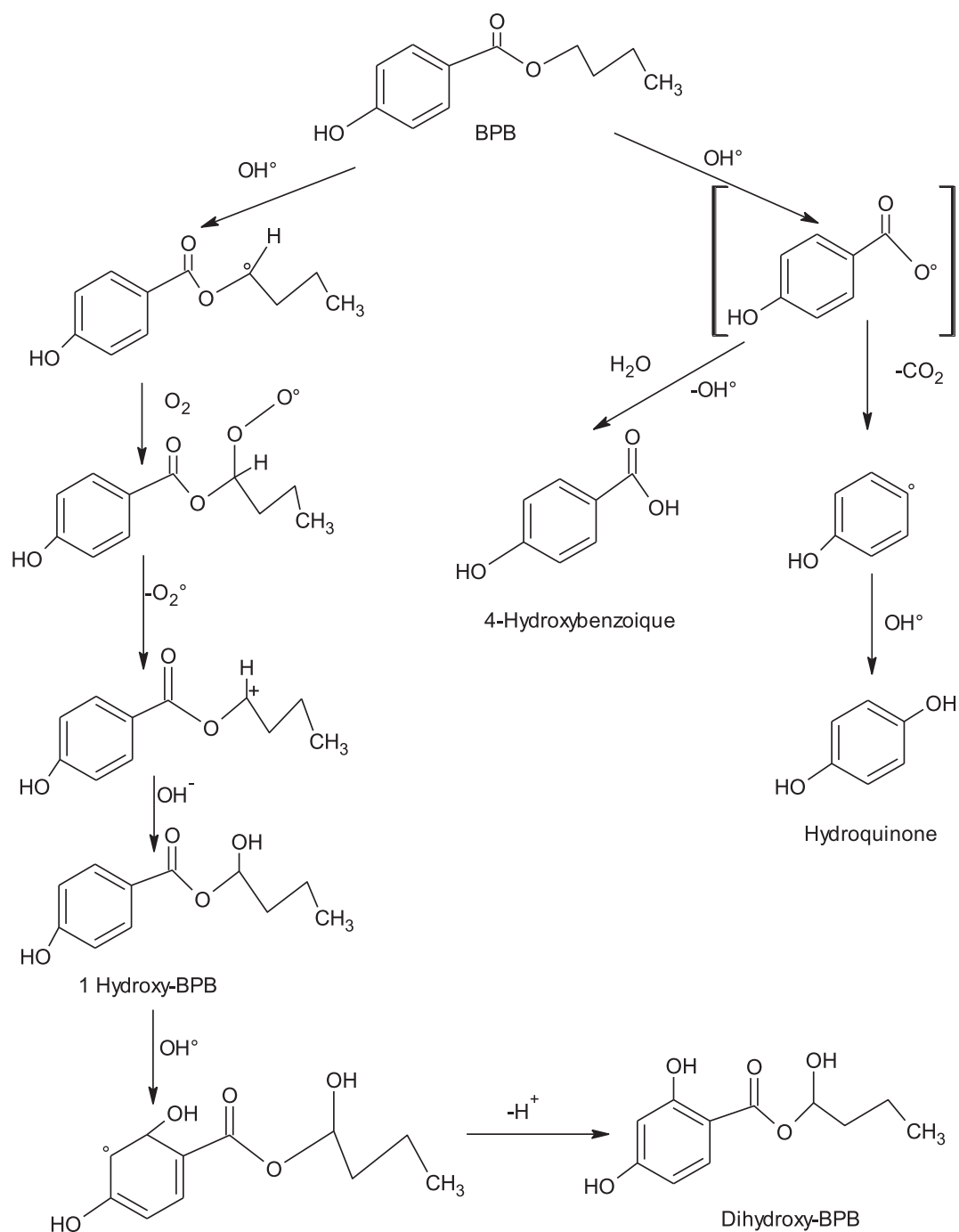


Fig. 6. The chemical structure and the proposed reaction pathway for the US/UV degradation of BPB.

transformation of BPB are shown in Fig. 5 and a plausible mechanism of BPB degradation by the UV/US process is depicted in Fig. 6. The formation of ester chain hydroxylation products began with the abstraction of hydrogen to produce the intermediate radical which reacts with dissolved oxygen to form peroxy radical. This peroxy radical could further dissociate into carbocation that reacts with OH• to form ester chain hydroxylation product 1-hydroxy-BPB ($m/z = 209.21$; $t_R = 18.08$ min). Besides, hydroxylation of BPB was found to be a significant reaction mainly at the aromatic ring. Hydroxylation at the aromatic ring is occurred via a direct reaction with OH• and ensures the formation of dihydroxy-BPB ($m/z = 225.14$; $t_R = 16.40$ min). It could be also possible that BPB reacts with OH• produced by the US/UV process to form other by-products (Tay et al., 2010a, 2010b). However, these two by-products were not monitored by LC/MS/MS. The breakdown of the C–O bond by OH• forms a radical intermediate. This intermediate radical could directly react with water to give 4-hydroxybenzoic acid. The intermediate radical could also rearrange to lose CO₂ and subsequently reacts with OH• to form hydroquinone.

On the other hand, the residual concentration of TOC recorded at the end of treatment was 6.8 ± 0.2 mg/L compared to 12.0 ± 0.10 mg/L measured in the initial BPB solution. The relatively low yield of TOC removal (approximately 43.3%) indicated that only a small fraction of BPB was completely oxidized into water and carbon dioxide. The majority of the pollutant was transformed into by-products.

Besides, Microtox tests carried out under optimal conditions show a decrease in the percentage of luminescence inhibition while applying the US/UV process. At an exposure time of 15 min, the percentage of the inhibition initially measured was 78.5%, whereas the percentage of the inhibition recorded at the end of the treatment was 39.8%. Under these conditions, toxicity was reduced, but still remained in the treated water. The residual concentration of BPB and by-products (1 hydroxy BPB, dihydroxy BPB, hydroquinone and 4-hydroxybenzoic acid) remained toxic for *V. fischeri*.

3.5. Kinetic study

To evaluate the oxidation rate of BPB, the kinetic data were analyzed using pseudo-first order kinetic model. The kinetic parameters were

estimated by a regression analysis method using Excel software. The pseudo-first order kinetic model is described by the following equation:

$$\ln \frac{C_0}{C} = k_1 t \quad (10)$$

where C_0 is the initial concentration of BPB, C is the concentration of BPB at time t , k_1 is the first order reaction rate constant (min^{-1}) and t is the reaction time.

Fig. 7 shows that the BPB degradation using the US/UV process follows a pseudo-first-order kinetic model. Higher correlation coefficient ($R^2 = 0.9726$) was obtained for pseudo-first-order kinetic model. The first-order kinetic reaction rate constant recorded was 0.0367 min^{-1} . This high removal rate of BPB was mainly attributed to ROS (namely hydroxyl radical) continuously produced over time. In our experimental conditions (optimal conditions), the ROS production rate was estimated to be $17.31 \cdot 10^{-3} \text{ mM h}^{-1}$, in which the value can be compared to that recorded ($22.6 \cdot 10^{-3} \text{ mM h}^{-1}$) by Daghrir et al. (2013) while treating a p-nitrosodimethylaniline solution using a photo-electro-catalytic oxidation process. It is interesting to compare the kinetic constant recorded in our study (0.0367 min^{-1}) with values obtained in other experimental conditions. Tay et al. (2010a, 2010b) indicated that the degradation rate of BPB (500 μM) by ozonation process (0.67 g O₃/h, at pH 6.9) is well described by the first order kinetic model and occurs with two ozonation stages ($k_{1\text{obs}} = (2.24 \pm 0.04) \cdot 10^{-1} \text{ min}^{-1}$ and $k_{2\text{obs}} = (4.2 \pm 0.3) \cdot 10^{-1} \text{ min}^{-1}$). However, pseudo-second order kinetic model for the BPB degradation (from $4.2 \pm 0.6 \cdot 10^2 \text{ M}^{-1} \text{ s}^{-1}$ to $1.38 \pm 0.05 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$) has been recorded by Tay et al. (2010a, 2010b) while using the same technique (ozonation process). The type of oxidant species produced could influence the kinetic rate of pollutant degradation (Tay et al., 2010a, 2010b).

Finally, the US/UV treatment cost of BPB (including only energy consumption) recorded in the optimal conditions was estimated to be $4.84 \text{ \$/m}^3$. The treatment cost was also put into evidence by Hansen and Andersen (2012) while treating the BPB using a hybrid process H₂O₂/UV. The treatment cost of BPB was around $0.47 \text{ \$/m}^3$. The treatment cost recorded ($4.84 \text{ \$/m}^3$) in our study was ten times higher than that proposed by Hansen and Andersen (2012). However, this

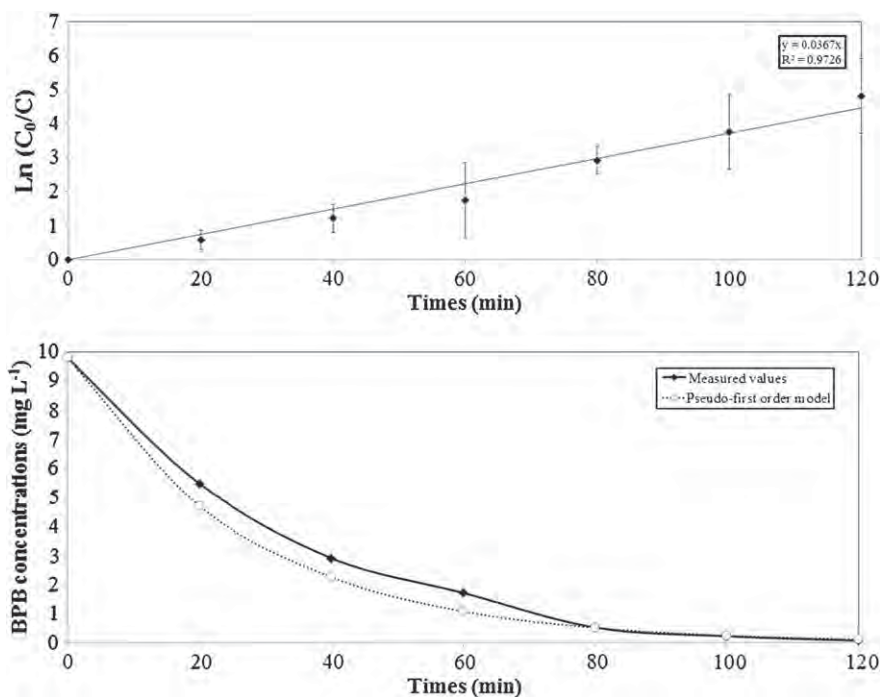


Fig. 7. Kinetic degradation of BPB by US/UV process.

relatively high cost can be compensated by several advantages such as easy operation, compactness of equipment, no transportation, no storage of chemicals and no handling of chemicals.

4. Conclusion

In this study, the degradation efficiency of BPB using US/UV process has been investigated. It showed that the treatment time and calorimetric power were found to be the most influent parameters. The contributions of treatment time and calorimetric power on BPB degradation were 45.2% and 22.6%, respectively, whereas the contributions of pH and pollutant concentration were 20.1% and 9.61%, respectively. A central composite design was employed to define the optimal operating conditions for BPB oxidation. The US/UV process applied under optimal conditions (at a calorimetric power of 40 W during 120 min, under pH 7 and using 10 mg/L as initial concentration of BPB) is able to oxidize $99.2 \pm 1.4\%$ of BPB and to record a partial mineralization (43.3%). The analysis using LC/MS/MS technique shows that 1 hydroxy BPB, dihydroxy BPB, hydroquinone and 4-hydroxybenzoic acid are the main by-products of BPB. The kinetic study shows that the pseudo-first-order kinetic model (0.0367 min^{-1}) describes well the oxidation of BPB by US/UV process.

Conflict of interest

This work has been financed by the National Sciences and Engineering Research Council of Canada (NSERC). So, no conflict of interest is presented.

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