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Kinetics of the degradation of *n*-butyl benzyl phthalate using O₃/UV, direct photolysis, direct ozonation and UV effects

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Abstract The aim of this work is to study the degradation kinetics of the endocrine disruptor benzyl butyl phthalate using ozone and UV radiation. The model comprises four parallel subsystems that are identified and isolated: (1) direct photolysis, (2) direct ozonation in the absence of hydroxyl radicals, (3) complete ozonation (direct+indirect oxidation), and (4) ozone+UV. To determine the nature of ozone attacks and the influence of ·OH radicals on O₃ activity, two sets of experiments were performed: (i) conventional ozonation and (ii) the same ozonation experiments in the presence of *tert*-butanol as radical scavenger, where only the reactions involving molecular ozone are present. The explored variables were (i) ozone concentration, (ii) incident radiation rate at the reactor windows, (iii) reaction pH, and (iv) the presence of radical scavengers. Major intermediates of BBP degradation were identified. Degradation kinetics was correctly modeled by a pseudo-second-order kinetic model based on the sum of all the effects occurring during the treatment. The corresponding kinetic constants were obtained, and the relative contributions of each of the considered subsystems were evaluated.

Keywords Ozone · Benzyl butyl phthalate · UV radiation · Direct and indirect oxidation · Degradation kinetics · Endocrine disruptor

Introduction

Phthalate esters (PEs) represent a large family of industrial chemicals most widely used as plasticizers, primarily in the

production of polyvinyl chloride (PVC) resins, adhesives, and as cellulose film coatings (Esplugas et al. 2007; Chatterjee and Dutta 2008a; Xu et al. 2009). They are also used to improve the mechanical properties of plastic resins, particularly flexibility (Serôdio and Nogueira 2006).

In recent years, phthalates have attracted much attention because even at low concentration levels, they are suspected of interfering with reproductive and behavioral health in humans and wildlife, through disturbance of the endocrine system (Psillakis et al. 2004). Due to their potential risks for human health and the environment, several phthalates have been listed as priority substances by many national and international regulatory organizations. Particularly, di-*n*-butyl phthalate, butyl benzyl phthalate, and di-2-ethylhexyl phthalate have been included by the European Union in the list of endocrine-disrupting chemicals (EDCs) (Serôdio and Nogueira 2006).

Given their physical rather than chemical incorporation into the polymeric matrix, phthalates easily migrate into foods, beverages, and drinking water from the packaging or bottling material or manufacturing processes (Psillakis et al. 2004; Serôdio and Nogueira 2006) and have been found in sediments, natural waters, and soils (Chatterjee and Karlovsky 2010; Rocha et al. 2013). They have also been detected in aquatic organisms as in human serum and plasma (Staples et al. 1997; Chatterjee and Dutta 2008a).

n-Butyl benzyl phthalate (BBP) is one of the most frequently identified phthalates in diverse environmental samples including drinking water, soil, lake and marine sediments, groundwater, and river and ocean water (Xu et al. 2009). BBP has been tested for estrogenic properties both in vivo and in vitro (Harris et al. 1997); on this basis, it has been classified as one of the most important environmental contaminants with documented adverse health effects (Chatterjee and Karlovsky 2010) and considered one of the major endocrine-disrupting chemicals. Because of its low solubility

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in water (Gledhill et al. 1980), BBP is presented in a stable form at very low concentrations, complicating its removal.

Different chemical, physical, and biological treatment processes are currently proposed for the removal of PEs. Several studies were conducted on PEs degradation by photolysis (Lau et al. 2005), electrocoagulation (Kabdaşlı et al. 2009), ozonation (Li et al. 2006; Oh et al. 2006; Chen et al. 2011; Ferreira de Oliveira et al. 2011a,b; Wen et al. 2011), aerobic and anaerobic biodegradation (Chatterjee and Dutta 2008a,b), Fenton and photo-Fenton processes (Rocha et al., 2013), UV/H₂O₂ (Xu et al. 2007; Medellin-Castillo et al. 2013), and photocatalysis (Sharma et al. 2010; Sin et al. 2012), among others. In the case of BBP, most studies consist biological processes (Chatterjee and Dutta 2008a, b; Yang et al. 2013). There are also reports concerning the sonochemical (Psillakis et al. 2004) and photocatalytic (Xu et al. 2009) degradation of BBP. Fenton and photo-Fenton processes were studied (Rocha et al. 2013) as well as the treatment performance of different wastewater treatment procedures for the removal of seven selected EDCs, including BBP (Balabanić et al. 2012).

Ozone is widely used in drinking water treatment for organic matter decomposition and microbiological disinfection. Several kinds of phthalates were degraded by this technology. However, no report about BBP degradation by O₃ or O₃/UV process could be found in the literature, except for the results reported by Balabanić et al. (2012), but the authors neither identified any intermediates of the degradation process nor performed any kinetic analyses regarding the ozonation treatment.

Although all AOPs have in common the participation of hydroxyl radicals as nonselective oxidizing agents, they differ in the mechanisms through which these radicals are generated. In some cases, other compounds capable of directly reacting with pollutants are also involved, giving rise to parallel paths of reaction (e.g., direct ozonation, UV photolysis). The combined processes can be more efficient for degrading complex molecules since different reaction pathways coexist. During ozonation, ·OH radicals can react nonselectively with most of the organic compounds in water, whereas O₃ with its electrophilic nature can react selectively with electron-rich reaction site of organic compounds (Tay et al. 2013). Therefore, organic compounds in water may be degraded by both O₃ and ·OH through a series of oxidation and radical reactions. They may also be strongly enhanced by the inclusion of UV radiation (Benitez et al. 2004).

The study of the potential "oxidation/mineralization" of a complex system such as the one originated in the oxidation of BBP using O₃/UV is interesting since a special difficulty arises in the process under consideration. The system becomes complex with competitive parallel reaction paths, such as photolysis and selective oxidation reactions produced directly by O₃ and indirect reactions where ·OH radical takes part in a nonselective form (see Fig. 1).

This work studies the kinetics of the degradation of BBP using O₃/UV process isolating the effects of photolysis, the

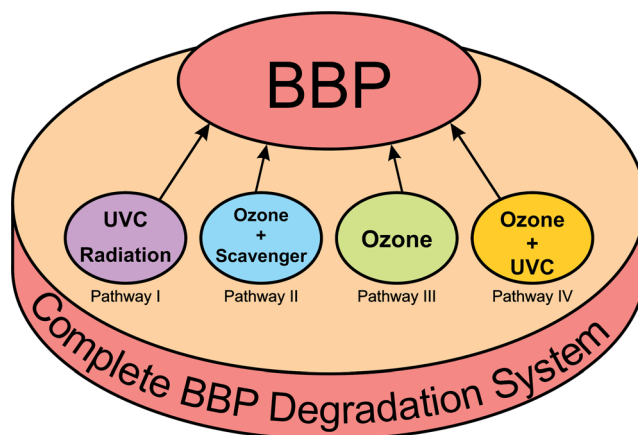


Fig. 1 Parallel paths of the reacting system

action of the molecular ozone in the absence of ·OH radicals, the action of O₃ when the ·OH radical is present, and the increase in the reaction rate by the presence of UV radiation. In this way, it is possible to complete a kinetic study of this reaction.

Materials and methods

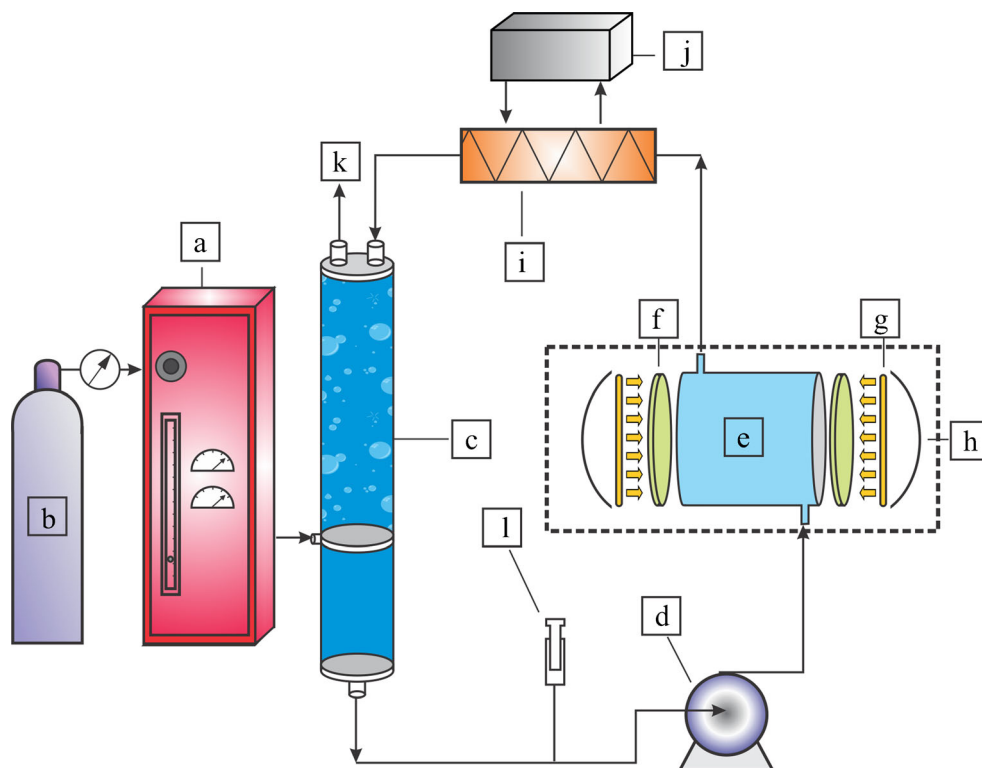
Experimental device

Figure 2 shows the experimental setup. O₃ was produced from pure O₂ by an ozone generator (Fischer 503). The photoreactor was a cylinder made of Teflon closed in both extremes with two flat circular windows made of quartz. The reactor could be operated in the dark or could be irradiated by means of two low-pressure Hg germicidal lamps. Three different radiation levels were used: two Heraeus NNI 40/20 lamps ($\lambda=253.7$ nm, 40 W each) and the same lamps with one or two pairs of neutral filters. The corresponding incident radiation intensities at the reactor windows (G_w) were determined by actinometry (4.81 , 1.94 , and 1.08×10^{-8} Einstein $\text{cm}^{-2} \text{s}^{-1}$). The photoreactor was part of a recirculating system that included an absorption column, a centrifugal pump and a heat exchanger connected to a thermostatic bath to keep the system temperature constant at 20 °C, a sampling port, and a venting outlet to eliminate the excess of O₂/O₃ fed to the absorption column. For all species except O₃, the recycling system was a well-mixed batch reactor. For O₃, the system operated continuously. The total liquid volume was 1,700 cm³.

Experimental procedure

The stabilization of the system was performed according to Gilliard et al. (2013). The initial concentration of BBP was 2.64 ± 0.16 ppm in all cases. The pH of the solution was the natural one produced by the dissolution of BBP in ultra-purified water (Osmon). To study the

Fig. 2 Experimental Setup. **a** O₃ generator, **b** O₂ supply, **c** absorption column, **d** centrifugal pump, **e** photoreactor, **f** neutral filters, **g** UV lamps, **h** parabolic reflectors, **i** heat exchanger, **j** thermostatic bath, **k** O₃ vent, and **l** sampling port



pH effects, one set of experimental runs was made at pH 4 and 10. The solution pH was kept constant using $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffer and was controlled along the reaction by means of a digital thermo pH meter. For experimental runs involving $\cdot\text{OH}$ inhibition, *t*-BuOH was utilized as radical scavenger, in a molar relationship $t\text{-BuOH}:\text{O}_3=1.5$, greatest than the value of 1 which is considered sufficient for the radical-mediated mechanism inhibition (López et al. 2007).

The ozone concentration in the system is constant. This condition is ensured with the employed apparatus that includes a regulated, continuous feed and a very gentle ozone output stream through a venting hole. In every reaction in which ozone participates, the recycling system is a well-stirred, semi-batch reactor. The ozone consumed in all the reaction steps in which it intervenes must be replenished to keep its concentration constant, which is the proposed operating condition. Based on the mass flow of ozone and the total liquid volume, according to Silva et al. (2009), the applied doses of ozone assume values of 0.64, 1.01, and 1.23 g O₃/L.

Analyses

The BBP concentration was measured using HPLC (Waters 2487 Dual λ Absorbance) with a UV detector ($\lambda=245\text{ nm}$); Supelco LC-18 column; and mobile phase acetonitrile/water 80/20, 1 mL min⁻¹. Mineralization was evaluated by means of total organic carbon (TOC) measurements (Shimadzu TOC-5000A). Residual O₃ in the aqueous phase was monitored

using the indigo method. Analyses were made immediately after sampling. Reproducibility tests were made for all runs, and analytical determinations were triplicated.

In order to identify reaction intermediates, the liquid samples were acidified to pH=1.5 using HCl. Then a liquid–liquid extraction was performed using methylene chloride. The organic extract was evaporated under a stream of dry N₂. The methyl derivatives were obtained using MeOH and H₂SO₄ and incubating at 60 °C for 45 min. CH₂Cl₂ was added, and samples were stirred for 2 min. The methylene chloride phase was injected into the gas chromatograph (Kitson et al. 1996). Analyses were carried out on a Shimadzu GC-17A system, equipped with a Shimadzu QP-5000 MS and HP 5 phenyl methyl silicone column. Helium was employed as carrier gas. The identification was based on electronic impact and chemical ionization mass spectral interpretation and on the comparison between the mass spectra obtained and the spectra contained in the NIST database and reported data (Nativelle et al. 1999).

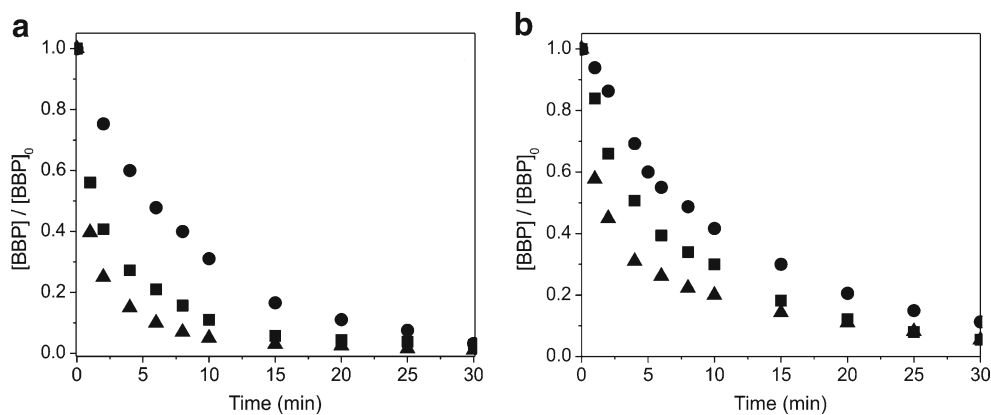
Results and discussion

Ozone effects

Complete ozonation reactions

Figure 3a presents the experimental results of BBP degradation using O₃ in the absence of UV radiation. In this case, it is

Fig. 3 Effect of O₃ concentration on BBP degradation. **a** O₃ alone and **b** O₃+*t*-BuOH. [O₃]=black circle 2.97×10⁻⁴ M, black square 3.38×10⁻⁴ M, and black triangle 3.88×10⁻⁴ M



necessary to bear in mind that the O₃ incorporated into the system is capable of oxidizing BBP by the molecular track or through the ·OH radicals.

The different values of reaction progress for a given time allow inferring that there is a strong dependence between the kinetics of the process and the concentration of oxidant (see Table 1). For all the studied conditions, the higher conversions are achieved in a relatively short time, although from this information, it is not possible to determine the relative contribution of each of the reaction "steps or paths" involved.

Direct ozonation

One aim of this work is to independently study and evaluate the kinetics of each of the oxidation processes involved. Then, experimental runs were conducted using *t*-BuOH as a radical scavenger where only the reactions involving molecular O₃ attack are present. The experimental results of the degradation of BBP using the same concentrations of O₃ as those utilized in the previous section are presented in Fig. 3b. The comparison of the results obtained for ozonation in the presence of

t-BuOH shows that the presence of the ·OH radicals completely changes the progress of the reaction, increasing the degradation rate of BBP. Table 1 presents a comparison of the half-life (*t*_{1/2}) obtained for each process, which can be uncoupled in order to quantify the relative contributions of oxidation by molecular O₃ and ·OH radicals as it will be described in subsequent sections.

Considering the use of O₃ as a tertiary or complementary water treatment, where the pH was usually closer to neutral, the most experimental pH study in this work was near 7 without adjustments. The objective of this work was to study the degradation of BBP in natural conditions (i.e., pH values near 7). However, a set of experimental runs was made to qualitatively evaluate the effects of reaction pH. Experiments were carried on at three constant pH values. For a reaction time of 15 min, BBP conversions were 65, 83, and 91 % for pH 4, 7, and 10, respectively (see Fig. 4). The results show that an increase in the reaction pH enhances the degradation rates, in agreement with literature results (Ferreira de Oliveira et al. 2011a). However, the quantification of this trend exceeds the scope of this paper.

Table 1 Summary of characteristic kinetics values

Half-life <i>t</i> _{1/2} [minute]				
<i>C</i> _{O₃} × 10 ⁻⁴ M	Process			
	Total ozonation ^a (O ₃ +·OH)	Ozonation ^a (O ₃ + <i>t</i> -BuOH)	UV alone ^{a,b} (photons)	UV+O ₃ ^{a,b} (O ₃ +·OH)
2.97	5.6	8.18	–	2.04
3.38	1.2	4.32	–	1.13
3.88	0.9	1.59	–	0.45
0	–	–	30	–
Estimated kinetic parameters				
<i>k</i> _{O₃} = 1.08 [M ⁻¹ s ⁻¹] <i>k</i> _{O₃} = 0.14 [M ⁻¹ s ⁻¹] φ = 5 × 10 ⁻⁴ [mol Einstein ⁻¹] <i>k</i> _{·OH} = 0.94 [M ⁻¹ s ⁻¹] , <i>k</i> _{O₃} = 0.14 [M ⁻¹ s ⁻¹]				

^a pH=7

^b *G*_w=4.81 × 10⁻⁸ Einstein cm⁻² s⁻¹

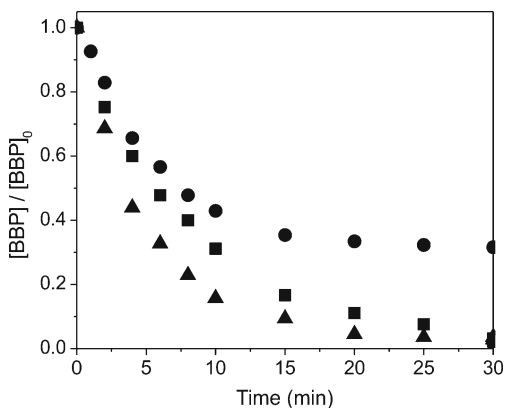


Fig. 4 Effect of pH on BBP degradation. pH=black circle 4, black square 7, and black triangle 10. $[O_3]=2.97 \times 10^{-4}$ M

Radiation effects

Direct photolysis-ozone+UV

Figure 5a shows the time evolution of BBP concentration using UV alone. From the comparison with the results obtained using O_3 , it is clear that the conversions are smaller. Moreover, when the processes are simultaneous (O_3+UV), direct photolysis is expected to have a minor impact because O_3 competes with BBP for the photons (see next section)

Figure 5b shows the experimental data when the UV process is combined with the addition of O_3 under various UV irradiation rates at the reactor windows. It must be considered that the concentration of $\cdot OH$ radicals is increased by the effect of UV radiation on the decomposition of O_3 (Gilliard et al. 2013). Table 1 shows the characteristic half-life for the different experimental conditions studied.

The complete kinetic modeling

As mentioned in the “Introduction,” this combined reacting system has a very complex scheme that must take into consideration different parallel pathways: (i) direct photolysis, (ii) direct ozonation, and (iii) ozonation plus UV radiation. The

objective is to find a complete model that satisfies the following requisites: in the absence of O_3 and in the presence of UV radiation, it must reproduce direct photolysis; with O_3 alone, it must portray complete ozonation or only direct ozonation using $t\text{-BuOH}$; in the presence of O_3 and UV radiation, it must describe the complete sequence including the enhancement of the reaction rate by $\cdot OH$ radicals. The working equations necessary to analyze the experimental results and to obtain the kinetic parameters require the resolution of the mass and radiant balances, as follows.

The reactor mass balance

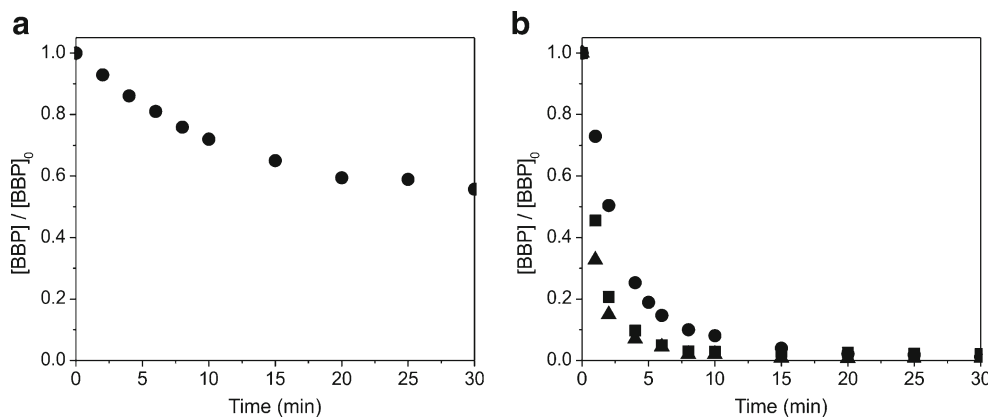
Considering the experimental setup shown in Fig. 2, it is important to establish several considerations: (i) the mass balance equations should differentiate the existence of illuminated and dark sections of the reacting system as well as the integration volumes of each one; (ii) the recycling system is a well-mixed batch reactor; and (iii) the O_3 consumed must be replenished to keep its concentration constant. Therefore, the reactions that involve radiation absorption take place only in the irradiated part of the system (the reactor volume, V_R), while the ozonation reactions proceed in the whole volume (the total system volume, V_T). With the following hypotheses—the reactor volume is smaller than the total volume, there is perfect mixing in the whole recycling system, high recirculation flow rate is applied, and there is isothermal operation—the average mass balance equations result in the following:

$$\left. \frac{dC_{BBP}(t)}{dt} \right|_{Dark} = \left\langle R_{BBP, Dark}(x, t) \right\rangle_{V_{Tot}} \tag{1}$$

$$\left. \frac{dC_{BBP}(t)}{dt} \right|_{UV} = \left(\frac{V_R}{V_{Tot}} \right) \left\langle R_{BBP, UV}(x, t) \right\rangle_{V_R} \tag{2}$$

$$\left. \frac{dC_{BBP}(t)}{dt} \right|_{Tot} = \left\langle R_{BBP, Dark}(x, t) \right\rangle_{V_{Tot}} + \left(\frac{V_R}{V_{Tot}} \right) \left\langle R_{BBP, UV}(x, t) \right\rangle_{V_R} \tag{3}$$

Fig. 5 Effect of UV radiation on BBP degradation. **a** Direct photolysis. **b** O_3+UV , $[O_3]=$ black circle 2.97×10^{-4} M, black square 3.38×10^{-4} M, and black triangle 3.88×10^{-4} M, $G_w=4.81 \times 10^{-8}$ Einstein $cm^{-2} s^{-1}$



From the condition of a very good mixing operation, all concentrations are constant in space. Consequently, the only relevant variable that must be calculated is the local volumetric rate of photon absorption e_i^a that participates in the photochemical steps. The local and averaged values of e_i^a must be obtained from a photon balance for the different species (i).

The radiation balance

Using a one-dimensional radiation model, employing lamps with monochromatic emission where the reactor irradiated from both sides, the following expression results for the absorbed radiation of species (i):

$$\langle e_i^a \rangle_{V_R} = \frac{2 \alpha_i C_i G_W}{\sum_j \alpha_j C_j L_R} \left\{ 1 - \exp \left[- \left(\sum_j \alpha_j C_j \right) L_R \right] \right\} \quad (4)$$

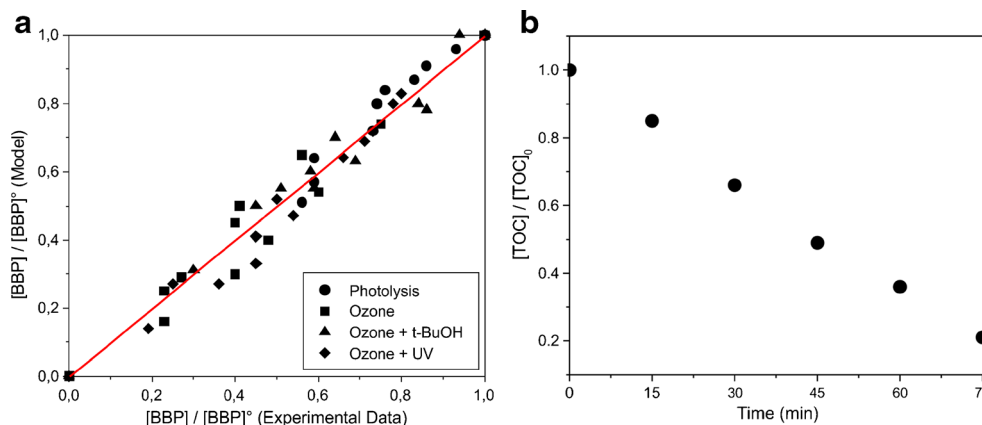
where (i) could be BBP or O_3 :

$$\langle e_{BBP}^a \rangle_{V_R} = \frac{2 \alpha_{BBP} C_{BBP} G_W}{(\alpha_{BBP} C_{BBP} + \alpha_{O_3} C_{O_3}) L_R} \{ 1 - \exp [- ((\alpha_{BBP} C_{BBP} + \alpha_{O_3} C_{O_3})) L_R] \} \quad (5)$$

$$\langle e_{O_3}^a \rangle_{V_R} = \frac{2 \alpha_{O_3} C_{O_3} G_W}{(\alpha_{BBP} C_{BBP} + \alpha_{O_3} C_{O_3}) L_R} \{ 1 - \exp [- ((\alpha_{BBP} C_{BBP} + \alpha_{O_3} C_{O_3})) L_R] \} \quad (6)$$

G_w represents the incident radiation at the reactor wall and α_i is the molar absorption coefficient for (i) species, namely, O_3 and BBP. As has been said, the values of $\langle e_i^a \rangle_{V_R}$ for BBP with and without the presence of O_3 could be calculated to evaluate the effect produced on the radiation field by the presence of O_3 , which competes for the absorption of photons. Even if the lowest O_3 concentration is used, the relationship $\langle e_{BBP}^a \rangle_{V_R, O_3/UV} / \langle e_{BBP}^a \rangle_{V_R, Photolysis}$ has a value of $f=0.12$. Then, in the case of the O_3+UV system, the contribution of direct photolysis to the global reaction is very low.

Fig. 6 **a** Correlation between experimental data and model results. *Black circle* photolysis: $G_w=4.81 \times 10^{-8}$ Einstein $cm^{-2} s^{-1}$, *black square* ozonation: $[O_3]=2.97, 3.38,$ and 3.88×10^{-4} M, *black triangle* O_3+t -BuOH: $[O_3]=2.97, 3.38,$ and 3.88×10^{-4} M, $[t$ -BuOH]/ $[O_3]=1.5$, *black diamond* O_3/UV : $[O_3]=2.97 \times 10^{-4}$ M, $G_w=4.81, 1.94,$ and 1.08×10^{-8} Einstein $cm^{-2} s^{-1}$ and **b** mineralization of BBP: $[O_3]=2.97 \times 10^{-4}$ M



The complete derivation of the mass and radiation balance equations can be reviewed in literature (Gilliard et al. 2013).

The kinetic model

The following assumptions were taken into account: (i) the short half-life of BBP in order to determine initial reaction rates, (ii) the greatest radiation absorption rate $\langle e_i^a \rangle$ of O_3 against BBP, (iii) O_3 concentration is constant in each experiment and proportional to $\cdot OH$ concentration (this allows arriving at a pseudo-second order model), and (iv) the kinetic constants of each process are independent. The kinetic expressions of each of the processes represented in Fig. 1 are determined by the following:

Direct photolysis (photons):

$$R_{BBP, phot.} = -\Phi_{BBP} e_{BBP}^a, \quad \Phi_{BBP} = \text{quantum yield} \left[\frac{\text{Einstein}}{\text{mol}} \right] \quad (7)$$

Direct oxidation (O_3):

$$R_{BBP, direct} = -k_{O_3} C_{BBP} C_{O_3} \quad (8)$$

Hydroxyl oxidation ($\cdot OH$)

$$R_{BBP, \cdot OH} = -k_{\cdot OH} C_{BBP} C_{\cdot OH} \quad (9)$$

Finally, the total BBP degradation rate could be predicted by a kinetic model based on the sum of all the effects occurring during the treatment:

$$R_{BBP, T} = \sum R_{BBP, i} = -(\Phi_{BBP} e_{BBP}^a + k_{O_3} C_{BBP} C_{O_3} + k_{\cdot OH} C_{BBP} C_{\cdot OH}) = -(\Phi_{BBP} e_{BBP}^a + k_{O_3} C_{BBP} C_{O_3} + k_{\cdot OH}^* C_{BBP} C_{O_3}) \quad (10)$$

It is important to notice that by the combination of experiments using O_3 alone and with O_3+t -BuOH, it is possible to estimate the value of the kinetic constant of the direct oxidation.

Introducing the corresponding kinetic equations and $\langle e_i^a(t) \rangle_{V_R}$ values in the different mass balances and using regression techniques, the numerical values of the reaction constants were estimated. Table 1 shows the kinetics parameters obtained. Finally, Fig. 6a presents the correlation between the set of experimental data and the model results obtained using the final equation ($r^2=0.95$).

This results show that the use of O_3 and O_3/UV is an effective technique for the degradation of BBP. The half-life time calculated in this study, even using ozone in absence of UV radiation and the lower ozone concentration, is more than 10 times lower than reported by Xu et al. (2009) for the photocatalytic degradation of BBP. Using a similar initial concentration of BBP (2.5 ppm), the authors found that the degradation of BBP was only 37 % after 30 min of photocatalytic treatment. The observed kinetic constant was more than two times lower than calculated in this work. Regarding the degradation of total organic carbon, Xu et al. (2009) reported a TOC reduction of 60 % after a reaction time of 80 min, using an initial concentration of BBP of 1 ppm (lower than us).

Ferreira de Oliveira et al. (2011a) studied the degradation of diethyl phthalate (DEP) using ozone. The authors found, in agreement with our results on the degradation of BBP, that an increase in the reaction pH causes an increase in the degradation rate of DEP. For a reaction pH of 7.2, the values reported for the direct kinetic constant are very similar to the results found in this report. The authors found that the contribution of

OH radicals to DEP degradation was 86.1 and 98.4 % at pH 2.5 and 7.2, respectively. In our report, we found that the contribution of OH radicals to BBP degradation at pH=7 was 87 %.

Identification of BBP intermediates and final products

To explore the degradation mechanism of BBP, the intermediate products formed in the ozonation process were identified GC–MS methods as described before. Comparison with available standard compounds, instrumental library searches, literature data, and mass fragmentation pattern were used to identify degradation intermediates. Mono-butyl phthalate, mono-benzyl phthalate, butanoic acid, benzyl alcohol, benzoic acid, phthalic acid, and *n*-butanol were identified as intermediate products of BBP degradation, in agreement with literature data (Chatterjee and Dutta 2008b; Xu et al. 2009).

Based on the identification of intermediates and literature, a summarized reaction scheme for the degradation of BBP was consolidated. As will be shown below, the final products are mineralized compounds.

The loss of butanol or benzyl alcohol from BBP could lead to the formation of the observed products mono-butyl phthalate and mono-benzyl phthalate. These intermediates may undergo further oxidations to produce phthalic acid.

The degradation of *n*-butanol leads to the formation of butyraldehyde that is oxidized to produce butanoic acid.

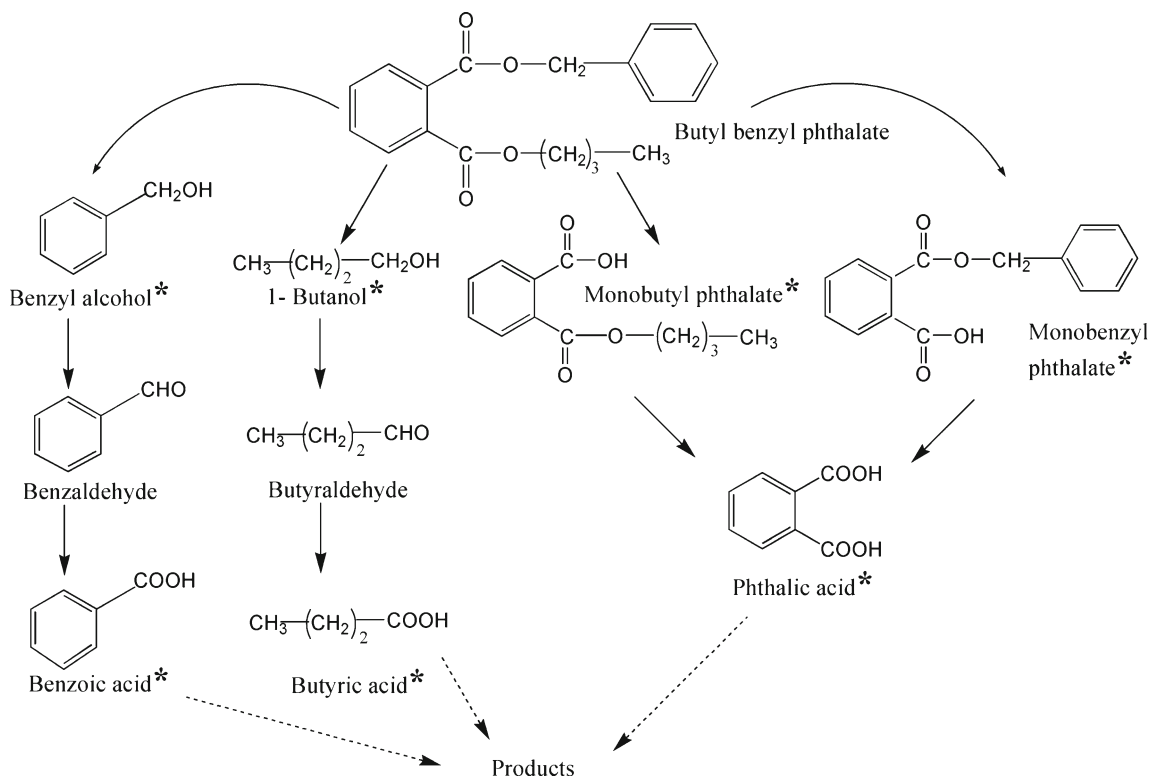


Fig. 7 Summarized reaction scheme for the degradation of BBP by ozonation (*asterisks*) Compounds identified in this study

This last oxidation occurs very fast, and butyraldehyde could not be identified in this study. The oxidation of benzyl alcohol produces benzaldehyde that is oxidized to benzoic acid in a similar way.

Regarding the ability of oxidation/mineralization process, Fig. 6b shows the time variation of total organic carbon. It can be noticed that the removal of TOC was approximately 80 % after degradation time of 75 min which indicated that most of BBP and the intermediate products would be mineralized to final products CO₂ and water. Figure 7 shows the proposed reaction scheme for the degradation of BBP.

Conclusions

Effects of ozone concentration, pH, UV radiation, and scavengers on the degradation of BBP by O₃/UV process were investigated. It was determined that (i) an increase in dissolved O₃ concentration enhances the degradation of BBP; (ii) the presence of *t*-BuOH decreases the reaction rate; (iii) the use of O₃/UV is much more effective than O₃ alone for BBP oxidation; (iv) the efficiency of BBP degradation increases when pH value increases; and (v) the reaction shows sensitivity to the irradiation rates. Major intermediates of the BBP degradation were identified and are in agreement with those detected in microbiological and photocatalytic processes. A summarized degradation scheme was proposed. The degradation kinetics was correctly modeled by a pseudo-second-order kinetic model based on the sum of all the effects occurring during the treatment, and the corresponding kinetic parameters were obtained. The results obtained give good expectation to be applied with success for the treatment of water contaminated with BBP.

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