



# Ozonation and peroxone oxidation of benzophenone-3 in water: Effect of operational parameters and identification of intermediate products

Pablo Gago-Ferrero<sup>a</sup>, Kristof Demeestere<sup>b,\*</sup>, M. Silvia Díaz-Cruz<sup>a</sup>, Damià Barceló<sup>a,c</sup>

<sup>a</sup> Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18–26, 08034 Barcelona, Spain

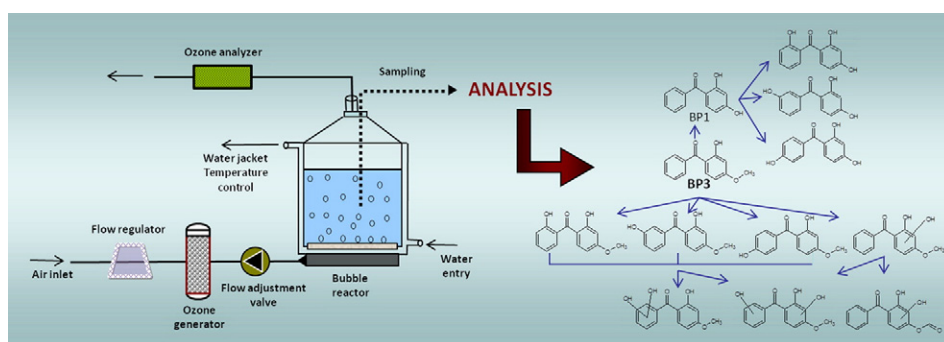
<sup>b</sup> Research Group EnvOC, Department of Sustainable Organic Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium

<sup>c</sup> Catalan Institute for Water Research (ICRA), Parc Científic i Tecnològic de la Universitat de Girona, C/ Emili Grahit, 101 Edifici H2O, E-17003 Girona, Spain

## HIGHLIGHTS

- ▶ Ozonation shows to be a promising technology for the elimination of BP3.
- ▶ New data are obtained on the effect of process parameters on BP3 removal.
- ▶ Conditions favoring hydroxyl radical formation accelerate the degradation process.
- ▶ The reactivity is higher through radicalar pathways compared to direct ozonation.
- ▶ Seven major transformation products of BP3, including BP1 and DHMB, are identified.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 10 July 2012

Received in revised form 21 September 2012

Accepted 2 October 2012

Available online 25 November 2012

### Keywords:

UV filters  
Advanced oxidation  
Water treatment  
Parameter study  
Degradation pathways

## ABSTRACT

The goal of this study was to bring forward new data and insights with respect to the effect of operational variables and reaction pathways during ozonation and peroxone oxidation of the UV filter compound benzophenone-3 (BP3) in water. A systematic parameter study, investigating the effect of the ozone inlet concentration, temperature, pH, H<sub>2</sub>O<sub>2</sub> and t-butanol addition in a lab-scale bubble reactor, showed the promising potential of ozonation towards BP3 degradation. pH showed to be a major process parameter, with half-life times (5.1–15.0 min) being more than two times shorter at pH 10 compared to neutral and acid conditions. This indicates the important role of hydroxyl radicals as supported by the addition of H<sub>2</sub>O<sub>2</sub> and t-butanol as HO• promoter and scavenger, respectively. Ozonation intermediate products were identified by liquid chromatography coupled to quadrupole-time-of-flight mass spectrometry (HPLC–QqTOF-MS/MS). Demethylation and non-selective HO• attack proved to be the major reaction mechanisms. Where available, identified intermediates were confirmed using analytical standards, and concentration profiles along the ozonation process were determined through selective targeted MS/MS analysis. Benzophenone-1 (BP1), also being a UV-filter compound, and 2,2'-dihydroxy-4-methoxybenzophenone (DHMB) revealed to be the major BP3 degradation products, showing a maximum concentration at about the half-life time of BP3.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Benzophenone-3 ((2-hydroxy-4-methoxyphenyl)-phenylmethadone, BP3) absorbs and dissipates UV irradiation, and constitutes one of the most commonly used UV filters. This compound is used in personal care products such as cosmetics, beauty creams, lotions and shampoos, or as

\* Corresponding author. Tel.: +32 9 264 59 65; fax: +32 9 264 62 43.  
E-mail address: [Kristof.Demeestere@UGent.be](mailto:Kristof.Demeestere@UGent.be) (K. Demeestere).

an additive in polymeric materials that have to be protected from sunlight-initiated disruption (FDA, 1999; Council Directive, 1976).

Recent studies (Fent et al., 2010a; Gago-Ferrero et al., 2012a) indicate that sunscreen agents, including BP3, are persistent and bio-accumulative compounds (Log  $K_{OW}$ =3.79, <http://www.syrres.com/esc/physdemo.htm>). The increasing use of UV filters constitutes a potential risk for the environment. BP3 was detected in several environmental matrices such as in surface waters (Balmer et al., 2005), sediments (Gago-Ferrero et al., 2011a) and fish (Fent et al., 2010a), as well as in human milk (Hany and Nagel, 1995; Schlumpf et al., 2010). BP3 shows estrogen-like activity in vitro and in vivo assays (Schlumpf et al., 2004; Calafat et al., 2008; Blüthgen et al., 2012). Dermal and oral administration of BP3 to rats and mice has shown alterations in liver, kidney, and reproductive organs (Calafat et al., 2008). A recent study of Kunisue et al. (2012) indicates that exposure to elevated levels of benzophenone type UV filter compounds may be associated with estrogen-dependent diseases such as endometriosis.

Current wastewater treatment techniques are not effective in removing UV filters (Li et al., 2007; Negreira et al., 2009). These compounds are preferably retained in sewage sludge (Gago-Ferrero et al., 2011b; Negreira et al., 2011), which might be further used as a fertilizer. BP3 was measured at relatively high values (37 to 3810 ng L<sup>-1</sup>) in raw wastewater and primary effluent (Snyder et al., 2006). The latter value is not far from the predicted no observed effect concentration (PNEC) for BP3 (6000 ng L<sup>-1</sup>, chronic effects), as estimated in a recent tentative environmental risk assessment for fish and *Daphnia magna* (Fent et al., 2010b). In this context, there is an urgent need of new approaches for wastewater treatment for the removal of UV-absorbing compounds.

Advanced oxidation processes (AOPs), which generate hydroxyl radicals (HO•), are a promising tool for the removal of persistent organic pollutants (POPs) at an acceptable cost (0.05–0.20 euros per m<sup>3</sup> for ozonation) (Joss et al., 2008). There is abundant information about removal of pharmaceuticals and pesticides via innovative physical–chemical processes, but for personal care products the data available are limited. The feasibility of BP3 removal from sewage or treated gray water by ozone has been demonstrated in a few studies (Table 1), but a detailed insight in the mechanisms and the parameters affecting ozonation and perozone oxidation processes are lacking so far. There are some studies reporting the conversion of BP3 into other benzophenone-type degradation products like BP1 during fungal biodegradation (Gago-Ferrero et al., 2012b) or human metabolism (Okereke et al., 1993, 1995; Kunisue et al., 2012), but its behavior during advanced oxidation processes is largely unknown. Moreover, apart from mechanistic considerations, also the data reported on removal efficiency are somewhat ambiguous. For example, whereas Rosal et al. (2010) did not detect any BP3 elimination by ozone, other studies report removal efficiencies above 80%. Hernández-Leal et al. (2011) recently studied BP3 degradation in Milli-Q water along with 17 other micropollutants and their results evidenced that BP3 was removed up to 94% (from 673 to 40 ng L<sup>-1</sup>).

Given the lack of data and knowledge in this field, the aim of this research was to systematically investigate the removal of BP3 in water when treated with ozone and/or hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The scope is twofold. First, the focus is put on the effect of operational

variables on BP3 removal and on the ozone consumption. To the author's best knowledge, this study constitutes the first one investigating the effect of important process parameters like pH, H<sub>2</sub>O<sub>2</sub> addition, temperature, and inlet ozone concentration on the ozonation of UV filters. Second, by use of advanced analytical techniques based on liquid chromatography coupled to quadrupole-time-of-flight tandem mass spectrometry (HPLC–QqTOF-MS/MS), BP3 main ozonation and perozone byproducts are identified and structurally characterized to gain insight in the advanced oxidation pathway of BP3 in water.

## 2. Materials and methods

### 2.1. Standards and reagents

BP3 (CAS N. 131-57-7) and BP1 (CAS N. 131-56-6) were purchased from Sigma-Aldrich (Germany). 2,2'-dihydroxy-4-methoxybenzophenone (DHMB, CAS N. 131-53-3) and 2,3,4-trihydroxybenzophenone (THB, CAS N. 1143-72-2) were supplied by Dr. Ehrenstorfer (Germany). The isotopically labeled compound 2-hydroxy-4-methoxy-2',3',4',5',6'-d5 (BP3-d5), used as an internal standard, was obtained from CDN isotopes (Canada). The organic solvents (>99.8% purity) methanol, acetone, acetonitrile and HPLC grade water were provided by Biosolve (The Netherlands). H<sub>2</sub>O<sub>2</sub> (35 wt.%), KH<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub> and NaB<sub>4</sub>O<sub>7</sub>·10(H<sub>2</sub>O) were supplied by Acros Organics (Belgium). H<sub>3</sub>PO<sub>4</sub> (≥85%, 15 M) was obtained from Merck (Belgium). Clean dry air ([H<sub>2</sub>O]<3.0 ppm<sub>v</sub>; [CO<sub>2</sub>]v; [C<sub>x</sub>H<sub>y</sub>]v) was provided by L'Air Liquide (Belgium). Solid phase extraction (SPE) was carried out with Oasis HLB cartridges (60 mg sorbent, Waters, Spain).

### 2.2. Experimental setup

The ozonation experiments were performed in a temperature controlled bubble column with a height of 41.8 cm and an inner and outer diameter of 10.3 and 14.1 cm, respectively. Ozone was generated in dry air by a LAB2B ozone generator (Ozononia, Switzerland) and after flow adjustment dosed through a sintered glass plate at the bottom of the reactor. The reaction solution was prepared by adding BP3 powder (0.219 mmol L<sup>-1</sup> (50.0 mg L<sup>-1</sup>)) to deionized water at controlled temperature conditions. After stirring this oversaturated solution for 24 h, the undissolved fraction was removed by filtration over a 0.45 μm filter, and the reactor was filled with 2.4 L of the BP3 saturated aqueous solution (dissolved concentration, 22.3 μmol L<sup>-1</sup> (5.1 mg L<sup>-1</sup>); RSD=5%, n=10). At the standard conditions, i.e. those applied during the initial experimental setup, the ozone inlet concentration was 85.7 μmol L<sub>gas</sub><sup>-1</sup>, the gas flow rate 120 mL min<sup>-1</sup>, and the reactor temperature 25 °C. The ozone mass transfer coefficient (k<sub>l,a</sub>) in the bubble column was determined to be 5.5 h<sup>-1</sup> (De Witte et al., 2010). The gas holdup and specific gas–liquid contact area are calculated (Tizaoui et al., 2009; Heynderickx et al., 2011) to be 0.014 (dimensionless) and 15 m<sup>2</sup>m<sup>-3</sup>, respectively. The water was buffered by a 10.12 mM phosphate buffer (pH 3 and pH 7) or a 2.5 mM borax buffer (pH 10). For the perozone experiments, H<sub>2</sub>O<sub>2</sub> was added in concentrations of 10–600 μM. Ozonated liquid samples were taken by a tap at 6 cm water height. Since the liquid phase in

**Table 1**  
Overview of reported studies dealing with the ozonation of BP3 in sewage water.

Type of water	Scale	Mode	Time (min)	AOD <sup>a</sup> (mg L <sup>-1</sup> )	C <sub>0</sub> <sup>b</sup> (ng L <sup>-1</sup> )	Removal (%)	Reference
STP effluent	Lab-scale	Semi-batch	15	16.3	123	NR <sup>c</sup>	Rosal et al. (2010)
Tertiary effluent	Pilot-scale	Continuous	24	7.3	6	>83	Snyder et al. (2006)
Tertiary effluent	Full-scale	Continuous	180	5–6	311	20	Li et al. (2007)
Aerobically treated gray water	Lab-scale	Batch	45	1.22	285	>94	Hernández-Leal et al. (2011)

<sup>a</sup> AOD: applied ozone dose.

<sup>b</sup> C<sub>0</sub>: initial BP3 concentration.

<sup>c</sup> NR: not removed.

Download English Version:

<https://daneshyari.com/en/article/6333359>

Download Persian Version:

<https://daneshyari.com/article/6333359>

[Daneshyari.com](https://daneshyari.com)