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Chlorination of oxybenzone: Kinetics, transformation, disinfection byproducts formation, and genotoxicity changes

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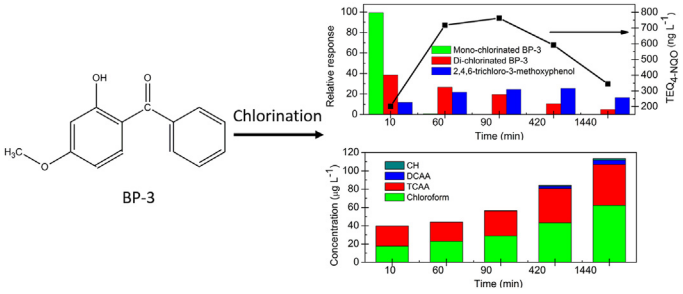
HIGHLIGHTS

- Oxybenzone reacted quickly with chlorine.
- Transformation product 2,4,6-trichloro-3-methoxyphenol was comparably stable.
- High amounts of chloroform and TCAA were formed during chlorination of oxybenzone.
- Significantly elevated genotoxicity was observed after chlorination of BP-3.

GRAPHICAL ABSTRACT



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ABSTRACT

UV filters are a kind of emerging contaminant, and their transformation behavior in water treatment processes has aroused great concern. In particular, toxic products might be produced during reaction with disinfectants during the disinfection process. As one of the most widely used UV filters, oxybenzone has received significant attention, because its transformation and toxicity changes during chlorine oxidation are a concern. In our study, the reaction between oxybenzone and chlorine followed pseudo-first-order and second-order kinetics. Three transformation products were detected by LC-MS/MS, and the stability of products followed the order of tri-chloro-methoxyphenoyl > di-chlorinated oxybenzone > mono-chlorinated oxybenzone. Disinfection byproducts (DBPs) including chloroform, trichloroacetic acid, dichloroacetic acid and chloral hydrate were quickly formed, and increased at a slower rate until their concentrations remained constant. The maximum DBP/oxybenzone molar yields for the four compounds were 12.02%, 6.28%, 0.90% and 0.23%, respectively. SOS/umu genotoxicity test indicated that genotoxicity was highly elevated after chlorination, and genotoxicity showed a significantly positive correlation with the response of tri-chloro-methoxyphenoyl. Our results indicated that more genotoxic transformation products were produced in spite of the elimination of oxybenzone, posing potential threats to drinking water safety. This study shed light on the formation of DBPs and toxicity changes during the chlorination process of oxybenzone.

1. Introduction

UV filters are an important ingredient in personal care products to protect humans from sun exposure. They are increasingly used

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because of concern over UV irradiation and skin carcinoma. Apart from that, UV filters are also applied as additives in various plastic products to prevent yellowing and degradation (Zenker et al., 2008). UV filters frequently end up in aquatic environments as a direct or indirect consequence of human activities, directly through recreational activities (i.e., swimming in surface waters) and industrial wastewater discharges and indirectly through wastewater effluent containing UV filters (Santos et al., 2012).

Oxybenzone (BP-3) is one of the most frequently used benzophenone (BP) type UV filters. The additive amount of BP-3 in sunscreen products was reported to be as high as 10% (Kim and Choi, 2014). Many studies have confirmed the endocrine-disrupting effects of BP-3 both *in vivo* and *in vitro* (Schreurs et al., 2005; Díaz-Cruz and Barceló, 2009). Specifically, BP-3 showed significant estrogenic effects during *in vitro* studies on MCF-7 human breast cancer cells, and the relative estradiol (E2) effect can be as high as 105% (Schlumpf et al., 2001). After exposure to BP-3, significant induction of vitellogenin was observed in rainbow trout and Japanese medaka (Coronado et al., 2008). Considering the high K_{OW} value of BP-3 (Log $K_{OW} = 3.79$), it has the potential to accumulate in living creatures and pose potential threats to human health and other living creatures.

BP-3 has frequently been detected in aquatic environments, and ranks higher than other UV filters in terms of concentration level (typically in the magnitude of ng L^{-1} to μg L^{-1}) and detection frequency (Balmer et al., 2005; Kameda et al., 2011; Diaz-Cruz et al., 2012; Jurado et al., 2014; Tsui et al., 2014). One thing of great concern is that extraordinarily high levels of BP-3 were observed in tap water in Barcelona, Spain, with a maximum value of 363 μg L^{-1} (Diaz-Cruz et al., 2012). High levels of BP-3 were detected in waters used for recreational purposes. Up to 2013 ng L^{-1} BP-3 was detected in seawater near a popular beach in South Carolina, USA (Bratkovics and Sapozhnikova, 2011), and concentration in swimming pools in Greece and Germany was 2400–3300 ng L^{-1} (Lambropoulou et al., 2002), and 1200 ng L^{-1} (Zwiener et al., 2007), respectively.

Disinfection is the final protection of drinking water before it is distributed to consumers. It is effective in inactivating pathogens. However, the micropollutants which are not removed by the traditional drinking water treatment (coagulation, sedimentation, and filtration) are likely to be oxidized in the disinfection process (Westerhoff et al., 2005). Chlorine is the most commonly used disinfectant in the world. Despite its efficiency in killing pathogens, DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs) can be formed through the reaction between natural organic matter (NOM) and chlorine. Apart from the formation of DBPs from NOM, chlorine can also react with anthropogenic organic pollutants forming DBPs. Despite the fact that the concentration level of BP-3 should be low in aquatic environments, elevated levels have been observed in many waters used for recreational purposes. Thus, research on formation of DBPs is important for assessing water safety and human health impact. Moreover, other transformation products might also be formed during the chlorination process (Bedner and MacCrehan, 2005; Chen and Westerhoff, 2010; Tawk et al., 2014). In recent years, numerous studies have focused on the identification of transformation products from organic pollutants by chlorination, e.g., pharmaceuticals and personal care products (PPCPs), and possible implications to the aquatic environment since the overall toxicity of parent compounds after chlorination has been observed to increase (Hu et al., 2002; Tawk et al., 2014).

Chlorination behavior of BP-3 in aquatic environments has not caused concern until recently. Negreira et al. (2008) studied chlorination kinetics of BP-3 and identified transformation products by gas chromatography - mass spectrometry (GC-MS). The first-order and second-order kinetics and the influence of pH on the degradation behavior of BP-3 were comprehensively studied, and the chloroform formation potential was also investigated by Duirk et al. (2013). Zhuang et al. (2013) investigated stability of transformation products and acute toxicity changes using tests by *Vibrio fischeri*. Lately, Manasfi et al. (2015) studied the formation patterns of brominated products of BP-3 and bromoform formation in an artificial seawater swimming pool. Chlorination kinetics, transformation products, and genotoxicity changes of the compound 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (BP-4), which shares similar structure to BP-3, was also evaluated (Negreira et al., 2012; Xiao et al., 2013). To our knowledge, no research has ever focused on the genotoxicity changes after chlorination of BP-3, and the relationship between transformation products and toxicity has not been investigated. The formation of other DBPs from chlorination of BP-3, such as HAAs, are not known. Thus, genotoxicity changes measured using SOS/umu test and DBP formation from chlorination were evaluated in this study, as well as degradation kinetics and product identification.

2. Materials and methods

2.1. Chemicals

Oxybenzone (>98%, analytical grade), sodium hypochlorite solution (available chlorine 4.00–4.99%), ammonium acetate for mass spectrometry (>99%, eluent addictive for LC-MS) were purchased from Sigma-Aldrich (St. Louis, MO, USA). EPA 551A, 551B halogenated volatile mixture containing trihalomethanes (THMs), haloketones (HKs), haloacetonitriles (HANs), chloral hydrate (CH) and EPA 552.2 haloacetic acids mix were purchased from Supelco (Bellefonte, PA, USA). Methyl *tert*-butyl ether (MtBE) and methanol of HPLC grade were purchased from Fisher Scientific (Geel, Belgium) and J.T. Baker (USA), respectively. Stock solution of BP-3 was prepared in methanol with a concentration of 1 g L^{-1}. The pH value was adjusted by 10 mM phosphate buffer (mixture of 10 mM disodium hydrogen phosphate dodecahydrate and 10 mM sodium dihydrogen phosphate dihydrate) in this study, and determined by a pH meter (Thermo Scientific). Ultra-pure water used in the study was produced by a Mill-Q purifier (Millipore). All the glass vials were rinsed with acetone, methanol, and ultra-pure water in sequence before use.

2.2. Chlorination kinetics of BP-3

In order to have better knowledge of the chlorination rate of BP-3, the degradation kinetics experiment was conducted in a 150 mL amber glass bottle equipped with a small magnetic stir bar to ensure homogeneity of the solution. The experiment was carried out at room temperature (approximately 24 °C), and pH was controlled at 7 ± 0.1. The initial concentration of BP-3 was 1 mg L^{-1}, and different free chlorine doses were spiked to analyze the influence of chlorine dose on the reaction kinetics. In order to ascertain that the reaction was performed under pseudo-first-order conditions, the free chlorine dose was spiked at least ten times higher than that of BP-3 (the molar ratios of Cl_2/BP-3 = 9.6, 11.2, 12.8, 13.7, and 16.0, respectively). At given time intervals, 1 mL of aliquot was sampled, and transferred to a 2 mL injection vial containing excess $Na_2S_2O_3$ to quench the residual chlorine. The samples were analyzed by LC-MS/MS as soon as possible. The kinetic study was also conducted under pH 6 and 8 to assess the influence of pH on the reaction rate.

2.3. Chlorination products identification

The products identification experiment was carried out in a