Chlorination and chloramination of benzophenone-3 and benzophenone-4 UV filters

Peizeng Yang[a], Deyang Kong[b], Yuefei Ji[a], Junhe Lu[a,*], Xiaoming Yin[a], Quansuo Zhou[a]

[a] Department of Environmental Science and Engineering, Nanjing Agricultural University, Nanjing 210095, China
[b] Nanjing Institute of Environmental Science, Ministry of Environmental Protection of PRC, Nanjing 210042, China

ABSTRACT

The objective of this research was to explore the fundamental reactions between chlorine/chloramine and 2-hydroxyl-4-methoxyl benzophenone (BP3)/2-hydroxyl-4-methoxyl benzophenone-sulfonic acid (BP4), which were the most common reactions in benzophenone-type UV filters during drinking water treatment processes. Both BP3 and BP4 could react with free chlorine and chloramine, with reactions following pseudo-first-order kinetics in excess of chlorine (HClO) and chloramine (NH_2Cl). Generally, chlorination was more rapid than chloramination. BP4 was less reactive than BP3 toward both chlorine and chloramine, due to the presence of an electron-accepting sulfonate group. Therefore, BP3 had a significantly higher disinfection by-products (DBP) formation potential than BP4. Chlorination of BP3 and BP4 generated remarkably higher levels of DBPs than chloramination, with high pH conditions facilitating the formation of chloroform but inhibiting the formation of haloacetic acid (HAAs). Comparison of the reaction behavior of two different BP-type UV filters, i.e., BP3 and BP4, revealed that certain functional groups significantly affected the reactivity of BP-type UV filters in chlorination and chloramination processes. This contribution may provide new insights into the reaction behavior of UV filters during drinking water disinfection process using chlorine and/or chloramine as disinfectant, and provide guidelines for drinking water safety management.

1. Introduction

UV filters are active ingredients widely used in a variety of products, such as plastic additives to prevent yellowing and degradation of plastic products, or in sunscreens to protect the skin from UV damage such as sunburn, photo-ageing and even cancer (Brooke et al., 2008; Gackowska et al., 2014; Kupper et al., 2006; Ramos et al., 2016). Despite the growing health concerns (Langford et al., 2015; Ramos et al., 2016; Santos et al., 2013; Tsui et al., 2014b), sunscreen products, especially those contain several different UV filters with high sun protection factor (SPF), remain popular among consumers. Benzophenone (BP)-type UV filters are a commercially important group of UV filters, which contain a benzophenone backbone. According to the number and types of functional groups attached to the backbone, a total of 12 BP-type UV filters are commercially used (Karthikraj et al., 2017; Santos et al., 2012). Among them, 2-hydroxyl-4-methoxyl benzophenone (BP3, pK_a = 9.65) (Li et al., 2016a, 2016b) and 2-hydroxyl-4-methoxyl benzophenone-sulfonic acid (BP4, pK_{a1} = −0.7, pK_{a2} = 7.3) (De et al., 2013; Negreira et al., 2009) are two of the most abundantly used. Their usage is approved in EU, USA, Japan and many other countries (Shaath, 2010). The content of BP3 or BP4 in sunscreen agents can account for up to approximately 10% of the total formulation (Kim and Choi, 2014).

Although UV filters can protect the skin from damage caused by UV radiation, the BP-type UV filters have been shown to exhibit potential endocrine disrupting activity and genotoxicity (Diaz-Cruz et al., 2009; Kunz and Fent, 2009; Xiao et al., 2013; Zhao et al., 2013). BP-type UV filters can bio-accumulate in vivo and mimic hormones. The Japanese Ministry of Environment has classified the BP-type UV filters as a group of chemicals with suspected endocrine disrupting effects (Molins-Delgado et al., 2016; MOE, 2000).

Owing to their chemical stability and resistance to biodegradation, BP3 and BP4 are frequently detected in aquatic environments, which is of significant environmental concern. BP3 concentration of 363 ng L^{-1} was detected in tap water in Barcelona (Spain) (Diaz-Cruz et al., 2012). Up to 1548 ng L^{-1} BP4 was detected in influents of wastewater treatment plants (WWTP) in Catalonia (NE, Spain) (Gago-Ferrero et al., 2013a, 2013b). Similar or higher concentrations of BP3 and BP4 were

also reported in WWTP effluents in Hongkong and the surface water at Jamaica Bay in New York (Tsui et al., 2014a). In particular, higher levels of BP3 were found in waters used for recreational purposes. For example, up to 1258 ng L^{-1} BP3 was reported at Tropical (TP) beach in Okinawa Island (Japan) in August (Tashiro and Kameda, 2013). BP3 concentrations as high as 2400–3300 ng L^{-1} and 1200 ng L^{-1} were reported in swimming pools in Greece and Germany, respectively (Lambropoulou, 2002; Zwiener, 2007).

Washing off from human's skins into recreational water bodies, such as swimming pool waters, represents a direct pathway through which BP3 and BP4 release into the environment (Santos et al., 2012). The high persistence of most UV filters results in wastewater treatment plants failing to completely remove them. Their presence in natural water bodies is therefore inevitable. WWTP effluents are generally discharged into surface waters directly, and the effluent-driven organic compounds can contaminate surface waters which, in some cases, are used as drinking water supplies (Li et al., 2016a, 2016b; Xiao et al., 2013). To ensure pathogens inactivation, disinfection is typically applied in drinking water treatment before finished water is delivered to consumers through distribution systems. In addition, micropollutants that are not effectively removed by traditional drinking water treatment processes (e.g., coagulation, sedimentation, and filtration) can be degraded in the final disinfection process (Deborde et al., 2004; Von, 2003; Lu et al., 2004; Postigo et al., 2014; Westerhoff et al., 2005; Gong and Zhang, 2015). The disinfectants most commonly used in drinking water treatment include chlorine and chloramine, with the former being more cost-effective and providing a good level of disinfection. Chloramine is a secondary disinfectant which is formed when free chlorine is added to water containing ammonia (NH$_3$). Despite the importance of chlorine and chloramine to pathogens disinfection and micropollutants oxidation, chlorination can produce certain transformation products which may be more toxic than their parent compounds (Negreira et al., 2008, 2009; Rule et al., 2005; Sherwood et al., 2012; De et al., 2013; Lu et al., 2018; Duirk et al., 2013a, 2013b). Another major drawback of chlorination is the formation of disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), through reactions between dissolved natural organic matter (NOM) and chlorine (Abdallah et al., 2015; Li et al., 2016a, 2016b; Negreira et al., 2008; Xiao et al., 2013; Zhang et al., 2016). DBPs have been reported to induce carcinogenicity, toxicity and teratogenicity, with dichloroacetic acids (DCAA) and trichloroacetic acids (TCAA) found to be hepatotoxic and potentially cause neuropathy and fetal abnormality (Tawk et al., 2014; Zhuang et al., 2013; Xiao et al., 2013; Zhang et al., 2016). The disinfection by chloramine is less efficient; however, it can also generate DBPs, albeit to a lesser extent (Bougeard et al., 2010; Xie, 2003). Therefore, studies on the potential for forming transformation products and DBPs in drinking water chlorination/chloramination are important for assessing water safety and human health.

UV filters that are present in water supplies can be exposed to disinfectants which have the potential to induce degradation and form byproducts with varying levels of toxicity compared to their parent compounds (Hu et al., 2002). In fact, several papers have been published in recent years on the transformation of BP-type UV filters by chlorine (Li et al., 2016a, 2016b; Negreira et al., 2008; Xiao et al., 2013; Zhang et al., 2016). For instance, Zhang et al. (2016) detected three chlorinated products of BP3 which displayed substantially enhanced bio-toxicity. Negreira et al. (2008) have demonstrated that 2,4-dihydroxybenzophenone (BP1) and BP3 were unstable in chlorinated water, resulting in the formation of several chlorinated intermediates and DBPs via cleavage of the benzene ring. Xiao et al. (2013) have also detected chlorinated intermediates with relatively high genotoxicity during the BP4 chlorination process. While these studies have demonstrated that chlorinated intermediates and DBPs, such as HAAs and chloroform, can be formed from the reaction between free chlorine and BP-type UV filters, few studies have focused on the transformation of

UV filters by chloramine, which is a priority focus in the present study. In addition, comparison of the reaction behavior of BP3 and BP4, revealed that certain functional groups significantly affected the reactivity of BP-type UV filters in chlorination and chloramination processes. This contribution may provide new insights into the reaction behavior of UV filters during drinking water disinfection process using chlorine and/or chloramine as disinfectant, and provide guidelines for drinking water safety management.

2. Materials and methods

2.1. Chemicals

BP3 and BP4 (with purities > 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). 1 g L^{-1} stock solutions of each BP were prepared in methanol and kept at 4 °C before usage. Sodium hypochlorite solution (NaOCl, available chlorine > 4%) was purchased from Nanjing Chemical Reagent (Nanjing, China), with the absolute chlorine concentration established using the DPD method (APHA/AWWA/WEF, 2005). Chloramine was prepared by adding sodium hypochlorite to an excess ammonium solution at pH 8–9 (ratio 1:1.2), resulting in the formation of a monochloramine solution. Potassium dihydrogen phosphate (KH$_2$PO$_4$), sodium hydroxide (NaOH), anhydrous sodium sulfate (Na$_2$SO$_4$), sodium sulfite (Na$_2$SO$_3$), sodium bicarbonate (NaHCO$_3$), sulfuric acid (H$_2$SO$_4$) and ammonium chloride (NH$_4$Cl) were purchased from J&K (Beijing, China). All chemicals were of the purest available quality and all diluted solutions were prepared with ultra-pure water (18.2 MΩ cm) produced using a Milli-Q (Millipore) water purification system. A calibration mixture containing trihalomethanes (THMs), 1,2-dibromopropane and haloacetic acids (HAAs) and trichloropropane (TCP) were also purchased from Sigma-Aldrich (St. Louis, MO, USA). Methyl *tert*-butyl ether (MTBE), methanol, acetonitrile, formic acid and acetic acid were all HPLC grade and were purchased from Fisher (Waltham, MA, USA). All experiments were performed at room temperature (20 °C).

2.2. Kinetics experiments

The chlorination and chloramination kinetics experiments were conducted in 60 mL brown glass vials with magnetic stirring to ensure homogeneity of the reaction solution. Initial BP concentration was diluted from the stock solution to 1 mg L^{-1}, using ultra-pure water. The reaction was initiated by rapidly mixing each BP solution in combination with chlorine or chloramine, with phosphate buffer (10 mM) added to maintain pH 7 conditions. To ascertain whether the reaction occurred under pseudo-first-order conditions, the molar ratio of chlorine or chloramine to BP was maintained at 10:1, respectively. At pre-set time intervals, a 1 mL aliquot was collected and transferred to a 2 mL injection vial containing an excess of Na$_2$SO$_3$ to quench any residual chlorine and stop the reaction.

BP3 and BP4 concentrations were analyzed using high performance liquid chromatography (HPLC, Hitachi L-2000, Japan), with separation performed using a LaChrom C18 reversed phase column (Hitachi LaChrom, 5 μm × 250 nm × 4.6 mm). An isocratic elution gradient was applied, consisting of 70% acetonitrile (with 0.1% acetic acid) and 30% water (with 0.1% acetic acid) for BP3, or 60% acetonitrile (with 0.1% acetic acid) and 40% water (with 0.1% acetic acid) for BP4, at a flow rate of 1 mL min^{-1}. The detection limits of BP3 and BP4 were 30 μg/L and 80 μg/L, respectively.

2.3. Identification of transformation products of BP3 and BP4

The chlorination and chloramination products identification experiments were conducted in 250 mL beaker flasks in the dark. Initial concentrations of BP3 and BP4 were both 1 mg L^{-1}. The reaction was initiated by rapidly mixing each BP solution with chlorine or