Journal of Hazardous Materials 324 (2017) 626–633

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Research paper

Effect of bromide on the transformation and genotoxicity of octyl-dimethyl-p-aminobenzoic acid during chlorination

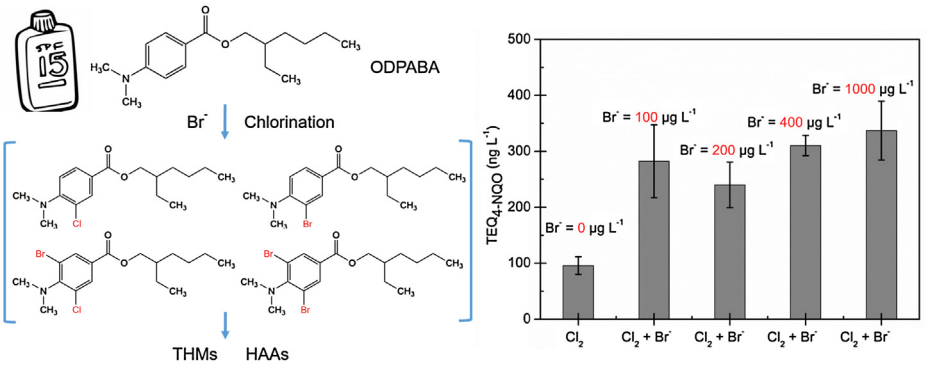
Qiwan Chai[a,1], Shujuan Zhang[b,1], Xiaomao Wang[a], Hongwei Yang[a,*], Yuefeng F. Xie[a,c]

[a] State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China
[b] International Publishing Center, China National Knowledge Infrastructure, Beijing 100192, China,
[c] Environmental Engineering Programs, The Pennsylvania State University, Middletown, PA 17057, USA

HIGHLIGHTS

- Kinetics data of ODPABA chlorination affected by bromide were acquired.
- Cl-Br-ODPABA and Br_2-ODPABA were firstly identified as transformation products.
- ODPABA cannot be readily chlorinated into HAAs and THMs.
- Appearance of bromide elevated genotoxicity of ODPABA chlorination.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 September 2016
Received in revised form 7 November 2016
Accepted 10 November 2016
Available online 15 November 2016

Keywords:
Octyl-dimethyl-*p*-aminobenzoic acid
Chlorination
Bromide
Transformation products
Genotoxicity

ABSTRACT

Octyl-dimethyl-p-aminobenzoic acid (ODPABA), one of the most commonly used organic UV filters, can undergo considerable transformation in water when entering into the disinfection process. The impacts of bromide on degradation kinetics, formation and speciation of transformation products, regulated disinfection by-products (DBPs) as well as genotoxicity changes during ODPABA chlorination were investigated in this study. Results indicated that the reaction of ODPABA with chlorine followed pseudo-first-order and second-order kinetics. Adding bromide noticeably enhanced the degradation rate of ODPABA, but reduced the impact of chlorine dose. Four halogenated transformation products (Cl-ODPABA, Br-ODPABA, Cl-Br-ODPABA and Br_2-ODPABA) were detected by LC–MS/MS. Mono-halogenated products were stable during 24-h chlorination, while di-halogenated products constantly increased. The total yields of trihalomethanes (THMs) and haloacetic acids (HAAs) were both low, but predominated by bromine substitution at high levels of bromide. In addition, SOS/umu tests showed that genotoxicity was generated after ODPABA chlorination, which was increased at least 1.5 times in the presence of bromine. Whereas, no significant genotoxicity variation was observed following bromide concentration change.

1. Introduction

UV filters, especially various kinds of organic compounds, are important constituents in sunscreens, body lotions, cosmetics, lipsticks, and many other personal care products(PCPs) for pro-

* Corresponding author.
E-mail address: yanghw@tsinghua.edu.cn (H. Yang).
[1] These authors contributed equally to this study and share first authorship.

http://dx.doi.org/10.1016/j.jhazmat.2016.11.035
0304-3894/

tecting individuals from harmful UV radiation. Besides, they are also widely added in a variety of plastic materials and equipment, such as plastic packaging, glasses, building materials and automobile components to work against degradation and yellowing [1,2]. Coinciding with their functions, most of the organic UV filters contain one or several aromatic structures attached with lipophilic groups. UV filters constantly enter into the aquatic environments through two main pathways: (a) directly by recreational activities like swimming and bathing as well as industrial wastewater discharge; (b) indirectly by domestic wastewater effluent [3]. The accumulation of UV filters has caused serious concern, because they are resistant to conventional water treatment processes [4,5]. Furthermore, many of them are related to environmental risks, especially when entering into food chains [6].

Octyl-dimethyl-*p*-aminobenzoic acid (ODPABA), a derivative of *p*-aminobenzoic acid (PABA), is one of the most frequently used UV filters. In USA, UK, AUS and China, the maximum addition of ODPABA in sunscreens is regulated to be 8% [7,8]. Recreational activities pose a strong impact on the level of ODPABA in the aquatic environments. Previous studies reported ODPABA of 111 ng L^{-1} in seawater from Folly Beach in United States [9], up to 110 ng L^{-1} in tap water in Spain [10], only 1 – 2 ng L^{-1} in moderately polluted rivers in Japan [11]. In China, ODPABA has been detected in a range of 95 – 182 ng L^{-1} in surface water for recreational purposes in Hong Kong [5], and this compound was found in 100% of surface water samples in Nanjing with the maximum concentration of 30 ng L^{-1} [12]. More recently, ODPABA was still detected in Korea's sewage treatment plants with the average concentration below 50 ng L^{-1}, though it has been prohibited in Korea as a UV filter [13]. Researches have shown that ODPABA is able to activate transcription of human estrogen receptor α (ERα) [14] and proliferate breast cancer cells in *vitro* system [15]. Besides, endocrine disruption effects for invertebrates were also reported [16].

Conventional water treatment processes (i.e., coagulation, sedimentation, and filtration) cannot effectively remove organic micropollutants [17]. These persistent pollutants may react with disinfectants during the disinfection process. Chlorine is the most commonly used disinfectant in the world due to its low cost, reliability, and convenience of maintenance. However, large amounts of regulated and emerging disinfection byproducts (DBPs) can be generated via oxidation and substitution reactions of chlorine with organic matters [18,19]. Moreover, bromide is considered as an important DBP precursor, with a concentration from ~10 to >1000 μg L^{-1} in natural fresh waters [20,21]. Bromide can be oxidized by chlorine to hypobromous acid (HOBr), which has been proved to react more effectively with aromatic species than chlorine [22]. To date, the amount studies concerning chlorination fate of ODPABA are limited. The first report was published by Sakkas et al. [23], which identified chlorinated by-products in swimming pool water with photolysis taken into account. Negreira et al. [24] discussed degradation kinetics of ODPABA during chlorination under the condition of neutral pH and chlorine doses in artificial and tap water. Nakajima et al. [25] investigated the impact of different pH on chlorine demands and by-product levels of ODPABA. However, the effect of bromide concentrations on kinetics as well as the formation and speciation of DBPs during ODPABA chlorination has not yet been studied.

Toxicology studies have showed that chlorination of some aromatic micropollutants can generate more genotoxic halogenated products than their parent compounds [26,27]. On the other hand, brominated species of regulated DBPs as well as some aromatic byproducts, are generally more genotoxic and carcinogenic than their chlorinated analogues [28,29]. One of the UV filters, benzophenone-4 (BP-4), has been proved that the acute toxicity would amount after its chlorination in the presence of bromide [30]. Thus, the existence of bromide can raise more risks for drinking water safety. Nakajima et al. [25] studied the mutagenicity during chlorination of ODPABA in modelling swimming pools. Although a decrease in the mutagenicity was observed, the toxicity is not sure when bromide is present in the water system.

In this study, the degradation behavior of ODPABA was investigated in simulated chlorinated water with various levels of bromide. Besides, SOS/umu tests were carried out to study genotoxicity changes in chlorinated water samples. Degradation kinetics, transformation products, regulated DBPs formation, and genotoxicity evaluation were comprehensively assessed.

2. Material and methods

2.1. Chemicals

ODPABA was provided by Dr. Ehrenstorfer (Germany). Ammonium acetate and sodium hypochlorite solution were purchased from Sigma-Aldrich (St. Louis, MO, USA), and EPA 551A, 551 B halogenated volatile mixture of 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), methanol, and dichloromethane of HPLC grade were purchased from Fisher Scientific (Geel, Belgium). A stock solution of ODPABA with the concentration of 1 g L^{-1} was prepared in methanol. Ultra-pure water, produced by a Mill-Q purifier (Millipore), was used in order to exclude the interference it might cause when natural water samples were utilized.

2.2. Chlorination of ODPABA

The chlorination kinetics study was carried out in a 150 mL amber glass bottle equipped with a small magnetic stir bar at room temperature (approximately 15 °C), and pH was controlled at 7 ± 0.2 with a 10 mM phosphate buffer. The initial spiked concentration of ODPABA was 1 mg L^{-1}, and this concentration was applied during all the experiments. In the chlorination experiment, different chlorine doses with molar ratios of Cl_2/ODPABA = 11.7, 15.6, 19.5, 23.4, and 27.3, respectively, were used. ODPABA was spiked first, and the reaction was initiated by the addition of calculated volume of free chlorine. 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. More samples were taken with the spiked chlorine concentration of 3 mg L^{-1} till 24 h in order to identify transformation byproducts and their variations.

In order to explore the influence of bromide on the degradation of ODPABA, 100 μg L^{-1} bromide was spiked into the solution in which chlorine doses were 2, 3, and 4 mg L^{-1}, respectively. Besides, different bromide doses of 50, 100, 200, and 400 μg L^{-1} were spiked into the solution in which chlorine dose was 3 mg L^{-1}. The samples were analyzed by LC–MS/MS as soon as possible.

2.3. Analysis of ODPABA and transformation products

Analysis of ODPABA and its transformation products was performed by Triple Quad LC–MS/MS (Agilent Technologies 1290-6460) equipped with a C18 column (2.1 mm × 50 mm × 2.5 μm, Waters XBridge, Ireland) and an electrospray (ESI) source. Pure methanol and 0.5 mM ammonium acetate in ultra-pure water were used as the mobile phases, and the flow rate was 0.2 mL min^{-1}. The elution gradient was as follows: 5% methanol initially was increased to 80% in 1 min, increased to 100% in 2 min, decreased to 5% in 6.1 min, and kept for 0.4 min. Post-run time was 2 min. Temperature of column was maintained at 30 °C. Chlorination products