



## Comparative evaluation of iodoacids removal by UV/persulfate and UV/H<sub>2</sub>O<sub>2</sub> processes



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### ABSTRACT

To develop a cost-effective method for post-formation mitigation of iodinated disinfection by-products, degradation of iodoacids by UV, UV/PS (persulfate), and UV/H<sub>2</sub>O<sub>2</sub> was extensively investigated in this study. UV direct photolysis of 4 iodoacids followed first-order kinetics with rate constants in the range of  $2.43 \times 10^{-4}$ – $3.02 \times 10^{-3}$  cm<sup>2</sup> kJ<sup>-1</sup>. The derived quantum yields ( $\Phi_{254}$ ) of the 4 iodoacids range from 0.13 to 0.34, respectively. A quantitative structure-activity relationship (QSAR) model was subsequently established and applied to predict the direct photolysis rates of 6 other structurally similar iodoacids whose standards are commercially unavailable. At a UV dose of 140 mJ cm<sup>-2</sup> which is typically applied for disinfection of drinking water, the removal percentages of 4 iodoacids were only between 3.35% and 34.7%. Thus, ICH<sub>2</sub>CO<sub>2</sub>H (IAA), the most photo-recalcitrant species, was selected as the target compound for removal in the UV/PS and UV/H<sub>2</sub>O<sub>2</sub> processes. The IAA degradation rates decreased with increasing pH from 3 to 11 in both processes. Humic acid (HA) and HCO<sub>3</sub><sup>-</sup> had inhibitory effects on IAA degradation in both processes. Cl<sup>-</sup> adversely affected the IAA degradation in the UV/PS process but had no effect in the UV/H<sub>2</sub>O<sub>2</sub> process. Generally, in the deionized (DI) water, surface water, treated drinking water, and secondary effluent, UV/PS process is more effective than UV/H<sub>2</sub>O<sub>2</sub> process for IAA removal, based on the same molar ratio of oxidant: IAA. SO<sub>4</sub><sup>-</sup> generated in the UV/PS process yields a greater mineralization of IAA than HO<sup>•</sup> in the UV/H<sub>2</sub>O<sub>2</sub> process. IO<sub>3</sub><sup>-</sup> was the predominant end-product in the UV/PS process, while I<sup>-</sup> was the major end-product in the UV/H<sub>2</sub>O<sub>2</sub> process. The respective contributions of UV, HO<sup>•</sup>, and SO<sub>4</sub><sup>-</sup> for IAA removal in the UV/PS process were 7.8%, 14.7%, and 77.5%, respectively, at a specific condition (1.5 μM IAA, 60 μM oxidant, and pH 7). Compared to UV/H<sub>2</sub>O<sub>2</sub> process, UV/PS was also observed as more cost-effective process based on the electrical energy per order (EE/O) and chemical cost.

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### 1. Introduction

Haloacetic acids (HAAs) represent the second largest group of disinfection by-products (DBPs). When iodide is present in the source water, iodoacids including iodinated haloacetic acids can be formed as iodinated disinfection by-product (I-DBPs) during the

oxidative and disinfection processes (Plewa et al., 2004). Iodoacids as a class of emerging DBPs have been detected in drinking water in some countries (Plewa et al., 2004; Krasner et al., 2006; Richardson et al., 2008; Wei et al., 2013). For example, in an occurrence study, 5 iodoacids including iodoacetic acid (IAA), bromoiodoacetic acid, (Z)-3-bromo-3-iodo-propenoic acid, (E)-3-bromo-3-iodo-propenoic acid, and (E)-2-iodo-3-methylbutenedioic acid were found at sub-μg L<sup>-1</sup> to μg L<sup>-1</sup> levels in the chloraminated and chlorinated drinking waters from 23 cities in USA and Canada (Richardson et al., 2008). In another occurrence study, IAA was also detected at sub-μg L<sup>-1</sup> to μg L<sup>-1</sup> levels in the drinking waters from 13 water plants in

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Shanghai, China (Wei et al., 2013). There is a rising concern of iodoacids due to their strong toxicities. Recent toxicity studies demonstrated that iodoacids are more cytotoxic and genotoxic than their brominated and chlorinated analogues (Plewa et al., 2004; Cemeli et al., 2006; Richardson et al., 2008). For example, IAA was 2.0 times and 47 times more genotoxic in Chinese hamster ovary (CHO) cells than bromoacetic acid (BAA) and chloroacetic acid (CAA), respectively. The cytotoxicity of IAA in CHO cells was 3.0 times and 287 times higher than BAA and CAA, respectively (Plewa et al., 2004). Generally, IAA is the most cytotoxic and genotoxic DBP in mammalian cells among the haloacetic acids. Thus, some research efforts have been directed toward the analysis, occurrences, formation, and toxicities of iodoacids (Richardson et al., 2008; Plewa et al., 2010; Li et al., 2012; Liu et al., 2013; Wei et al., 2013; Ye et al., 2013). However, to the best of our knowledge, there is still no well-documented study on the post-formation mitigation of iodoacids during water and wastewater treatment processes.

Besides post-chlorination, pre-chlorination and intermediate-chlorination are also applied in some water treatment plants. Pre-chlorination removes the odor and taste compounds and also enhances the following coagulation. The intermediate-chlorination is applied at settled water to prevent fouling of sand filter or ultra-filtration/microfiltration membrane. DBPs including I-DBPs could be generated during pre-chlorination, intermediate-chlorination and post-chlorination processes. Compared to that at the stage of post-chlorination process, I-DBPs are more easily generated during pre-chlorination and intermediate-chlorination processes, as the concentrations of DBPs precursor and iodide at these two stages are higher than those at the stage of post-chlorination. Thus, UV facilities can be considered to be installed after post-chlorination of the sand-filtered water to mitigate the formed DBPs including iodoacids.

In the past decades, the UV/H<sub>2</sub>O<sub>2</sub> process, one of the most common advanced oxidation processes (AOPs), has been extensively studied and applied in the advanced treatment of drinking water and wastewater. In the UV/H<sub>2</sub>O<sub>2</sub> process, the degradation of the target pollutant involves both UV direct photolysis and hydroxyl radical (HO<sup>•</sup>)-assisted indirect photolysis. Another type of AOP, the UV/PS (persulfate) process, has recently attracted significant scientific interest for the destruction of recalcitrant organic pollutants via the generation of sulfate radical (SO<sub>4</sub><sup>•-</sup>) (Tsitonaki et al., 2010; He et al., 2014a, 2014b; Oh et al., 2016). Since SO<sub>4</sub><sup>•-</sup> can be transformed to HO<sup>•</sup> to some extent depending on pH of the reaction solution, the degradation of the target pollutant in the UV/PS process is attributed to UV direct photolysis, as well as SO<sub>4</sub><sup>•-</sup> and HO<sup>•</sup>-assisted indirect photolysis (He et al., 2014b; Yuan et al., 2014). It is worthy to mention that the UV/PS process has been demonstrated to remove some carboxylic acids effectively through decarboxylation by SO<sub>4</sub><sup>•-</sup> (Madhavan et al., 1978; Davies et al., 1985; Criquet and Leitner, 2009). Furthermore, the efficiency of both UV/PS and UV/H<sub>2</sub>O<sub>2</sub> processes are affected by operating parameters such as UV dose, pH, oxidant dose, and water quality etc (Criquet and Leitner, 2009; Tan et al., 2013; Kwon et al., 2015).

In this study, UV direct photolysis of 4 iodoacids was firstly investigated. A quantitative structure-activity relationship (QSAR) model was established and applied to predict the direct photolysis rates of 6 other commercially unavailable iodoacids. Subsequently, degradation of IAA, the most photo-recalcitrant and toxic species among all iodoacids, by the UV/PS and UV/H<sub>2</sub>O<sub>2</sub> processes was compared in terms of the effect of pH, oxidant dose, and matrix species such as humic acid (HA) and HCO<sub>3</sub><sup>-</sup> on its photodegradation rate as well as the end-products and operating cost. Different types of water including DI water, surface water and treated drinking water (from a water treatment plant, Singapore), and secondary

effluent (from a municipal wastewater treatment plant, Singapore) were used as water matrix to further evaluate the effectiveness of these AOPs for IAA removal. The respective contributions of UV, HO<sup>•</sup>, and SO<sub>4</sub><sup>•-</sup> for IAA removal in the UV/PS process were also determined.

## 2. Materials and methods

### 2.1. Reagent and solution preparation

Synthetic solution for UV direct photolysis and UV-based advanced oxidation were prepared using deionized (DI) water. Iodochloroacetic acid (IClCHCO<sub>2</sub>H, 99+%), iodobromoacetic acid (IBrCHCO<sub>2</sub>H, 90+%), and diiodoacetic acid (I<sub>2</sub>CHCO<sub>2</sub>H, 95+%) were purchased from Cansyn Chemical Corp (Canada). Iodoacetic acid (ICH<sub>2</sub>CO<sub>2</sub>H, 99%), H<sub>2</sub>O<sub>2</sub> (35% w/w aqueous solution), and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (99%) were purchased from Alfa Aesar (Singapore). In the following, IAA and PS refer to ICH<sub>2</sub>CO<sub>2</sub>H and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, respectively.

### 2.2. Chemical analysis

Micro liquid-liquid extraction with methyl *tert*-butyl ether (MTBE) at acidic condition was adopted for extraction of iodoacids, and both NaCl and H<sub>2</sub>SO<sub>4</sub> were added to water samples to improve the extraction efficiency. The extracted iodoacids reacted with MeOH in the presence of H<sub>2</sub>SO<sub>4</sub> at 50 °C for 2 h to produce the corresponding methyl esters, which were then determined by GC (Agilent, 6890A)/ECD (Electron Capture Detector) according to U.S. EPA method 552. A DB-225 column (J&W) with helium as carrier gas was used. Nitrobenzene (NB), *p*-nitrobenzoic acid (pNBA), *p*-chlorobenzoic acid (pCBA) and *m*-toluic acid (mTA) were determined by HPLC with a photodiode array detector (Agilent, 1100 serial). I<sup>-</sup> and IO<sub>3</sub><sup>-</sup> were detected by an ion chromatography (IC) coupled with ICP-MS (Agilent, G3151A). Formic acid (HCO<sub>2</sub>H) and oxalic acid were analyzed by IC coupled with thermal conductivity detector (Dionex, ICS-3000). Formaldehyde (HCHO) was determined by headspace sampler coupled with GC (Agilent, 7890A)/FID (Flame Ionization Detector). Total organic carbon (TOC) was analyzed by a TOC analyzer (Shimadzu, TOC-VCSH). UV254 absorbance of water samples were measured by a UV/vis spectrophotometer (Shimadzu, UV-2550). H<sub>2</sub>O<sub>2</sub> concentration was measured by a WTW Photolab S12.

### 2.3. Photoreactor and photodegradation experiments

Photodegradation experiments were conducted in a 740 mL cylindrical photoreactor. A low-pressure mercury vapour lamp (5 W, emission at 254 nm, Philips) was placed in a quartz sleeve which was aligned coaxially with the photoreactor. UV direct photolysis of 4 iodoacids (each at initial concentration of 1.5 μM) in the multi-species system was conducted in DI water. UV/PS and UV/H<sub>2</sub>O<sub>2</sub> treatment of IAA (1.5 μM) were conducted in two separate series of experiments. Samples were withdrawn at the pre-determined time intervals and analyzed immediately. Since most water and wastewater treatment processes in practice are operated at circumneutral condition, the reaction solution was adjusted to pH 7 by phosphate buffer solution (5 mM) in the present study unless otherwise stated. For other pH values (3, 5, 9, and 11), the pH adjustment was carried out using 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> or NaOH solution.

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