Effects of typical water components on the UV_{254} photodegradation kinetics of haloacetic acids in water

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ABSTRACT

This study investigated a range of typical water components and parameters, including pH, carbonate, bicarbonate, halides, nitrate, dissolved organic matter (DOM), free chlorine, and initial concentration, on the photodegradation kinetics of seven different haloacetic acids (HAAs) with different halogen substitutions. The results show that the photolysis rates can generally be enhanced by additions of free chlorine and iodide yet decelerated by increases of DOM and bromide. In contrast, pH and feeding HAA concentration did not affect the photodegradation of HAAs significantly over pH ranges from 6 to 11 or doses from 0.05 to 50 mg/L. One exception existed that hydroxide, bicarbonate, and carbonate apparently inhibited the photolysis kinetics of monochloroacetic acid, suggesting that indirect photolysis via hydroxyl radical was partially responsible for this compound. As for the combined influences of water matrix, the photolysis rates of HAAs dosed into tap, lake, and ocean waters were lower than those dosed into ultrapure water by on average 21–38%, indicating that most components in these real waters tended to suppress the photolysis. The study therefore demonstrates the complexity of DBP removal using a UV system, and such results may help assessment of the real potential of UV photolysis for HAA control in water.

1. Introduction

Disinfection of drinking water, swimming water, and recycling wastewater are essential to protect the public from water-borne diseases. Since the 20th century, disinfectants like chlorine and chloramine have been widely used to inactivate pathogens in water around the world. However, in 1974, disinfection by-products (DBPs), typically including trihalomethane (THM) and haloacetic acid (HAA), were found to be formed in the reactions between disinfectant and DBP precursors [1,2]. Attention therefore shifted to the undesirable side effects of disinfection, triggering numerous studies to explore solutions that would minimize DBP formation without compromising disinfection performance. To date, HAAs have been detected in all types of disinfected waters [3–6], and occasionally they are even identified as the dominant species of DBP [7,8]. Given that they may have carcinogenic [9], cytotoxic, genotoxic [10–12], oxidative [13], reproductive [14], and developmental effects on humans [12,15,16], certain HAAs are already regulated by authorities in the USA, China, Canada, and Austria. It is noteworthy that some highly toxic HAAs [17], such as iodinated species, are not yet regulated, meaning that the risk posed by HAAs might still be underestimated.

As for DBP control, based upon over 40 years of research, a consensus has been reached that a combined effort involving water source protection, treatment process optimization, distribution system maintenance, and point-of-use control are needed [4]. Of all available measures, the most cost-effective approach to control DBP is to prevent its formation by removing DBP precursors (e.g., via activated carbon, coagulation, or biodegradation) [18,19] or by applying alternative disinfectants (e.g., chloramine), and both methods can be implemented in water treatment plant (WTP). However, once DBP is formed, it becomes more expensive and difficult to control it. Although some DBP precursors can be removed from the WTP, they cannot be completely eliminated [18]. To the best of the authors' knowledge, the most efficient (although maybe not the most cost-effective) approach for control of existing DBPs in drinking water is reverse osmosis [20–22], which may be employed in household water treatment (HWT) facilities. Other HAA removal methods have also been examined, and their performance is highly dependent upon the physicochemical properties of DBPs. For example, due to their high water dissociative ability (pK_a, < 3), HAAs mostly exist in deprotonated forms in ambient water and therefore can be neither volatilized nor absorbed readily by common absorbents like activated carbon [23]. In contrast, based upon their strong

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hydrophilicity, studies have reported effective biodegradations of HAAs by microbes colonizing in sand filters [24], pipes [25,26], cultural media [27], and activated carbon [28–30] when disinfectant is absent. Other methods for HAA reduction include the use of zero valent iron [31,32] and corrosive iron materials [33] or oxidization by electrochemical processes [34,35].

Recently, the removal of HAAs by ultraviolet (UV)-based methods, using UV radiation either alone or in tandem with catalysts like TiO_2, has also gained considerable attention, because of its potential application in HWT [36] or swimming pool facilities [6,37]. In the natural environment, photochemical conversion of DBPs has also been tested to detoxify chlorinated seawater [38]. However, earlier studies usually focused on the mechanisms, products, and pathways of HAA photolysis using laboratory synthetic waters [39], and relatively less is known about the influences of specific water components in real water on HAA photostability. Existing knowledge may therefore be insufficient to assess the real potential of UV photolysis for reducing the risks posed by HAAs.

In order to fill these knowledge gaps, this study aims to investigate the effects of a range of typical water components and water quality parameters on HAA photodegradation kinetics. The selected seven HAAs represent diverse halogenation degree and types of HAAs, including monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), monoiodoacetic acid (MIAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), and trichloroacetic acid (TCAA). The water components are classified according to their characteristics and potential effects, including three pH adjusting and potential radical scavenging components (i.e., hydroxide, bicarbonate, and carbonate), three halides (i.e., chloride, bromide, and iodide), , two chromophoric and radical generating components (i.e., nitrate and dissolved organic matter [DOM]), free chlorine (a common oxidant in drinking water), and initial HAA concentration. In addition to ultrapure water, three types of real water samples were collected and dosed with HAAs for comparison study. Because these selected components are likely implicated in multiple, contrasting mechanisms that can facilitate and/or hinder photolysis, we have made substantial discussion of their ultimate effects using the information from this study and literature.

2. Materials and methods

2.1. Reagents and samples

All HAA reagents were purchased in powder forms (AR grade, > 98% purity) from either Aladdin or Sigma-Aldrich Co., Ltd. Prior to experiments, stock solutions (1 g/L) were prepared separately for each HAA using ultrapure water and stored in a cooler at 4 °C. The purpose of separate tests for each HAA was to avoid producing interfering effects among HAA compounds. A humic acid product was obtained as an example of DOM from Aladdin Inc. (Category No.: H102874). Ultrapure water with electric resistance of 18.2 MΩ was produced by a Millipore water generator with a UV sterilizer (Direct-Q_3). In addition, three typical real waters were collected to analyze the effects of the water matrix. The characteristics of real waters are provided in Table 1.

2.2. Analytical methods

HAAs were detected by a gas chromatograph (GC) equipped with an electron capture detector (GC-9720, Fuli, China) according to the EPA method 552.3, with their method detection limits (MDLs) below 1 μg/L and data variations less than 10% for each sample. For quality control and assurance purpose, a stock solution with 100 μg/L TCAA was monitored every week to check the GC performance. Free chlorine was analyzed by a spectrophotometer (Hach 3900, USA) according to the EPA method 330.5. Anions including chloride, bromide, iodide, and nitrate were detected by an ion chromatograph (IC) equipped with both conductivity and UV detectors (IC-2010 Tosoh, Japan.), and their MDLs were less than 10 μg/L. DOM was measured by a total organic carbon (TOC) analyzer (TOC-L_{CPH}, Shimadzu, Japan) according to the EPA method 415.3, yielding an MDL of 0.1 mg-C/L. Water pH was determined by a pH probe (Thermo Fisher 8103BN, USA). The method for estimating MDL is based upon a EPA method [40]. Student-*t* test was extensively employed as a statistical tool to determine the significance of difference among results [41].

2.3. Photoreactor

The experiments were carried out in three parallel, stainless, column-shaped sterilizers with 4 cm diameter and 450 ml water volume. Low pressure mercury lamps (UV-Tec, 12 W, Co., Ltd, China) emitting 253.7 nm light were deployed in the middle of the chambers and shielded by quartz tubes. Using H_2O_2 as an actinometer [42], the photon intensity per volume of water (I_0) and the effective optical path length were determined as 9.66×10^6 E L^{-1} s^{-1} and 1.4 cm, respectively, which correspond to a photon flux of 1.35×10^{-8} E cm^{-2} s^{-1} and a UV intensity of 6.37 mW cm^{-2}, respectively. A typical dose of UV water disinfection in practice in WTP is 40 mJ cm^{-2} [43]. Aliquots were retrieved at designated time intervals from the sampling points of the reactors without stopping the irradiation process. Although water temperature reached up to 40 °C from ambient 20 °C during photolysis process, less than 10% HAAs were reduced in control tests where samples were held in the dark at 40 °C for 6 hr (Figure S1), proving that the HAA losses during the UV irradiation period were mostly attributed to photolysis instead of thermal hydrolysis. All photolysis experiments were tested in duplicate or replicate to ensure that the error bars were less than 10% for all data.

3. Results and discussions

3.1. Effects of pH, hydroxide, bicarbonate, and carbonate

Water pH in real water is an important water quality parameter mainly controlled by buffering compounds like bicarbonate. When pure HAAs are spiked into ultrapure water, HAAs will dissociate to their deprotonated forms, leading to a weakly acidic solution. However, it is currently unknown if experiments conducted under laboratory conditions may lead to different performance from those done with natural waters. In order to better understand the pH effect, this study first designed experiments to evaluate the influences of two buffering compounds (i.e., bicarbonate and carbonate) and a pH-adjusting chemical (i.e., sodium hydroxide) on the photodegradation rates of HAAs. The

Table 1
Characteristics of real waters used for evaluation.

	TDS (mg/L)	TOC (mg/L)	pH	Alkalinity (mg/L as CaCO$_3$)	Free chlorine	Chloride (mg/L)	Nitrate (mg/L)
Tap water	54.4	2.05	7.9	30.8	0.17	14.3	2.6
Lake water	63.9	6.18	8.1	49.8	ND	31.5	ND
Sea water	3.0×10^4	ND	8.1	113.4	ND	18,638	1.7

ND: not detected.