Separation and Purification Technology 203 (2018) 260–267

Contents lists available at ScienceDirect

Separation and Purification Technology

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

A new approach to controlling halogenated DBPs by GAC adsorption of aromatic intermediates from chlorine disinfection: Effects of bromide and contact time

Jingyi Jiang[1], Wanxin Li[1], Xiangru Zhang*, Jiaqi Liu, Xiaohu Zhu

Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Hong Kong, China

ARTICLE INFO

Keywords:
Disinfection byproducts
DBPs
Chlorination
GAC adsorption

ABSTRACT

Granular activated carbon (GAC) adsorption has been traditionally used to remove natural organic matter (NOM), the major precursor of halogenated disinfection byproducts (DBPs), in drinking water treatment plants. Recently, a new approach has been developed to effectively control the formation of trihalomethanes, haloacetic acids, and total organic halogen (TOX) in chlorinated drinking water by targeting intermediate aromatic halogenated DBPs instead of NOM using GAC adsorption. However, the applicability of this new approach to different source water matrices and disinfection conditions remained unclear. In this study, the effects of bromide and contact time on the performance of the new approach for DBP control were investigated. Same source waters were also treated with the traditional approach (i.e., using GAC to remove NOM prior to chlorination) and with chlorination only for comparison. With increasing the initial bromide level from 0 to 2 mg/L, the TOX removal with the new approach increased from 52% to 74%, while the removal with the traditional approach increased from 18% to 37%. Besides, as the chlorine contact time increased from 0.5 to 3.0 h, the TOX removal with the new approach increased from 61% to 75%, while the removal with the traditional approach increased from 21% to 36%. Increasing the bromide level and chlorine contact time enhanced the halogenated DBP removal with both new and traditional approaches, but the removal with the new approach was always two times higher or more than that with the traditional approach, which justified the superiority of the new approach. Moreover, various intermediate aromatic halogenated DBPs were detected in the chlorinated water samples and their levels were significantly decreased after the GAC adsorption, which further corroborated the effectiveness of the new approach for DBP control.

1. Introduction

Chlorine is an extensively used disinfectant, which can effectively inactivate most of planktonic bacteria and limit the growth of heterotrophic microorganisms in source waters [1–3]. During chlorination, the dosed chlorine may react with inorganic halides and natural organic matter (NOM) to form organic halogens, i.e., halogenated disinfection byproducts (DBPs). Epidemiological studies have suggested an association between the consumption of chlorinated drinking water and the increased risks of spontaneous abortions, birth defects, and bladder and colorectal cancers [4–7]. Toxicological studies have shown that many halogenated DBPs are genotoxic, cytotoxic, and developmentally toxic to laboratory organisms [8–11]. Notably, due to the presence of bromide in source waters, the formation of brominated DBPs has drawn increasing concerns because they are usually tens-to-hundreds of times more toxic than their chlorinated analogs [8,10,11].

Most DBPs formed during chlorination still remain unknown. Total organic halogen (TOX), as a collective surrogate, is widely used to represent all forms of organic halogen-bonded DBPs regardless of their identification [12,13]. TOX can be further specified into total organic chlorine (TOCl), total organic bromine (TOBr), and total organic iodine. Many studies have demonstrated that TOX in a chlorinated drinking water sample is positively correlated to the toxicity of the sample [14–16]. Although there is no regulation for TOX in chlorinated drinking water so far, it is indispensable to measure TOX to quantify DBP formation during chlorination and evaluate adverse effects of halogenated DBPs in disinfected water.

Recently, many polar halogenated DBPs have been detected by a novel precursor ion scan (PIS) method using electrospray ionization-triple quadrupole mass spectrometry (ESI-tqMS). By setting PISs of *m/z*

* Corresponding author.
E-mail address: xiangru@ust.hk (X. Zhang).
[1] Shared first authorship.

https://doi.org/10.1016/j.seppur.2018.04.050
Received 26 January 2018; Received in revised form 5 April 2018; Accepted 19 April 2018
Available online 21 April 2018
1383-5866/

35/37 and 79/81, almost all polar chlorinated and brominated DBPs in a water sample can be selectively detected [17,18]. By coupling the ESI-tqMS with ultra-performance liquid chromatography, numerous new halogenated DBPs have been identified in drinking water, and most of them are aromatic halogenated DBPs [19,20]. These aromatic halogenated DBPs have been found to act as intermediate DBPs, and they can decompose to form the regulated DBPs, including trihalomethanes (THMs) and haloacetic acids (HAAs), with further chlorination [19]. Besides, it has been reported that these newly identified aromatic halogenated DBPs generally presented considerably higher developmental toxicity and growth inhibition than the regulated aliphatic DBPs [10,11]. To mitigate the adverse effects of DBPs, it is vital to remove aromatic halogenated DBPs from chlorinated drinking water.

In addition, the formation of halogenated DBPs is complicated by the presence of bromide. Bromide is commonly observed in source waters and its concentration ranges from ~10 μg/L to > 2 mg/L [21–23]. When applying chlorination to bromide-containing waters, bromide can be oxidized by chlorine to form hypobromous acid/hypobromite ion, which is usually more reactive toward aromatic compounds through substitution reactions than hypochlorous acid/hypochlorite ion [24–26]. Pan and Zhang [20] have demonstrated that increasing the bromide level in source water shifted the formation of chlorinated aromatic DBPs, to chlorobromo-aromatic DBPs, and even to their fully brominated analogs. Other researchers have also reported the enhanced formation of brominated halobenzoquinones, diclofenac, and HAAs with increasing the bromide level [26–28]. Besides, the chlorine contact time is another important factor. The formation of major aliphatic DBPs (including THMs and HAAs) and overall halogenated DBPs (represented by TOX) usually increases with increasing chlorine contact time [19,28–30]. The decomposition of some aliphatic halogenated DBPs in the presence of residual chlorine has also been reported. At pH 7, the levels of dichloro-propanone and total halo-acetonitriles decreased with increasing chlorine contact time from 0.5 to 72 h [30], while the level of total *N*-nitrosamines increased with increasing chlorine contact time from 0.5 to 24 h and decreased from 24 to 72 h [28]. As aforementioned, the newly identified aromatic halogenated DBPs are intermediate DBPs during chlorination, and they present relatively high levels in chlorinated water samples with chlorine contact time ranging from 1 to 9 h [19]. Notably, the DBP compositions in water samples with different chlorine contact times are different. With the increase of contact time, hydrolysis, auto-decomposition, dehalogenation and other reactions might occur [28,30–32].

A new approach has been developed to effectively remove intermediate aromatic halogenated DBPs via granular activated carbon (GAC) adsorption after chlorination, rather than to remove NOM by GAC adsorption prior to chlorination (i.e., traditional approach) [33]. This new approach has been demonstrated to be substantially more effective than the traditional approach in controlling aromatic halogenated DBPs, regulated DBPs (including THMs and HAAs), overall halogenated DBPs (represented by TOX), and overall toxicity in a simulated drinking water [33]. As the bromide level in source water and chlorine contact time may vary spatially and temporally with the drinking water treatment plant, an important and practical question is whether this new approach can be applied to source water with different bromide levels and water utilities with different chlorine contact times. Accordingly, the effects of initial bromide level (i.e., the bromide level in source water) and chlorine contact time on the performance of the new approach for controlling halogenated DBPs were investigated in this study. As a comparison, samples with chlorination only (i.e., control samples without GAC adsorption during the treatment) and with the traditional approach (i.e., using GAC to remove NOM prior to chlorination) were also prepared. TOX was measured for evaluation and comparison of the effectiveness of the new and traditional approaches in controlling overall halogenated DBPs. To verify the removal of intermediate aromatic halogenated DBPs with the new approach, a PIS approach using ESI-tqMS was used to detect polar halogenated DBPs, including intermediate aromatic halogenated DBPs.

2. Materials and methods

2.1. Materials

A NaClO (> 50,000 mg/L as Cl_2) stock solution was purchased from Sigma–Aldrich. A working solution was prepared by diluting the commercial stock and its concentration was determined by the DPD–FAS titration method [34]. Suwannee River humic acid (SRHA, 2R101H) was supplied by the International Humic Substances Society. Coconut-based GAC with a low chloride background (< 0.1 mg as Cl/1 g GAC, TX070, Mitsubishi) was used in the micro-column test for GAC adsorption and the TOX measurement. Ultrapure water (18.2 MΩ·cm) was provided by a water purification system (Cascada I, PALL). Methyl-*tert*-butyl-ether (MtBE), acetonitrile (ACN) and other chemicals involved in this work were HPLC- or reagent-grade and provided by Sigma–Aldrich.

2.2. Preparation of simulated source water samples

Three simulated source water samples were prepared with ultrapure water by dissolving SRHA (3 mg/L as C), $NaHCO_3$ (90 mg/L as $CaCO_3$, for alkalinity) and KBr (0, 1.0, and 2.0 mg/L as Br^-). The relatively high bromide levels were used for amplifying the formation of brominated DBPs [19,20,33].

2.3. Experimental design of the traditional and new approaches

As illustrated in Fig. 1a–c, the simulated source water samples (i.e., SRHA samples) were treated with chlorination only, the traditional approach, and the new approach, respectively. For the traditional approach, the source water was pretreated with GAC adsorption and then chlorinated; while for the new approach, the source water was chlorinated followed by GAC adsorption. To simulate the performance of the GAC adsorption in both approaches, micro-column tests were conducted by using an adsorption module (TXA-03, Mitsubishi Chemical Corp.), which included a piston-pump, Teflon tubings, and one glass micro-column (with a length of 20 mm and an inner diameter of 3 mm). The column was prepacked with 40-mg fresh GAC with particle sizes of 100 × 200 mesh (i.e., with a mean particle diameter of 112 μm). The flow rate of a water sample through the GAC column was set at 3 mL/min [35]. In the micro-column tests, all the materials in contact with water were made of Teflon or glass. Notably, the micro-column adsorption test is a small-scale column test, which can be regarded as a proof of concept prior to the scaling up and application of a GAC filtration unit in real drinking water treatment utilities.

In general, the SRHA samples containing different initial bromide levels with different chlorine contact times were treated with the

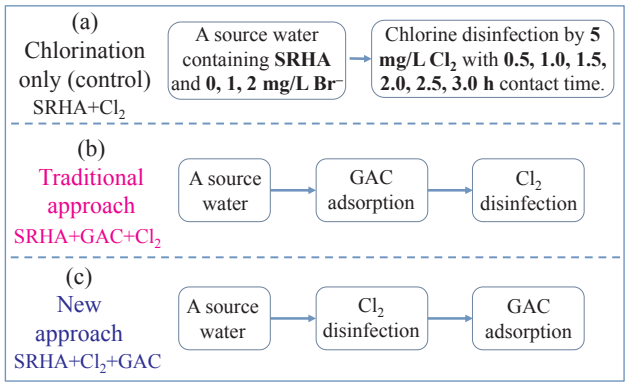

Fig. 1. The experimental schemes with the control, traditional and new approaches.