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Drinking water disinfection by-products detection, formation and the precursors removal study

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DRINKING WATER DISINFECTION BY-PRODUCTS DETECTION, FORMATION AND THE PRECURSORS REMOVAL STUDY

by

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ABSTRACT

Haloacetic acids (HAAs) and trihalomethanes (THMs) are two groups of commonly found disinfection by-products (DBPs). Iodinated THMs and HAAs were observed after disinfection of water containing high level of iodide and are proved to be more toxic than their corresponding chlorinated and brominated species. In the presented dissertation, a novel rapid and sensitive high performance ion chromatography-tandem mass spectrometry (HPIC–MS/MS) method has been developed for simultaneous analysis of all these HAAs, bromate, bromide, iodide, and iodate, seventeen compounds in total, without any tedious sample preparation. Besides an efficient analytical method for the detection of DBPs, seeking for a green disinfectant with a low formation of DBPs is necessary. Peracetic acid (PAA) has been demonstrated to be a possible green disinfectant that has the potential to reduce the formation of THMs, HAAs and other DBPs. The formation potential of HAAs and THMs, especially the iodinated forms, from PAA disinfection has been investigated and compared with that from FC treatment. Another efficient way to control DBPs is to remove their precursors. When using breakpoint chlorination to disinfect the source water containing high concentration of ammonia, high levels of THMs and HAAs will form. In addition, if N-nitrosamine precursors are present, highly toxic N-nitrosamines may form during water treatment process. In the third part of this dissertation, zeolites and activated carbon were examined for ammonia and N-nitrosamine precursors removal when incorporated into drinking water treatment processes.

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SECTION

1. INTRODUCTION

1.1. HALOACETIC ACIDS (HAAS), TRIHALOMETHANES (THMS) AND N-NITROSAMINES DISINFECTION BY-PRODUCTS (DBPS)

Disinfection by-products (DBPs) are the products of the reaction between disinfectants and the naturally occurring organic matter (NOM), iodide, bromide and other organic and inorganic pollutants (Richardson et al., 2007). Commonly used disinfectants include chlorine, chloramine, chlorine dioxide, ozone and peracetic acid. HAAs and THMs are the two most commonly found DBPs formed in chlorinated drinking water (Krasner et al., 2006). United State Environmental Protection Agent (US EPA) has set regulations to control the concentrations of THMs and HAAs in drinking water. The regulated THMs are usually referred as THM4, and regulated HAAs referred as HAA5. THM4 includes chloroform, bromodichloromethane, chlorodibromomethane and bromoform. HAA5 includes chloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid, and dibromoacetic acid. The maximum contamination level (MCL) of THM4 and HAA5 are 80 and 60 μg/L, respectively (US EPA, 2006). Research has shown the correlation between these DBPs and the bladder cancer (Costet et al., 2011; Villanueva et al., 2004; Villanueva et al., 2007), adverse pregnancy outcomes (Grellier et al., 2010) and teratogenic in rats (Narotsky et al., 2011).

Iodo-acids and Iodo-THMs are two types of emerging DBPs. Iodo-acids include monoiodoacetic acid (MIAA), diiodoacetic acid (DIAA), chloroiodoacetic acid (CIAA), bromoiodoacetic acid (BIAA), (Z)-3-bromo-3-iodopropenoic acid, (E)-3-bromo-3-iodopropenoic acid, and (E)-2-iodo-3-methylbutenedioic acid, which have been identified in drinking water system (Richardson et al, 2008a, 2008b; Wei et al, 2013). Iodo-THMs include dichloroiodomethane, bromochloroiodomethane, dibromoiodomethane, chlorodiiodomethane, bromodiiodomethane and iodoform. When high level of iodide presents in the source water, it would be oxidized by the disinfectant to form hypoiodous acid (HIO), which will further react with NOM to form Iodo-DBPs (Richardson, 2005). For the source water in coastal cities which is impacted by seas, the level of iodide is usually high thus the formation potential of iodinated DBPs is significant (Richardson and Postigo, 2011). Another source of iodine in the formation of Iodo-DBPs is iodinated X-ray contrast media (ICM) (Duirk et al., 2011). Iodo-DBPs have enhanced mammalian cell cytotoxicity and genotoxicity when compared to their brominated and chlorinated analogues (Richardson et al., 2008a). The order of genotoxicity of mono- haloacetic acids from high to low is iodoacetic acid > bromoacetic acid >> chloroacetic acid. In addition, the cytotoxicity of iodoacetic acid in S. typhimurium is 2.9x and 53.5x higher than that of bromoacetic acid and chloroacetic acid, respectively (Plewa et al., 2004).

The use of chloramine as disinfectant has shown to decrease the formation of HAA5 and THM4. However, chloramination increases the formation of nitrogen-containing DBPs, such as N-nitrosamines, which are generally more genotoxic and cytotoxic than that of without nitrogen (Richardson and Postigo, 2011). N-nitrosamines include N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), and N-nitrosopyrrolidine (NPyr), N-nitrosodi-n-propylamine (NDPA), N-nitrosomorpholine (NMor), N-nitrosodi-n-butylamine (NDBA), N-nitrosomethylethylamine (NMEA), N-nitrosopiperidine (NPip), and N-nitrosodiphenylamine (NDPhA). NDMA, NDEA and NPyr are more frequently detected (Asami et al, 2009; Charrois et al, 2007; Jurado-

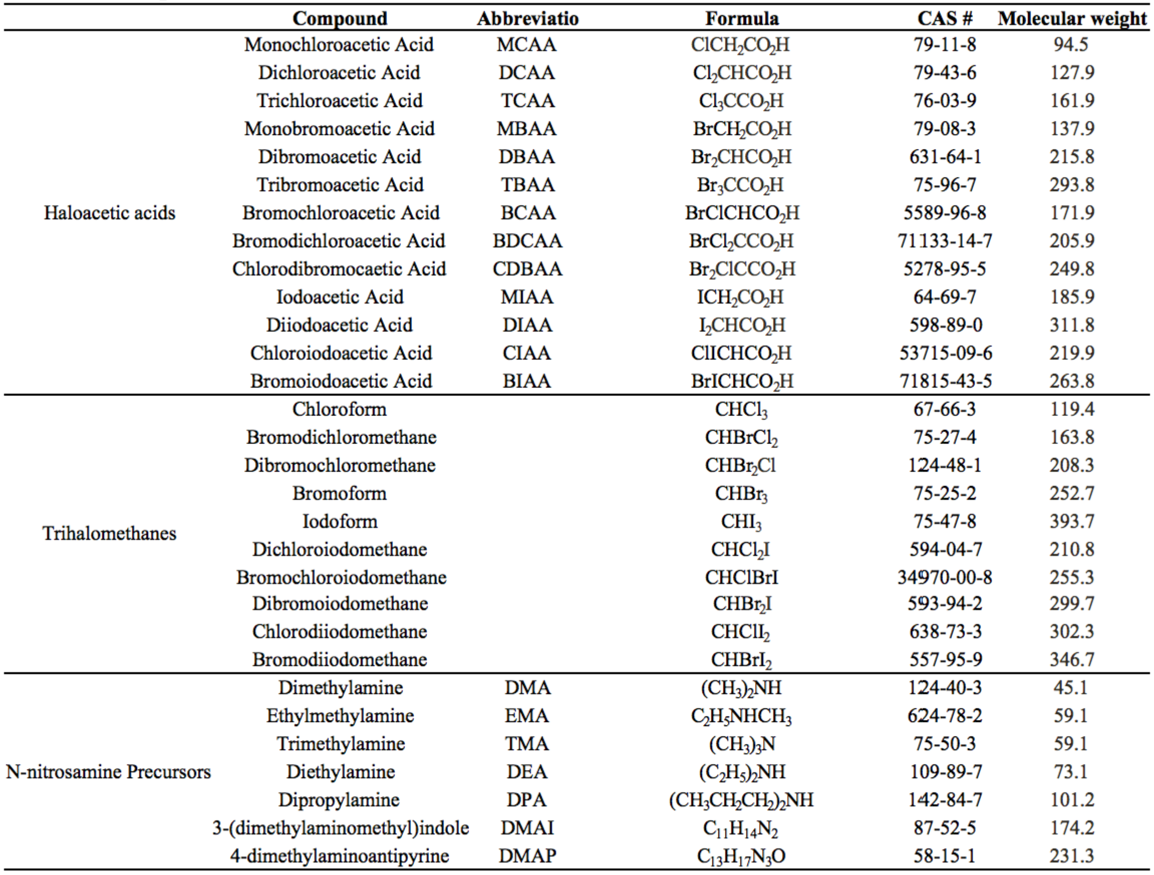
Sanchez et al, 2010) in drinking water system. NDMA has been classified as probably human carcinogens (Group B2) by the Integrated Risk Information System (IRIS) and is associated with an excess lifetime cancer risk of 10^{-5} when its concentration is equal or higher than 7 ng/L (US EPA, 1987). N-nitrosamine is formed during the chloramination or ozonation of water with dimethylamine (DMA) (Andrzejewski et al, 2008; Choi and Valentine, 2002; Mitch and Sedlak, 2002), chlorination of water containing ammonia and/or organic nitrogen (Charrois et al, 2007), or in the reaction of DMA with nitrite by the addition of HOCl (Choi and Valentine, 2003). In addition, the use of nitrogen-containing coagulants or ion-exchange resin in the water treatment process can also result in the formation of N-nitrosamine (Wilczak et al, 2003). A group of PPCPs (20 in total) containing amine groups has been demonstrated to be nitrosamine precursors during chloramine disinfection (Shen and Andrews, 2011). Secondary amines, such as DMA, ethylmethylamine (EMA), diethylamine (DEA), and dipropylamine (DPA), are reported as the most important precursors of N-nitrosamines (Wu et al., 2015a). Tertiary amines, such as trimethylamine (TMA), 4-dimethylaminoantipyrine (DMAP), and 3-(dimethylaminomethyl)indole (DMAI), can also contribute the formation of N-nitrosamines during chloramination disinfection (Selbes et al., 2013).

The basic information of 13 HAAs, 10 THMs and 7 N-nitrosamine precursors studied in this dissertation is showed in Table 1.1.

1.2. HAAS AND THMS DETECTION

The standard method for chloroacetic acids (CAAs), bromoacetic acids (BAAs) detection is US EPA method 552.3 (US EPA, 2003) and 557 (US EPA, 2009). EPA method 552.3 involves liquid-liquid extraction (LLE) and derivatization with the use of methyl tert-butyl ether (MTBE), sodium sulfate and sodium bicarbonate, then the extracted HAAs are identified and quantified by gas chromatography - electron capture detection (GC-ECD). Method 557 uses ion chromatography coupled with negative-ion electrospray ionization tandem mass spectrometry (IC-ESI-MS/MS) to detect CAAs, BAAs, bromate and dalopon in finished drinking water without the need of sample preconcentration or cleanup. Several more methods have been developed for the determination of HAAs in water. A summary of selected HAAs detection methods with different analytical techniques is listed in Table 1.2.

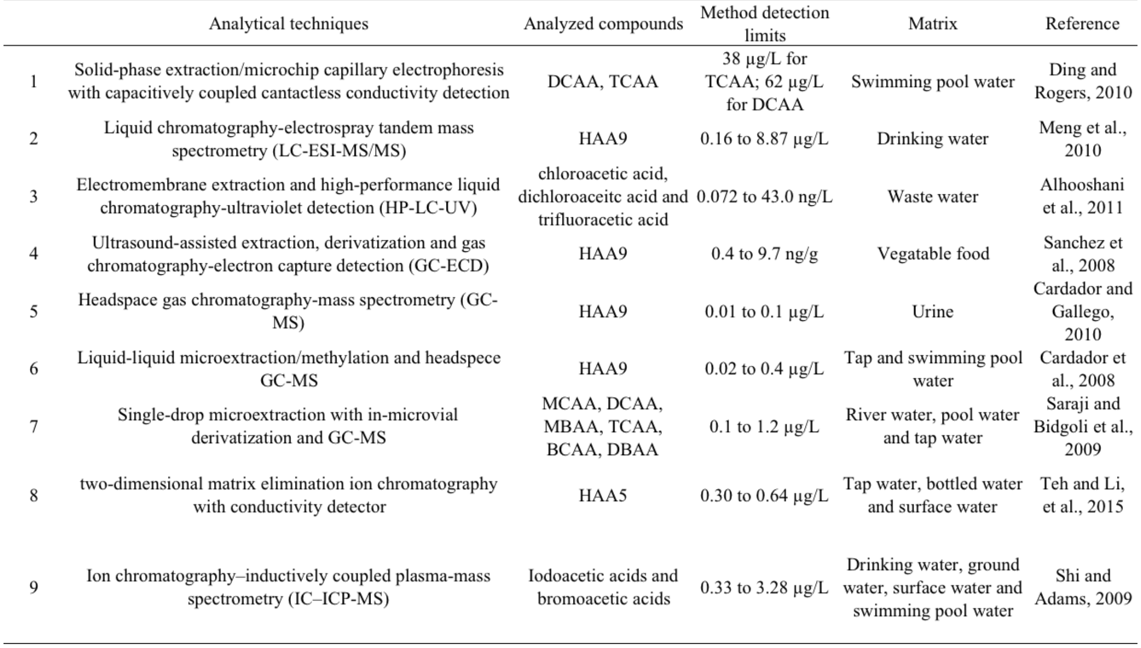
Table 1.1. The characteristics of 13 haloacetic acids, 10 trihalomethanes and 7 N-nitrosamine precursors.



	Compound	Abbreviatio	Formula	CAS #	Molecular weight
Haloacetic acids	Monochloroacetic Acid	MCAA	$ClCH_2CO_2H$	79-11-8	94.5
	Dichloroacetic Acid	DCAA	Cl_2CHCO_2H	79-43-6	127.9
	Trichloroacetic Acid	TCAA	Cl_3CCO_2H	76-03-9	161.9
	Monobromoacetic Acid	MBAA	$BrCH_2CO_2H$	79-08-3	137.9
	Dibromoacetic Acid	DBAA	Br_2CHCO_2H	631-64-1	215.8
	Tribromoacetic Acid	TBAA	Br_3CCO_2H	75-96-7	293.8
	Bromochloroacetic Acid	BCAA	$BrClCHCO_2H$	5589-96-8	171.9
	Bromodichloroacetic Acid	BDCAA	$BrCl_2CCO_2H$	71133-14-7	205.9
	Chlorodibromocaetic Acid	CDBAA	Br_2ClCCO_2H	5278-95-5	249.8
	Iodoacetic Acid	MIAA	ICH_2CO_2H	64-69-7	185.9
	Diiodoacetic Acid	DIAA	I_2CHCO_2H	598-89-0	311.8
	Chloroiodoacetic Acid	CIAA	$ClICHCO_2H$	53715-09-6	219.9
	Bromoiodoacetic Acid	BIAA	$BrICHCO_2H$	71815-43-5	263.8
Trihalomethanes	Chloroform		$CHCl_3$	67-66-3	119.4
	Bromodichloromethane		$CHBrCl_2$	75-27-4	163.8
	Dibromochloromethane		$CHBr_2Cl$	124-48-1	208.3
	Bromoform		$CHBr_3$	75-25-2	252.7
	Iodoform		CHI_3	75-47-8	393.7
	Dichloroiodomethane		$CHCl_2I$	594-04-7	210.8
	Bromochloroiodomethane		$CHClBrI$	34970-00-8	255.3
	Dibromoiodomethane		$CHBr_2I$	593-94-2	299.7
	Chlorodiiodomethane		$CHClI_2$	638-73-3	302.3
	Bromodiiodomethane		$CHBrI_2$	557-95-9	346.7
N-nitrosamine Precursors	Dimethylamine	DMA	$(CH_3)_2NH$	124-40-3	45.1
	Ethylmethylamine	EMA	$C_2H_5NHCH_3$	624-78-2	59.1
	Trimethylamine	TMA	$(CH_3)_3N$	75-50-3	59.1
	Diethylamine	DEA	$(C_2H_5)_2NH$	109-89-7	73.1
	Dipropylamine	DPA	$(CH_3CH_2CH_2)_2NH$	142-84-7	101.2
	3-(dimethylaminomethyl)indole	DMAI	$C_{11}H_{14}N_2$	87-52-5	174.2
	4-dimethylaminoantipyrine	DMAP	$C_{13}H_{17}N_3O$	58-15-1	231.3

Though there are a lot of methods for HAAs detection with different types of instrumentations and/or samples preparations available, general screening methodology is lacking and necessary for simultaneously monitoring chloro-, bromo-, and iodoacetic acids, along with the related halogenated water contaminants.

Table 1.2. A summary of selected HAAs detection methods with different analytical techniques



	Analytical techniques	Analyzed compounds	Method detection limits	Matrix	Reference
1	Solid-phase extraction/microchip capillary electrophoresis with capacitively coupled cantactless conductivity detection	DCAA, TCAA	38 μg/L for TCAA; 62 μg/L for DCAA	Swimming pool water	Ding and Rogers, 2010
2	Liquid chromatography-electrospray tandem mass spectrometry (LC-ESI-MS/MS)	HAA9	0.16 to 8.87 μg/L	Drinking water	Meng et al., 2010
3	Electromembrane extraction and high-performance liquid chromatography-ultraviolet detection (HP-LC-UV)	chloroacetic acid, dichloroaceitc acid and trifluoracetic acid	0.072 to 43.0 ng/L	Waste water	Alhooshani et al., 2011
4	Ultrasound-assisted extraction, derivatization and gas chromatography-electron capture detection (GC-ECD)	HAA9	0.4 to 9.7 ng/g	Vegatable food	Sanchez et al., 2008
5	Headspace gas chromatography-mass spectrometry (GC-MS)	HAA9	0.01 to 0.1 μg/L	Urine	Cardador and Gallego, 2010
6	Liquid-liquid microextraction/methylation and headspece GC-MS	HAA9	0.02 to 0.4 μg/L	Tap and swimming pool water	Cardador et al., 2008
7	Single-drop microextraction with in-microvial derivatization and GC-MS	MCAA, DCAA, MBAA, TCAA, BCAA, DBAA	0.1 to 1.2 μg/L	River water, pool water and tap water	Saraji and Bidgoli et al., 2009
8	two-dimensional matrix elimination ion chromatography with conductivity detector	HAA5	0.30 to 0.64 μg/L	Tap water, bottled water and surface water	Teh and Li, et al., 2015
9	Ion chromatography–inductively coupled plasma-mass spectrometry (IC–ICP-MS)	Iodoacetic acids and bromoacetic acids	0.33 to 3.28 μg/L	Drinking water, ground water, surface water and swimming pool water	Shi and Adams, 2009

Note: MCAA: monochloroacetic acid; DCAA: dichloroacetic acid; TCAA: trichloroacetic acid; MBAA: monobromoacetic acid; DBAA: dibromoacetic acid; BCAA: bromochloroacetic acid; HAA5: MCAA, DCAA, TCAA, MBAA, DBAA; HAA9: MCAA, DCAA, TCAA, MBAA, DBAA, tribromoacetic acid (TBAA), BCAA, bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA).

The standard method of THM4 detection is EPA method 552.3 (US EPA, 1995), which includes LLE with MTBE and detection with GC-ECD. Afterwards, more methods have been developed for the detection of THMs (Cancho, et al., 2000; Kozani et al, 2007;

Vora-adisak and Varanusupakul et al., 2006; Zhao et al., 2004). To avoid the time-consuming LLE process and the use of hazardous organic solvent, solid-phase microextraction (SPME) technique has been applied to the detection of THMs (Shi and Adams, 2012; Silva et al., 2006). SPME uses a fiber coated with adsorbent, for example polydimethylsiloxane (PDMS), carboxen/polydimethylsiloxane (CAR/PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB) and so on, to adsorb volatile compounds under certain temperature for a certain time until a distribution equilibrium of the analytes has been reached between the sample and the fiber coating. The analytes are then desorbed from the fiber under a high temperature. Allard et al. developed a SPME-GC-MS method, by which 10 THMs, including bromo-, chloro- and iodo- THMs, can be detected simultaneously in water (2012). A rapid SPME-GC/MS method has been developed for analysis of 20 emerging volatile DBPs, including iodo- THMs, haloacetonitriles (HANs) and halonitromethanes (HNMs) (Luo et al., 2014).

1.3. FORMATION OF HAAS AND THMS

The formation of HAAs and THMs is related to the concentration and speciation of precursors, such as NOM, iodide, bromide, in the source water and the choice of disinfectants. Iodide and bromide can be oxidized by disinfectants to form HIO and hypobromous acid (HOBr) (Bichsel and Von Gunten, 1999; Hua et al., 2006), which can react with NOM to form brominated and iodinated DBPs (Bichsel and Von Gunten, 2000; Hua et al., 2006). With different combination of chlorine, bromine and iodine, a total of 10 THM and 19 HAAs can form (Hua et al., 2006). More brominated DBPs will form with the increase of bromide concentration, while the total organic halogen decrease with the increase of iodide concentration (Hua et al., 2006). More THMs were formed than HAAs at pH 8, while HAAs are formed more at pH 6 (Liang and Singer, 2003).

Chlorine has been used for the water disinfection for a long time. To comply with the HAAs and THMs regulations, monochloramine (MCA) is suggested to use as a secondary disinfectant due to the reduced THM4 and HAA5 formation (Bougeard et al., 2010). However, the use of MCA is reported to promote the formation of iodinated DBPs because HIO cannot be further oxidized by MCA to form iodate which serve as a natural sink for iodide (Bichsel and Von Gunten, 1999; Richardson, 2005). Peracetic acid (PAA) is a green disinfectant with decomposition products of acetic acid, hydrogen peroxide, oxygen and water (Gehr and Cochrane., 2002). It is usually used in wastewater treatment (Gehr and Cochrane., 2002), food and beverage industries, and textile bleaching (Kitis, 2004). It has the potential to be used as an alternative drinking water disinfectant, however, the formation of DBPs, especially the iodinated form, needs to be investigated in detail.

1.4. REMOVAL OF HAAS, THMS AND N-NITROSAMINES

HAAs, THMs and N-nitrosamines removal is an effective way to control their harmful effect to human body. For HAAs, different methods or materials for its removal have been investigated, including biologically active carbon (BAC) processes (Wu and Xie, 2005), dehalogenation by using zero-valent iron (Fe^0) or other element doped Fe^0 (Hozalski et al., 2001; Tang et al., 2013), electrochemical reductive treatment (Li et al., 2012; Zhao et al., 2014). Among all these methods, some of them can also effectively remove THMs. For example, Fe^0 immobilized on activated carbon nanocomposite shows best THMs removal capacity, followed by Fe^0 and powdered activated carbon (PAC)

(Xiao et al., 2015). Besides that, reverse osmosis (RO) has been used to remove THMs and shows great efficiency on the removal of chloroform (Mazloomi et al., 2010). For N-nitrosamines removal, advanced oxidation using a combination of UV with hydrogen peroxide (H_2O_2) has been proven to be effective for the removal of NDMA (Sedlak and Kavanaugh, 2006). N-nitrosamines can also be removed by RO membranes, however, the removal efficiency is effected by several parameters, like feed temperature, membrane permeate flux, feed solution pH and ionic strength (Fujioka et al., 2012).

Removal of the precursors is another effective way for the control of DBPs. Various approaches have been studied for the removal of NOM, such as advanced oxidation processes (AOP) (Chin and Berube, 2005; Matilainen and Sillanpaa, 2010), PAC coupled with enhanced coagulation (Kristiana et al., 2011), ultrafiltration and nanofiltration (Lamsal et al., 2012). Study shows that the combination of ozone or UV with H_2O_2 results in greater total organic carbon (TOC) removal than the individual process. In addition, the AOPs tends to decrease the aromaticity of NOM, precursors of THMs, more effectively. Therefore, the decrease of THMs formation is greater than that of HAAs (Lamsal et al., 2011). High concentration of ammonia in the source water complicate the disinfection process. When a high concentration of chlorine is dosed to reach breakpoint chlorination, high levels of THMs and HAAs will form (Blute et al., 2012). Therefore, the removal of ammonia before chlorination disinfection is necessary for the control of THMs and HAAs.

Pre-oxidation has been reported as one possible way to remove the N-nitrosamine precursors, for example, ferrate (Fe(VI)) has been used to oxidize NDMA precursors which leads to the removal of NDMA of 46 to 84% in river water (Lee et al., 2008). Chen and Valentine found out that the amount of NDMA formed is significantly reduced by preoxidation of its precursors with free chlorine, permanganate, H_2O_2, and ozone before the MCA added (2008). Besides, adsorption technique, like PAC and zeolite, have also been used for N-nitrosamine precursors' removal. Wu et al found out that zeolites can remove most of the secondary and tertiary amines precursors, and PAC shows better removal efficiency for the less hydrophilic tertiary amines (2015b).

With so many methods available for the control of HAAs, THMs and N-nitrosamines, an efficient and cheap method is desired if it can contribute to the control of all the three DBPs simultaneously. Moreover, the method's applicability in real water treatment process also needs to be investigated.

1.5. RESEARCH OBJECTIVES

This work aims to improve the understanding and monitoring of HAAs, THMs and N-nitrosamines during drinking water treatment process. And the whole work including three parts:

(1) Developing a general screening method for simultaneously monitoring chloro-, bromo-, and iodoacetic acids, along with the related halogenated water contaminants without tedious sample preparation process.

(2) Studying the formation of HAAs and THMs, especially the iodinated forms, during PAA disinfection.

(3) Investigating the removal of ammonia and N-nitrosamine precursors by mordenite zeolite and PAC, and the suitable addition point of these adsorbents in drinking water treatment process.

PAPER

I. Rapid Simultaneous Analysis of 17 Haloacetic Acids and Related Halogenated Water Contaminants by High-Performance Ion Chromatography-Tandem Mass Spectrometry

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ABSTRACT

Haloacetic acids (HAAs), which include chloroacetic acids, bromoacetic acids, and emerging iodoacetic acids, are toxic water disinfection byproducts. General screening methodology is lacking for simultaneously monitoring chloro-, bromo- and iodoacetic acids. In this study, a rapid and sensitive high-performance ion chromatography–tandem mass spectrometry method for simultaneous determination of chloro-, bromo-, and iodo-acetic acids and related halogenated contaminants including bromate, bromide, iodate, and iodide was developed to directly analyze water samples after filtration, eliminating the need for pre-concentration and chemical derivatization. The resulting method was validated in both untreated and treated water matrices including tap water, bottled water, swimming pool water, and both source water and drinking water from a drinking water treatment facility to demonstrate application potential. Satisfactory accuracies and precisions were obtained for all types of tested samples. The detection limits of this newly developed method were lower or comparable to similar techniques without the need for extensive sample treatment requirement and it includes all HAAs and other halogenated compounds. This provides a powerful methodology to water facilities for routine water quality monitoring and related water research, especially for the emerging iodoacetic acids.

Key words: Haloacetic acids, iodoacetic acid, water disinfection byproducts, high performance ion chromatography-mass spectrometry, bromate

1. Introduction

Haloacetic acids (HAAs) are a group of disinfection byproducts (DBPs) formed during water disinfection [1-5]. HAAs, which comprise chloroacetic acids (CAAs), bromoacetic acids (BAAs), and iodoacetic acids (IAAs), have become a public health concern due to their cytotoxicity and carcinogenicity as well as their prevalence in chlorinated water [6-9]. The toxicity of monohalogenated acetic acids (monoHAAs) increases with the mass of the halogen, following an order of IAAs > BAAs >> CAAs which is related to their alkylating potential and the propensity of the halogen leaving group [7]. According to current United States Environmental Protection Agency (US EPA) regulations, the maximum contamination level (MCL) of the sum of the concentration of five major HAAs (HAA5), namely monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA), is 60 μg/L in drinking water [10]. The World Health Organization (WHO) suggests that regulatory levels of MCAA, DCAA and TCAA to be 20, 50, and 200 μg/L, respectively [11]. During drinking water disinfection process, iodide in source water is oxidized to form hypoiodous acid, which will further react with natural organic matter to form iodo-DBPs [12]. IAAs were found in drinking water samples from source water with a high bromide/iodide concentration when disinfected with chloramine [13]. They are highly cytotoxic and more genotoxic in mammalian cells than BAAs. The cytotoxicity of iodoacetic acids in S. typhimurium was 2.9 times and 53.5 times higher than BAAs and CAAs [13]. Bromate is another regulated DBP that is usually formed after ozonation or sodium hypochlorite disinfection in bromide containing water [14] with toxic effects to humans and animals [15-17]. The

International Agency for Research on Cancer (IARC) has classified bromate as a Group 2B carcinogen (possibly carcinogenic to humans) [1] and is regulated by the US EPA with an MCL of 10 μg/L [10].

Due to increasing awareness and concern regarding to these DBPs, it is imperative to develop rapid and robust methods for their quantitation in disinfected water. The standard method for CAAs and BAAs detection is US EPA method 552.3 [18] and 557 [19] using gas chromatography - electron capture detection (GC-ECD) and ion chromatography electrospray ionization tandem mass spectrometry (IC-ESI-MS/MS), respectively. EPA method 552.3 requires liquid-liquid extraction and derivatization before analysis which is time-consuming and requires the use of organic solvents. EPA method 557 requires no sample pre-concentration or cleanup and has a total run time of 55 minutes. However, neither method includes IAAs which are more toxic and require low detection limits. Ion chromatography - mass spectrometry (IC-MS) [20] and high-performance ion chromatography - inductively coupled plasma - mass spectrometry (HPIC-ICP-MS) [21, 22] methods have been developed to address these challenges; however, current IC-MS techniques only screen for HAA5, monoiodoacetic acid (MIAA), and bromate, while the HPIC-ICP-MS method only includes BAAs and IAAs, not CAAs, with detection limits ranging from 0.13 to 3.28 μg/L. Gas chromatography-mass spectrometry (GC-MS) has been used for the detection of nine HAAs and dalapon [23]. However, time consuming liquid-liquid extraction and acidic methanol derivatization, are needed. Another GC-MS method utilizing chemical ionization has been developed to detect HAAs in tap water with detection limits ranging from 8 ng/L to 94 ng/L [24]; however, pentafluorobenzyl esterification and toxic 2,3,4,5,6-

Pentafluorobenzyl bromide are needed for sample pretreatment, while IAAs were not included in this method. Several methods [25-27] have been developed using liquid chromatography–tandem mass spectrometry (LC-MS/MS). In a study by Luo et al. [27], 13 HAAs were separated by three UPLC columns. Acid or acidic buffer and volatile ion pair reagent were added in the mobile phase. The detection limits ranged from 0.15 to 1.5 μg/L. A method to detect four Iodo-HAAs was developed using LC/MS/MS but CAAs and BAAs are not included [28].

The standard methods for bromate detection are EPA methods 321.8 [29] and 557 [19] using ion chromatography/inductively coupled plasma-mass spectrometry (IC/ICP-MS) and IC/ESI-MS/MS with detection limits of 0.3 μg/L and 0.02 μg/L, respectively. Teh et al. developed a two-dimensional matrix elimination ion chromatography method for simultaneous detection of bromate, chlorite and HAA5 with detection limit ranging from 0.30 to 0.64 μg/L [30]. More recently, a more sensitive high-performance ion chromatography-tandem mass spectrometry (HPIC-MS/MS) method was developed for the simultaneous detection of perchlorate and bromate with the detection limits of 0.04 and 0.01 μg/L, respectively [31]. Although there are a number of methods have been developed for bromate detection, it will be highly beneficial if it is analyzed with HAAs and other halogenated compounds simultaneously, rather than by separate methods to reduce time and monitoring costs.

The objective of this study was to develop a simple, rapid, and sensitive HPIC-MS/MS method for simultaneous detection of all chloro-, bromo-, and iodoacetic acids, bromate, and other related halogenated compounds, a total of 17 compounds, with minimal sample preparation. The method was successfully developed and applied to untreated and treated water analysis including tap water, bottled water, swimming pool water, and both source and drinking water from a drinking water treatment facility. This method can be used for all HAAs analysis, especially the more toxic IAAs detection, without applying any time-consuming preparation or toxic organic solvent.

2. Materials and Methods

2.1 Chemicals and Standards Preparation

MIAA (98%), MBAA (99+ %), bromochloroacetic acid (BCAA, 97%), bromodichloroacetic acid (BDCAA, 99.7%), MCAA (99%), CDBAA (99.9%), DBAA (97.4%), DCAA (99+ %), TBAA (99%), and TCAA (99+ %) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Diiodoacetic acid (DIAA, 90%), chloroiodoacetic acid (CIAA, 90%) and bromoiodoacetic acid (BIAA, 85%) were products of CanSyn Chem. Corp. (Toronto, ON, Canada). Sodium bromate (99+ %), sodium iodide (99.99%), potassium bromide (99.99%), and methylamine (40% wt. in water) were purchased from Sigma Aldrich (St. Louis, MO, USA). Potassium iodate (99.4+ %) and sodium thiosulfate (98+ %) were purchased from Fisher Scientific (Pittsburgh, PA, USA). Ultra-high purity water (18.2 MΩ.cm) was prepared by an Elix-3 water purification system (Millipore, Billerica, MA, USA) and degassed by vacuum filtration using 0.22 μm nylon membrane filter prior to standard or mobile phase preparation. Stock standard solutions were prepared at 2000 mg/L in ultra-high purity water except iodide, which was prepared in 0.5% ammonium hydroxide aqueous solution to minimize the potential oxidation. Stock standard solutions were stored in amber glass vials with Teflon-lined caps in refrigerator. A secondary standard mixture containing all 17 compounds was prepared in ultra-high purity water at concentration of 10 mg/L each in amber glass vial, stored in a refrigerator at 4˚C and re-prepared every two months (stabilities were tested and they were all stable for at least for two months). Working standard solutions were freshly diluted before use in 100 mg/L sodium thiosulfate prepared in ultra-high purity water.

2.2 HPIC Separation

A Shimadzu ultra-fast performance liquid chromatography (UFLC) system (Columbia, MD) including two pumps (LC-20 AD XR), an autosampler (SIL-20AC XR), an online degasser (DGU-30A3) with a Dionex (Sunnyvale, CA, USA) Ionpac AS 21 ion exchange column (2 x 250 mm) and an AG 21 guard column (2 x 50 mm) was used for separation. Injection volumes of 50 and 5 µL were used for samples analysis with different matrices. Mobile phase A was ultra-high purity water and mobile phase B was 200 mM methylamine in ultra-high purity water operated under gradient elution. The elution flow rate was 0.3 mL/min with a gradient elution program as follows: separation began with 7% mobile phase B for 9 minutes, ramping to 18% B by 9 minutes, hold at 18% B for one minute and then ramping to 60% at 19.5 minutes, stayed at 60% B for 8 minutes, then returned to 7% B at 28 minutes where it was held for 8 more minutes before next injection.

2.3 MS/MS Detection

A 4000Q Trap mass spectrometer (AB Sciex, Foster City, CA) was operated under negative electrospray ionization (ESI) and multiple reaction monitoring (MRM) detection. Individual analytes were sequentially infused into the MS/MS system for compound parameter optimization. Specifically, declustering potentials (DP), collision energies (CE), and collision cell exit potentials (CXP), were optimized for the two most sensitive ion transitions (one for quantification ion pair and the other for confirmation ion pair) for each analyte. Flow injection analysis (FIA) was performed to optimize ion source conditions including ion source temperature, ion spray voltage, and various gas flows. Analytes which co-eluted were discriminated by unique ion pairs.

2.4 Water Sample Collection

Several types of water samples were analyzed, including 100 mg/L sodium thiosulfate prepared in ultra-high purity water, tap water, bottled water, swimming pool water, and source and drinking water from a drinking water treatment facility. Tap water was collected from local laboratory with 0.64 mg/L residual free chlorine (FC), 0.74 mg/L total chlorine and 0.17 mg/L DOC. The tap water utilized local groundwater as source water, and chlorine was used for disinfection. Bottled water was purchased from a local grocery store with 0.13 mg/L DOC and non-detectable FC residual. Swimming pool water was collected from a local public swimming pool with 1.23 mg/L residue FC, 1.93 mg/L total chlorine and 7.54 mg/L DOC (Rolla, MO, USA). The source of swimming pool was local tap water, with chlorine as disinfectant. A drinking water treatment plant near St. Louis, MO, USA was also selected to collect water samples. Creek water was used as source water with DOC concentration of 2.53 mg/L. After chlorination disinfection, DOC was 1.65 mg/L in the finished drinking water.

Samples were quenched by sodium thiosulfate at the time of sample collection to prevent further formation of DBPs. To test the effects of the quenching agent on the detection of target compounds, a standard mixture of each compound at 10 µg/L was prepared in 100 mg/L sodium thiosulfate solution and analyzed. Recoveries were within 81.1-113% which demonstrated that sodium thiosulfate can be used to quench residual disinfectants in water samples without affecting the detection of target analytes. All water samples were collected in pre-cleaned amber glass bottles containing sodium thiosulfate (100 mg/L). Sample bottles were filled such that no headspace was permitted without overfilling. When collecting samples from a water tap, the tap was opened for 5 min until the water temperature stabilized to ensure the sample was representative of the original water samples without any contamination from the water pipes. Samples were placed in coolers filled with ice and transported to lab within 12 hours from collection and stored at 4 ºC prior to analysis. After filtration by 0.22 µm nylon syringe filters (LabTech America, Inc., Hopkinton, MA), samples were injected directly for HPIC-MS/MS detection. All analyses were completed within 14 days following sample collection, within EPA method 557 suggested sample storage limit [19].

3. Results and Discussions

3.1 HPIC-MS/MS Method Optimization

The method is a novel combination of HPIC separation with negative electrospray ionization and tandem mass spectrometry detection. The HPIC separation was achieved by using a regular high performance liquid chromatography (HPLC) and directly hyphenated with a mass spectrometer, no separate ion chromatography instrument is needed except an IC column. This provides convenience to the users who do not have an IC system. Conventionally used nonvolatile base, such as sodium or potassium hydroxide, or sodium or potassium carbonate salt for HPIC, is not suitable for mobile phase of ESI-MS/MS detection. Instead, volatile additives were examined in mobile phase for this method development. Ammonium nitrate, ammonium acetate, and methylamine were tested with varying concentrations in water as mobile phase B. Methylamine at concentration 200 mM was selected as the optimized mobile phase B because it resulted in superior separation and analyte sensitivity. Mobile phase A was ultra-high purity water for optimal chromatographic resolution using a gradient elution as described in the experimental section. An Ionpac AS11-HC ion exchange column (4.0 x 250 mm) and Ionpac AS 21 ion exchange column (2 x 250 mm) (Dionex, Sunnyvale, CA) were evaluated for analytes separation. Ionpac AS21 column was found more ideal for chromatography resolution and sensitivity of detection, and was used for all the subsequent experiments for this developed method. Different gradient profiles were tested to separate analytes and to minimize matrix interferences. A representative chromatogram with injection volume of 50 µL at concentration of 20 µg/L is shown in Figure 1 with peak identification and retention times shown in Table 1. All compounds eluted in less than 20 minutes. The reproducibility of retention time was tested by injections of standard mixture spiked in ultra-high purity water and in real water samples collected in this study. Excellent reproducibility of retention time was observed with percent relative standard deviation (%RSD) of five injections ranging from 0.12-0.28% in ultra-high purity water and 0.0-1.2% in real water samples. For more complex water matrices, smaller injection volume of 5 µL was used to avoid column overloading by matrices. Reproducibility of retention time with smaller injection volume was tested with relative standard deviation of five injections ranging from 0.057-0.51% in real water (swimming pool water) samples.

The optimized MS/MS conditions were as follows: ion source temperature of 550℃, ion spray voltage of -4500 V, curtain gas pressure at 35 psi, ion source gas 1 pressure at 45 psi, and ion source gas 2 pressure at 35 psi. The entrance potential was -10 V for all compounds. Though optimal ion source temperature for TCAA detection was reported of 200℃ [32], the ion source temperature of 550℃ was selected for this method because this temperature had optimal performance for most of the other analytes, especially IAAs in this study. When tested separately for TCAA at 200℃ ion source temperature, TCAA detection limit was 0.5 µg/L for injection volume of 50 µL and 2 µg/L for injection volume of 5 µL. Other compound dependent parameters are listed in Table 2. The precursor ions for HAAs were [M-H]- except TBAA, BDCAA and CDBAA, for which [M-COOH]- was selected. For iodide and bromide, specific halogen ions were selected as both precursor ions and product ions. For bromate and iodate, specific halogen ions were selected as precursor ions and product ions were precursor ions with the loss of one oxygen atom.

3.2 Detection Limits

The detection limits were determined by injecting standards prepared in reagent water containing 100 mg/L sodium thiosulfate. The limits of detection (LOD) and limits of quantification (LOQ) were at the concentrations where signal to noise ratio (S/N) was at 3-5 and 9-10, respectively. The detailed results are shown in Table 3 and 4. For injection volume of 50 µL, the LODs for most of the analytes were between 0.01 to 0.1

µg/L, except for TCAA (1.00 µg/L). For injection volume of 5 µL, the LODs for most of the analytes were between 0.02 to 0.20 µg/L, except for TCAA (5 µg/L).

Fig. 1 Representative chromatograms of HPIC-MS/MS method

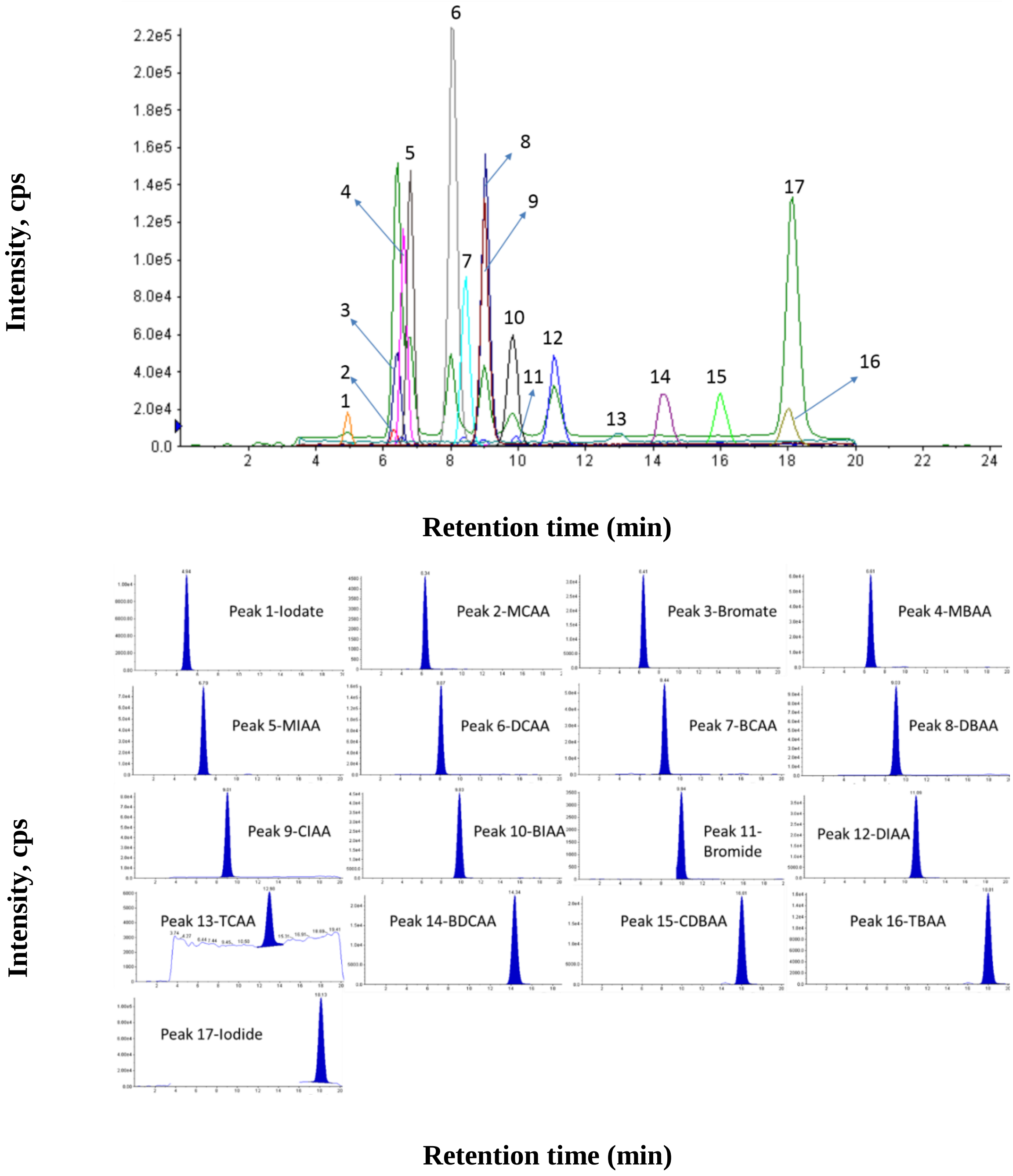


Table 1 Analyte general information, retention times (RT) and precision (n=5) with 50 µL injection of standard (20 µg/L) prepared in reagent water

Compound	Abbreviation	Formula	CAS #	Molecular weight	Peak #	RT (%RSD)
Iodate	Iodate	IO_3^-	7681-55-2	174.9	1	4.94 (0.25)
Monochloroacetic Acid	MCAA	$ClCH_2CO_2H$	79-11-8	94.0	2	6.35 (0.18)
Bromate	Bromate	BrO_3^-	7789-38-0	126.9	3	6.41 (0.18)
Monobromoacetic Acid	MBAA	$BrCH_2CO_2H$	79-08-3	137.9	4	6.61 (0.24)
Iodoacetic Acid	MIAA	ICH_2CO_2H	64-69-7	185.9	5	6.80 (0.28)
Dichloroactic Acid	DCAA	Cl_2CHCO_2H	79-43-6	127.9	6	8.09 (0.22)
Bromochloroacetic Acid	BCAA	$BrClCHCO_2H$	5589-96-8	171.9	7	8.46 (0.19)
Dibromoacetic Acid	DBAA	Br_2CHCO_2H	631-64-1	215.8	8	9.06 (0.17)
Chloroiodoacetic Acid	CIAA	$ClICHCO_2H$	53715-09-6	219.9	9	9.03 (0.18)
Bromoiodoacetic Acid	BIAA	$BrICHCO_2H$	71815-43-5	263.8	10	9.86 (0.22)
Bromide	Bromide	Br^-	7758-02-3	78.9	11	9.95 (0.19)
Diiodoacetic Acid	DIAA	I_2CHCO_2H	598-89-0	311.8	12	11.13 (0.17)
Trichloroacetic Acid	TCAA	Cl_3CCO_2H	76-03-9	161.9	13	13.02 (0.23)
Bromodichloroacetic Acid	BDCAA	$BrCl_2CCO_2H$	71133-14-7	205.9	14	14.40 (0.25)
Chlorodibromoacetic Acid	CDBAA	Br_2ClCCO_2H	5278-95-5	249.8	15	16.07 (0.15)
Tribromoacetic Acid	TBAA	Br_3CCO_2H	75-96-7	293.8	16	18.06 (0.19)
Iodide	Iodide	I^-	7681-82-5	126.9	17	18.15 (0.12)

Table 2 Optimized HPIC-MS/MS conditions

Compound	Quantification ion pair	Confirmation ion pair	DP (V)	CE_1 (V)	CE_2 (V)	CXP_1 (V)	CXP_2 (V)
Iodate	175/159	175/143	-50	-40	-38	-9	-7
MCAA	93/35	NA	-30	-16	NA	-3	NA
Bromate	127/111	127/79	-40	-30	-80	-5	-1
MBAA	137/79	NA	-25	-18	NA	-3	NA
MIAA	185/127	NA	-20	-16	NA	-7	NA
DCAA	127/83	NA	-20	-14	NA	-3	NA
BCAA	173/81	173/129	-35	-26	-14	-13	-7
DBAA	217/173	217/81	-35	-18	-40	-9	-3
CIAA	219/127	219/175	-20	-12	-16	-9	-9
BIAA	263/127	263/219	-35	-34	-16	-5	-13
Bromide	81/81	79/79	-100	-54	-54	-5	-5
DIAA	311/127	311/267	-40	-48	-14	-5	-17
TCAA	161/35	161/117	-25	-28	-10	-3	-7
BDCAA	163/81	163/79	-25	-14	-14	-3	-3
CDBAA	207/79	207/81	-25	-24	-22	-13	-3
TBAA	251/79	251/81	-20	-28	-30	-3	-7
Iodide	127/127	NA	-60	-54	NA	-5	NA

Note 1. DP-Declustering potential, CE_1-Collision energy for quantification ion pair, CE_2 Collision energy for confirmation ion pair, CXP_1-Collision cell energy for quantification ion pair, CXP_2-Collision cell energy for confirmation ion pair.

Note 2. No confirmation ion pairs were detected for MCAA, MBAA, MIAA and DCAA because their intensities were too low to be detected.

3.3 Calibration Linearity, Accuracy, and Precision

An external calibration curve in 100 mg/L sodium thiosulfate was constructed to quantify HAAs and related halogenate compounds. The calibration curves displayed good linearity with $R^2>0.99$ for each analyte. The precision and reproducibility of this method was evaluated by analyzing five replicates of the standard mixture prepared in ultra-high purity water at concentration of 5 μg/L for injection volume of 50 μL and 20 μg/L for injection volume of 5 μL with recoveries ranging from 94.2 to 116% and relative standard deviation ranging from 0.027 to 0.86%, indicating good method accuracy in reagent water. The detailed method performance results are shown in Table 3 and 4.

Table 3 Performance of the HPIC-MS/MS method for 50 µL injection

Compound	LOD (µg/L)	LOQ	Calibration range	R^2	5 µg/L in Reagent Water	
		(µg/L)	(µg/L)		%recovery	%RSD (n=5)
Iodate	0.02	0.05	0.05-100	0.9985	101	0.23
MCAA	0.05	0.10	0.10-100	0.9997	97.2	0.12
Bromate	0.01	0.02	0.02-100	0.9994	96.7	0.057
MBAA	0.01	0.02	0.02-100	0.9994	99.6	0.10
MIAA	0.01	0.02	0.02-100	0.9980	98.2	0.027
DCAA	0.01	0.02	0.02-100	0.9990	104	0.053
BCAA	0.02	0.05	0.05-100	0.9991	100	0.12
DBAA	0.02	0.05	0.05-100	0.9998	104	0.22
CIAA	0.02	0.05	0.05-100	0.9982	102	0.18
BIAA	0.02	0.05	0.05-100	0.9984	103	0.15
Bromide	0.10	0.20	0.20-100	0.9998	103	0.14
DIAA	0.02	0.05	0.05-100	1.0000	100	0.18
TCAA	1.00	2.00	2.00-100	0.9907	104	0.47
BDCAA	0.01	0.02	0.02-100	0.9996	100	0.16
CDBAA	0.01	0.02	0.02-100	0.9996	101	0.17
TBAA	0.01	0.02	0.02-100	1.0000	108	0.25
Iodide	0.10	0.50	0.50-100	0.9993	96.6	0.035

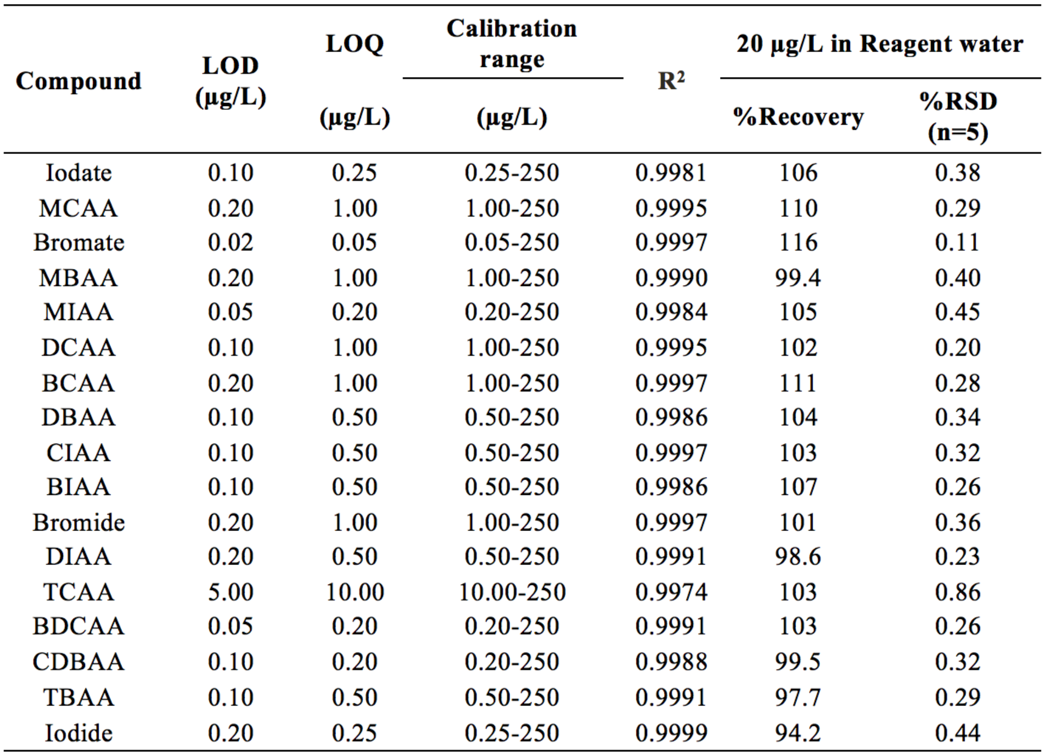
Note: Limits of detection (LOD) were determined where the S/N = 3-5; Limits of quantification (LOQ) were determined where S/N = 9-10.

3.4 Real Water Sample Analysis

To assess the robustness of the developed method in various sample matrices, several types of water samples were analyzed using the developed HPIC-MS/MS method. Satisfactory spike recoveries were obtained in all tested samples. Method performance was accurate with spike recoveries ranging from 81.7% to 119% and relative standard deviation less than 16%. To avoid ion suppression from matrix anions, such as chloride, nitrate and sulfate [30] or other unknown compounds, or possible overload of column capacity, a smaller injection volume (5 µL) was applied when testing swimming pool water, and both source and drinking water from the drinking water treatment plant.

Table 5 shows the occurrence of the 17 analytes in the tap water, bottled water, swimming pool water and both source and drinking water from a drinking water treatment facility. Samples were directly analyzed after filtration without any other sample preparation. The total concentrations of HAA5 were 0.19 µg/L in tap water, 18.26 µg/L in drinking water, and were below the detection limits in bottled water and source water. MIAA was detected in tap water (0.12 µg/L), swimming pool water (0.61 µg/L), and drinking water from the drinking water treatment facility (1.13 µg/L). CIAA, BIAA and DIAA were not found above the detection limits in tap water, bottled water and source water from the drinking water treatment facility, while CIAA was found in swimming pool water (0.96 µg/L) and drinking water from the drinking water treatment facility (0.56 µg/L). Bromate was below the detection limit in tap water, bottled water, and both types of water samples from the drinking water treatment facility. High concentrations of bromate (149.55 µg/L) and TCAA (156.42 µg/L) were detected in swimming pool water, presumably due to water reuse and repeat disinfections for the high DOC water. Study has shown that organic matters from swimmers, such as sweat, urine, skin and cosmetics, are likely to serve as a source of HAAs precursors [33].

Table 4 Performance of the HPIC-MS/MS method for 5 µL injection



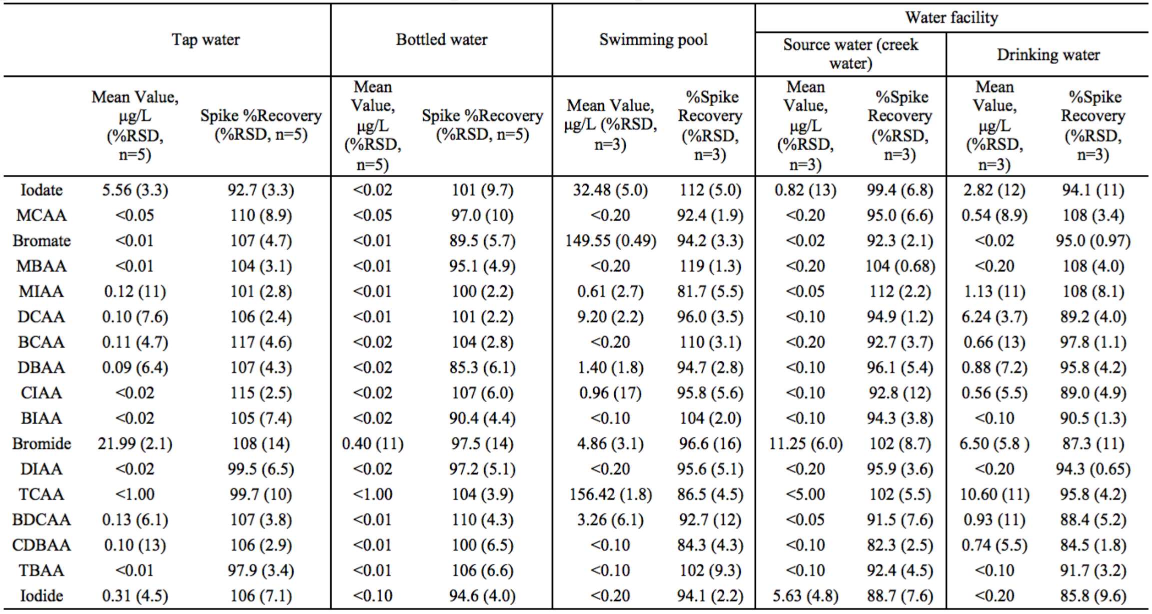
Compound	LOD (µg/L)	LOQ (µg/L)	Calibration range (µg/L)	R^2	20 µg/L in Reagent water %Recovery	20 µg/L in Reagent water %RSD (n=5)
Iodate	0.10	0.25	0.25-250	0.9981	106	0.38
MCAA	0.20	1.00	1.00-250	0.9995	110	0.29
Bromate	0.02	0.05	0.05-250	0.9997	116	0.11
MBAA	0.20	1.00	1.00-250	0.9990	99.4	0.40
MIAA	0.05	0.20	0.20-250	0.9984	105	0.45
DCAA	0.10	1.00	1.00-250	0.9995	102	0.20
BCAA	0.20	1.00	1.00-250	0.9997	111	0.28
DBAA	0.10	0.50	0.50-250	0.9986	104	0.34
CIAA	0.10	0.50	0.50-250	0.9997	103	0.32
BIAA	0.10	0.50	0.50-250	0.9986	107	0.26
Bromide	0.20	1.00	1.00-250	0.9997	101	0.36
DIAA	0.20	0.50	0.50-250	0.9991	98.6	0.23
TCAA	5.00	10.00	10.00-250	0.9974	103	0.86
BDCAA	0.05	0.20	0.20-250	0.9991	103	0.26
CDBAA	0.10	0.20	0.20-250	0.9988	99.5	0.32
TBAA	0.10	0.50	0.50-250	0.9991	97.7	0.29
Iodide	0.20	0.25	0.25-250	0.9999	94.2	0.44

Note: Limits of detection (LOD) were determined where the S/N = 3-5; Limits of quantification (LOQ) were determined where S/N = 9-10.

4. Conclusions

A simple and sensitive HPIC-MS/MS method was developed for simultaneous analysis of 17 compounds including chlorinated, brominated, and iodinated HAAs, bromate, bromide, iodate, and iodide. It is the only method reported for simultaneous analysis of all HAAs, bromate, and related halogenated compounds. The method was applied to tap water, bottled water, swimming pool water, and both source water and drinking water from a drinking water treatment facility. The method is applicable for occurrence monitoring as well as disinfection byproduct formation potential and control studies in drinking water and surface water. This method will save time and resources for water treatment facilities that routinely monitor the evaluated DBPs by analyzing multiple compounds in a single method with minimal sample pre-treatment. The method will also be suitable for emerging iodo-DBPs related research and formation kinetics studies.

Table 5 Detection of HAAs, bromate, and related halogenated compounds and method performance in different water samples. (%RSD: percent relative standard deviation)



	Tap water		Bottled water		Swimming pool		Water facility			
							Source water (creek water)		Drinking water	
	Mean Value, µg/L (%RSD, n=5)	Spike %Recovery (%RSD, n=5)	Mean Value, µg/L (%RSD, n=5)	Spike %Recovery (%RSD, n=5)	Mean Value, µg/L (%RSD, n=3)	%Spike Recovery (%RSD, n=3)	Mean Value, µg/L (%RSD, n=3)	%Spike Recovery (%RSD, n=3)	Mean Value, µg/L (%RSD, n=3)	%Spike Recovery (%RSD, n=3)
Iodate	5.56 (3.3)	92.7 (3.3)	<0.02	101 (9.7)	32.48 (5.0)	112 (5.0)	0.82 (13)	99.4 (6.8)	2.82 (12)	94.1 (11)
MCAA	<0.05	110 (8.9)	<0.05	97.0 (10)	<0.20	92.4 (1.9)	<0.20	95.0 (6.6)	0.54 (8.9)	108 (3.4)
Bromate	<0.01	107 (4.7)	<0.01	89.5 (5.7)	149.55 (0.49)	94.2 (3.3)	<0.02	92.3 (2.1)	<0.02	95.0 (0.97)
MBAA	<0.01	104 (3.1)	<0.01	95.1 (4.9)	<0.20	119 (1.3)	<0.20	104 (0.68)	<0.20	108 (4.0)
MIAA	0.12 (11)	101 (2.8)	<0.01	100 (2.2)	0.61 (2.7)	81.7 (5.5)	<0.05	112 (2.2)	1.13 (11)	108 (8.1)
DCAA	0.10 (7.6)	106 (2.4)	<0.01	101 (2.2)	9.20 (2.2)	96.0 (3.5)	<0.10	94.9 (1.2)	6.24 (3.7)	89.2 (4.0)
BCAA	0.11 (4.7)	117 (4.6)	<0.02	104 (2.8)	<0.20	110 (3.1)	<0.20	92.7 (3.7)	0.66 (13)	97.8 (1.1)
DBAA	0.09 (6.4)	107 (4.3)	<0.02	85.3 (6.1)	1.40 (1.8)	94.7 (2.8)	<0.10	96.1 (5.4)	0.88 (7.2)	95.8 (4.2)
CIAA	<0.02	115 (2.5)	<0.02	107 (6.0)	0.96 (17)	95.8 (5.6)	<0.10	92.8 (12)	0.56 (5.5)	89.0 (4.9)
BIAA	<0.02	105 (7.4)	<0.02	90.4 (4.4)	<0.10	104 (2.0)	<0.10	94.3 (3.8)	<0.10	90.5 (1.3)
Bromide	21.99 (2.1)	108 (14)	0.40 (11)	97.5 (14)	4.86 (3.1)	96.6 (16)	11.25 (6.0)	102 (8.7)	6.50 (5.8)	87.3 (11)
DIAA	<0.02	99.5 (6.5)	<0.02	97.2 (5.1)	<0.20	95.6 (5.1)	<0.20	95.9 (3.6)	<0.20	94.3 (0.65)
TCAA	<1.00	99.7 (10)	<1.00	104 (3.9)	156.42 (1.8)	86.5 (4.5)	<5.00	102 (5.5)	10.60 (11)	95.8 (4.2)
BDCAA	0.13 (6.1)	107 (3.8)	<0.01	110 (4.3)	3.26 (6.1)	92.7 (12)	<0.05	91.5 (7.6)	0.93 (11)	88.4 (5.2)
CDBAA	0.10 (13)	106 (2.9)	<0.01	100 (6.5)	<0.10	84.3 (4.3)	<0.10	82.3 (2.5)	0.74 (5.5)	84.5 (1.8)
TBAA	<0.01	97.9 (3.4)	<0.01	106 (6.6)	<0.10	102 (9.3)	<0.10	92.4 (4.5)	<0.10	91.7 (3.2)
Iodide	0.31 (4.5)	106 (7.1)	<0.10	94.6 (4.0)	<0.20	94.1 (2.2)	5.63 (4.8)	88.7 (7.6)	<0.20	85.8 (9.6)

Note: For tap water and bottled water, injection volume was 50 µL; Spike was 0.5 µg/L for most of the analyties except for bromide and iodate in tap water and TCAA in both water samples (5 µg/L); for swimming pool water and both source and finished water from the drinking water treatment facility, injection volume was 5 µL; Spike was 5 µg/L for most of analytes except for bromate and iodate in swimming pool water and TCAA in all of the water samples (50 µg/L).

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II. Evaluation of Haloacetic Acids and Trihalomethanes Formation by Peracetic Acid Disinfection

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ABSTRACT

Free chlorine (FC) is commonly used as a disinfectant in the United States; however, disinfection by-products (DBPs) are formed when FC reacts with natural organic matter (NOM) in the source water. Haloacetic acids (HAAs) and trihalomethanes (THMs) are two groups of commonly-found DBPs. Iodinated HAAs and THMs are found during the disinfection of water containing high levels of iodide and are much more toxic than their chlorinated and brominated analogs. Peracetic acid (PAA) is a strong antimicrobial disinfectant that has the potential to reduce the formation of HAAs and THMs. In this study, the formations of 13 HAAs and 10 THMs, especially the iodinated forms, have been investigated during PAA disinfection. The formations under different iodide concentrations, pHs, and contact times were systematically studied. Two types of commercial PAAs containing different concentrations of PAA and H_2O_2 were studied, and FC disinfection was also tested in parallel for comparison. THMs were detected by solid-phase microextraction gas chromatography/mass spectrometry (SPME-GC/MS) method. HAAs were analyzed by following a recently developed high performance ion chromatography-tandem mass spectrometry (HPIC-MS/MS) method. Results show that the ratio of PAA and H_2O_2 concentration significantly affected the formation of THMs and HAAs. During PAA disinfection with lower PAA than H_2O_2, no detectable levels of THMs and HAAs were observed. During PAA disinfection with higher PAA than H_2O_2, low levels of monoiodoacetic acid, diiodoacetic acid, and iodoform were formed, and these levels were enhanced with the increase of iodide concentration (up to 240 μg/L).

Keywords: Peracetic acid disinfection, iodinated THMs, iodoacetic acids, water disinfection by-products, SPME GC-MS

Highlights

- Haloacetic acids and trihalomethanes formation during peracetic acid disinfection.
- The detection of THM4 and 6 iodinated THMs with SPME GC-MS
- Iodinated HAAs and THMs formed more with the increase of iodide concentration.
- No formation of HAAs and THMs was observed during PAA treatment with $[PAA]<[H_2O_2]$.
- Only MIAA, DIAA and CHI_3 were formed during PAA treatment with $[PAA]>[H_2O_2]$.

1. Introduction

Disinfection by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs), as well as other types of organic by-products, are formed during the disinfection of waters containing natural organic matters (NOM), bromide and iodide. United States Environmental Protection Agency (US EPA) has set regulations for THM and HAA levels in drinking water. The maximum contamination level (MCL) of the sum of the concentration of five HAAs (HAA5, namely monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA)) and four THMs (THM4, namely bromodichloromethane ($CHBrCl_2$), bromoform ($CHBr_3$), chloroform ($CHCl_3$) and dibromochloromethane ($CHBr_2Cl$)) are 60 and 80 μg/L in drinking water, respectively (US EPA, 1998).

Studies have shown that the concentrations of halogen ions such as bromide and iodide play a role on the formation and speciation of HAAs and THMs (Criquet, et al., 2012; Ding, et al., 2013). Iodide and bromide can be oxidized by different disinfectants, such as ozone, chlorine, and chloramine to form hypoiodous acid (HIO) and hypobromous acid (HOBr) (Bichsel and Von Gunten, 1999). Similar to hypochlorous acid (HOCl), the formed HIO and HOBr can react with NOM to form brominated and iodinated DBPs (Bichsel and Von Gunten, 2000; Hua et al., 2006; Richardson, 2005; Richardson et al., 2003;). Through different substitution and combination of chlorine, bromine and iodine, a total of 10 THMs and 19 HAAs can theoretically form during chlorination (Hua et al., 2006). With the addition of bromide, concentrations of brominated and mixed HAAs increase substantially, while chlorinated HAAs decrease slightly (Cowman and Singer, 1995; Wu and Chadik, 1998). This phenomenon is because bromine reacts faster and substitutes more efficiently than chlorine when reacting with NOM (Westerhoff et al., 2004). The yields of THMs and HAAs increase with the increase of initial bromide concentration (Plewa et al., 2004; Shah et al., 2015a), while the total organic halogen decrease with increasing initial iodide concentration (Hua et al., 2006). Iodo-trihalomethanes (IodoTHMs), which can be responsible for taste and odor problems, are formed by the reactions between HIO and NOM. The formed HIO can be further oxidized to form iodate (IO_3^-) by ozone and chlorine, but not by monochloramine (MCA), which favors the formation of iodoorganic compounds during the disinfection of drinking water (Bichsel and Von Gunten, 1999). The iodoform (CHI_3) formation in the oxidation of natural waters containing iodide increases in the order of $O_3 < Cl_2 < NH_2Cl$ (Bichsel and Von Gunten, 2000; Pan et al., 2016a). Similarly, chlorine's competing reaction to form iodate as a sink for the natural iodide leads to more iodo-acids forming during chloramination treatment than chlorination (Plewa et al., 2004; Richardson, 2005).

In common drinking water sources, the bromide and iodide concentrations are typically low (Shah et al., 2015a), which leads to relatively low formation of bromo- and iodo- DBPs. However, bromo- and iodo- DBPs have been shown to be significantly more cytotoxic and genotoxic than the corresponding chloro- DBPs (Richardson et al., 2007). The cytotoxicity of iodoacetic acids in S. typhimurium is 2.9 times and 53.5 times higher than bromoacetic acids and chloracetic acids (Plewa et al., 2004). In addition, iodoTHMs has been found in drinking water distribution systems (Ding, et al., 2013; Ioannou, et al., 2016). Iodo- DBPs are detected during cooking processes when chloraminated tap water and iodized table salt are used (Pan et al., 2016b).

Peracetic acid (PAA) has been used in wastewater treatment (Baldry et al., 1991; Gehr and Cochrane, 2002; Sánchez-Ruiz et al., 1995; Wagner et al., 2002). PAA is commercially available in the form of a quaternary equilibrium mixture containing acetic acid (AA), hydrogen peroxide (HP), PAA, and water. It shows great effectiveness against a wide spectrum of microorganisms including bacteria, fungi, spores, viruses, and protozoan cysts (Liberti and Notarnicola, 1999). PAA is a green disinfectant, the decomposition products of which are AA, HP, oxygen, and water (Gehr and Cochrane, 2002; Wagner et al., 2002). The formation of DBPs during PAA treatment has been studied (Dell'Erba et al., 2007; Shah et al., 2015a); however, this formation is still unclear, especially in the application of drinking water treatment. In addition, studies regarding to the formation of iodinated THMs and HAAs during PAA treatment are lacking. CHI_3, monoiodoacetic acid (MIAA), diiodoacetic acid (DIAA) and triiodoacetic acid (TIAA) are the major species of iodinated DBPs formed during chloramination of iodide containing water (Liu et al., 2017). Bromate, brominated, and chlorinated THMs and HAAs have been found in brackish waters treated with PAA, but the formation was affected by the ratio between PAA and H_2O_2 in PAA mixture, which can be minimized by the presence and high concentration of H_2O_2 (Shah et al., 2015b).

This study is focuses on the formation of HAAs and THMs, especially the iodinated form, when using PAA as a disinfectant. The influence of iodide concentrations, pHs, and contact times on the formation were systematically studied. Samples were also disinfected by FC in parallel to compare the influence of different types of disinfectants.

2. Experimental section

2.1 Chemicals and materials

The standards of HAAs and other halogenated compounds used were same with those the HAAs method development paper published recently (Xue et al., 2016). Sodium iodide (99.99%) and THM4 standard mixture at concentration of 200 mg/L were purchased from Sigma-Aldrich (St. Louis, MO, USA). Iodide stock solution at concentration of 1000 mg/L was prepared by dissolving sodium iodide in ultra-high purity water. Iodinated THMs (I-THMs) including CHI_3 (100%), bromodiiodomethane ($CHBrI_2$, 95%), bromochloroiodomethane (CHBrClI, 100%), chlorodiiodomethane ($CHClI_2$, 100%), dibromoiodomethane ($CHBr_2I$, 97.6%) and dichloroiodomethane ($CHCl_2I$, 100%) were purchased from CanSyn Chem. Corp. (Toronto, ON, Canada). Stock solutions of I-THMs were made by dissolving the chemicals into methanol and stored in a freezer. Diethyl-p-phenylenediamine (DPD) test kits were purchased from HACH company (Loveland, CO, USA). Two types of PAA were used. PAA1 was from Solvay chemicals, Inc. (Vandalia, IL, USA) which contains 12.2% PAA and 19.4% H_2O_2. PAA2 was from PeroxyChem LLC (Philadelphia, PA, USA), which contains 35.5% PAA and 6.5% H_2O_2. Anhydrous sodium sulfate (≥99%) and sodium thiosulfate (>98%) were purchased from Fisher Scientific (Fisher Scientific, Pittsburgh, PA, USA). Ultra-high purity water (18.2 MΩ cm) was prepared by an Elix-3 water purification system (Millipore, Billerica, MA, USA).

2.2 Disinfection treatment procedures

Missouri river water was used to establish the water matrix and filtered by 0.45 μm nylon membrane filter by vacuum filtration before experiments. Initial water parameter at 20 ˚C was pH of 8.34, dissolved organic carbon (DOC) of 4.0 mg/L, UV_{254} absorption of 0.0851, and an initial concentration of iodide and bromide of 20 and 60 μg/L, respectively. Two pHs, pH 6.6 and 8.6, were studied. pH 8.6 was adjusted using sodium hydroxide and pH 6.6 was adjusted using sulfuric acid with 10 mM phosphate buffer.

The dosages of disinfectant, FC and PAA, were determined by a preliminary demand test. Filtered Missouri river water was disinfected by FC and PAA at concentrations of 5 and 10 mg/L, respectively. After 4 hours’ reaction, the residue concentrations of disinfectants were measured. The disinfectant demand was determined by the difference between initial dosage and final residue. To reach the target disinfectant residue of 2-4 mg/L after 4-hours’ contact time, the requisite doses were 6 mg/L FC and 5 mg/L PAA.

Three levels of iodide concentrations were studied (20, 120, and 240 μg/L) to determine the effect of iodide concentration on the formation and speciation of THMs and HAAs. The iodide concentration was adjusted by adding iodide stock standards into the water samples to obtain the desired concentration. After the addition of disinfectant, water samples were agitated at 130 rpm continuously for 4 hours. Meanwhile, samples were taken at time points of 5, 10, 30, 60, 120, 240 minutes for analyses. Residue disinfectant was measured immediately. Samples for HAAs, THMs, bromide, iodide, bromate, and iodate detection were quenched immediately with 100 mg/L sodium thiosulfate.

2.3 Analytical methods

Thirteen HAAs and four halogenated compounds were quantified by a high performance ion chromatography-tandem mass spectrometry (HPIC-MS/MS) method (Xue et al., 2016). Ten THMs were determined by upgrading a solid-phase microextraction gas chromatography-mass spectrometry (SPME GC-MS) method (Shi and Adams, 2012) to include six iodinated THMs. The temperature program was modified as follows: initial temperature at 40 ˚C for 2 minutes, ramp to 150 ˚C at 20 ˚C/min and hold for 2 minutes, ramp to 250 ˚C at 20 ˚C/min and hold for 0.5 minutes. The total run time was 15 minutes. The desorption temperature was changed to 200 ˚C to avoid the degradation of CHI_3 (Allard et al., 2012).

DOC was tested by using a TOC-L analyzer with ASI-L liquid autosampler (Shimadzu, Columbia, MD, USA). UV_{254} absorbance was monitored with a Cary 50 UV-Vis Spectrometer (Agilent, Santa Clara, CA, USA). pH was tested with a Thermo Orion 3 Star pH meter (Thermo Fisher Scientific, Waltham, MA, USA). The concentrations of FC and PAA were tested with HACH DR/2010 portable datalogging spectrophotometer (Loveland, CO, USA) by following the standard methods for examination of water and wastewater (Eaton and Franson, 2005).

3. Results and discussion

3.1. Method performance of 10 THMs detection with SPME GC-MS method

The detection limits of $CHCl_3$, $CHCl_2I$, $CHBr_2Cl$, $CHBr_3$, CHBrClI, $CHClI_2$, $CHBrI_2$ were 0.01 µg/L; $CHBrCl_2$, $CHBr_2I$ were 0.02 µg/L; and CHI_3 was 0.2 µg/L. A representative chromatogram of standard prepared in reagent water is shown in Figure 1 with peak identification and retention times shown in Table 1. The method was validated with various water matrices, including reagent water, Missouri River water and tap water. Method performance was accurate with spike recoveries ranging from 81.0 to 115% and relative standard deviation of less than 9.3%.

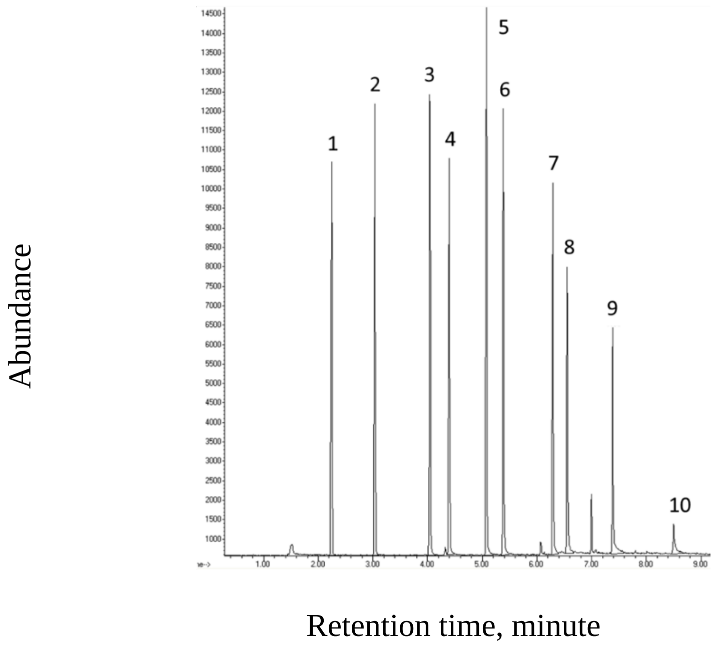


Figure 1. Representative chromatograms of ten THMs (5 µg/L each) prepared in reagent water: 1. $CHCl_3$, 2. $CHBrCl_2$, 3. $CHBr_2Cl$, 4. $CHCl_2I$, 5. $CHBr_3$, 6. CHBrClI, 7. $CHBr_2I$, 8. $CHClI_2$, 9. $CHBrI_2$, 10. CHI_3

Compound	Abbreviation	Retention time (minutes)	LOD (µg/L)	LOQ (µg/L)	Calibration range (µg/L)	R^2	5 µg/L in Reagent Water		5 µg/L in Missouri River water		5 µg/L in Tap Water	
							%Recovery	%RSD (n=3)	%Recovery	%RSD (n=3)	%Recovery	%RSD (n=3)
Chloroform	$CHCl_3$	2.24	0.01	0.05	0.05-50	0.9995	95.5	3.5	101	2.2	85.3	3.2
Bromodichloromethane	$CHBrCl_2$	3.03	0.01	0.05	0.05-50	0.9976	91.1	2.4	84.3	5.1	96.4	2.6
Dibromochloromethane	$CHBr_2Cl$	4.04	0.01	0.05	0.05-50	0.9946	87.5	5.9	86.9	7.6	115	3.4
Dichloroiodomethane	$CHCl_2I$	4.39	0.01	0.05	0.05-10	0.9945	85.1	4.5	91.6	9.3	96.2	4.8
Bromoform	$CHBr_3$	5.07	0.01	0.05	0.05-50	0.9916	84.9	3.6	90.9	1.4	103	3.1
Bromochloroiodomethane	$CHBrClI$	5.38	0.01	0.05	0.05-10	0.9996	83.6	4.5	88.2	6.7	87.1	2.6
Dibromoiodomethane	$CHBr_2I$	6.29	0.01	0.05	0.05-10	0.9999	81.0	2.1	107	4.3	90.2	5.5
Chlorodiiodomethane	$CHClI_2$	6.55	0.01	0.05	0.05-10	0.9998	94.3	1.5	89.8	2.8	89.3	1.4
Bromodiiodomethane	$CHBrI_2$	7.38	0.01	0.05	0.05-10	0.9997	88.1	2.8	94.7	5.1	87.3	4.6
Iodoform	CHI_3	8.50	0.20	0.50	0.20-20	0.9905	90.0	4.6	87.1	7.4	112	3.3

Note: Limits of detection (LOD) were determined where the Signal/Noise (S/N) = 3-5; Limits of quantification (LOQ) were determined where S/N = 9-10.

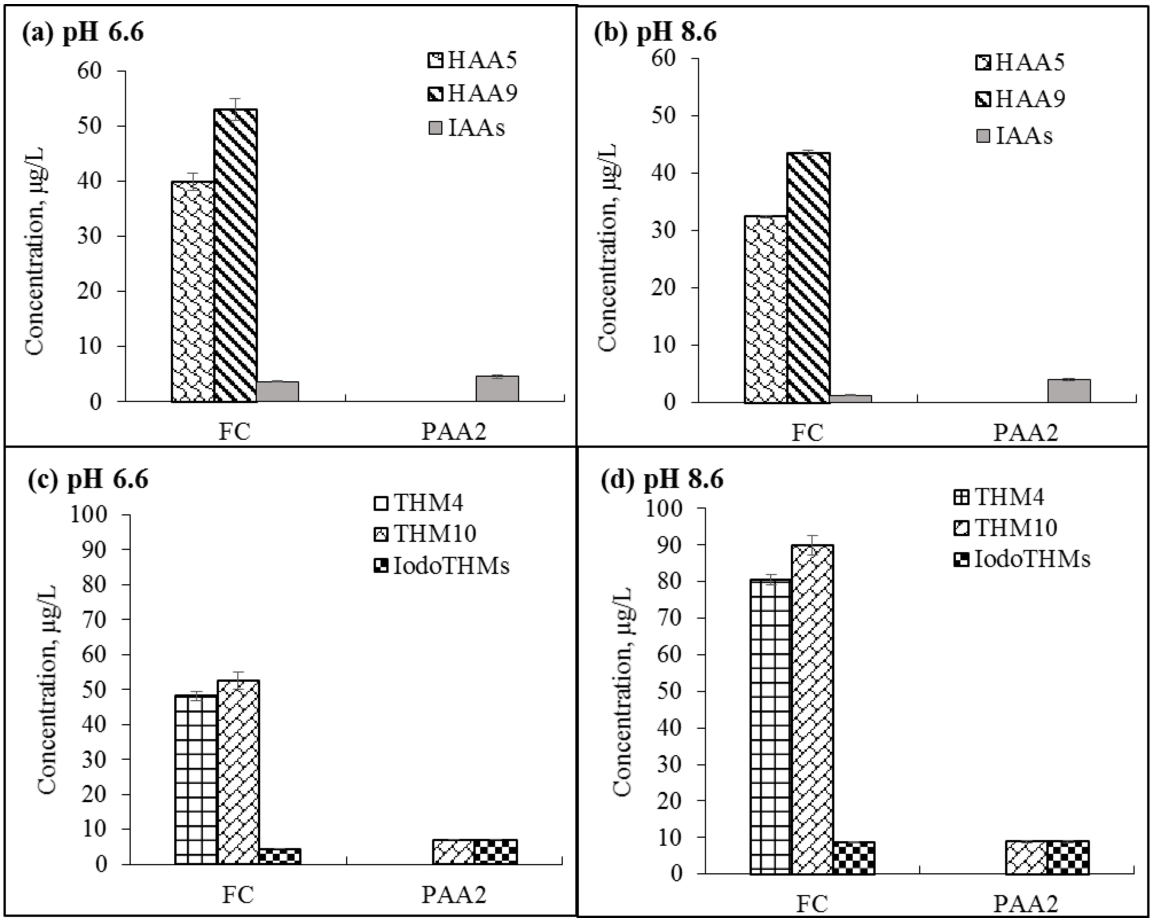
Table 1. Performance of the GC/MS method for ten THMs

3.2. Formation of HAAs and THMs when disinfected by FC, PAA1, and PAA2

Figure 2 shows the formation of HAAs and THMs during FC and PAA2 treatment in filtered Missouri River water with iodide addition (to make iodide concentration of 240 µg/L) at pH 6.6 and 8.6. During FC treatment, the formation of chlorinated, brominated, and iodinated acetic acid (CAAs, BAAs, and IAAs) was observed, and DCAA and TCAA were the predominant species with concentrations of 14.79 and 22.45 µg/L at pH 6.6, and 15.07 and 15.55 µg/L at pH 8.6, respectively. Only MIAA and CIAA were identified during FC treatment after 4 hours' disinfection. And their concentrations were 2.34 and 1.31 µg/L at pH 6.6, and 0.63 and 0.60 µg/L at pH 8.6, respectively. No bromine-containing IAAs were found, presumably due to the low ambient bromide concentration in the water samples. Nine types of THMs were found with except of CHI_3 at pH 6.6 and the most abundant species was $CHCl_3$ (33.25 µg/L). All ten types of THMs were detected at pH 8.6. The most abundant species of iodo-THMs was $CHCl_2I$ at both pHs, and the concentrations were 2.55 µg/L at pH 6.6 and

4.48 μg/L at pH 8.6. During PAA1 treatment, no detectable HAAs and THMs were formed. In PAA1 solution, the concentration of H_2O_2 was higher than PAA (12.2% PAA and 19.4% H_2O_2). PAA can react with chloride, bromide, and iodide to form secondary oxidants (HClO, HBrO, and HIO), which would further react with NOM to form DBPs; however, H_2O_2 can reduce these secondary oxidants back to halide ions. Therefore, the formation of DBPs was limited during PAA1 treatment (Shah et al., 2015b). In PAA2 solution, the concentration of PAA was higher than H_2O_2 (35.5% PAA and 6.5% H_2O_2), and no brominated and chlorinated HAAs and THMs were found. MIAA and DIAA were formed at both pH 6.6 and 8.6. The most abundant species of the IAAs and Iodo-THMs were DIAA and CHI_3. Compared to that during FC treatment, the formation of IAAs and Iodo-THMs were higher when disinfected by PAA2. The oxidation of iodide and bromide is governed by a conjugate acid form of PAA (PAAH). The reaction of PAAH and iodide is approximately three orders of magnitude higher than that of the reaction between PAAH and bromide, and seven orders of magnitude higher than that of the reaction between PAAH and chloride (Shah et al., 2015b). This might cause the only formation of IAAs in water samples containing higher concentrations of iodide (120 and 240 μg/L) when disinfected by PAA2. Increasing pH from 6.6 to 8.6 increased the formation of THMs and decreased the formation of HAAs during both FC and PAA2 treatment. This was also observed by Liang and Singer (Liang and Singer, 2003) during chlorination disinfection.

No formation of bromate was observed during the treatment of both types of PAA solutions, while 3 μg/L of bromate was detected during FC treatment in water samples containing 60 μg/L of bromide at both pHs.



Note: HAA5 includes MCAA, DCAA, TCAA, MBAA and DBAA; HAA9 includes MCAA, DCAA, TCAA, MBAA, DBAA, TBAA, BCAA, BDCAA and CDBAA; IAAs includes MIAA, DIAA, BIAA and CIAA; THM4 includes $CHCl_3$, $CHClBr_2$, $CHCl_2Br$, $CHBr_3$; THM10 includes $CHCl_3$, $CHClBr_2$, $CHCl_2Br$, $CHBr_3$, CHI_3, $CHBrI_2$, CHBrClI, $CHClI_2$, $CHBr_2I$, $CHCl_2I$; Iodo-THMs include CHI_3, $CHBrI_2$, CHBrClI, $CHClI_2$, $CHBr_2I$, $CHCl_2I$.

Figure 2. THMs and HAAs formation during 6 mg/L FC and 5 mg/L PAA2 treatment in filtered Missouri river water with 240 µg/L iodide after 4 hours (a) HAAs formation at pH 6.6; (b) HAAs formation at pH 8.6; (c) THMs formation at pH 6.6; (d) THMs formation at pH 8.6

3.3 Effect of iodide concentration on the speciation and formation of HAAs and THMs

Three iodide concentrations, 20, 120, and 240 µg/L, were tested to investigate the effect of iodide concentration on the speciation and formation of HAAs and THMs. Three disinfectants, FC, PAA1, and PAA2, were used. Figure 3 shows the disinfectant depletion at pH 6.6.

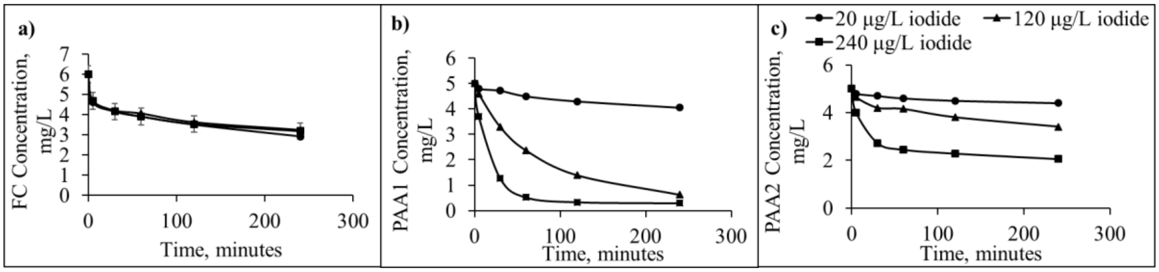
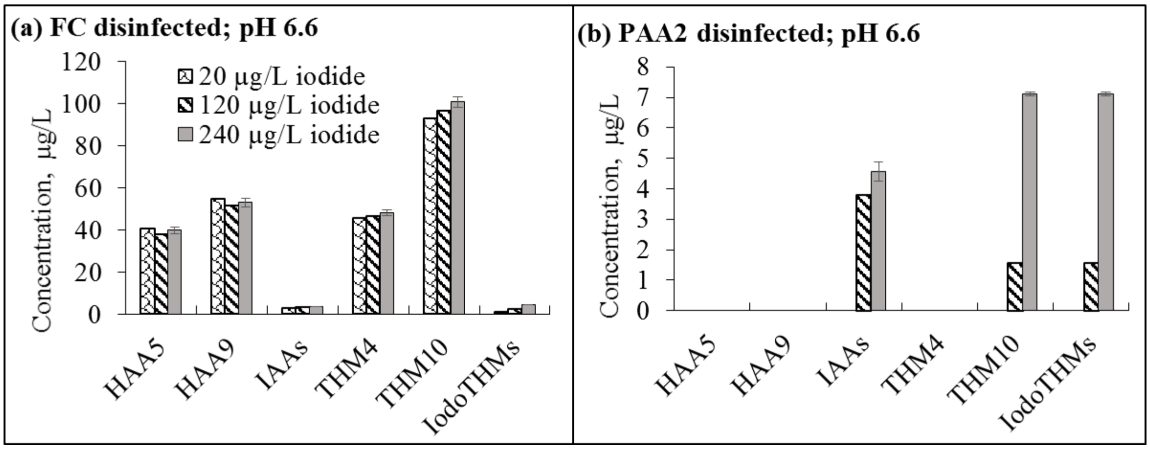


Figure 3. The effect of iodide concentration on disinfectant depletion at pH 6.6. a) FC; b) PAA1; c) PAA2

When increasing the concentration of iodide, the depletion of FC did not show much changes. However, the consumption of PAA increased, and the increase was more significant with PAA1. A similar depletion trend was found for FC, PAA1, and PAA2 at pH 8.6. This may be explained by the reactions between PAA, iodide, and H_2O_2 (Shah et al., 2015b). PAA can likely react with iodide to form secondary oxidant HIO, while H_2O_2 serves as an important sink for HIO and reacts with HIO to form iodide. Therefore, in this catalytic cycle reaction, more PAA will be consumed with a higher concentration of iodide when H_2O_2 is present. The reaction will continue until the complete consumption of H_2O_2 or PAA.

Figure 4 shows the impact of iodide concentration on the formation of THMs and HAAs. Increasing initial iodide levels from 20 to 240 µg/L had little effect on the formation of chlorinated and brominated HAAs and THMs during FC treatment, while there was a slight increase for IAAs and iodo-THMs. Hua et al (2006) also reported that no significant change in THM4 was found at iodide concentration of 2 μM/254 μg/L. IAAs and Iodo-THMs were detected during PAA2 treatment starting from 120 µg/L iodide and increased with the increase of iodide concentration more significantly than that during FC treatment. This is because 80% of iodide was oxidized by chorine to form iodate, while 20% of iodide formed iodate during PAA2 treatment at pH 6.6. The increase magnitude of IAAs at higher concentrations of iodide was less than that of the iodo-THMs.



Note: Filtered Missouri river water was used, pH 6.6, reaction time 4 hours

Figure 4. Effect of iodide concentration on the formation of THMs and HAAs. (a) 6 mg/L FC disinfection; (b) 5 mg/L PAA2 disinfection. The water sample was filtered Missouri river water at pH 6.6; reaction time was 4 hours

Figure 5 shows the formation of IAAs during FC and PAA2 treatment at pH 6.6 and 8.6. Different speciation and formation trends were observed when using FC and

PAA2 as disinfectant, respectively. MIAA and CIAA were the major species of IAAs formed during FC treatment, while MIAA and DIAA were formed during PAA2 treatment. In FC treatment, the formation of IAAs was more rapid in the first 60 min than from 60 min to 240 min, and CIAA was detected after 60 min. In PAA2 treatment, IAAs concentration increased gradually with the increasing reaction time. Similar formation trends were observed at higher pH when using the same disinfectant.

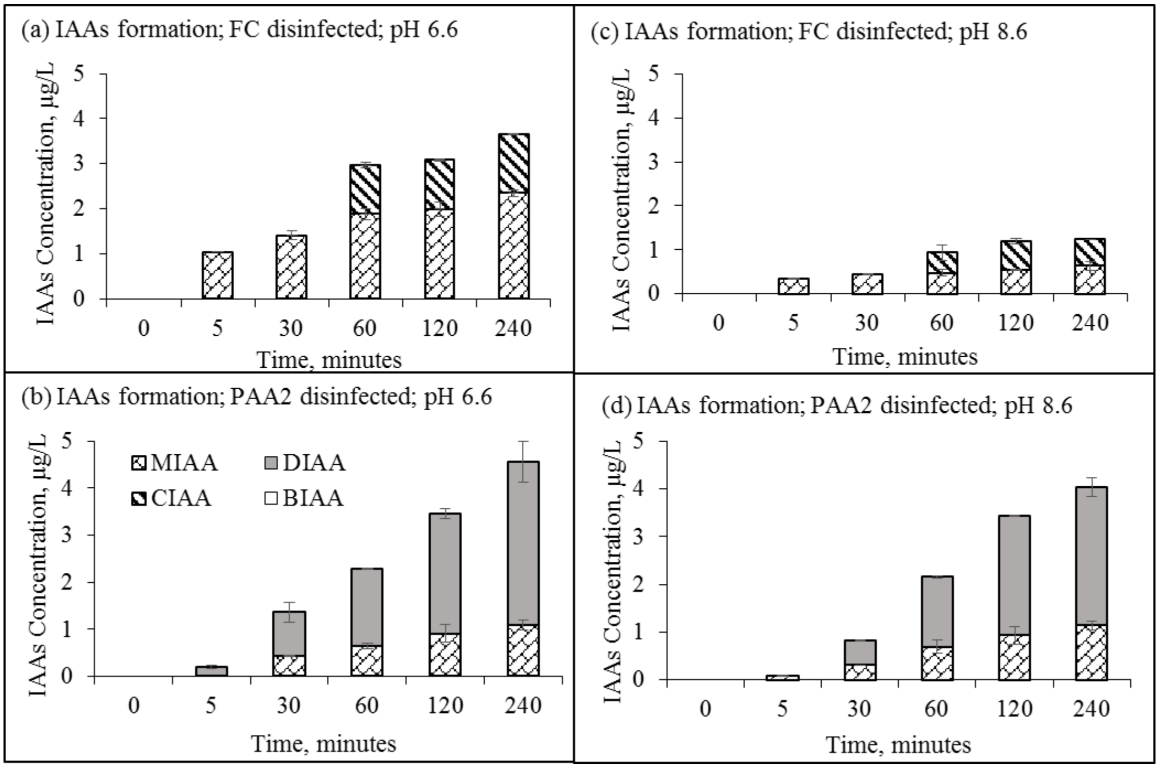


Figure 5. The formation of IAAs during FC and PAA2 treatment at pH 6.6 and 8.6 with 240 µg/L iodide. (a) FC disinfected, pH 6.6; (b) PAA2 disinfected, pH 6.6; (c) FC disinfected, pH 8.6; (d) PAA2 disinfected, pH 8.6

Figure 6 shows the formation of iodo-THMs during FC and PAA2 treatment at pH 6.6 and 8.6. During FC treatment at pH 6.6, five types of iodo-THMs were formed, including $CHCl_2I$, $CHBr_2I$, CHBrClI, $CHClI_2$, and $CHBrI_2$, among which $CHCl_2I$ and $CHBrI_2$ were the most and least abundant species, respectively. No CHI_3 was formed above detection limit. At pH 8.6, all six types of iodo-THMs were formed. $CHCl_2I$ was the most abundant species, while $CHBrI_2$ and CHI_3 were the least formed iodo-THMs. Most of the iodo-THMs were formed during first 30 mins, and the formation speed slowed down afterwards. The formation of iodo-THMs during PAA2 treatment was quite different from that during FC treatment. When using PAA2 as disinfectant, only CHI_3 formed and the formation increased gradually with time. The other iodo-THMs, if formed, were all below detection limits. There were 4.47 and 8.61 µg/L iodo-THMs formed in total during FC treatment, while there were 7.12 and 8.92 µg/L CHI_3 formed during PAA treatment when pH was 6.6 and 8.6, respectively.

No chlorinated or brominated THMs and HAAs were detected when using PAA as disinfectant, which serves as a good reason for drinking water treatment facilities to use PAA as alternative disinfectant to FC for the purpose of minimizing the formation of THM4 and HAA5 and meet the EPA regulation requirements. However, more iodo-THMs and IAAs were formed during PAA2 treatment than that of FC treatment when the source water contained higher concentrations of iodide, such as 240 µg/L. Iodo-THMs and IAAs have been demonstrated to be more toxic than their corresponding brominated and chlorinated forms (Richardson et al., 2007), even though they are not currently regulated by EPA.

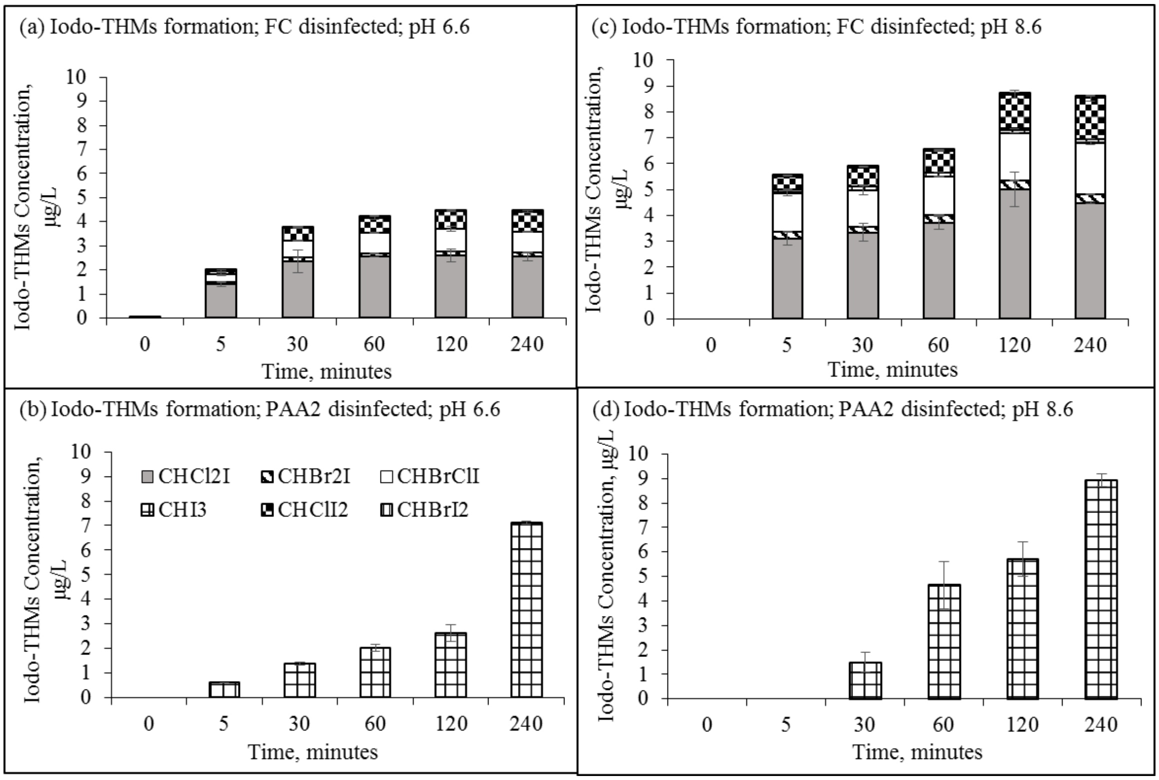


Figure 6. The formation of Iodo-THMs during FC and PAA2 treatment at pH 6.6 and 8.6 with 240 µg/L iodide. (a) FC disinfected, pH 6.6; (b) PAA2 disinfected, pH 6.6; (c) FC disinfected, pH 8.6; (d) PAA2 disinfected, pH 8.6

On the other hand, no HAAs and THMs were detected when using PAA1 as disinfectant, which demonstrates the potential to use PAA1 as an alternative disinfectant in drinking water treatment.

3.4 Effect of iodide on iodide substitution factor

The bromine substitution factor, which is the ratio of the molar concentration of bromine incorporated into a given class of DBP to the total molar concentration of chlorine and bromine, has been used as a measure of bromine substation among different DBP species (Obolensky and Singer, 2005). In this paper, similar to the bromine substitution factor, the iodide substitution factor (ISF) was used. The ISF is defined as the ratio of the molar concentration of iodine incorporated into a given class of DBP to the total molar concentration of chlorine, bromine, and iodine. Figure 7 shows the ISF changes along with the concentration of iodide when disinfected by FC for 4 hours. The 13 HAAs and 10 THMs exhibited similar ISF patterns with the addition of iodide. However, the ISF of 10 THMs increased more rapidly with the increase of iodide concentration. In addition, 13 HAAs showed higher ISF at pH 6.6 but lower ISF at pH 8.6, while the ISFs for 10 THMs were quite similar at two pHs.

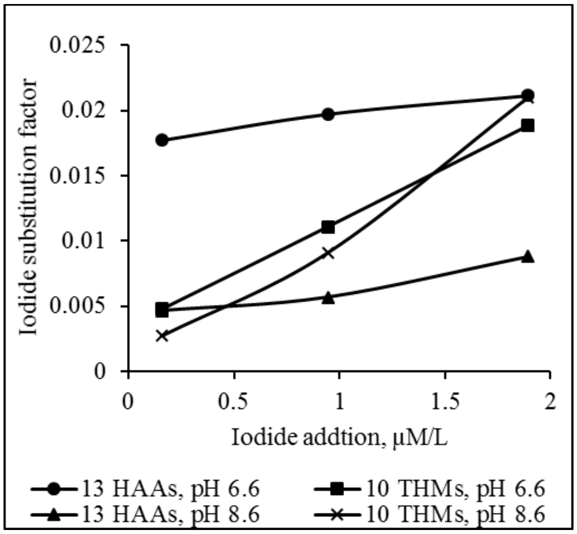


Figure 7. Effect of iodide on iodine substitution factor (ISF) in 13 HAAs and 10 THMs at pH 6.6 and 8.6 when disinfected by FC for 4 hours

4. Conclusions

The formation of THMs and HAAs during PAA treatment has been systematically investigated. The pH change showed that HAA formation was favored at lower pH, while THM formation was favored at higher pH for both FC and PAA treatment. When increasing the iodide concentration from 20 to 240 µg/L during FC treatment, the formation of chlorinated and brominated THMs and HAAs did not change significantly, while iodinated THMs and HAAs formed more at higher concentrations of iodide. The composition of H_2O_2 and PAA in the PAA solution showed great effect on the formation of THMs and HAAs. No detectable formation of THMs or HAAs was observed during PAA1 treatment, which contained more H_2O_2 than PAA. MIAA, DIAA, and CHI_3 were formed during PAA2 treatment, which contained more PAA than H_2O_2. This study demonstrated the potential use and possible concerns of PAA as an alternative disinfectant during drinking water treatment. Even though there was no formation of brominated and chlorinated HAAs and THMs when using both types of PAA, high levels of iodinated HAAs and THMs were observed during the treatment of PAA solution with higher PAA than H_2O_2 if the source water contains high level of iodide. Due to the high toxicity of iodinated HAAs and THMs, source water matrices, especially iodide concentration, need to be considered for drinking water treatment utilities to optimize their disinfection strategies to minimize DBP formation.

Acknowledgement

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Conflict of Interest

The authors declare no conflict of interest.

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III. Simultaneous Removal of Ammonia and N-Nitrosamine Precursors from High Ammonia Water by Zeolite and Powdered Activated Carbon

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ABSTRACT

When adding sufficient chlorine to achieve breakpoint chlorination to source water containing high concentration of ammonia during drinking water treatment, high concentrations of disinfection by-products (DBPs) may form. If N-nitrosamine precursors are present, highly toxic N-nitrosamines, primarily N-nitrosodimethylamine (NDMA), may also form. Removing their precursors before disinfection should be a more effective way to minimize these DBPs formation. In this study, zeolites and activated carbon were examined for ammonia and N-nitrosamine precursor removal when incorporated into drinking water treatment processes. The test results indicate that Mordenite zeolite can remove ammonia and five of seven N-nitrosamine precursors efficiently by single step adsorption test. The practical applicability was evaluated by simulation of typical drinking water treatment processes using six-gang stirring system. The Mordenite zeolite was applied at the steps of lime softening, alum coagulation, and alum coagulation with powdered activated carbon (PAC) sorption. While the lime softening process resulted in poor zeolite performance, alum coagulation did not impact ammonia and N-nitrosamine precursor removal. During alum coagulation, more than 67% ammonia and 70%-100% N-nitrosamine precursors were removed by Mordenite zeolite (except 3-(dimethylaminomethyl)indole (DMAI) and 4-dimethylaminoantipyrine (DMAP)). PAC effectively removed DMAI and DMAP when added during alum coagulation. A combination of the zeolite and PAC selected efficiently removed ammonia and all tested seven N-nitrosamine precursors (dimethylamine (DMA), ethylmethylamine (EMA), diethylamine (DEA), dipropylamine (DPA), trimethylamine (TMA), DMAP, and DMAI) during the alum coagulation process.

Keywords: Disinfection by-products; drinking water treatment; ammonia removal by zeolite; N-nitrosodimethylamine (NDMA); N-nitrosamines; N-nitrosamine precursor removal by zeolite and powdered activated carbon

1. Introduction

Many drinking water treatment systems, particularly small water systems that treat ground water, are facing issues of naturally-occurring high ammonia (NH_3 and NH_4^+) in their source water. When ammonia is present in high concentration, it reacts with free chlorine to form chloramines which have lower disinfection capacity (Blute et al., 2012). When a higher dose of chlorine is applied to reach the breakpoint chlorination, high levels of toxic disinfection by-products (DBPs) will form (Blute et al., 2012). On the other hand, ammonia can also be consumed by nitrifying bacteria to form nitrite and nitrate, and high nitrite would pose an acute health hazard (Blute et al., 2012). Thus, control and removal of ammonia in drinking water treatment is important. N-nitrosamines are a class of potential mutagenic and carcinogenic DBPs that form during drinking water or wastewater disinfection by chlorine or chloramines (Mitch et al., 2003) with N-nitrosodimethylamine (NDMA) as the predominant product. There are several hypotheses regarding their formation including the oxidation of intermediate formed by the reaction of dichloramine and dimethylamine (DMA) (Schreiber and Mitch, 2006), the formation of highly reactive nitrosating intermediate in water containing organic nitrogen precursor during chlorination (Choi and Valentine, 2003), and the reaction between monochloramine with either DMA (Selbes et al., 2013) or secondary amines (Zhou et al., 2014), or certain tertiary amines (Mitch and Sedlak, 2002a; Selbes et al., 2013). Several major precursors have been identified including DMA, ethylmethylamine (EMA), diethylamine (DEA), dipropylamine (DPA), trimethylamine (TMA), 4-dimethylaminoantipyrine (DMAP) and 3-(dimethylaminomethyl)indole (DMAI), all of which can be detected by a simple and rapid method developed using ultra-fast liquid chromatography-tandem mass spectrometry (UFLC-MS/MS) (Wu et al., 2015a).

Several methods have been used for ammonia removal including membrane distillation (Qu et al., 2013; Rezakazemi et al., 2012), air stripping (Yuan et al., 2016), breakpoint chlorination, biological treatment (Peng and Zhu, 2006), electrochemical oxidation (Li and Liu, 2009), and microwave radiation (Lin et al., 2009). However, since the ammonia concentration in source water varies and the risk of forming high levels of DBPs increases when using breakpoint chlorination, less expensive and less-DBP forming methods are needed. A UV/chlorine process has recently been developed for ammonia removal, which lowers chlorine demand and the formation of trihalomethanes (THMs) and haloacetic acids (HAAs). However, more haloacetonitriles (HANs) are formed (Zhang et al., 2015). In addition, the expense of the use of this UV/chlorine process is also another important factor that needs to be considered. There are also several methods developed for the removal of N-nitrosamines including reverse osmosis (RO) membranes (Fujioka et al., 2012), membrane bioreactor (Wijekoon et al., 2013), sand filtration (Krauss et al., 2009), and nanofiltration (Miyashita et al., 2009). Research has demonstrated that NDMA formation is attributable to the reaction between monochloramine and organic nitrogen-containing precursors (Gerecke and Sedlak, 2003; Krasner et al., 2013; Mitch and Sedlak, 2002a, 2002b). Therefore, a practical way to reduce the concentration of N-nitrosamines in water system is to remove their nitrogen-containing precursors.

Ion exchange is a promising ammonia and N-nitrosamine precursor removal method due to its low energy input and ease of operation (Demir et al., 2002; Gendel and

Lahav, 2013; Lin and Wu, 1996). However, using organic resin exchangers is costly (Huang et al., 2010), thus, the use of natural zeolite is considered to be a competitive and effective treatment due to its relatively less cost and simplicity of application and operation (Englert and Rubio, 2005; Huang et al., 2010; Karadag et al., 2006; Zhou and Boyd, 2014). Zeolite has also been used to remove ammonia during waste water treatment (Almutairi and Weatherley, 2015; Markou et al., 2014) and landfill leachate (Couto et al., 2016). Combined with alum and polyaluminum chloride, clinoptilolite zeolite can remove total organic carbon (TOC) in surface runoff significantly (Murnane et al., 2016). Zeolites are mainly composed of aluminosilicates (Englert and Rubio, 2005) with a three-dimensional structure formed by AlO_4 and SiO_4 tetrahedra that are connected by a shared oxygen atom (Englert and Rubio, 2005; Huang et al., 2010; Šiljeg et al., 2010). This open and stable structure contributes to high cation exchange capacity, cation selectivity, higher void volume and great affinity for cation ions like $NH_4^+{}_{(aq)}$ and other types of organic ions with positive charge (Farkaš et al., 2005; Huang et al., 2010; Rožić et al., 2000; Saltalı et al., 2007; Šiljeg et al., 2010; Wang and Peng, 2010; Wang et al., 2007). In a recent study, Mordenite zeolite has been shown to be an effective adsorbent to effectively remove most of the seven N-nitrosamine precursors previously identified in laboratory reagent water and untreated surface water (Wu et al., 2015b). However, the dual removal efficiencies of ammonia and N-nitrosamine precursors by zeolite have never been attempted in the drinking water treatment.

Powdered activated carbon (PAC) has been used for the removal of a wide range of emerging contaminants in water treatment (Bhatnagar et al., 2013; Mailler et al., 2015), usually at the step of alum coagulation. It shows low adsorption capacity on ammonia due to its non-polar surface (Halim et al., 2010), while can remove N-nitrosamine precursors (Beita-Sandí et al., 2016; Hanigan et al., 2012; Wu et al., 2015b). The effect of PAC on the ammonia and N-nitrosamine precursor removal during alum coagulation was also investigated.

We hypothesize that zeolite can effectively remove ammonia and N-nitrosamine precursors simultaneously, and by combination of zeolite and PAC, all the polar and less polar N-nitrosamine precursors can be well controlled during the drinking water treatment. The objectives of this study are to (1) identify the most effective zeolite for ammonia removal; (2) test the suitability of N-nitrosamine precursor removal by zeolite in combination with PAC; (3) apply zeolite and PAC in drinking water treatment processes by simulation of drinking water treatment steps of lime softening (add $Ca(OH)_2$ to reduce water hardness) and alum coagulation (add $Al_2(SO_4)_3 \cdot 14.3\ H_2O$ to destabilize water colloidal suspensions) through jar test. This aims to find out how to incorporate the zeolite and PAC in real drinking water treatment process.

2. Materials and Methods

2.1 Chemicals and Materials

Three types of zeolite including Bear River zeolite, Mordenite zeolite, and Zeolite Y used in the study were purchased from Bear River Zeolite Co. (Preston, ID, USA), Fisher Scientific (Pittsburgh, PA, USA), and Sigma Aldrich (St. Louis, MO, USA), respectively. Modified Bear River zeolite was prepared by mixing Bear River zeolite with 2 mol/L NaCl solution at 120 r/min and 36°C for 72 hr, then washing with ultra-high purity water three times and drying in an oven at 100°C (Šiljeg et al., 2010). HydroDarco

B PAC was purchased from Cabot Norit Americas Inc. (Marshall, TX, USA). The characteristics of each adsorbent (zeolites and PAC) are listed in Table 1.

Table 1 Characteristics of zeolites and PAC tested for ammonia and N-nitrosamine precursor removal.

Adsorbent	Source	Type	BET Surface Area (m^2/g)	Composition	Si/Al Molar Ratio
Bear River Zeolite	Natural zeolite	Clinoptilolite	375	K-Ca-Na-Al-Si	~15:1 to 20:1
Mordenite	Natural zeolite	Mordenite	425	$(Ca, Na_2, K_2) Al_2Si_{10}O_{24}\cdot 7H_2O$	13:1
Zeolite Y	Synthesized zeolite	Synthesized zeolite	450	$(Na_2,Ca,Mg)_{3.5}[Al_7Si_{17}O_{48}]\cdot 32(H_2O)$	200:1
Powered Activated Carbon	Lignite coal	PAC	510	Carbon	N/A

Seven N-nitrosamine precursor standards including DMA (40 wt.% in H_2O), TMA (25 wt.% in H_2O), DMAI (99%), DMAP, EMA (97%), DEA (≥99.5%), DPA (99%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Ammonium hydroxide standard solution (trace metal grade, 20%-22% as NH_3) and LC-MS grade methanol was purchased from Fisher Scientific (Pittsburgh, PA, USA). Formic Acid (LC-MS grade) was purchased from Sigma Aldrich (St. Louis, MO, USA). Ultra-high purity water was generated by a Millipore Elix 3 water purification system (Millipore, Billerica, MA, USA). Lime ($Ca(OH)_2$, >95%) and Alum ($Al_2(SO_4)_3\bullet 14.3\ H_2O$, >98%) used in the simulated drinking water treatment process were purchased from Fisher Scientific (Pittsburgh, PA, USA).

2.2 Water Sample Collection

Several types of water samples were used in this study including ultra-high purity water, surface (river) water, ground (well) water, and ground (well) water after certain treatment. Surface water was collected from the Missouri River (near Jefferson City, MO, USA). Ground water was collected from a shallow well (100 ft deep) near the Missouri River (MO, USA) that was influenced by the river water. The well water samples were collected at two different treatment steps, (1) after aeration but before lime softening (well water 1) and (2) after lime softening before recarbonation (well water 2) from a drinking water treatment facility.

All the water samples were collected in pre-cleaned 4-L amber bottles, placed in coolers filled with ice and transported to lab within 12 hr. The samples were stored in the refrigerator at 4°C unfiltered before use, then returned to room temperature before experiments were conducted.

2.3 Analytical Techniques

The water sample characterization was performed by following the standard methods for examination of water & wastewater (Eaton and Franson, 2005) and using commercially available HACH test kits (HACH, Loveland, CO). Ammonia concentrations were detected using HACH TNT 830 kits with a detection range of 0.015 to 2.00 mg/L NH_3-N (HACH, Loveland, CO). HACH DR 2800 spectrophotometer was used for ammonia detection (HACH, Loveland, CO). Dissolved organic carbon (DOC) was tested by using a TOC-L analyzer with ASI-L liquid autosampler with detection limit of 0.20 mg/L (Shimadzu, Columbia, MD, USA). pH was measured with a Thermo Orion

3 Star pH meter (Thermo Fisher Scientific, Waltham, MA, USA). Turbidity was measured using a TB200 Portable Turbidimeter (Orbeco-Hellige, Sarasota, FL, USA) and UV_{254} absorbance was monitored with a Cary 50 UV-Vis Spectrometer (Agilent, Santa Clara, CA, USA). Seven N-nitrosamine precursors were analyzed using a UFLC-MS/MS method with method detection limits ranging from 0.02 to 1 µg/L, except for EMA (5 µg/L) (Wu et al., 2015a). Briefly, a Shimadzu LC-20ADXR UFLC system (Columbia, MD) coupled with 4000 Q-trap mass spectrometer (AB Sciex, Concord, ON, CA) was used. The analysis was under positive electrospray ionization (ESI+) with multiple reaction monitoring (MRM) mode. Phenomenex polar-RP C18 column (Phenomenex, Torrance, CA) with dimensions of 150 × 2.0 mm i.d., particle size of 4 µm was used. Mobile phase A was ultra-high purity water with 0.1% formic acid and mobile phase B was methanol with 0.1% formic acid.

2.4 Water Treatment Procedures

2.4.1 Investigate ammonia removal efficiency by different types of zeolites

The ammonia removal efficiencies of Bear River (untreated and treated to improve adsorption), Mordenite, and Zeolite Y was tested and compared in untreated well water with naturally occurring ammonia concentration of 1.19 mg/L in small-scale tests. During this small-scale tests, water sample was added into 40 mL amber vials with addition of 1000 mg/L of specific type of adsorbent. Then the mixtures were shaken for 90 min. Afterwards, the water samples were filtered through 0.45 µm nylon membrane filter for ammonia analysis and 0.22 µm nylon membrane filter (both types of filters were purchased from LabTech America, Inc., Hopkinton, MA, USA) for N-nitrosamine precursor analysis.

2.4.2 Investigate the impacts of dosage, contact time, pH, and temperature on the removal of ammonia by the most effective zeolite

The most efficient zeolite was chosen to study the effects of dosage, contact time, pH and temperature on the removal of ammonia. Untreated well water (contains naturally occurring 1.19 mg/L ammonia) was used for all the following tests. The treatment procedures were same with those described in Section 2.4.1.

(1) During dosage test, three dosages including 100, 1000 and 5000 mg/L were used with contact time of 4 hr.

(2) During exposure time test, the adsorbent was allowed to contact for 5, 10, 30, 60, 120, 240, 1440 min. The dosage of adsorbent during exposure time test was decided during dosage tests.

(3) During pH test, pH was adjusted to 6, 7, and 8 using a 10 mmol/L phosphate buffer. Then the most efficient absorbent at the concentration decided during dosage tests was added and the mixture was agitated for 4 hr.

(4) During temperature tests, three temperatures, 2°C, room temperature, and 40°C, were investigated. The dosage and contact time in the temperature tests were determined during dosage tests and exposure time tests.

2.4.3 Investigate simultaneous removal of ammonia and N-nitrosamine precursors by small-scale test

The simultaneous removal of ammonia and N-nitrosamine precursors was first tested in small-scale with 40 mL vials. Ultra-high purity water dosed with 8 mg/L ammonia and 25 µg/L N-nitrosamine precursors was used. The most effective Mordenite zeolite was used and the dosage was 1000 mg/L with contact time of 30 min. The treatment procedures were same with Section 2.4.1.

2.4.4 Investigate simultaneous removal of ammonia and N-nitrosamine precursors by simulation of water treatment process using jar test

For practical application of the studied adsorbents to remove ammonia and N-nitrosamine precursors in drinking water treatment system, it is important to establish which water treatment step is the ideal step for adding these adsorbents. Simultaneous removal of ammonia and N-nitrosamine precursors was then tested through a simulated drinking water treatment process using a six-gang stirrer with 2-L square beakers (Phipps & Bird, Richmond, VA, USA). Three types of water were used for the simulation study, including well water 1 and 2 and Missouri River water. The concentrations of ammonia and N-nitrosamine precursors in water samples were adjusted to be 1.5 mg/L and 20 µg/L, respectively. Two commonly used drinking water treatment steps, lime softening and alum coagulation, were simulated. PAC was added at the step of alum coagulation to study its effect on the removal of ammonia and N-nitrosamine precursors.

During lime softening, excess lime was added to remove both Ca and Mg at pH 11; For alum coagulation, 50 mg/L $Al_2(SO_4)_3 \cdot 14.3\ H_2O$ was added; For alum coagulation with PAC sorption, 50 mg/L $Al_2(SO_4)_3 \cdot 14.3\ H_2O$ and 20 mg/L PAC was added. The chemicals were dosed into the water samples in specific reaction beakers of the six-gang stirring system. Mordenite was added into specific beakers simultaneously with lime, alum, or alum with PAC, followed by rapid mixing (30 sec at 300 r/min), flocculation (10 min each at 58, 42 and 28 r/min) and sedimentation (180 min at 0 r/min). After treatments, samples were filtered with 0.22 μm nylon membrane filters for N-nitrosamine precursor analysis and 0.45 μm the same type of filter for UV_{254} absorption and ammonia analysis. pH and turbidity were tested in unfiltered samples.

2.5 Quality Assurance and Control

US EPA quality control and assurance guideline was closely followed during this study. All the analytical methods have been validated to make sure certified performance before used for sample analysis. Method detection limits, reproducibility, calibration curve linearity, and matrix effect were all been tested to make sure they meet the performance criteria. During sample analysis, continuing quality control, including blank sample, duplicates of selected samples, and spiking recovery of samples, were performed for every batch or every 10-15 samples.

3. Results and Discussion

There were four types of water samples used in this study and their basic chemical and physical parameters were measured at room temperature (~20°C) and are listed in Table 2. Untreated well water was used for the study of ammonia removal by zeolites in small scales. Well water 1, well water 2 and Missouri River water were used for the study of simultaneous ammonia and N-nitrosamine removal through jar tests. Missouri River water contained high DOC (5.76 mg/L) and non-detectable NH_3-N, while in well water, the DOC level was relatively low and it contained around 1 mg/L of naturally occurring NH_3-N. Before lime softening, the hardness in well water samples was high.

Table 2 The basic parameters of tested water samples at 20 °C.

Water sample	pH	DOC	NH_3-N, mg/L	UV_{254} absorption	Calcium hardness as $CaCO_3$, mg/L	Total hardness as $CaCO_3$, mg/L	Alkalinity as $CaCO_3$, mg/L	Turbidity, NTU
Missouri River water	7.40	5.76	<0.015	0.1335	149	222	149	324
Well water (source water)	7.40	2.87	1.19	0.2040	410	570	603	142
Well water 1 (after aeration before lime softening)	7.72	2.80	1.02	0.0824	397	546	568	129.5
Well water 2 (after lime softening before recarbonation)	9.55	2.37	1.18	0.0516	69	186.5	161	2.31

3.1 Ammonia Removal by Zeolites

The ammonia removal efficiencies by different zeolites in untreated well water (naturally occurring ammonia concentration of 1.19 mg/L) were compared. The ammonia removal results are shown in Fig. 1. Ammonia removal efficiency was as follows: Mordenite > Modified BRZ > Zeolite Y > BRZ. Mordenite had the best removal efficiency (68%). This result can be explained by its low Si/Al molar ratio (Si/Al = 13:1) and moderate surface area (425 m^2/g) which contribute to a high cation-exchange capacity. For Bear River zeolite and Zeolite Y, although the former has higher Si/Al ratio, Bear River zeolite has lower surface area (375 m^2/g for Bear River zeolite and 450 m^2/g for zeolite Y), thus resulted in lower ammonia removal efficiency than that of Zeolite Y (Wu et al., 2015b). Modified BRZ showed better removal efficiency on ammonia than BRZ, which agrees with the previous published data and is because that the stability of NH_4^+ on Na-form of zeolite (modified BRZ) is higher than that on ordinary form of zeolite (Lin et al., 2013; Šiljeg et al., 2010; Soetardji et al., 2015).

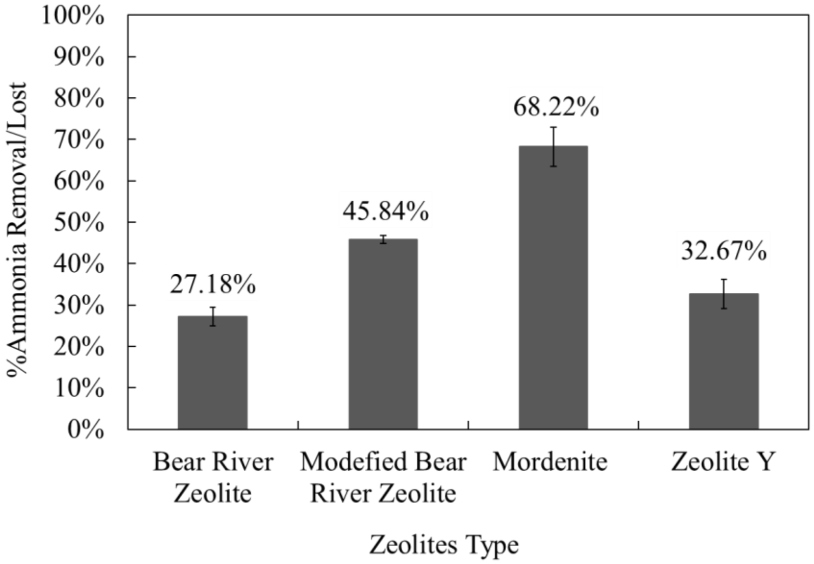


Fig. 1. Ammonia removal efficiencies by different types of zeolites at a dosage of 1000 mg/L in well water sample (ammonia concentration of 1.19 mg/L) after 4 hours' contact time (n=2, error bars represent the percent difference).

Zeolite dosage, exposure time, pH, and temperature impacts on the ammonia removal efficiency were evaluated in untreated well water (naturally occurring 1.19 mg/L ammonia) using the most efficient absorbent, Mordenite zeolite. Ammonia removal was 17%, 72% and 86% when 100, 1000, and 5000 mg/L Mordenite were added, respectively. Compared to that with 100 mg/L zeolite applied, the ammonia removal efficiency increased drastically with 1000 mg/L zeolite applied, but increased slowly when further increasing the zeolite concentration to 5000 mg/L. When adding higher concentration of zeolite, the solid/liquid ratios increases, the potential of aggregation or particles precipitation increases (Huang et al., 2010; Saltalı et al., 2007) which would affect the zeolite adsorption efficiency. This might be the reason why the removal of ammonia did not increase linearly with the increase of zeolite dosage from 100 to 5000 mg/L. Therefore, dosage of 1000 mg/L was selected for the following study.

Exposure time dependence was investigated by allowing Mordenite to contact for 5, 10, 30, 60, 120, 240, 1440 min. The removal kinetics were fast, with 66% of ammonia removed after 5 min of contact time but only 5% increased removal at the longest time point. Similar results have been obtained by other studies (Huo et al., 2012; Lin et al., 2013). The fast ammonia adsorption might result from excess adsorption sites on the zeolite at the beginning of the interaction (Du et al., 2005). Meanwhile, the adsorption of N-nitrosamine precursors by Mordenite is rapid, which reaches equilibrium within 10 min of contact (Wu et al., 2015b).

For pH and temperature dependence tests, no significant difference in ammonia removal was found for all the tested pHs (shown in Fig. 2**)**, and all the tested temperatures (shown in Fig. 3).

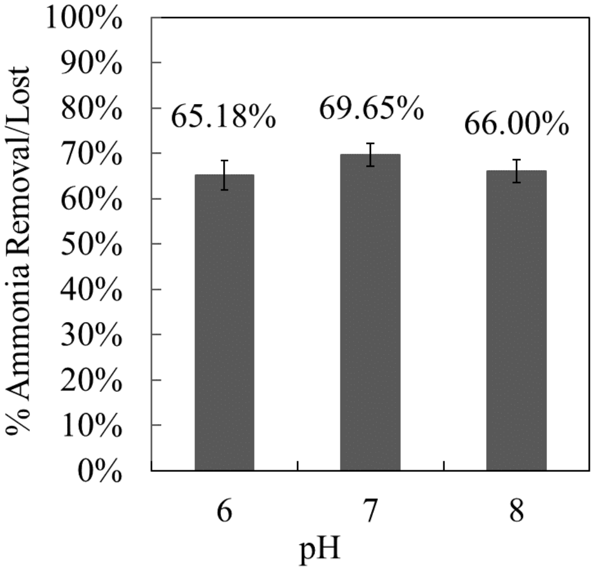


Fig. 2. Ammonia removal efficiencies by 1000 mg/L Mordenite zeolite in well water sample (ammonia concentration of 1.19 mg/L) at different pHs after 4 hours contact time (n=2, error bars represent the percent difference).

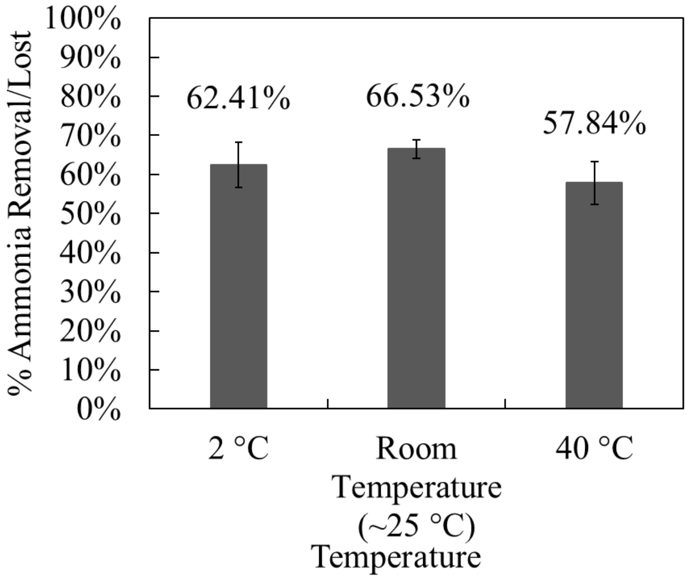


Fig. 3. Ammonia removal efficiencies by 1000 mg/L Mordenite zeolite in well water sample (ammonia concentration of 1.19 mg/L) at different temperatures after 5 minutes' contact time (n=2, error bars represent the percent difference).

3.2 Simultaneous Removal of Ammonia and N-Nitrosamine Precursors in Ultra-High Purity Water by Mordenite Zeolite

The most effective ammonia removal zeolite, Mordenite, was selected to determine the simultaneous removal efficiency of ammonia and N-nitrosamine precursors because of its high performance in ammonia removal. Mordenite effectively removed more than 95% of all the tested N-nitrosamine precursors, except DMAP, and 75% of the ammonia in ultra-high purity water in small-scale tests (Table 3). DMAP is aromatic amine which is less ionic and has weaker electrostatic interactions with zeolites, resulting in lower removal efficiency by Mordenite compared to the other precursors (Wu et al., 2015b).

Table 3 Ammonia and N-nitrosamine precursor removal in ultra-high purity water (spiked with 8 mg/L ammonia and 25 μg/L each of N-nitrosamine precursors) by Mordenite zeolite (1000 mg/L). Contact time for the removal was 30 minutes.

Sample ID	Mordenite (mg/L)	% Removal/Lost							
		DMA	EMA	TMA	DEA	DPA	DMAI	DMAP	Ammonia-N
Control	0	2.1	8.5	5.9	8.7	16.4	10.7	3.4	24.9
Sample	1000	100.0	97.1	95.9	100.0	98.3	98.5	0.0	75.1
Sample duplicate	1000	100.0	97.3	95.7	100.0	98.3	98.6	0.0	75.1

DMA: dimethylamine; EMA: ethylmethylamine; TMA: trimethylamine; DEA: diethylamine; DPA: dipropylamine; DMAI: (dimethylaminomethyl)indole; DMAP: dimethylaminoantipyrine.

3.3 Simultaneous Removal of Ammonia and N-Nitrosamine Precursors by Mordenite Zeolite during Simulated Water Treatments through Jar Tests

For practical applications, it is important to evaluate the removal efficiency of ammonia and N-nitrosamine precursors by Mordenite when combined with other drinking water treatment processes. The practical zeolite application for real drinking water treatment process should be coagulation processes including lime softening and alum coagulation. Alum has been used in the wastewater treatment and shows a great effect on the removal of dissolved phosphorus and total phosphorus (Brennan et al., 2012; O'Flynn et al., 2013) PAC is usually added during the step of alum coagulation in drinking water treatment plant. Using a six-gang stirrer, lime softening and alum coagulation with and without PAC sorption, were simulated with addition of 1000 mg/L Mordenite to evaluate the simultaneous removal of ammonia and N-nitrosamine precursor.

3.3.1 Ammonia and N-Nitrosamine precursor removal by mordenite zeolite during simulated lime softening treatment

Lime softening is a common early step in the drinking water treatment process. Thus, the removal of ammonia and N-nitrosamine precursors was first tested during lime softening. Well water 1 was used for the study after adjusting the concentration of ammonia and N-nitrosamine precursors to be 1.5 mg/L and 20 µg/L, respectively. In the first experiment, Mordenite with concentration of 1000 mg/L was added to the water samples and allowed to contact for 10 min. After 10 min, the removal efficiencies of ammonia and N-nitrosamine precursors were tested. Lime was then added without removing the Mordenite. After rapid mixing, flocculation and sedimentation, samples were taken for ammonia and N-nitrosamine precursor detection. In the second experiment, 1000 mg/L Mordenite was added together with lime and subjected to rapid mixing, flocculation, and sedimentation.

When mordenite was added before lime and allowed to contact for 10 min, 68% ammonia was removed. However, after adding lime, the removal of ammonia decreased to 29%, indicating that the ammonia was being replaced on the adsorbent during lime softening. In the samples dosed with Mordenite and excess lime simultaneously, only 15% ammonia removal was observed. This indicated that lime softening had a negative effect on ammonia removal by Mordenite zeolite. N-Nitrosamine precursor removal was largely unchanged between the two experiments, resulting in more than 95% removal except for TMA (60%), DMAI (8%) and DMAP (no removal) in each case.

During the softening process, the pH increased to 11. Ammonia has a pK_a of 9.4; above this pH, ammonia exists in molecular form rather than ionic. Thus, it was hypothesized that ammonia removal was pH dependent and that when pH above ammonia pK_a, ammonia removal would be minimal due to the ammonia equilibrium in water shifting to the molecular form. The effect of pH on ammonia and N-nitrosamine precursor removal was investigated by adjusting the pH of well water 1 to 6, 7, 8, 9, 10, and 11 using 1 mol/L sodium hydroxide and 10% sulfuric acid, with adjustment of ammonia and each precursor to be 1.5 mg/L and 20 µg/L, respectively, and contacting with 100 mg/L Mordenite for 30 min. The results can be seen in Table 4. Ammonia removal was between 12%-14% in samples at pH 6, 7, 8, decreased to 5% removal in samples at pH 9, and was not removed in samples at pH 10 and 11. N-nitrosamine precursor removal increased slightly as pH increased, most likely due to the relatively high pK_a values for most of the precursors ranging from 9.8-11 and less competition for ion exchange sites under basic conditions (Wu et al., 2015b).

Table 4 Ammonia and N-nitrosamine precursor removal efficiency by Mordenite zeolite (100 mg/L) in well water 1 (after aeration but before lime softening) with ammonia (1.5 mg/L) and N-nitrosamine precursor (20 µg/L each) at different pHs.

Sample ID	pH	Mordenite (mg/L)	% Removal/Lost							
			Ammonia	DMA	TMA	EMA	DEA	DPA	DMAI	DMAP
Well water 1--Control	8.08	0	0.0	0.0	0.0	21.7	7.2	7.0	1.2	1.9
Well water 1-6	6.02	100	11.8	26.2	15.5	36.1	22.9	56.4	3.1	1.2
Well water 1-7	6.93	100	13.5	26.0	11.5	30.9	24.8	50.8	5.1	8.2
Well water 1-8	8.08	100	13.5	45.0	16.2	40.2	25.3	59.8	5.4	5.3
Well water 1-9	8.96	100	4.7	34.8	17.7	58.1	29.2	75.2	9.5	6.8
Well water 1-10 (%RPD[a] , n=2)	9.96 (0.0)	100	0.0 (N/A[b])	55.1 (0.3)	23.1 (1.1)	65.9 (7.3)	34.5 (2.7)	65.2 (9.3)	21.5 (2.6)	7.6 (9.1)
Well water 1-11	10.97	100	0.0	51.4	47.2	72.3	42.4	68.5	21.3	7.8

[a] RPD means relative percent difference of duplicated samples.

[b] N/A means not applicable.

3.3.2 Ammonia and N-Nitrosamine precursor removal by mordenite during alum coagulation with and without PAC

Six-gang stirrer simulations were conducted to determine the effects on ammonia and N-nitrosamine precursor removal when alum and Mordenite were added simultaneously with and without PAC sorption. Three types of water were evaluated including well water 1, well water 2 and Missouri River water. The concentrations of ammonia and N-nitrosamine precursors in water samples were adjusted to 1.5 mg/L and 20 μg/L, respectively. During alum coagulation, pH was adjusted to around 7 from initial pH values of 7.72, 9.55, and 7.40 for well water 1, well water 2, and Missouri River water, respectively. Since the optima pH range for alum coagulation is 6-7, in general acid is used in addition of the coagulant during drinking water treatment process to reduce the amount of coagulant needed and effectively lower chemical costs. Turbidity decreased significantly after coagulation for well water 1 and Missouri River water, indicating an efficient coagulation process. The detailed results of pH, UV_{254} absorption, and turbidity change before and after each treatment are shown in Table 5. Ammonia and N-nitrosamine precursor removal after the different treatments in each type of water is shown in Table 6. In the experiment with well water 1, duplicates were conducted for samples with the addition of alum and Mordenite, or alum, PAC and Mordenite. In the experiment with well water 2 and Missouri river water, four replicates were conducted for the above mentioned samples. Acceptable reproducibility for the removal of ammonia and N-nitrosamine precursors was achieved in all three types of water matrices with the percent of relative standard deviation ranging from 0.0 to 21.3%. Without Mordenite addition during alum coagulation, no ammonia removal was observed and less than 25%

of the precursors were removed except for DMAI and DMAP in samples treated with PAC. When Mordenite was added during alum coagulation without PAC addition, more than 67% ammonia and 70%-100% precursors were removed except DMAI and DMAP, indicating that the addition of alum did not affect the ion exchange sites on the zeolite.

Table 5 Values of pHs, UV$_{254}$ absorption, Turbidity of water matrixes tested after different treatments.

Water samples	**Treatments**[a]	**[c]pH (%RSD[b])**	**UV$_{254}$ Absorption (%RSD)**	**Turbidity (NTU) (%RSD)**
Well water 1 (after aeration before lime softening)	No treatment (n=1)	7.72	0.0824	129.5
	Alum (n=1)	7.68	0.0552	0.4
	Alum+PAC (n=1)	7.56	0.0455	0.2
	Alum+Mordenite (n=2)	7.45 (0.7)	0.0575 (8.0)	2.4 (12.2)
	Alum+PAC+Mordenite (n=2)	7.40 (0.5)	0.0488 (3.1)	2.4 (11.3)
Well water 2 (after lime softening before recarbonation)	No treatment (n=1)	9.55	0.0516	2.3
	Alum (n=2)	7.07 (0.7)	0.0421 (1.0)	0.4 (2.6)
	Alum+PAC (n=2)	7.04 (0.4)	0.0332 (8.4)	0.3 (7.4)
	Alum+Mordenite (n=4)	7.06 (0.7)	0.0452 (6.0)	1.9 (18.4)
	Alum+PAC+Mordenite (n=4)	7.02 (0.1)	0.0372 (4.3)	1.4 (15.9)
Missouri River water	No treatment (n=1)	7.40	0.1335	324.0
	Alum (n=2)	6.95 (1.2)	0.0929 (6.1)	0.5 (8.7)
	Alum+PAC (n=2)	7.06 (0.4)	0.0808 (6.8)	0.7 (14.5)
	Alum+Mordenite (n=4)	7.16 (0.3)	0.0999 (1.2)	2.2 (20.6)
	Alum+PAC+Mordenite (n=4)	7.16 (0.2)	0.0904 (2.9)	2.0 (17.3)

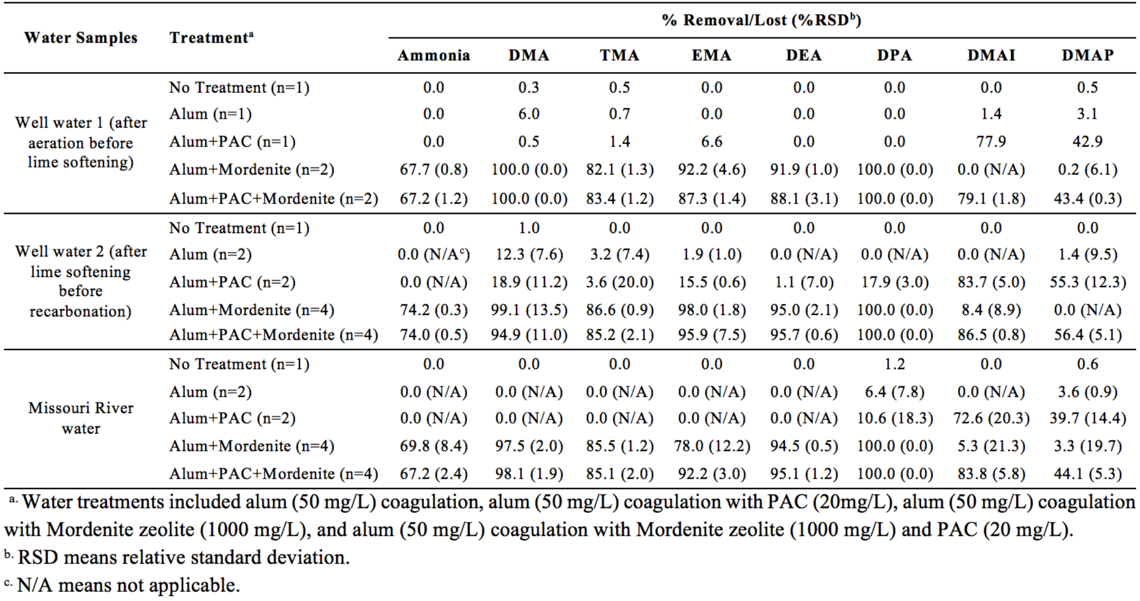
[a] Water treatments included alum (50 mg/L) coagulation, alum (50 mg/L) coagulation with PAC (20 mg/L) addition, alum (50 mg/L) coagulation with Mordenite zeolite (1000 mg/L), and alum (50 mg/L) coagulation with Mordenite zeolite (1000 mg/L) and PAC (20 mg/L).

[b] RSD means relative standard deviation of replicated samples.

[c] pHs for all three types of water matrix were adjusted to be within 7 to 8 with sodium hydroxide or sulfuric acid after the addition of alum

During alum coagulation with PAC sorption process, more than 67% of ammonia was removed when Mordenite was added. N-nitrosamine precursor removal was similar to the test results without PAC addition, except for DMAI and DMAP. When PAC was added, more than 73% DMAI and 40% DMAP were removed. PAC is a highly porous material with a large surface area to which natural organic matter can adsorb, especially hydrophobic compounds (Nam et al., 2014). Therefore, DMAI and DMAP were removed when PAC was added, similar to results from a previous study (Wu et al., 2015b). Due to its non-polar surface, PAC did not have much adsorption of ammonia (Halim et al., 2010). In the samples dosed with alum, PAC, and Mordenite, more than 75% precursors were removed except DMAP (43% removal). This demonstrated that the combination of Mordenite and PAC was an efficient way for the control of both ammonia and N-nitrosamine precursors. Alum coagulation did not show negative effect on the adsorption process of both Mordenite zeolite and PAC.

Table 6 Percent removal/lost of ammonia and N-nitrosamine precursors in different water matrixes after different types of water treatments.



Water Samples	Treatment[a]	% Removal/Lost (%RSD[b])							
		Ammonia	DMA	TMA	EMA	DEA	DPA	DMAI	DMAP
Well water 1 (after aeration before lime softening)	No Treatment (n=1)	0.0	0.3	0.5	0.0	0.0	0.0	0.0	0.5
	Alum (n=1)	0.0	6.0	0.7	0.0	0.0	0.0	1.4	3.1
	Alum+PAC (n=1)	0.0	0.5	1.4	6.6	0.0	0.0	77.9	42.9
	Alum+Mordenite (n=2)	67.7 (0.8)	100.0 (0.0)	82.1 (1.3)	92.2 (4.6)	91.9 (1.0)	100.0 (0.0)	0.0 (N/A)	0.2 (6.1)
	Alum+PAC+Mordenite (n=2)	67.2 (1.2)	100.0 (0.0)	83.4 (1.2)	87.3 (1.4)	88.1 (3.1)	100.0 (0.0)	79.1 (1.8)	43.4 (0.3)
Well water 2 (after lime softening before recarbonation)	No Treatment (n=1)	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0
	Alum (n=2)	0.0 (N/A[c])	12.3 (7.6)	3.2 (7.4)	1.9 (1.0)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	1.4 (9.5)
	Alum+PAC (n=2)	0.0 (N/A)	18.9 (11.2)	3.6 (20.0)	15.5 (0.6)	1.1 (7.0)	17.9 (3.0)	83.7 (5.0)	55.3 (12.3)
	Alum+Mordenite (n=4)	74.2 (0.3)	99.1 (13.5)	86.6 (0.9)	98.0 (1.8)	95.0 (2.1)	100.0 (0.0)	8.4 (8.9)	0.0 (N/A)
	Alum+PAC+Mordenite (n=4)	74.0 (0.5)	94.9 (11.0)	85.2 (2.1)	95.9 (7.5)	95.7 (0.6)	100.0 (0.0)	86.5 (0.8)	56.4 (5.1)
Missouri River water	No Treatment (n=1)	0.0	0.0	0.0	0.0	0.0	1.2	0.0	0.6
	Alum (n=2)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	6.4 (7.8)	0.0 (N/A)	3.6 (0.9)
	Alum+PAC (n=2)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	10.6 (18.3)	72.6 (20.3)	39.7 (14.4)
	Alum+Mordenite (n=4)	69.8 (8.4)	97.5 (2.0)	85.5 (1.2)	78.0 (12.2)	94.5 (0.5)	100.0 (0.0)	5.3 (21.3)	3.3 (19.7)
	Alum+PAC+Mordenite (n=4)	67.2 (2.4)	98.1 (1.9)	85.1 (2.0)	92.2 (3.0)	95.1 (1.2)	100.0 (0.0)	83.8 (5.8)	44.1 (5.3)

[a] Water treatments included alum (50 mg/L) coagulation, alum (50 mg/L) coagulation with PAC (20mg/L), alum (50 mg/L) coagulation with Mordenite zeolite (1000 mg/L), and alum (50 mg/L) coagulation with Mordenite zeolite (1000 mg/L) and PAC (20 mg/L).

[b] RSD means relative standard deviation.

[c] N/A means not applicable.

4. Conclusions

In this study, ammonia removal efficiencies by using different types of zeolites including Bear River zeolite, modified Bear River zeolite, Mordenite zeolite, and Zeolite

Y was investigated in high ammonia water. Mordenite zeolite was demonstrated to be the most efficient adsorbent for ammonia removal. The removal of ammonia by Mordenite was very fast and reached equilibrium in about 5 min. pHs lower than the p*K*a value of ammonia (6, 7, and 8) and temperature (2°C, Room Temperature, 40°C) did not show significant effects on the removal efficiencies. Mordenite zeolite was subsequently used to study the simultaneous removal of N-nitrosamine precursors and ammonia in ultra-high purity water spiked with ammonia and N-nitrosamine precursors during small-scale tests, and in real water samples with concentration adjustment of ammonia and N-nitrosamine precursors during simulated drinking water treatments. The simulated drinking water treatments included lime softening and alum coagulation with and without PAC addition. The lime softening process had negative effects on the removal of ammonia by Mordenite zeolite due to increased pH (up to 11) and the low pK_a (9.4) of ammonia. Above pH 9.4, ammonia existed in molecular form and seemed to be no longer participating in ion exchange. Mordenite zeolite efficiently removed most of the ammonia and N-nitrosamine precursors (except DMAI and DMAP) during alum coagulation without PAC. PAC showed a good removal efficiency for aromatic and less hydrophilic amines DMAI and DMAP. Therefore, the combination of two types of adsorbents is a good choice for removal of ammonia and N-nitrosamine precursors from drinking water system.

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SECTION

2. CONCLUSIONS

A rapid and sensitive HPIC-MS/MS method for simultaneous determination of chloro-, bromo-, and iodo- acetic acids and related halogenated contaminants including bromate, bromide, iodate, and iodide was developed to directly analyze water samples after filtration, eliminating the need for pre-concentration and chemical derivatization. The method was further used for investigating the formation of HAAs and THMs, especially the iodinated form, during PAA disinfection. PAA is a strong antimicrobial disinfectant that has the potential to reduce THMs and HAAs formation. According to the results, the composition of H_2O_2 and PAA in the PAA solution showed great effect on the formation of HAAs and THMs. When using PAA solution with higher concentration of H_2O_2 than PAA as disinfectant, no detectable formation of HAAs and THMs was observed. When using PAA solution with higher concentration of PAA than H_2O_2 as disinfectant, high levels of iodinated HAAs and THMs were observed.

Besides the study of the detection and formation of THMs and HAAs, an efficient and economic method was investigated for the control of DBPs. Results showed that mordenite zeolite efficiently removed most of the ammonia and N-nitrosamine precursors (except DMAI and DMAP) during alum coagulation treatment process. The addition of PAC helped with the removal of DMAI and DMAP. Therefore, the combination of mordenite zeolite and PAC is a good choice for removal of ammonia and N-nitrosamine precursors from drinking water system.

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