Separation and Purification Technology 156 (2015) 980–986

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Effect of pH on the formation of disinfection byproducts in ferrate(VI) pre-oxidation and subsequent chlorination

Xin Yang [a,b], Wenhui Gan [a], Xing Zhang [a], Huang Huang [a], Virender K. Sharma [c,*]

[a] SYSU-HKUST Research Center for Innovative Environmental Technology, School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China
[b] Research Institute of Sun Yat-sen University in Shenzhen, Shenzhen, China
[c] Department of Environmental and Occupational Health, School of Public Health, Texas A&M University, 1266 TAMU, College Station, TX 77843, USA

ARTICLE INFO

Article history:
Received 2 April 2015
Received in revised form 22 August 2015
Accepted 24 September 2015
Available online 26 September 2015

Keywords:
Ferrate
Chlorine
Organic matter
Disinfection by-products
Trihalomethanes

ABSTRACT

This study investigated the effect of pH on the formation of disinfection by-products (DBPs) during pre-oxidation with ferrate(VI) ($Fe^{VI}O_4^{2-}$, Fe(VI)) and subsequent chlorination of either a source water from a treatment plant, or a representative solution of natural organic matter from the Suwannee River NOM (SRNOM). The studied DBPs include trihalomethanes (THMs), chloral hydrate (CH), haloacetonitriles (HANs), and trichloronitromethane (TCNM). The results show that increasing pH from 5.0 to 9.0 increased THMs formation during chlorination of source water and Fe(VI) pre-oxidation generally decreased the concentration of THMs, except pH 9.0. The formation of CH and TCNM were not greatly influenced by pH in chlorination. But Fe(VI) pretreatment before chlorination enhanced CH and TCNM formation in acidic pH while lessened their formation in alkaline pH. HANs were detected in acidic pH whereas almost no formation of HANs was observed in basic pH. Similar experiments were conducted with SRNOM water to assess the variation of DBPs at different pHs with/without Fe(VI) pre-oxidation. Reactivity, products of fractions, and moieties of organic matter involved in Fe(VI) per-oxidation and subsequent chlorination reasonably explained the trends of the formation of DBPs under acidic to basic conditions.

1. Introduction

Disinfection using chlorine is widely applied to control microbial pathogens in drinking water. However, chlorination has raised a public health concern with the detection of potential toxic disinfection by-products (DBPs), such as trihalomethanes (THMs) and chloral hydrate (CH), generated from the reaction of chlorine with organic components of water [1,2]. Much of the research in the last decade has focused on nitrogen-containing DBPs (N-DBPs) because of their production during chloramination, an alternation process which produces lower THM concentrations than chlorination [3–7]. Examples of N-DBPs include nitrosoamines, halonitriles, haloacetamides, and halonitroalkanes, which can be produced. N-DBPs are more acutely carcinogenic, genotoxic, and cytotoxic than chlorinated DBPs [8,9]. If chlorine is used as a disinfectant, DBP production should be minimized by a pre-oxidation process before its application.

With chlorination, natural organic matter (NOM) in water contributes to the formation of DBPs [5,10,11]. NOM can be characterized by hydrophilic and hydrophobic constituents of different molecular sizes as well as by aliphatic and aromatic contents [12,13]. Importantly, NOM contains precursors of different moieties that play important roles in the formation of DBPs [2,11]. Results have shown that chemical oxidation of NOM can increase hydrophilicity and produce compounds with small molecular weights such as ketones and carboxylic acid and thus influence the formation of DBPs during subsequent chlorination [14]. These chemical oxidants include chlorine dioxide, hydrogen peroxide, ozone, and potassium permanganate and can be pre-oxidants to decrease the levels of DBPs before applying chlorine to drinking water [15–18]. Chlorine dioxide and ozone have shown the formation of potential carcinogenic chlorite and bromate ions, respectively, while chloramine as a pre-oxidant forms nitrosoamines [3,19,20]. In the past decade, ferrate((VI) ($Fe^{VI}O_4^{2-}$) has emerged as a greener oxidant in sustainable treatment processes [21–24] and can be an effective pre-oxidant to control the concentrations of DBPs in water treatment. However, limited work has been conducted to demonstrate its potential as a pre-oxidant followed by chlorination [25,26].

A recent work showed that moieties of Suwannee river natural organic matter (SRNOM) greatly influenced the formation of DBPs during chlorination with and without Fe(VI) as a pre-oxidant [26]. The water pH can affect the reactivity of the moieties with

---

* Corresponding author.
E-mail address: vsharma@sph.tamhsc.edu (V.K. Sharma).

http://dx.doi.org/10.1016/j.seppur.2015.09.057
1383-5866/

chlorine [27,28], but no study on the formation of DBPs at different pHs has been performed during Fe(VI) pre-oxidation followed by chlorination. The main aim of the current paper is to determine the effect of pH on DBP formation in the absence and presence of Fe(VI) pre-oxidation of source water and SRNOM water, followed by chlorination. Formation of DBPs in the pH range from 5.0 to 9.0 was studied by determining the concentrations of THMs, CH, haloacetonitriles (HANs), and trichloronitromethane (TCNM). This paper has the following objectives: (i) to study the interaction of Fe(VI) with the source water in order to understand how different fractions of NOM in source water will affect DBP formation during subsequent chlorination, (ii) to understand the variation in DBP production with varied pH, and (iii) to characterize the involvement of natural organic matters of source water in DBP formation by performing similar experiments with water containing SRNOM.

2. Materials and methods

2.1. Reagents and solutions

A mixed standard containing a THM mixture standard, CH, HANs and TCNM and internal and surrogate standards were purchased from Supelco (St. Louis, MO, USA). High performance liquid chromatography (HPLC)-grade methanol, acetonitrile, and formic acid were obtained from Sigma–Aldrich (St. Louis, MO, USA). The chlorine solution of 1000 mg/L as Cl_2 was prepared by diluting a stock solution, which was earlier obtained from 5% sodium hypochlorite (NaOCl). The chlorine solution was titrated against diethyl-p-phenylene diamine (DPD)-ferrous ammonium sulfate (FAS) titration. All solutions were prepared using ultrapure water (~18 MΩ cm).

Solid potassium ferrate(VI) (K_2FeO_4) (~99%) was prepared using a wet chemistry method in which ferric nitrate was oxidized to ferrate(VI) with hypochlorite [29]. Solutions of Fe(VI) were prepared by adding solid K_2FeO_4 to 2 M NaOH solution to produce a concentration of 1000 mg/L as Fe. Experiments using ferrate were performed within 30 min of ferrate solution preparation. The ferrate (VI) concentration at pH 9.0 was calculated using a molar absorption coefficient of $\varepsilon_{505\ \mathrm{nm}} = 1150\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ [30].

A stock solution of NOM was prepared from Suwannee River NOM isolate (Cat. No. 1R101N, International Humic Substances Society, St. Paul, MN, USA). An aliquot of the NOM isolate was dissolved into ultrapure water and subsequently filtered; this sample is referred as the SRNOM water. The values of dissolved organic carbon (DOC) and specific UV absorbance (SUVA) were 5 mg/L and 4 L/mg/m, respectively. The properties of the SRNOM water are given in Table SM-1. In carrying out experiments with Fe(VI), solutions were diluted with water in order to obtain a concentration of 3.0 mg/L DOC of SRNOM water.

A water sample was collected from the source water of a water treatment plant Guangdong Province, China. After collection, the source the source was shipped to the laboratory and stored at 4 °C until analysis. The concentrations of DOC, total nitrogen, ammonia, nitrite, and bromide and the value of SUVA were measured and are summarized in Table SM-1. The water sample was diluted with ultrapure water prior to conducting experiments to achieve 3.0 mg/L DOC.

2.2. NOM fractionation methods

In order to obtain information on the hydrophobicity and molecular weight distribution as well as the spectral characteristics of fluorescence, excitation–emission (EEM) experiments were conducted with aliquots of the source water of 3 mg/L DOC and of pH 7.0. A ferrate dose of 1 mg/L or 20 mg/L was applied. DAX-8 (Supelco, St. Louis, MO, USA) was applied to fractionate hydrophobic and hydrophilic portions of aliquots (Fig. SM-1). Before passing each aliquot through the resin, the filtered source water was acidified to pH 2.0 using concentrated sulfuric acid. The column distribution coefficient was 50. The fraction retained by the resin was referred to as hydrophobic NOM while the eluent was the hydrophilic fraction.

Another portion of the source water was fractionated using Millipore YM10, YM1 ultrafiltration membranes (Amicon, Beverly, MA, USA) with MW cut-offs of 10 and 1 kDa, respectively [26]. A sequential ultrafiltration was carried out on a stirred 200 mL Amicon Ultrafiltration cell (EMD Millipore, Billerica, Massachusetts, USA) (Fig. SM-2). Filtration was stopped when the volume of retentate decreased from an initial volume of 200 mL to 50 mL in application of the YM10 membrane. Permeate was collected for subsequent ultrafiltration with YM1 membrane. The volume was increased back to 200 mL by using ultrapure water and filtration was subsequently continued until the volume decreased again to 50 mL. This flushing step was repeated twice and the retentate was collected and diluted to 200 mL. This cycle continued through the YM1 membrane. Overall, this process produced fractions from the source water with nominal MWs of >10, 1–10, and <1 kDa.

2.3. DBP formation potentials

The formation of DBPs in chlorinated waters was measured in the pH range from 5.0 to 9.0 with and without pre-oxidation with ferrate at room temperature (22 ± 1 °C). Chlorination experiments were conducted in capped amber glass bottles in the dark. Both SRNOM and source waters were buffered using 10 mM phosphate buffer prior to their use. Free chlorine (20 mg/L as Cl_2) was added to the samples, followed by incubation for 1 day. The experiments with pre-oxidation with ferrate, 20 mg/L of ferrate was added to waters and mixed solution were allowed to react for 360 min before chlorination. All samples were filtered with 0.45 μm filter paper and subjected to the tests for the formation of DBPs.

2.4. Analytical methods for water quality parameters

Values of DOC and total nitrogen were determined using a Shimadzu TOC-V_{CPH} analyzer (Kyoto, Japan). UV measurements were carried at 254 nm and were measured with a UV–visible spectrophotometer (Shimadzu, Multispec-1501, Kyoto, Japan). Nitrite, nitrate and bromide was measured using an ion chromatograph (Metrohm 882 compact IC plus) equipped with an anionic column (MetrosepA supp 5). Ammonia was measured using a flow injection analyzer (FIA, QuickChem FIAþ, 8000 Series). Fluorescence EEM measurements were carried out with a Hitachi F-4500 spectrometer, which had a xenon excitation source with slits set to 10 nm for both excitation and emission. The excitation wavelengths were from 200 to 400 nm in 5-nm increments while detected emission wavelengths were from 290 to 500 nm in 5-nm steps.

Analyses of THMs, CH, HANs, HNM were accomplished using USEPA Method 551.1 [31]. This method used gas chromatograph (Agilent 7890A, Santa Clara, California, USA) with an electron capture detector (ECD). The column was an HP-5 fused silica capillary column (30 m × 0.25 mm I.D. with 0.25 μm film thickness, J&W Scientific, Santa Clara, California, USA). The temperature program was as follows: initial temperature of 35 °C for 6 min, ramping to 100 °C at 10 °C/min and holding for 5 min, ramping to 200 °C at 20 °C/min and holding for 2 min.