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The formation and distribution of haloacetic acids 9 in copper pipe during chlorination

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Abstract

The formation and distribution of HAAs in copper pipe during chlorination was investigated. To determine the material influence of copper pipe, parallel experiments were performed in glass pipe. Results showed that there was no obvious difference between the sum of haloacetic acids (HAAs) and trihalomethanes (THMs) produced in copper pipe compared to that produced in glass pipe over a 12 h period. However, significant differences were observed about the distribution of five haloacetic acids in copper pipe and in glass pipe. Relatively less trichloroacetic acid (TCAA) and more monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA) and trihalomethanes (THMs) were produced in copper pipe than those in glass pipe. Corrosion scale on the wall of copper pipe was analyzed using X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The results showed the scales on the pipe surface mainly consisted of Cu_2O, CuO and Cu $(OH)_2$ or $CuCO_3$. During 24 h stagnation, copper released gradually from copper pipe. The influences of copper (II) and copper oxides on the distribution of HAAs were investigated in designed experiments. Results showed that less amount of TCAA, more amounts of DCAA and MCAA were formed with increasing concentration of copper (II). It was because the accelerative effect of copper (II) on the depletion of chlorination restricted the formation of TCAA precursor and the further formation of TCAA. Owing to the transformation of DCAA precursor to TCAA precursor was limited, more DCAA precursor could yield DCAA. The influences of Cu_2O and CuO on the distribution of TCAA and DCAA were the result of copper released at higher content.

Keywords: Chlorination; Disinfection by-products (DBPs); Haloacetic acids (HAAs); Copper pipe

1. Introduction

Chlorine is the predominant disinfectant in drinking water treatment because of its highly effectiveness on restraining most microorganisms and its being the cheapest one of all chemical disinfectants [1]. However, potentially harmfully disinfection byproducts (DBPs) are generated simultaneously during chlorination process [2–5]. Due to the health risk of DBPs, extensive researches have been performed on the formation of DBPs, with emphasis on trihalomethanes (THMs) and more recently, haloacetic acids (HAAs), which are the two most important DBPs. HAAs include monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA) and dibromochloroacetic acid (DBCAA). Among the nine HAAs species, only first five of them were regulated by the United States Environmental Protection Agency (EPA) and the current maximum concentration level for HAAs (the sum of the MCAA, DCAA, TCAA, MBAA and DBAA) is regulated at 60 μg/L in the US Stage 1 Disinfectants/Disinfection Byproducts Rule (D/DBPR) [6].

Distribution system of drinking water is an important place of disinfection byproducts formation [7,8]. After chlorinated water leaving the treatment plant, the possible growth of DBPs in distribution system was important to understand the higher level at the system extremities. In general, the evaluation of DBPs

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growth was conducted in a glass pipe for a certain reaction time. Only limited amount reports were relative to the effect of pipe materials on the formation of disinfection byproducts [8].

Copper pipe is widely used in the distribution systems of drinking water throughout the world due to its killing effect on certain bacterial specie [9]. However, copper ion was released and copper oxides were formed on the pipe wall during copper corrosion [10]. Copper acting as a transition metal played catalytic role in many reaction processes. Industrial catalysts of dehydrogenation of cyclohexanol to cyclohexanone are generally based on copper as an active component of catalytic systems [11]. Copper oxides have been tested as active components of catalysts in the oxidation of water pollutants [12]. Blatchley et al. reported catalytic effect of copper in THM formation and proposed a hypothesized mechanism that copper catalysis for citrate and β-ketoglutaric acid is based on information pertaining to copper complexation. It is believed that the attachment of copper on the molecule promotes the decarboxylation due to the effects of electron cloud transposition [13].

Based on the studies described above, it is hypothesized that copper and copper oxides could play an important role in the DBPs formation in copper pipe during chlorination. In this paper, haloacetic acids (HAAs) were chosen as one of the most important objective DBPs to be investigated during chlorination in copper pipe under stagnant condition. Little is known about how the growth of HAAs in drinking water is affected in copper pipe. Whether there are differences of HAAs production in copper pipe and in glass pipe and what contribute to the differences were the interests of this study.

After chlorinated water containing humic acid (HA) and bromide ion entering into copper pipe, it reacts with surface compounds on the pipe wall and results in the continued release of copper into the water bulk and the formation of copper oxides, which may influence the formation and distribution of HAAs. Based on the hypothesis above, besides the investigation of formation and distribution of HAAs in copper pipe and in glass pipe, copper release from copper pipe was studied as a function of time. The surface character of copper pipe was determined by XPS, SEM and EDS during the stagnation experiments. Finally, designed experiments in glass pipes were conducted with copper (II), cupric oxide and cuprous oxide, which were detected on the surface of pipe, at different dosages to understand why the differences of HAAs formation and distribution between copper pipe and glass pipe occurred.

2. Materials and methods

2.1. Materials

Analytical standards for DCAA and TCAA were obtained from Acros Organics. MCAA, MBAA and DBAA were obtained as 1000 μg/mL solution in MTBE from Ultra Scientific. Chloroform, bromodichloromethane, dibromochloromethane and bromoform were purchased from Chinese National Research Centre for Certified Reference Materials. Copper sulfate ($CuSO_4 \cdot 5H_2O$, reagent grade) was dissolved into deionized water for the copper (II) stock solution preparation of 1 mg/mL. Cupric oxide and cuprous oxide were the productions of Bei Hua Fine Chemicals Limited Company (Beijing, China) and Tianjin FuChen Chemical Reagent Factory (China), respectively. Stock solutions of chlorine of 25.4 g/L were prepared by diluting a commercial solution of sodium hypochlorite (NaOCl >10% available chlorine) and periodically standardized by N, *N*-diethyl-*p*-phenylenediamine (DPD) methods. Potassium bromide stock solution of 500 mg/L was prepared to increase the bromide content of selected tests. Humic acid (HA) was purchased from Tianjin Chemical Reagent Development Center (China). The elemental composition of humic acid was determined to be C 14.98%, H 1.829% N 0% (Elementar Vario EL, Germany). The humic acid stock solution of 500 mg/L was prepared by dissolving an amount of material into deionized water in base condition (pH 12) and then filtered by a 0.45 μm filter paper.

2.2. Analytical procedures

Measurement of total organic carbon (TOC) concentration was undertaken using a Multi N/C 3000 TOC analyzer (AnalytikjenaAG, Germany). Measurements of free chlorine were conducted using DPD spectrophotometry at 510 nm. Analysis of total copper (II) was performed by Flame Atomic Absorption Spectrophotometer 3100 (USA, PekinElmer Co.) after acidified at pH <2 with nitric acid, whereas soluble copper was operationally defined using filtering through a 0.45 μm pore size syringe filter before acidification.

THMs analysis were quantified by liquid/liquid extraction with hexane (HPLC grade) and by gas chromatography (Agilent 6890N Series, Japan) and electron capture detection (GC/ECD) according to USEPA method 551.1 [14]. 18 ml of the dechlorinated sample were extracted with 3.0 ml of hexane. The vial was shaken for 2 min and then the phases were allowed to separate for another 10 min. HAAs compounds were analyzed by liquid/liquid extraction with high purity methyl-*t*-butyl-ether (MTBE), using 1,2-dibromopropane as an internal standard, followed by derivatization with acidic methanol and by GC/ECD according to USEPA method 552.3 [15]. The extracted compounds are methylated with methanol and sulfuric acid solution to produce methyl ester derivatives that can be separated chromatographically. Separation of species was performed on a HP-5 fused silica capillary column (30 m × 0.32 mm × 0.25 μm). THMs and HAAs were measured under the following temperature program: (1) THMs: hold at 35 °C for 4 min, ramp to 100 °C at 10 °C/min and hold 3 min; (2) HAAs: hold at 35 °C for 4 min, ramp to 65 °C at 2 °C/min. The speciation and quantities of the formed THMs and HAAs were obtained by comparing the chromatograms of the samples with the calibration curves developed for THMs and HAAs. Total HAAs and THMs were determined by simple summation of individual components.

Several surface characterization techniques were employed to identify the corrosion products of copper pipe. X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) analyses were performed in this research. After treated by vacuum freeze drying, the samples cut from pipe coupons were stored in a desicca-