

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 $\text{Cu}(\text{OH})_2$ 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.

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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 harmful 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 (DBCBA). 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 $60 \mu\text{g/L}$ 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 species [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 $\mu\text{g}/\text{mL}$ solution in MTBE from Ultra Scientific. Chloroform, bromodichloromethane, dibromochloromethane and bromoform were purchased from Chinese National Research Centre for Certified Reference Materials. Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 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 \times 0.32 mm \times 0.25 μm). THMs and HAAs were measured under the following temperature program: (1) THMs: hold at 35 $^\circ\text{C}$ for 4 min, ramp to 100 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$ and hold 3 min; (2) HAAs: hold at 35 $^\circ\text{C}$ for 4 min, ramp to 65 $^\circ\text{C}$ at 2 $^\circ\text{C}/\text{min}$. 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-

tor before further analysis. The XPS scan was performed by Thermo VG scientific (UK). The base pressure during analysis was 10^{-8} mbar. The excitation source was Al K α radiation (photoelectron energy of 1486.6 eV). The absolute binding energies of different surface species were calibrated using the C (1 s) line at 284.6 eV. The micrographs of corrosion morphology and the elemental analysis of corrosion product were conducted by an SEM analysis using field emission scanning electron microscope instrument XL-30 (ESEM-FEG, FEI, USA) with EDS capability.

2.3. Quality control

Various quality control (QC) measures were undertaken to ensure the analytical precision and accuracy. (1) High purity solvents (HPLC grade) were used in analyses. All other chemicals were at least of analytical grade. (2) At the beginning of each analytical run, solvent blanks and solvent samples containing the internal standard were injected to condition the GC and to verify that interferences were absent. (3) All standards were run at the end of the sample analysis. For all analyses, four THMs mixture standards and five HAAs mixture standards were injected into the GC every day of experimentation to obtain calibration curves. The ranges of standards were from 0.5 to 300 $\mu\text{g/L}$ ($R^2 > 0.99$) and 1.0 to 200 $\mu\text{g/L}$ ($R^2 > 0.99$) for THMs and HAAs measurements, respectively.

2.4. Chlorination procedure

The experiments were performed in pipe-rigs. The copper pipes (internal diameter 13 mm, length 50 cm) contain approximately 80 mL water. The ends of each pipe were plugged by rubber stoppers wrapped with Teflon tape. Before every experiment, the pipes were carefully flushed at least three times with deionized water.

Beijing tap water treated by activated carbon was used as base water (pH 7.50 ± 0.1 , TOC 1.30 mg/L, conductivity 318 $\mu\text{s/cm}$ and residual chlorine 0.016 mg/L). After addition of humic acid stock solution and KBr solution to the base water, a certain volume of sodium hypochlorite stock solution was added under stirring condition, and then pH was adjusted with hydrochloric acid and sodium hydroxide. Conditions used in the pipe rig tests were pH 8.0, 5.86 mg/L of TOC, 16.2 mg/L (as Cl_2) chlorine dose and 0.3 mg/L of bromine. After the water introduced, the copper pipes and the glass pipes were sealed and lay in incubator at 20 °C in the dark. The copper pipes and the glass pipes were all headspace free to avoid volatilization. Water samples were taken from different pipes after 1, 2, 4, 8, 12, 24 h and measured residual chlorine, copper concentration, THMs and HAAs. At the start of each experiment, the total organic carbon (TOC) was measured. The samples were unbuffered, but the pH was measured at the beginning and end of each experiment. The pH decreased slightly (generally less than one pH unit) after experiment. Experiments were repeated three times (each) in copper pipes and in glass pipes.

After collection the water samples were terminated by addition of sodium hyposulfite immediately and divided into two

parts, one was extracted with hexane for THMs analyses, and the other was extracted with MTBE for HAAs analyses. The sampling bottles were all amber glass pipes with polypropylene screw caps and PTFE-faced silica septa

During stagnation, dissolved copper released was observed and surface analysis of corrosion scales indicated the existence of Cu_2O , CuO in the scales on pipe surface. To further understand what contribute to the differences of distribution of HAAs in copper pipe and in glass pipe, designed experiments were performed with copper (II), cuprous oxide and cupric oxide in glassware to test whether they had effects on formation and distribution of HAAs. Chlorination experiments with varying concentration of copper and copper oxides were performed. An amount of copper (II), CuO and Cu_2O respectively were added to 150 mL aqueous solution containing 5.73 mg/L of humic acid, 16.3 mg/L of chlorine and 0.3 mg/L of bromine to produce concentrations of copper (II) of 0 mM, 0.0079 mM, 0.079 mM and 0.79 mM, concentrations of CuO of 0 mM, 0.31 mM, 0.63 mM, 1.26 mM and 6.3 mM, concentrations of Cu_2O of 0 mM, 0.17 mM, 0.35 mM, 0.7 mM and 3.5 mM. All pH values were adjusted to 8.0 by adding hydrochloric acid or sodium hydroxide. The designed experiments were conducted in an automated shaker (HZ-9610K, HALIDE, China) and shaken at 150 rpm. The temperature was controlled at 20 ± 1 °C. Samples were withdrawn from the glass pipes after 20 h to detect HAAs, soluble copper concentration and residual chlorine.

3. Results and discussion

3.1. Effect of reaction time on formation and distribution of HAAs

The reaction time of the precursors and disinfectant was an important factor affecting DBPs formation [16]. The effect of reaction time on HAAs formation was studied by measuring samples taken after 1, 2, 4, 8, 12, 24 h. Fig. 1(a)–(d) present the results of individual HAAs species in copper pipe and in glass pipe (due to its consistent low formation during the experiment, the results of MBAA were not reported). Results showed similar trends—the formation of HAAs in copper pipe and in glass pipe both increased with time. However, higher productions of HAAs species were observed in copper pipe than that in glass pipe. As compared to glass pipe, the level of MCAA, DCAA, and DBAA in copper pipe increased 152%, 71% and 117% respectively after 12 h. Trichloroacetic acid, on the other hand, showed a very pronounced difference in yield between copper pipe and glass pipe. The formation of TCAA in copper pipe was much slower than in glass pipe, with the levels of TCAA only 38.4%. Rossiman et al. surveyed the DBPs formation in unlined ductile iron pipe and they found the similar tendency [8]. More DCAA and less TCAA were produced in unlined ductile iron pipe than the glass bottle.

This phenomenon may be attributable to two possibilities. One was on the base of the mechanism that dichloroacetic acid does not readily undergo chlorine substitution to give trichloroacetic acid [17–19]. Rook [19] proposed a mechanism of formation of DCAA and TCAA from the chlorination of

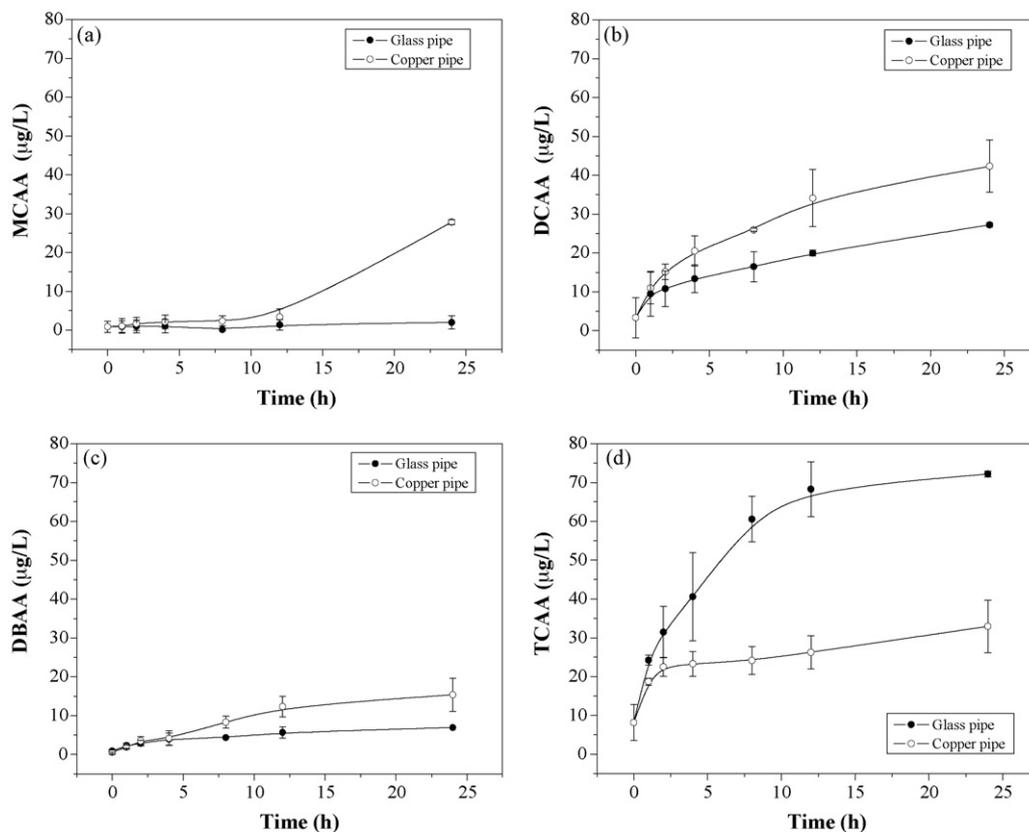


Fig. 1. (a) MCAA, (b) DCAA, (c) DBAA, (d) TCAA formation in copper pipe and in glass pipe as a function of time.

hypothetical resorcinol moiety in HA (Fig. 2). The suggested trichlorinated structure II will undergo ring opening to form a δ -ketocarboxylic acid III, still linked to the macromolecule. Cleavage of structure III induced by OH^- attack could produce either dichloroacetic acid (pathway b) or methylene chloride (pathway a). Continued chlorination of structure III would form structure IV. Cleavage of this trichlorinated structure would yield chloroform (pathway a) or trichloroacetic acid (pathway b). One can infer that the different distribution of HAAs speciation in copper pipe and in glass pipe was due to the presence of reaction promoting DCAA production and restraining formation of TCAA in copper pipe according Fig. 2.

Another possibility may due to the presence of analogous reactions in cast iron piping [20]. Proposed pathways for the degradation of TCAA, BDCAA and DBCAA in the presence of Fe^0 are given in Fig. 3. For each species, reduction occurs via hydrolysis with MCAA as the terminal product.

The formations of THMs in copper pipe and in glass pipe were investigated. The production of THMs in copper pipe and in glass pipe both increased with increasing time. However, slightly higher production of THMs was observed in copper pipe than in glass pipe. The increase was 22% in copper pipe at 12 h. The effect of reaction time on the sum of HAAs and THMs formation is shown in Fig. 4(a).

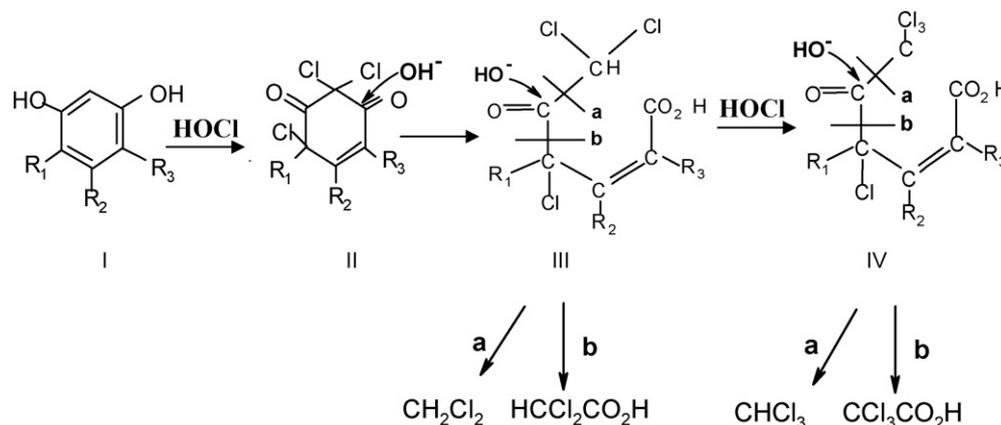


Fig. 2. Chlorination of hypothetical resorcinol moiety in HA (adapted from Rook [19]).

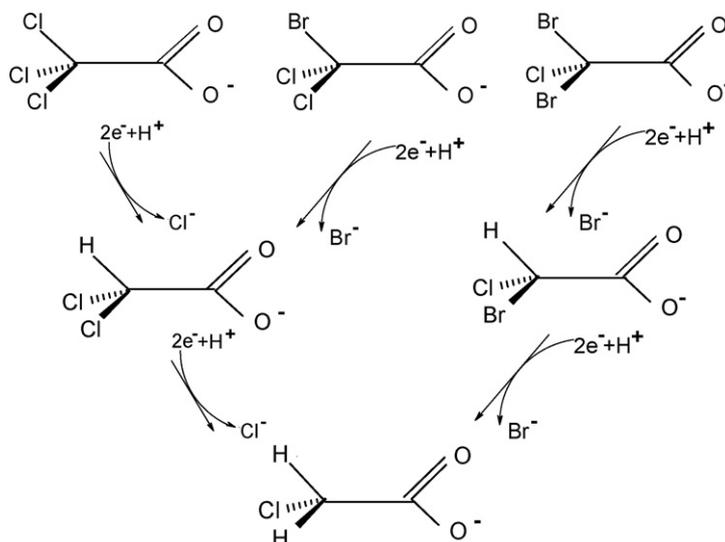


Fig. 3. Reaction pathways for the degradation of TCAA, BDCAA and CDBAA with Fe⁰ (adapted from Hozalski et al. [20]).

The finding presented in Fig. 1 and Fig. 4 indicates that the reaction in copper pipe results in merely a trade-off among the formation of DBPs. The overall yields of HAAs and THMs were essentially the same between the copper pipe and the

glass pipe. At 12 h, speciation in glass pipe is in the order: TCAA (71.0%) > DCAA (20.8%) > DBAA (5.9%) > MCAA (1.4%) > MBAA (0.88%); however the order in copper pipe was: DCAA (44.3%) > TCAA (34.1%) > DBAA (16.0%) > MCAA (4.4%) > MBAA (1.2%). After 12 h, the individual species formations were different between copper pipe and glass pipe. Among those HAAs species, TCAA was the most abundant species than DCAA and DBAA in glass pipe. However DCAA exceeded TCAA and became the most abundant species in copper pipe after 12 h chlorination, and an obvious increase of DBAA also found. To compare the distribution of THMs and HAAs, it can be concluded that at first 12 h, more trihalomethanes and less haloacetic acids were formed in copper pipe than in glass pipe. The percentage of THMs in sum of HAAs and THMs at 12 h was 66.3% and 56.4% in copper pipe and in glass pipe respectively, which indicated there were reactions shifting the DBPs species to THMs species in copper pipe. After 24 h, the sum of HAAs and THMs in copper pipe was higher than that in glass pipe due to increasing of MCAA and THMs.

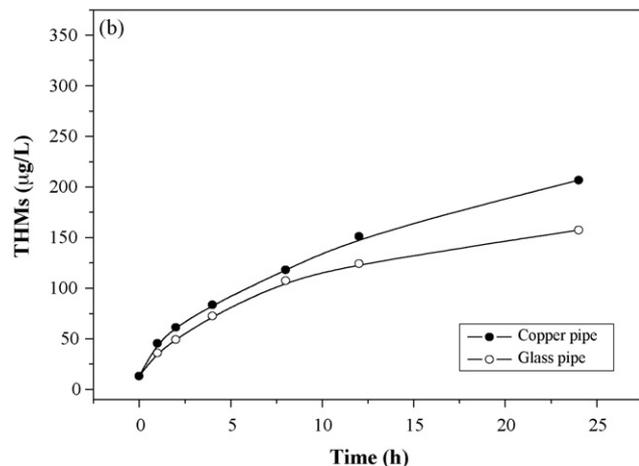
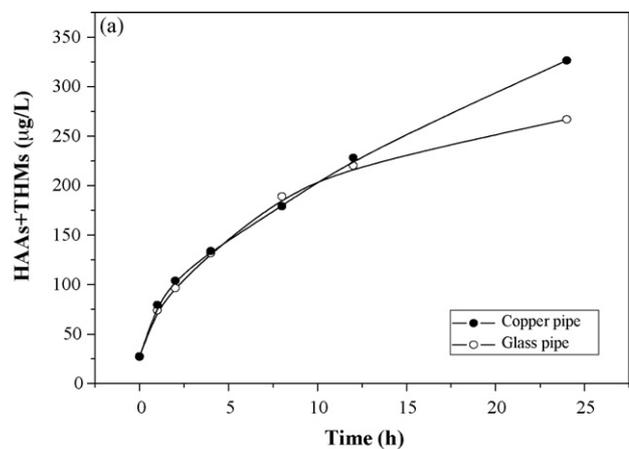


Fig. 4. (a) HAAs + THMs, (b) THMs formation in copper pipe and in glass pipe as a function of time.

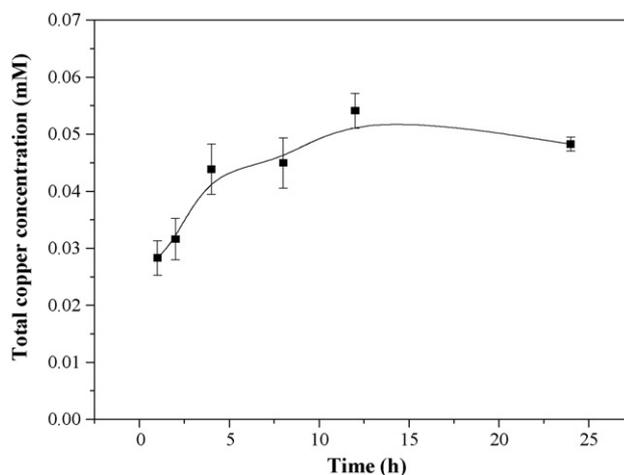
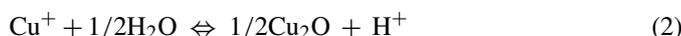


Fig. 5. Released copper in copper pipe as a function of time.

3.2. Copper released and Surface characters of copper pipe

Pipe surfaces in water distribution systems are often covered by corrosion solids, the metal ion released and the corrosion products in the pipe wall may influence the HAAs in water distribution systems. In order to explain the difference of individual species between copper pipe and glass pipe, the copper released was measured and the surface analysis of corrosion scales after 6 days immersion in chlorinated water was investigated by using X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). Fig. 5 presents the concentration of total copper released from copper pipe as a function of time. As shown, during stagnation the copper was released gradually from the pipe and reach up to 0.054 mM after 12 h.

Due to the presence of dissolved oxygen and chlorine in drinking water, the following reactions may occur in copper pipe:



Based on Eqs. (1)–(5), it can speculate that cupric oxide, cuprous oxide and cupric hydroxide or cupric carbonate were all the composition of the corrosion scale.

Fig. 6 shows the results of Cu 2p_{3/2} XPS spectra of the formed oxides film of copper pipe after 6 days immersion in chlorinated water. The three peaks at binding energies of 932.5, 934, and 935 eV represent Cu₂O, CuO and Cu(OH)₂ or CuCO₃, respectively. It indicates the presence of Cu₂O, CuO and Cu(OH)₂ or CuCO₃ on the scale of the pipe surface. In order to confirm the XPS findings, the morphology and elemental composition of the scale were analyzed by SEM and EDS technologies.

Fig. 7 shows SEM photomicrography of the corrosion products formed before and after immersion in chlorinated water. The atomic percentages ratios of copper to oxygen for the scale were approximate 10:1 for the oxide film before immersion and

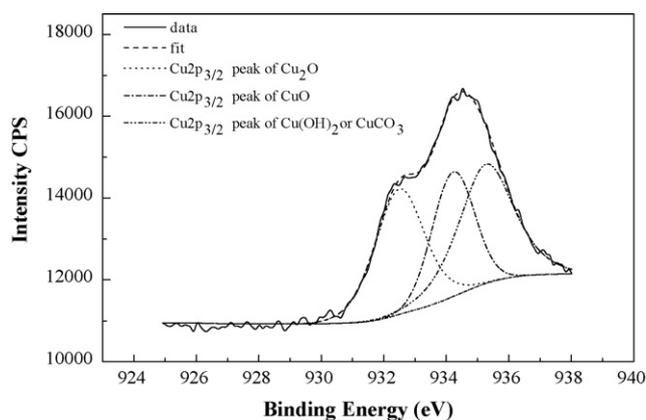


Fig. 6. Cu 2p XPS spectra of the oxide film formed after 6 days immersion.

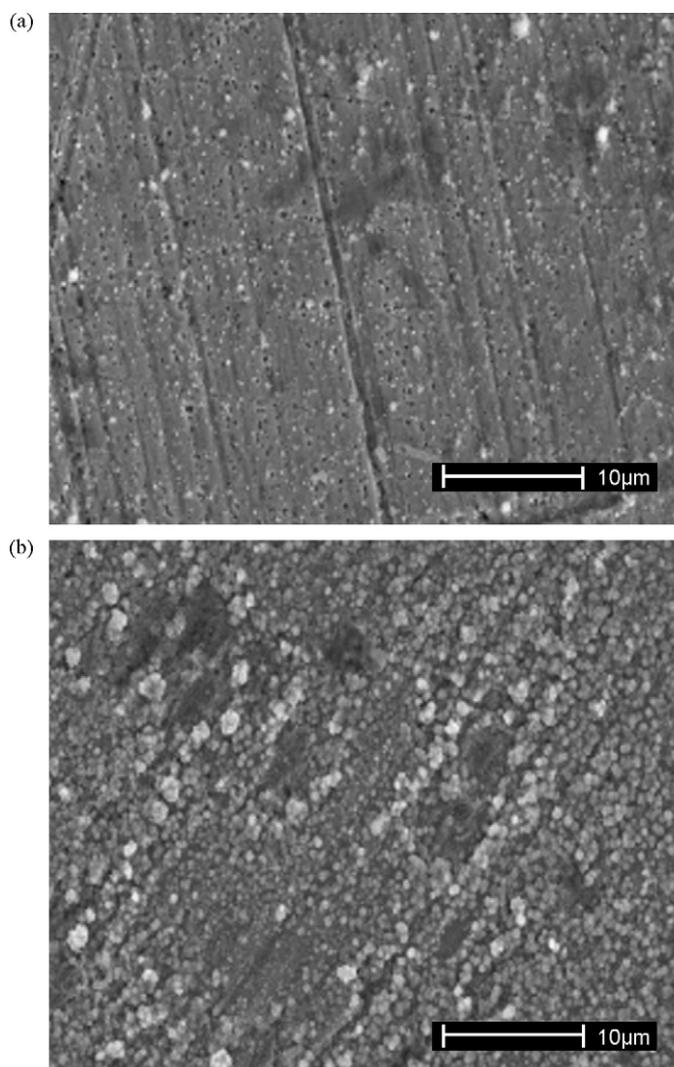


Fig. 7. An SEM photograph of copper surfaces (a) before immersion; (b) after 6 days immersion (2000× magnification).

about 2:1 after 6 days immersion. The low ratio of copper to oxygen indicates copper oxides have formed on the copper pipe surfaces.

3.3. Effect of copper (II) and copper oxides on formation and distribution of TCAA and DCAA

Based on the understandings above, copper (II) released and copper oxides formed on the scales could all have influence on the formation and distribution of HAAs.

Due to the yields of TCAA and DCAA were significant different in copper pipe and in glass pipe, designed experiments focused on the effects of copper (II) and copper oxides on the formation and distribution of TCAA and DCAA. Molar concentrations are used in the following discussion to account for the effect. The mole fraction of a particular HAAs species equals its molar concentration divided by sum of the molar concentrations of all HAAs species.

Fig. 8 presents the mole fraction of individual HAAs species after 20 h chlorination in case of (a) copper (II), (b) cupric

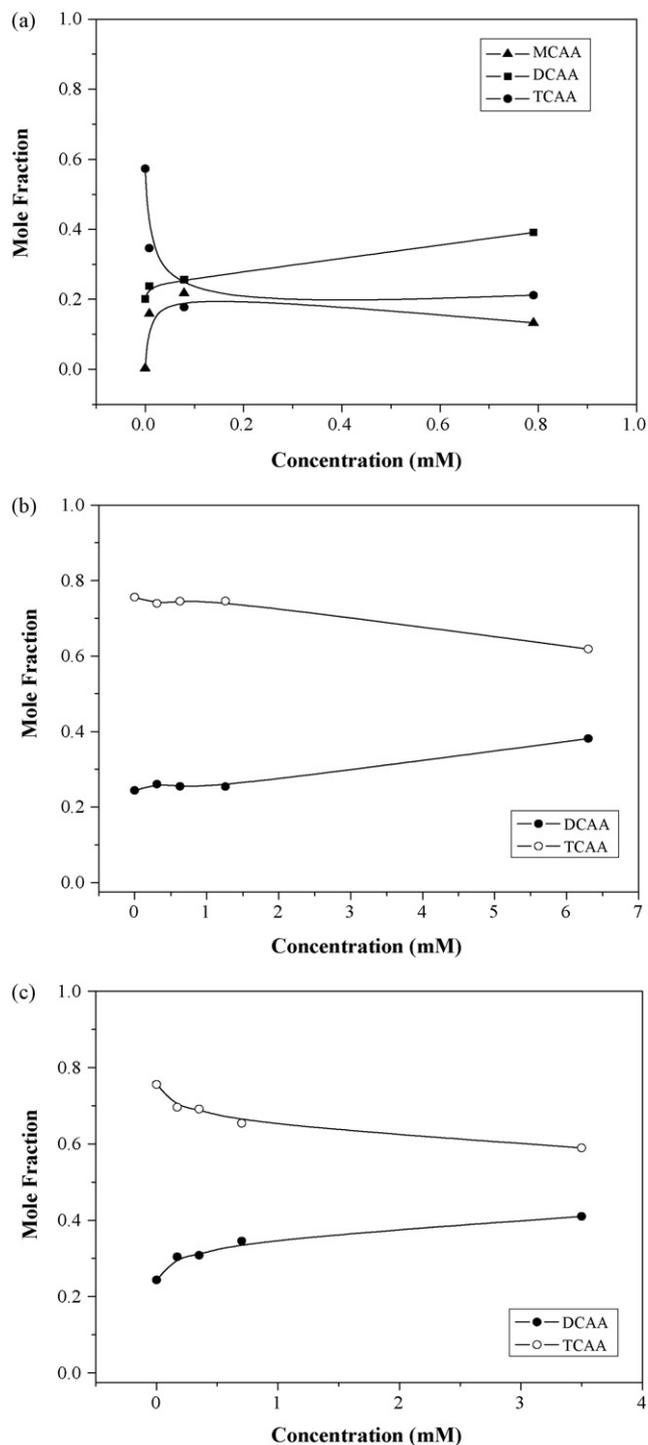


Fig. 8. Effect of dosage of (a) copper (II), (b) CuO, (c) Cu₂O on the distribution of HAAs.

oxide and (c) cuprous oxide respectively. As shown in Fig. 8(a), increasing copper (II) dosage increased DCAA and MCAA formation but decreased TCAA formation. When the concentration of copper (II) above 0.079 mM, the mole fraction of TCAA was at a stable value, but the mole fraction of DCAA was still increased. The tendency of TCAA, DCAA and MCAA in the case of copper (II) was similar to the tendency in copper pipe. One can infer that the different distribution of HAAs between copper pipe and glass pipe was relative to effect of copper (II).

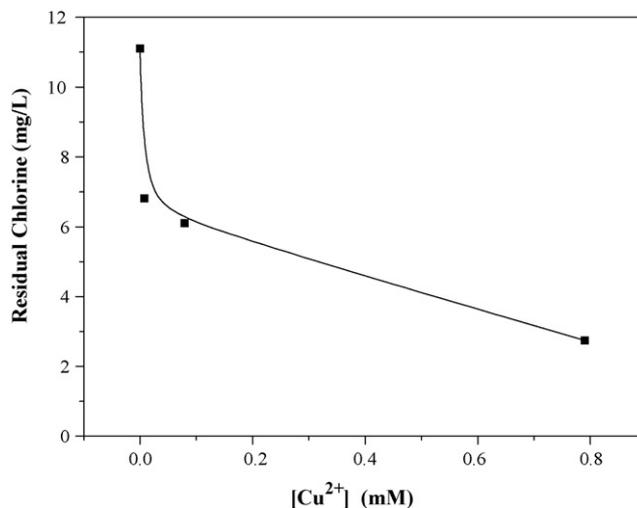


Fig. 9. Chlorine consumption as a function of dosage of copper (II).

Fig. 9 presents the effect of dosage of copper (II) on the consumption of chlorine. As shown in Fig. 9, the depletion of chlorine increased with the increasing dosage of copper (II). The mechanism presented in Fig. 2 indicates that the formation of TCAA would demand more HOCl than that of DCAA. It could be concluded that due to the accelerative effect of copper (II) on chlorination consumption restricted the formation of TCAA precursor IV and the further formation of TCAA according to the mechanism proposed by Rook. Owing to the transformation of DCAA precursor III to TCAA precursor IV was limited, more DCAA precursor III could yield DCAA (pathway b in Fig. 2).

Fig. 8(b) displays the influence of CuO on the distribution of TCAA and DCAA. As shown in Fig. 8(b), the addition of CuO to the system yielded no discernable influence when the dosage of CuO was below 1.26 mM, but a significant change was observed when the dosage was 6.3 mM. As shown in Fig. 8(c), the concentration of DCAA increased and the concentration of TCAA decreased with the increasing dosage of Cu₂O. The tendency was similar but the degree was less than that in the case of copper (II).

The dissoluble copper was investigated during the designed experiments. As shown in Fig. 10, the concentration of dissoluble copper increased with the increasing dosages of CuO and Cu₂O. However, the level of dissoluble copper in the case of CuO was lower as compared to Cu₂O. The concentration of copper released was below 6 μM when the dosage of CuO was below 1.26 mM and the level was increased to 15.7 μM when the dosage increased to 6.3 mM. The effect of CuO dosage on the dissoluble copper was similar to the effect of CuO dosage on the distribution of TCAA and DCAA. That is, a significant change of distribution of TCAA and DCAA was observed when the dosage of CuO was above 6.3 mM, and little difference was found when the dosage of CuO was below 1.26 mM.

The effect dosage of Cu₂O on dissoluble copper showed the same tendency to the effect of Cu₂O dosage on the distribution of TCAA and DCAA. The concentration of dissoluble copper increased more rapidly with the increasing dosage of Cu₂O, the concentration of dissoluble copper was 10.6 μM and 14.9 μM

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