Effect of zinc on the transformation of haloacetic acids (HAAs) in drinking water

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ABSTRACT

Suspected carcinogen haloacetic acids (HAAs), as a major class of disinfection byproducts, are widespread in drinking water. Batch experiments were conducted to investigate the effect of zinc, a metal component of galvanized pipe in water distribution systems, on the fate of the HAAs. Results showed that zinc could induce sequential dehalogenation of HAAs. All brominated acetic acids were transformed to acetate ultimately, and chloroacetic acid (MCAA) was the final product for the dehalogenation of trichloroacetic acid (TCAA) and dichloroacetic acid (DCAA). The concentrations of the parent compounds as a function of time were fitted pseudo-first-order kinetic model with $R^2 > 0.904$. Brominated acetic acids were more activated than chlorinated acetic acids in the reaction with zinc and the activity of HAAs decreased with the number of substituents reduced. While flowing through galvanized pipe, brominated and chlorinated acetic acids except MCAA would decrease to 1% of their initial concentrations in 2.11–6.34 h, and the rates would not be affected obviously by the hydrodynamic or duct conditions. The health risk due to TCAA, DCAA in drinking water tends to be magnified, and that due to TBAA, DBAA tends to be first increased and then decreased, also that due to MBAA tends to be decreased.

1. Introduction

Haloacetic acids (HAAs) are a class of important disinfection byproducts (DBPs) in drinking water which can be formed by disinfection with chlorine, chloramines, chlorine dioxide, and ozone, and are generally formed at highest levels with chlorination [1,2]. They are commonly concerned due to their ubiquitous distribution in drinking water and suspected carcinogenesis [3–5]. The United States Environmental Protection Agency (EPA) regulated the current maximum allowable running annual average (RAA) level for HAA₅ (the sum of chloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid, and dibromoacetic acid) at 60 μg/L in the US Stage 1 Disinfectants/Disinfection Byproducts Rule (D/DBPR), and 30 μg/L in Stage 2 D/DBPR [6].

Some studies showed that the varieties and concentrations of DBPs in drinking water may transfer through water distribution systems [7,8]. On the one hand, DBPs may aggrandize along the pipe due to the persistent interaction between residual natural organic matter (NOM) and the disinfectant [9]. On the other hand, DBPs may be translated via hydrolysis, biological transformation, and abiotic reduction to a variety of degradation products [10,11]. Also they

may be sorbed at or react within the pipe surface [12,13]. Thus, pipe surface is a crucial gist affecting all of the processes above. Until now, research regarding the influence of pipe surfaces to the fate of DBPs, including HAAs, has mostly focused on iron and its corrosion products [14–17]. Iron is a powerful reductant which led HAAs degraded via sequential hydrogenolysis, and the pseudo-first-order degradation rates for these reactions ranged from 0.08 to 10.6 h⁻¹ [14,15]. While in the presence of synthetic goethite and magnetite, trichloroacetic acid was unreactive [16]. Also, these studies were mainly concerned with the reaction pathways, but paid little attention to the influence of hydrodynamic and duct conditions.

Galvanized pipe is still widely used in water distribution systems even though it has been phased out in some countries. According to the survey of American Water Works Association (AWWA) in 2003, 8% of customer service lines (totally surveyed 14,120,646) in USA were composed of galvanized iron [18]. As it is reported that some chlorocarbons may be degraded rapidly by zincky metals [19–21], we speculated that zinc would react with HAAs and then affect their fate in distribution systems.

In this paper, the effect of zinc on the transformation of HAAs was investigated in laboratory model systems, and the corresponding mechanisms and kinetics were also discussed. The influence of some main hydrodynamic and duct conditions was also speculated from correlative experimental parameters. The purpose of our work was to better understand the fate of DBPs in drinking water distribution systems and to further predict and control the health risk due to these DBPs in the whole water distribution process.

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Nomenclature

a	the ratio of metal surface area to volume of solution (m^{-1})
D	diffusivity (cm^2/s)
K_m	mass transfer coefficient (m/h)
K_{obs}	pseudo-first-order rate constant (h^{-1})
K_s	rate constant for the surface interaction normalized on the basis of external geometric surface area of the particles (m/h)
K_t	overall rate constant (h^{-1})
Re	Reynolds number (dimensionless)
Sc	Schmidt number (dimensionless)
Sh	Sherwood number (dimensionless)
U_t	terminal settling velocity (m/s)
V	molal volume of solute at normal boiling point ($cm^2/g\,mol$)

Greek symbols
ν	kinetic viscosity (m^2/s)
ρ	fluid density (kg/m^3)
ρ_p	particle density (kg/m^3)

2. Materials and methods

2.1. Materials

Tribromoacetic acid (TBAA), dibromoacetic acid (DBAA), bromoacetic acid (MBAA), trichloroacetic acid (TCAA), dichloroacetic acid (DCAA), chloroacetic acid (MCAA) were obtained from Acros Organics with the purities greater than 99%. Their stock solutions were prepared in methyl tertiary-butyl ether (MTBE) and diluted to a series of concentrations via a methanolic spike (resulting in 0.3–0.4% methanol by weight) with deionized water (ultra pure grade). Selected physicochemical properties of the six HAAs are listed in Table 1.

The zinc was cleaned with 0.4% H_2SO_4 for 10 min to remove surface oxides using the procedure described in previous studies [22]. The acid-washed metals were rinsed 3 times with deoxygenated deionized water and acetone successively, then dried under nitrogen at 100 °C for 30 min and used within 24 h in order to avoid the metal activity decreased. The surface area was 2.19 m^2/g measured via BET. The particle diameter was 4062.7 nm measured by 90 Plus Particle Size Analyzer (Brookhaven Inst rument Corp., Holt sville, NY), and the external surface area assuming spherical particles was 2.58×10^{-2} m^2/g.

2.2. Experimental systems

All batch experiments were carried out in 25 mL glass centrifuge tubes or 1 L bottles which were all topped with teflon caps (results

showed reaction rates were not affected by solution volume). Acid-washed electrolytic zinc was added to the solutions which was degassed by ultrasonic instrument, and then was mixed horizontally in the dark shaker to prevent photodecomposition reactions. All batch experiments were performed at constant temperature ($25 \pm 0.2\,°C$).

At a given time, samples were filtered through a 0.22 µm filter into glass vials for ICP analysis, and some groups with high zinc concentrations were centrifuged at 3000 rpm for 10 min before filtration. Zinc concentrations were measured by atomic absorption spectrometer (AAnalyst 700, PerkinElmer). The pH of the solutions was measured by a pH meter (Mettler Toledo, Seven Multi).

2.3. Analytical methods

HAAs, acetate, chloride, and bromide ions were analyzed with IC system (Dionex, ICS1000 series, USA) which consisted of an IonPac AG19 guard column (Dionex, 4 mm × 50 mm, USA) and an IonPac AS19 separation column (Dionex, 4 mm × 250 mm, USA) for sample separation. The elution of sample was achieved with KOH from 10 to 45 mmol/L. The current of the suppressor was set at 130 mA. The flow rate of the eluent was kept at 1.0 mL/min. The determination was performed at 30 °C.

Ion concentrations were calibrated using standard concentrations covering the concentrations studied. Concentrations and the corresponding responses of IC for all identified ions followed linear relationships with $R^2 > 0.999$.

3. Results and discussion

3.1. Reactions of HAAs with zinc and the pathways

To compare and summarize reaction pathways, batch experiments were conducted in 25 mL glass centrifuge tubes with 1 mg/L HAAs and 10 mg/L zinc at 150 rpm. Control samples were in three series: (1) the same amount of degassed deionized water and zinc loading but no HAAs, (2) the same amount of HAAs solution without zinc, and (3) the same amount of HAAs solution with zinc ion. Concentrations of selected HAA and corresponding products were detected as a function of time. The reaction courses are shown in Figs. 1 and 2. The detection courses were 24–48 h and only the transformations during the first 12 h were shown in the two figures till when all reactions had already reached equilibrium. Each point presented the average concentration of 3–4 replicates, and the relative standard derivations (RSD) were not more than 5%.

The degradation of TBAA in the presence of zinc resulted in the sequential formation of three major products, DBAA, MBAA, and acetate, as well as simultaneous release of bromide ion, as shown in Fig. 1(a). The concentration of TBAA had decreased from 3.49 to 0.35 µmol/L in 40 min. DBAA and MBAA could be detected 10 min after the beginning of the reaction, and then their concentrations increased rapidly to the maximum of 1.61 µmol/L at 1 h and 2.23 µmol/L at 4 h, respectively. Between 1 and 4 h, MBAA concen-

Table 1
Selected physicochemical properties of tested HAAs.

Compounds	Abbreviation	Formula	MW	pK_a[a]	Unit cancer risk $\times 10^{-6}$[b]
Chloroacetic acid	MCAA	$CH_2ClCOOH$	94.5	2.867	ND
Dichloroacetic acid	DCAA	$CHCl_2COOH$	128.9	1.26	2.6
Trichloroacetic acid	TCAA	CCl_3COOH	163.4	0.52	5.5
Bromoacetic acid	MBAA	$CH_2BrCOOH$	139.0	2.902	ND
Dibromoacetic acid	DBAA	$CHBr_2COOH$	217.8	1.39	ND
Tribromoacetic acid	TBAA	CBr_3COOH	296.8	−0.147	–

ND: non-detected.

[a] Values were taken from J.A. Dean, Lange's Handbook of Chemistry, 13th ed., McGraw-Hill, New York, 1985.

[b] Values were taken from R.J. Bull, F.C. Kopfler, Health Effects of Disinfectants and Disinfection By-Products, AWWA, Denver, 1991.
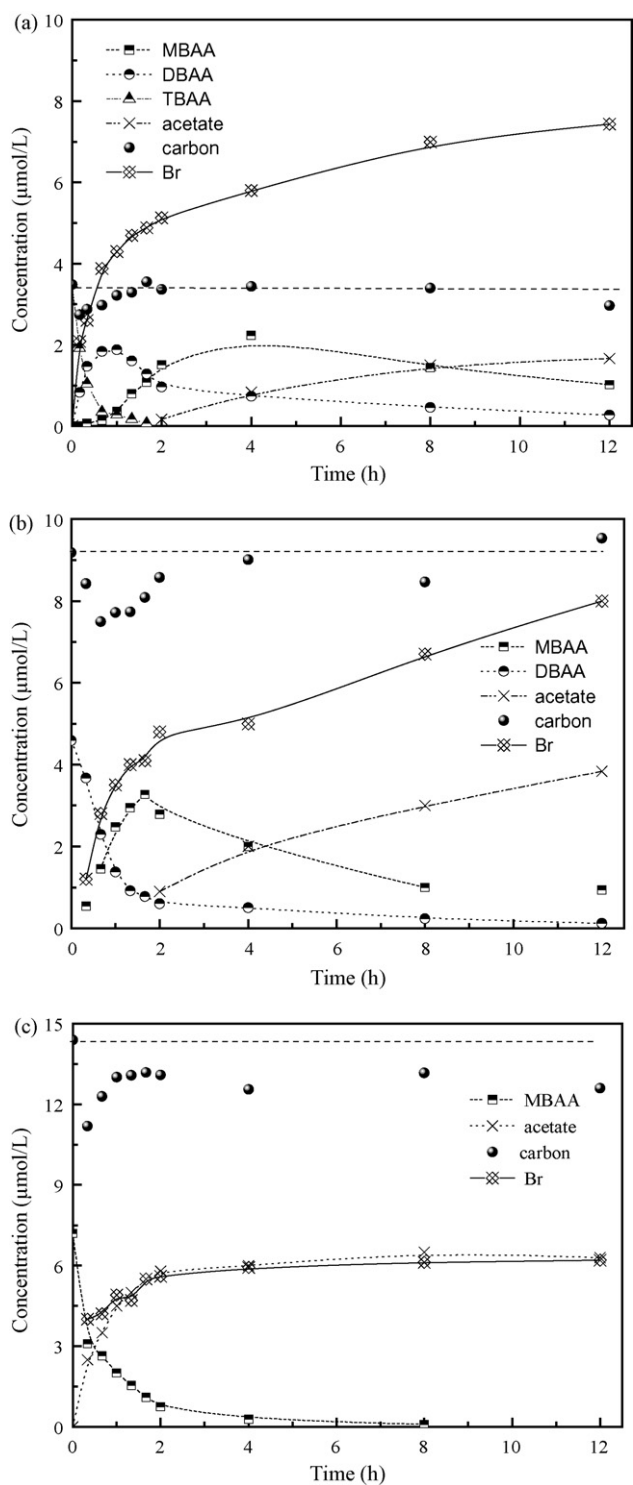
Fig. 1. Transformation of 1 mg/L brominated acetic acids (3.49 μmol/L TBAA, 4.59 μmol/L DBAA, 7.20 μmol/L MBAA) by 10 mg/L zinc: concentrations of MBAA, DBAA, TBAA, acetate, bromide (Br), and the sum of HAAs and acetate (carbon) as a function of time. (a), (b), and (c) represent the transformation of TBAA, DBAA, and MBAA respectively, n = 3 or 4, RSD $\leq$ 5%.

Fig. 2. Transformation of 1 mg/L chlorinated acetic acids (6.12 μmol/L TCAA, 7.75 μmol/L DCAA, 10.58 μmol/L MCAA,) by 10 mg/L zinc: concentrations of TCAA, DCAA, MCAA, chloride (Cl) and the sum of HAAs (carbon) as a function of time. (a), (b), and (c) represent the transformation of TCAA, DCAA, and MCAA respectively, n = 3 or 4, RSD $\leq$ 5%.

tration increased accelerately which was accompanying with the decrease of DBAA. After then, the reduction of MBAA was accompanied by the augment of acetate. The phenomena of these products increased one by one was consistent with the degradation proceeding via sequential hydrogenolysis from TBAA to acetate, meanwhile MBAA was detected at early time during the disappearance of TBAA,
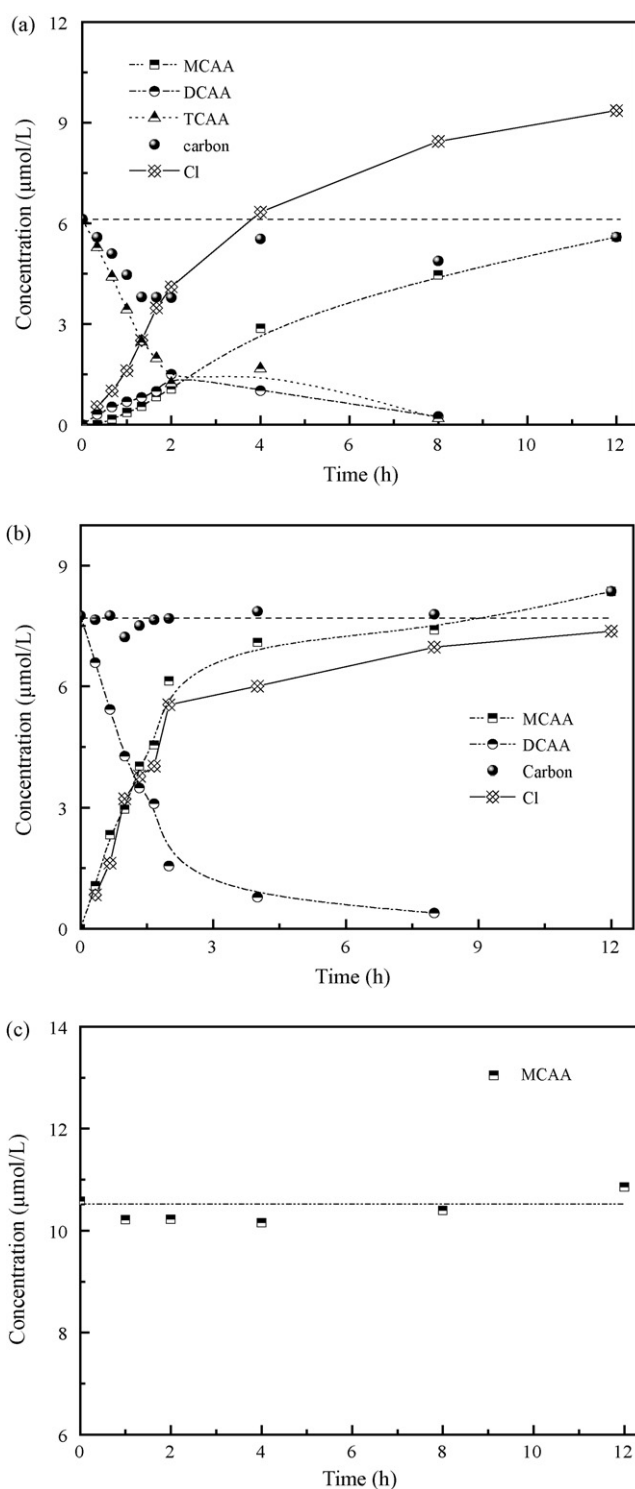
which demonstrated that α-elimination maybe occurred. In the whole process, the carbon mass balance was between 78.7% and 104.1%, and the bromine mass balance was between 86.0% and 96.2%. The lost mass may be adsorbed on the zinc surface. In addition, the minimal loss of TBAA in the control samples (2) and (3) showed that the sorption of TBAA to the teflon cap was neglectable

and the reduction of TBAA was not due to zinc ion but metallic zinc. A proposed pathway for the degradation of TBAA in the presence of zinc was shown as follows:
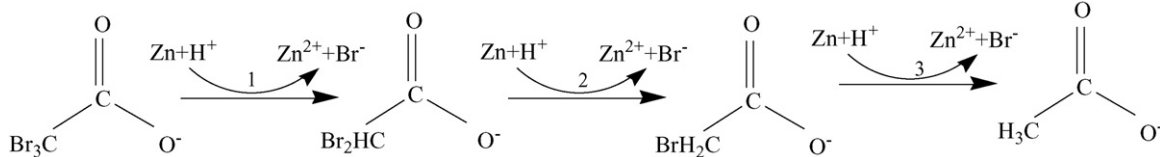

The redox couple formed by zero oxidation state metallic zinc and dissolved aqueous Zn^{2+} has a standard reduction potential of -0.763 V. This makes zinc a powerful reducing agent to the redox-labile substance TBAA. In the presence of a proton donor like water, TBAA typically undergo sequential reductive dehalogenation.

The reaction process between DBAA and zinc was demonstrated in Fig. 1(b). After 4 h, DBAA reduced from the initial 4.59 to 0.50 μmol/L, meanwhile MBAA and acetate were detected after 20 min and 8 h, respectively, also the maximum concentration of MBAA (3.27 μmol/L) emerged at 100 min. The carbon and bromine mass balance was between 84.0% and 103.8%, 87.2% and 99.0%, respectively. The process could be depicted by the latter two steps in the TBAA degradation.

During the reaction course between MBAA and zinc, MBAA concentration decreased from 7.19 to 0.75 μmol/L in 2 h while acetate concentration increased till 6.80 μmol/L, as shown in Fig. 1(c). The carbon and bromine mass balance was between 77.7% and 94.5%, 86.1% and 98.6%, respectively. This reaction was the last step in the pathway of TBAA degradation.

The transformation of TCAA in the presence of zinc was given in Fig. 2(a). Similar to the reactions of TBAA with zinc, TCAA was rapidly consumed with the concomitant formation of DCAA and MCAA. The concentration of TCAA had decreased from 6.12 to 0.18 μmol/L after 8 h, while DCAA increased to 1.50 μmol/L at 2 h and then decreased, similarly MCAA got to its maximum concentration of 5.59 μmol/L at 12 h. But acetate was not detected during the reaction of TCAA with zinc, which indicated the final dechlorination product was MCAA instead of acetate. In the detection process, the carbon mass balance was between 79.7% and 95.2%, and the chlorine mass balance was between 75.8% and 96.5%. A proposed pathway for the degradation of TCAA in the presence of zinc was as follows:
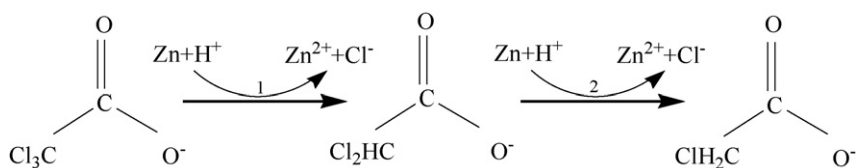
As shown in Fig. 2(b), DCAA was rapidly degraded (about 90% of DCAA was degraded after 4 h) and MCAA was sequentially formed in the presence of zinc, meanwhile acetate was not detected. The carbon and chlorine mass balances were ranged from 88.7% to 107.8%, 89.5% to 101.4% respectively. The process could be depicted by the last step in the process of TCAA degradation.
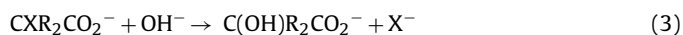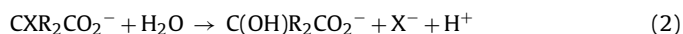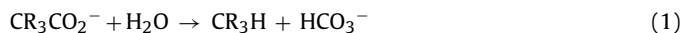
No obvious reduction of MCAA was shown in the presence of zinc, which was revealed in Fig. 2(c). The phenomena further confirmed the speculation from the experiments of TCAA and DCAA that the half-life of MCAA in the presence of zinc was much longer than 48 h. The carbon mass balance was between 95.9% and 105.1% and the chlorine mass balance was between 95.1% and 110.2%.

On the whole, the degradation of HAAs proceeded via sequential hydrogenolysis. The concentrations of the parent compounds as a function of time in the initial 2 h were simultaneously fit pseudo-first-order kinetic model with $R^2 > 0.904$. The pseudo-first-order rate constants (K_{obs}) calculated for all initial compounds were presented in Table 2.

The K_{obs} were reduced with the decrease of halogen atoms on HAAs, and brominated acetic acids reacted more quickly than chlorinated acetic acids. The reductive dehalogenation of chlorinated acetic acids was also incomplete which was supported by the accumulation of MCAA and the inability of detecting acetate in the batch tubes. It revealed that brominated acetic acids were more reactive than chlorinated acetic acids in these nucleophilic substitution reactions, probably due to the polarity of C-Br bond was higher than that of C–Cl bond.

Products other than dehalogenated ones were tried to be detected. In principle, HAAs in water can react in the other two ways [23]: (1) decarboxylation, which involves the spitting of a carbon–carbon σ-bond and loss of a molecule of CO_2 (or an ion of HCO_3^- or CO_3^{2-}) as in Eq. (1) where R may be Cl, Br, and H. (2) Nucleophilic substitution, in which OH as the nucleophile displaces a halide ion (X = Cl or Br) on the α-carbon atom. Because water is the most abundant nucleophile in the potable water system, this transformation is often regarded as a hydrolysis (Eq. (2)) but it can occur directly by hydroxide attack (Eq. (3)).

$$CR_3CO_2^- + H_2O \rightarrow CR_3H + HCO_3^- \tag{1}$$

$$CXR_2CO_2^- + H_2O \rightarrow C(OH)R_2CO_2^- + X^- + H^+ \tag{2}$$

$$CXR_2CO_2^- + OH^- \rightarrow C(OH)R_2CO_2^- + X^- \tag{3}$$

So, besides the dehalogenation products, halomethanes produced by decarboxylation and hydroxyethanoates produced through hydrolysis may emerge. In the experiment, halomethanes were also detected by headspace gas chromatography with electronic capture detector (HS-GC-ECD). However, the concentrations of all possible halomethanes were lower than detection limit. The existence of hydroxyethanoates were also ruled out by the GC-ECD spectra with no corresponding signals for them. From the appropriate mass balance and failure to detect other possible products, it is easy to conclude that sequential dehalogenation was the only pathway that zinc reacted with HAAs in water.

3.2. Kinetic analysis

Since the reaction happened on the interface between zinc and water, the rate-limiting step may represent either mass transfer of HAAs from bulk to zinc surface, or interaction at the surface. The overall rate constant (K_t) in such a case can be represented simply by a system of resistances in series:

$$\frac{1}{K_t} = \frac{1}{a}\left(\frac{1}{K_s} + \frac{1}{K_m}\right) \tag{4}$$

where K_s is the rate constant for the surface interaction normalized on the basis of external geometric surface area of the particles, K_m is the mass transfer coefficient, and a is the ratio of metal surface area to volume of solution. If mass transfer is slower than the

Table 2
Rate constants of HAAs reacted with zinc. (V: the molal volume of solute at normal boiling point, D: diffusivity, Sh: Sherwood number, K_m: the mass transfer coefficient, a: the ratio of geometric surface area of the particles to the volume of solution, K_{obs}: pseudo-first-order rate constants).

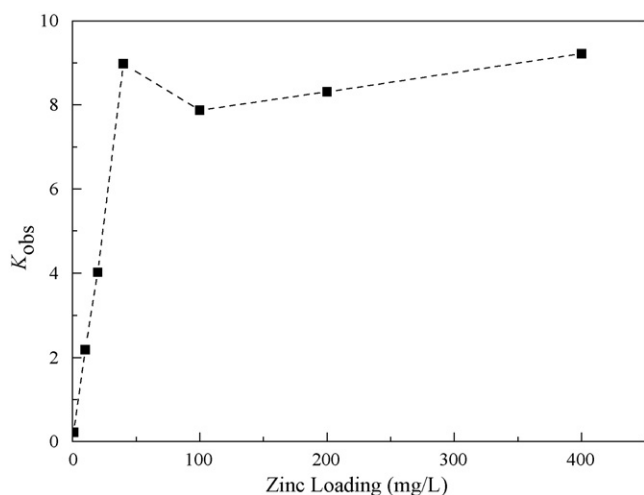| Compounds	V (cm^2/g mol)	$D \times 10^{-5}$ (cm^2/s)	Sh	$K_m a$ (h^{-1})	K_{obs} (h^{-1})
MCAA	80.1	1.215	2.324	9.701	–
DCAA	101	1.057	2.338	8.497	0.726
TCAA	121.9	0.9445	2.352	7.633	0.791
MBAA	82.5	1.194	2.325	9.539	1.182
DBAA	103.4	1.043	2.340	8.384	1.084
TBAA	124.3	0.9335	2.353	7.548	2.186

Fig. 3. The pseudo-first-order rate constants (K_{obs}) for transformation of 1 mg/L TBAA by zinc as a function of zinc loadings, $n = 3$ or 4, RSD $\leq 5\%$.

Fig. 4. The pseudo-first-order rate constants (K_{obs}) for transformation of 1 mg/L TBAA by 10 mg/L zinc as a function of mixing speeds, $n = 3$ or 4, RSD $\leq 5\%$.

surface interaction ($K_m \ll K_s$), mass transfer becomes the reaction bottleneck as $1/K_m a$ tends to dominate $1/K_t$.

Mass transfer rates are dependent on several factors, including fluid velocity, particle size, the density and viscosity of the fluid. In the experiment, increasing mixing speed tends to increase fluid velocity relative to the particles, which has the general effect of increasing K_m, thereby decreasing its impact on K_t but only down to a certain extent. Many previous studies demonstrated that independence of rate constant on mixing speed was a necessary, but was not a sufficient criterion to rule out mass transfer control [24].

If mass transfer is not the dominant part of K_t, the surface interaction should be the control process and divided into three continuous steps [25]: (1) adsorption of substrates to reactive sites at the surface, (2) reactions at the surface, and (3) desorption of the products. The rate-limiting step may be identified by examining the influence of initial substrate concentration on initial interaction rate. Main factors which determined or reflected the parameters a, K_s, and K_m are discussed below. In these experiments, TBAA, which was proved to be the most reactive species among testing HAAs, was chosen as the parent compound, for the active species was more susceptible to mass transfer limitation. As mass transfer condition of all HAAs was similar, it would not be the control step to other five HAAs if it were not the one to TBAA.

3.2.1. Effect of the metal loading

Experiments were conducted to investigate the effect of zinc loading. In these experiments, zinc loading ranged from 1 to 400 mg/L with 1 mg/L TBAA and the mixing speed was fixed at 150 rpm.

The K_{obs} at different initial zinc loadings were given in Fig. 3. The result indicated that the K_{obs} values were only directly proportional to metal loading over a limited range (1–40 mg/L). An explanation advanced by others is that a shift from kinetic to mass transfer con-
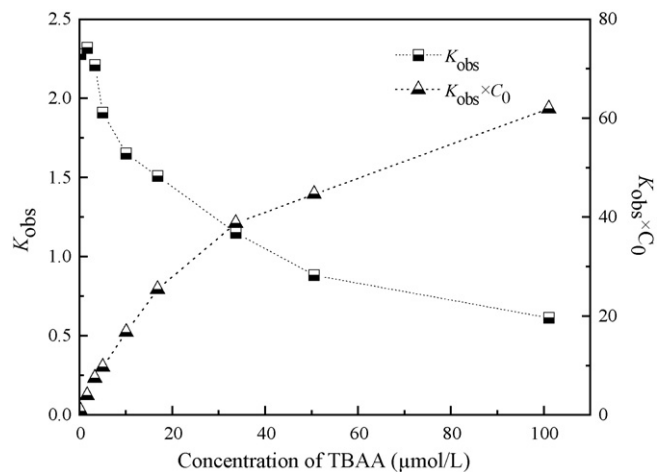
trol occurred [26]. However, the mass transfer rate coefficient, as well as the surface reaction coefficient, should be either directly proportional to metal loading, as shown in Eq. (4). Another explanation is inefficient mixing at the higher metal loadings [27]. This result indicated that Eq. (4) was tenable so that K_{obs} should be normalized by metal loading or a under zinc loading in the range of 1–40 mg/L.

3.2.2. Effects of the mixing speed

The influence of mixing speed on reaction between 10 mg/L zinc and 1 mg/L TBAA was surveyed. As shown in Fig. 4, little effect of mixing speeds on K_{obs} was discerned when they were between 100 and 300 rpm. The result eliminated mass transfer domination preliminarily.

Thus, the K_m needed to be known. When natural convection effect is absent and when Reynolds number (Re) is not much smaller than 1, the transfer rate for single spheres is given by following equation [28]:

$$Sh^* = \frac{K_m^* d_p}{D_{12}} = 2 + 0.6 Re^{1/2} Sc^{1/3} \tag{5}$$

in which Sherwood number (Sh) is determined by Schmidt number (Sc) and Re which are expressed in Eqs. (6) and (7) respectively. K_m^* is the uncorrected mass transfer coefficient (m/h), d_p is the particle diameter (m), and D is diffusivity (cm^2/s) expressed in Eq. (9).

$$Sc = \frac{\nu}{D} \tag{6}$$

where ν is kinetic viscosity (m^2/s).

$$Re = \frac{d_p U_t}{\nu} \tag{7}$$

U_t is the terminal settling velocity of metal powder (m/s) as following:

$$U_t = [\frac{2g}{27}(\frac{\rho_p}{\rho} - 1)]^{5/7} d_p^{8/7} \nu^{-3/7} \qquad (8)$$

here ρ_p and ρ are particle and the fluid density, respectively (kg/m^3), and

$$D = 7.4 \times 10^{-12} \frac{(xM)^{1/2}T}{uV^{0.6}} \qquad (9)$$

in which x is the association parameter, and the solvents were assumed approximately as water so that x is 2.6. M is the molecular weight of solvent, and V is the molal volume of solute at normal boiling point estimated via the previous method [29].

If the terminal velocity is used to calculate Re, Eq. (5) should give the minimum expected value of the transfer coefficient. Applying the correction factor for a system mixed by recirculating liquid, corrected K_m are obtained by $1.5 \times K_m^*$. The corrected K_m values for HAAs were listed in Table 2. It revealed that these reactions were all reaction limited as their calculated $K_m a$ values (assumed the particle as sphere, a is the ratio of geometric surface area of the particles to the volume of solution) were much higher than their K_{obs}.

3.2.3. Effects of the HAAs initial concentration

Further experiments were conducted at different initial concentrations of TBAA with 1 mg/L zinc and also mixed at 150 rpm. As shown in Fig. 5, the K_{obs} decreased with increasing concentrations in the range between 0.1 and 20 mg/L. The result demonstrated that competition for reactive sites existed. If the process is reaction-limited, the initial rates should increase with the increase of TBAA initial concentrations, and only up to a point [30]. As mass transfer was much faster than surface reaction and the K_{obs} were calculated by the concentrations in the incipient 2 h when the transformation was accordant with pseudo-first-order kinetic models, so the K_{obs} could represent initial interaction rate (K_0). as shown in Fig. 5, initial interaction rates ($R_0 = K_0 \times C_0 = K_{obs} \times C_0$, C_0 is the initial concentration of TBAA) were increased to a point then stayed constant. The phenomena was consistent with reaction-limited, so the reaction was the control step in the surface interaction between zinc and HAAs, probably including the transfer of electrons, the disruption and rebuilding of chemical bonds.

From the kinetic analysis, it is clear that the reaction process is much more significant than the mass transfer, adsorption and
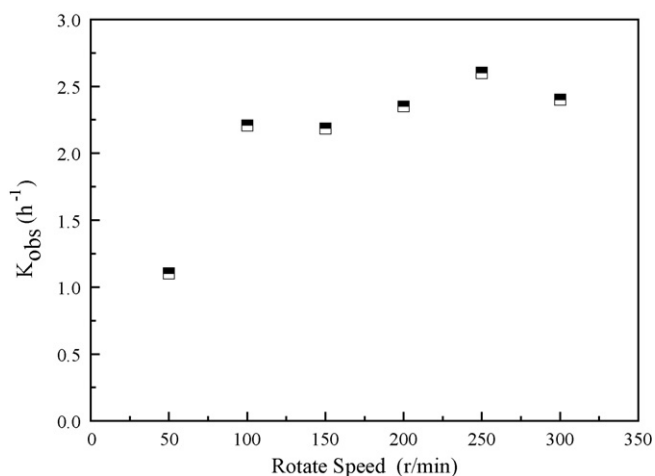

Fig. 5. The pseudo-first-order rate constants (K_{obs}) and initial action rates ($K_{obs} \times C$) for transformation of TBAA by 10 mg/L zinc as a function of TBAA initial concentrations, $n = 3$ or 4, RSD $\leq$ 5%.

Table 3
Degrading time of HAAs in galvanized pipe only considered the influence of zinc. (K_m: the mass transfer coefficient, a: the ratio of pipe surface to fluid volume, which was 266.67 m^{-1} here, k: the reduction rate constant of HAA along the pipe, t: the time that HAA decreases to 1% of its initial concentration).

HAAs	$K_m a$ (h^{-1})	k (h^{-1})	t (h)
MCAA	19.032	–	–
DCAA	17.345	0.726	6.34
TCAA	16.088	0.791	5.82
MBAA	18.809	1.182	3.90
DBAA	17.183	1.084	4.25
TBAA	15.963	2.186	2.11

desorption process. It was inferred that flowing through galvanized pipe, the degradation rates of HAAs are almost the same regardless of the duct and hydrodynamic conditions.

3.3. Environmental significance

Reduction of HAAs by zinc on the surface of galvanized pipe may play a role in determining the fate of HAAs in water distribution systems. A water distribution system calculation was shown below. A steady-state plug flow reactor equation was used to compute the concentration of HAAs along water distribution system:

$$C = C_0 \exp(-kt) \qquad (10)$$

where C is the concentration of a certain HAA along water distribution system, C_0 is the initial concentration, k is the reduction rate constant of HAAs along the pipe, and t is the reduction time of HAAs along the water distribution system.

A mass transfer correlation for a smooth pipe [31,32] was used to calculate mass transfer coefficients for HAAs in water distribution systems:

$$Sh = \frac{K_m d}{D} = 0.023 Re^{0.83} Sc^{0.333} \qquad (11)$$

$$Re = \frac{\rho u d}{\nu} \qquad (12)$$

where d is pipe diameter (15 mm), and u is flow velocity (0.3 m/s). The values of $K_m a$ (a is the ratio of pipe surface to fluid volume, which was 266.67 m^{-1} here) were listed in Table 3. Compared $K_m a$ with K_{obs} in Table 3, for TBAA, DBAA, MBAA, TCAA, and DCAA, the former was 7–24 times of the latter, so the influence of mass transfer was approximately negligible, then the k could be replaced by K_{obs}. Only considered the influence of zinc, all HAAs except MCAA would decrease to 1% of their initial concentrations in 2.11–6.34 h while flowing through galvanized pipe in water distribution systems.

The result proved that the influence of zinc to the transformation of HAAs should not be underestimated. After flowing through or staying in the galvanized pipe for a certain time, the categories and concentrations of HAAs may totally be changed. Some studies suggested that the toxicity of six chlorinated and brominated HAAs increased with a decrease in the number of halogen atoms per molecule [33], so the health risk due to the HAAs may be also changed in the water distribution process. As HAAs would be dehalogenated step by step and the final product for chlorinated acetic acids and brominated acetic acids are MCAA and acetate respectively, so the health risk due to TCAA, DCAA may magnify, while that due to TBAA, DBAA may increase firstly and vanish ultimately, and that due to MBAA will decrease to vanish directly.

4. Conclusions

Zinc would induce sequential dehalogenation of HAAs. The final product for brominated acetic acids was acetate, while TCAA and

DCAA were dechlorineted to MCAA. The K_{obs} were as follows: TBAA $(2.186\,h^{-1}) >$ MBAA $(1.182\,h^{-1}) >$ DBAA $(1.084\,h^{-1}) >$ TCAA $(0.791\,h^{-1}) >$ DCAA $(0.726\,h^{-1}) >$ MCAA, which indicated that in the reactions with zinc, brominated acetic acids were more activated than chlorinated acetic acids, and the reactivity of HAAs decreased when the number of substituents reduced. Batch studies also denoted that the K_{obs} of reaction between TBAA and zinc were only directly proportional to zinc loading over a limited range (1–40 mg/L), and decreased with increasing TBAA initial concentration between 0.1 and 20 mg/L, but not obviously affected by mixing speed between 100 and 300 rpm, which illustrated in all these reactions the influence of mass transfer, adsorption and desorption was all neglectable.

The reactions substantiated that zinc would induce TBAA, DBAA, MBAA, TCAA, DCAA decrease to 1% of their initial concentrations in 2.11–6.34 h while flowing through galvanized pipe. The health risk due to TCAA, DCAA may magnify, while that due to TBAA, DBAA may increase firstly and vanish ultimately, and that due to MBAA will decrease directly. Under different hydrodynamic and duct conditions, the surface interaction velocity of HAAs should be similar as it is determined by the reaction principle.

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