Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering)
ISSN 1673-565X (Print); ISSN 1862-1775 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
E-mail: jzus@zju.edu.cn

Factors influencing the formation of chlorination brominated trihalomethanes in drinking water*

Huan WANG[1], Dong-mei LIU[†‡1], Zhi-wei ZHAO[1], Fu-yi CUI[1], Qi ZHU[1,2], Tong-mian LIU[1]
([1]*State Key Laboratory of Urban Water Resources and Environments, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China*)
([2]*School of Chemistry and Material Sciences, Heilongjiang University, Harbin 150080, China*)
[†]E-mail: Mei18@hit.edu.cn

Received June 16, 2009; Revision accepted Oct. 16, 2009; Crosschecked Dec. 8, 2009

Abstract: The formation of brominated trihalomethanes (THMs-Br) which is proved more carcinogenic than their chlorinated analogues reported was very different at various water qualities. This study was performed to assess the effects of water quality parameters (bromide concentration, pH value and ammonia concentration), chlorination conditions (chlorine dose, reaction time) and ratios of Br^-/DOC and Br^-/Cl_2 consumption on the formation and distribution of THMs-Br in chlorination. The results showed good correlation between the bromine incorporation factor (BIF) n(Br) and Br^-/Cl_2 consumption ratio. The formation of total THM (TTHM) was found to decrease with increasing ammonia concentration but to increase with bromide concentration and pH value. The n(Br) trends were significantly affected by the presence of bromide concentration. The effects on the molar yields of THMs were more strongly influenced by bromide concentration and dissolved organic carbon (DOC) concentration than pH value and natural organic matter (NOM) source. High Br^-/DOC and Br^-/Cl_2 favor the formation of THMs-Br over chlorinated THMs (THMs-Cl). The experimental data including the main parameters such as bromide, DOC, ammonia, pH and reaction time were used for developing the predictive model for THMs-Br.

Key words: Brominated trihalomethanes (THMs-Br), Bromine incorporation factor (BIF), Total THM (TTHM), Chlorination, Predictive model
doi:10.1631/jzus.A0900343 **Document code:** A **CLC number:** X5

1 Introduction

The disinfection by chlorine is a normal water treatment process in China. Chlorine as a traditional disinfectant is popular due to its lower cost and higher oxidizing effect. However, the chlorine can also react with natural organic matter (NOM) and halides (e.g., Cl^- and Br^-) to form disinfection byproducts (DBPs) (Sketchell *et al*., 1995). Trihalomethanes (THMs) are identified as the main DBPs, and THMs consist of four chemical species which are chloroform ($CHCl_3$), dichlorobromomethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) (Chang *et al*., 2001; Panyapinyopol *et al*., 2005; Sorlini and Collivignarelli, 2005). Many researchers have observed that bromine incorporation into THMs is favored over chlorine incorporation when the molar concentration of chlorine and bromine is similar (Hua *et al*., 2006). Hypobromous acid (HOBr) is a stronger oxidant and is 20 times that of hydrochlorous acid (HOCl) (Cowman and Singer, 1996; Uyak and Toroz, 2007). In the bromide-containing water, bromide ions would substitute for the chloride to form the HOBr, which could then react with organic matters to form the brominated DBP (Singer, 1999).

Brominated trihalomethanes (THMs-Br) are suspected to be much stronger carcinogens and mutagens than their chloride-containing analogues (Richardson, 2003). Recently, special attention has

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‡ Corresponding author

* Project supported by the National Hi-Tech Research and Development Program (863) of China (No. 2006AA06Z311), the National Natural Science Foundation of China (No. 50808052)

been given to factors affecting and control of brominated THM species formation. The previous studies have investigated the effects of bromide, iodide concentration (Hua *et al.*, 2006; Sohn *et al.*, 2006; Sun *et al.*, 2009) and/or NOM concentration (Huang *et al.*, 2004; Lu *et al.*, 2009) and ammonia concentration (Yang and Shang, 2004; Chang *et al.*, 2008) on DBP formation during chlorination and ozonation. However, the fraction of THMs-Br formation at different water qualities reported has varied in the range of only approximately 6% with the low concentration of bromide in water of Korea (Yoon *et al.*, 2003) and a huge contrast exceeding 95% in bromide-rich lake water of Israel (Heller-Grossman *et al.*, 1993). To control chlorination THMs-Br, an understanding of the factors that influence their formation is required.

The objective of this work is to investigate THMs, in particular the THMs-Br formation from the filtered Songhua river water (at Harbin Shaohe Water Treatment Plant (SWTP) in China). The formation of the total trihalomethanes (TTHM) and the distribution of the individual species rely on the water characteristics, so we focused on how water quality conditions (e.g., reaction time, bromide concentration, pH value, ammonia concentration and incorporation factors) affect the percent conversion of bromide to THMs-Br. A predictive model for THMs-Br was developed from the experimental data to simulate the effects of the water and then compare predicted values to actual measurements.

2 Materials and methods

2.1 Sample preparation

Filtered water from SWTP (Harbin, China) and several solutions of humic acid (HA) extracts were used for the experiments. HA was used to provide the source of the precursors. Plants use conventional treatment processes and the characteristics of water for the experiment are listed in Table 1.

All experiments were performed at room temperature (20±2 °C). All glassware was cleaned with phosphate-free detergent and flushed with tap water and deionized water and heated in a muffle furnace at 400 °C for 2 h. Filtered water and solutions of humic materials were filtered (0.45 μm cellulose acetate filter) prior to the experiments.

Table 1 Water quality parameter characteristics

Parameter	A	B
TOC (mg/L)	2.54	1.97
DOC (mg/L)	2.53	1.97
UV_{254} (cm^{-1})	0.063	0.173
SUVA (L/(mg·m))[a]	2.49	8.78
Br^- (μg/L)[b]	8	100
pH	7.11	7.27
NH_3-N (mg/L)	1.23	0.14

A: the filtered surface water of SWTP; B: the solution of humic acid (HA) extracts was used for experiments. [a] Specific ultraviolet absorbance (SUVA) was calculated from ultraviolet absorbance at 254 nm (UV_{254}) divided by the dissolved organic carbon (DOC); [b] Bromide concentration after KBr was spiked into the samples. The concentration was verified by ion chromatography (IC) measurement

2.2 Materials

Methanol purge and methyl tert-butyl ether (MTBE) were purchased from Sigma-Aldrich. Primary standard solutions of THMs including $CHCl_3$ (>99% purity), $CHBr_2Cl$ (>98% purity), $CHBrCl_2$ (>98.6% purity) and HBr_3 (>99.5% purity) were obtained from the China National Analytical Center, Beijing. HA was purchased from Shanghai Jufeng Co., Ltd., China. All the other reagents were above analytical grade.

Chlorine concentration was determined using DPD (*N*, *N*-diethyl-*p*-phenylene-diamine) titration methods. Ammonia was measured with a spectrophotometer using the nesslerization method. DOC was measured with a total organic carbon analyzer (TOC-VCPH, Shimadzu). UV-absorbance was measured with a spectrophotometer (UV-2550, Shimadzu). Bromide was analyzed using an ion chromatography (ICS-3000, Dionex) with Environmental Protection Agency (EPA) method 300.0 A, and IonPac As19 analytical column was used with a 30 mmol/L potassium hydroxide eluant at a flow rate of 1.0 ml/min. THMs was measured by a liquid-liquid extraction (LLE) with a gas chromatography/electron capture detector (GC/ECD) (4890 N, Agilent) using a modified EPA Method 551.1. Briefly, a 35 ml water sample was placed in a 40 ml vial and then extracted with 2 ml MTBE. 6 g sodium sulfate anhydrous was added to enhance the extraction effect. The vial was sealed, shaken for 3 min, and left undisturbed for 5 min. 1 μl of the analytes in the solvent layer was then injected into the GC.

A molar fraction of halogen has been used as an unbiased measure of bromine substitution among different THMs categories (Obolensky and Singer 2005). The bromine incorporation factor (BIF) n(Br), which is a dimensionless factor used to assess bromine substitution in THM speciation, was first introduced by Gould *et al.* (1981). The n(Br) for THMs is given by

$$n(\mathrm{Br}) = \frac{C_{\mathrm{CHBrCl_2}} + 2C_{\mathrm{CHClBr_2}} + 3C_{\mathrm{CHBr_3}}}{C_{\mathrm{TTHM}}}, \quad 0 \le n \le 3, \tag{1}$$

where $C_{\mathrm{CHBrCl_2}} + 2C_{\mathrm{CHClBr_2}} + 3C_{\mathrm{CHBr_3}}$ is the molar amount of bromine in the THMs, μmol/L. and C_{TTHM} is the sum of four THMs, μmol/L.

3 Results

3.1 Effect of reaction time

Fig. 1a illustrates the formation of THMs as a function of chlorine reaction time in different bromide water samples. It can be seen that $CHCl_3$ and $CHBr_2Cl$ were formed rapidly in the first few hours and then the formation slowed with the chlorination reaction time. Small quantities of $CHCl_2Br$ and $CHBr_3$, however, did not change significantly. Fig. 1b illustrates that the waters with higher bromide concentration tended to have higher levels of TTHM formation. As shown, four species THMs formation rates were initially rapid from 0 to 48 h with the rapid consumption of chlorine, and thereafter decreased slightly. About 60% of TTHM were formed within the first 24 h.

The BIF value decreased initially and then increased, with the lowest point at about 0.56 occurring at 36 h (Fig. 1a). In contrast, the BIF increased and then decreased slightly in Fig. 1b.

3.2 Effect of bromide

When bromide ion concentration increase in accordance with constant DOC (increasing the Br^-/DOC), TTHM concentrations increase (Chellam and Krasner, 2001). In Fig. 2, TTHM concentration increased with increasing bromide ion concentration, and the molar increase of TTHM ranged from 0 to 54%. As the concentration of bromide increases, the yield of $CHCl_3$ decreases continuously, but those of THMs-Br increase almost linearly with the bromide concentration. According to Hutton and Chung (1994), the atomic mass of bromide ion is approximately twice that of the chloride ion, so THMs-Br increase the concentration of TTHM in water. Increasing the bromide concentration from 0.1 to 2.0 mg/L gradually shifted trihalomethanes from chlorinated species to the brominated species including mixed chlorobromo species and increased the n(Br) during chlorination. As HOBr is more oxidized than HOCl, firstly, HOCl rapidly oxidizes bromide to HOBr in the presence of bromide, and then the residual HOCl along with HOBr generated react with the precursor materials to produce mixed chlorobromo substitution products (Xue *et al.*, 2008).

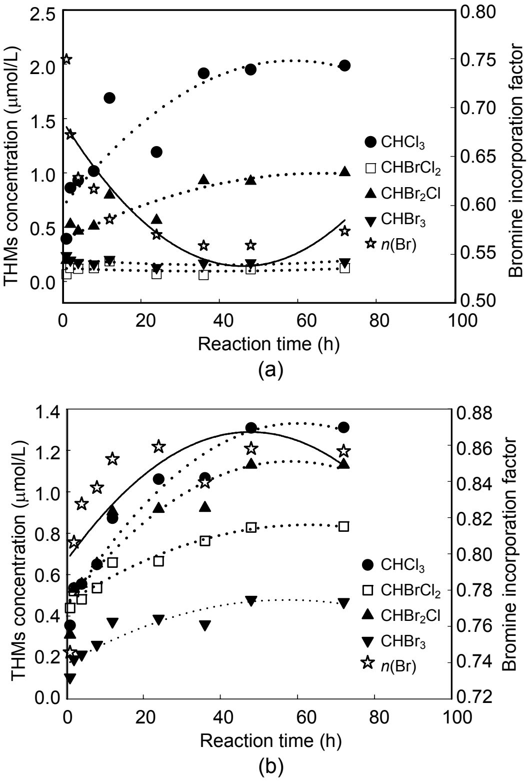

Fig. 1 Effect of reaction time on formation and distribution of THMs species from filtered surface water. (a) Br^-=0.1 mg/L; (b) Br^-=1 mg/L

Reaction conditions: DOC=2 mg/L; pH=7.1; Cl_2 dose=20 mg/L; temperature=20 °C

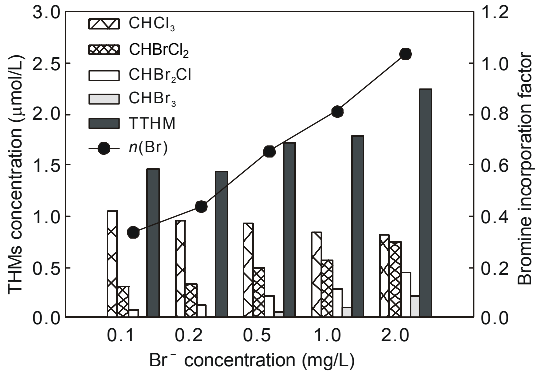

Fig. 2 Effect of bromide concentration on distribution of THMs species from filtered surface water

Reaction conditions: DOC=2.53 mg/L; Cl_2 dose=20 mg/L; reaction time=48 h; pH=7.1; temperature=20 °C

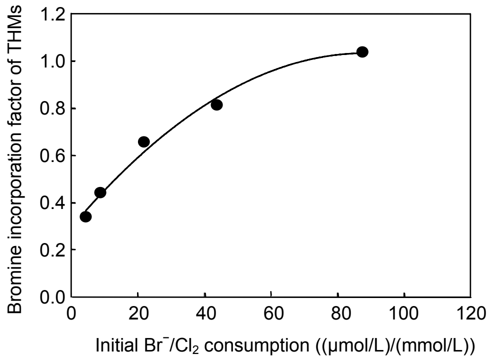

Fig. 3 Correlation between bromine incorporation factor of THMs and bromide-to-chlorine consumption ratio

So the ratio of Br^-/HOCl plays an important role in bromine substitution during THMs formation. As chlorine usually has higher orders of magnitude than bromide in concentration, and the oxidation of bromide by chlorine is very rapid, nearly all the bromide typically present in chlorinated water becomes oxidized to bromine and reacts with NOM (Huang *et al.*, 2004). Therefore, the ratio of initial bromide to chlorine consumed should give a reasonable approximation to the ratio of HOBr consumption to HOCl consumption (Hua *et al.*, 2006).

Fig. 3 shows that the BIF *n*(Br) of THMs increased substantially with increasing initial bromide to chlorine consumption ratio, which is consistent with (Symons *et al.*, 1993; Hua *et al.*, 2006). These researches were conducted on commercial humic substances or natural waters with different organic precursors. It suggests that Br^-/Cl_2 consumption ratio is a more important factor than the NOM type.

3.3 Effect of pH

The distribution of THMs mainly depends on the chlorination pH value and the Br^-/DOC ratio or Br^-/Cl_2 consumption ratio. The pH adjustment affects the DBP formation during chlorination in several major ways. First, the distribution of $HOCl/OCl^-$ depends on pH. HOCl, a more powerful oxidant than hypochlorite (OCl^-), is predominant at low pH values. Second, organic charge and reactivity are dependent on pH. Third, individual DBP formation can be affected by pH values (Hua and Reckhow, 2007).

As shown in Fig. 4a, increasing pH from 5 to 9 enhanced the THMs yields of $CHCl_3$ (1.24–2.34 μmol/L), $CHCl_2Br$ (0.34–0.97 μmol/L), $CHClBr_2$ (0.025–0.58 μmol/L), no $CHBr_3$, respectively. Similarly in Fig. 4b, the THMs yields were $CHCl_3$ (0.65–1.24 μmol/L), $CHCl_2Br$ (0.43–1.46 μmol/L), $CHClBr_2$ (0.58–1.23 μmol/L), $CHBr_3$ (0.23–1.34 umol/L), respectively. Compared with two water samples, in Fig. 4a, the ratios of Br^-/DOC and Br^-/Cl_2 were 24 and 18 times higher than those in Fig. 4b. Furthermore, in Fig. 4a, BIF value increased from 0.24 to 0.51 with increasing pH. A similar trend was also observed in Fig. 4b. BIF increased quickly to above 0.8. High Br^-/DOC and Br^-/Cl_2 favor the formation of THMs-Br over chlorinated THMs (THMs-Cl). The increase of the BIF with the pH in the range of 5 to 8 is probably due to the increment of alkaline hydrolysis of the THMs-Br determined by OH^-. The decrease at pH above 8 is attributed to the following disproportion of OBr^-, which can disassemble to bromate and bromide ions, neither of which reacts with HA. So the yield of the THMs-Br reduces at pH above 8 (Ichihashi *et al.*, 1999).

3.4 Effect of ammonia

THMs formation trends were significantly affected by the absence of ammonia. The incorporation of bromine changed the byproducts speciation toward brominated species and enhanced the yields of the TTHM. Comparing Fig. 5a with Fig. 5b, in the absence of ammonia, increasing the bromide concentration also decreased TTHM formation.

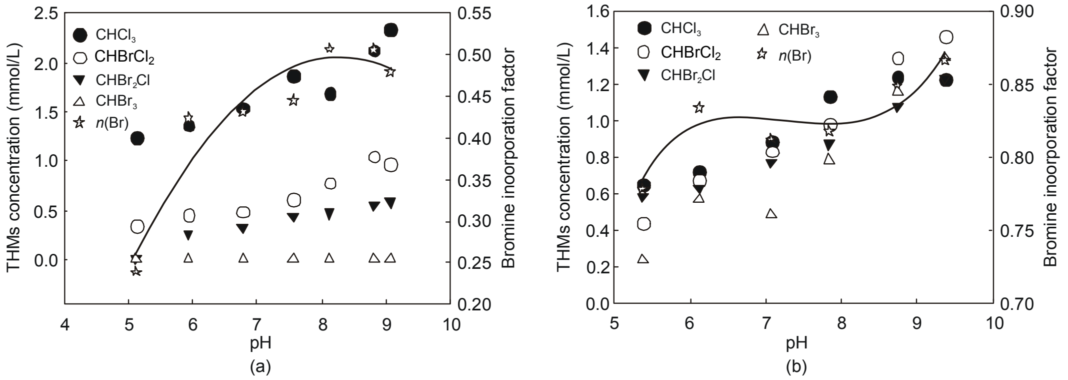

Fig. 4 Effect of pH on formation and distribution of THMs species from filtered surface water. (a) DOC=2.53 mg/L, Br^-=57 μg/L; (b) DOC=1.86 mg/L, Br^-=1 mg/L

Reaction conditions: Cl_2 dose=20 mg/L; reaction time=48 h; pH=7.0; temperature=20 °C

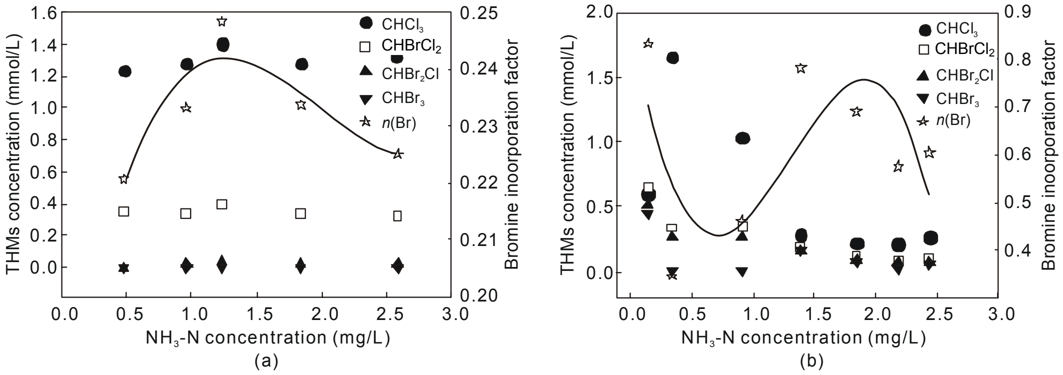

Fig. 5 Effect of ammonia concentrations on formation and distribution of THMs species. (a) DOC=2.53 mg/L; Br^-=57 μg/L; (b) DOC=1.86 mg/L; Br^-=1 mg/L

Reaction conditions: Cl_2 dose=20 mg/L; reaction time=48 h; temperature=20 °C

A possible explanation is that in the presence of ammonia, ammonia reacted with free chlorine to form monochloramine at a faster rate than the oxidation of bromide at 2 mg/L or less ($k_{\text{bromide-chlorine}}=3.8\times10^3\ (\text{mol/L})^{-1}\cdot\text{s}^{-1}$) (Yang and Shang, 2004). The remaining free chlorine continuously reacted with bromide ion to form hypobromous acid. Due to the formation of monochloramine limited generation of hypobromous acid, the formation of hypobromous acid in large quantities was impossible, which consequently led to lower yields of the THMs (Duong *et al.*, 2003). Inorganic bromochloramine can be formed from slow monochloramination of bromide ions ($k_{\text{bromide-monochloramine}}=3.5\times10^6\ (\text{mol/L})^{-2}\cdot\text{s}^{-1}$), and it is also known to react with organic precursors to form THMs-Br. Therefore, BIF increases with increasing bromide concentrations in ammonia solutions.

3.5 Combined effect of DOC, ammonia and pH

Substances including ammonia, bromide ions and HA in solution react with free chlorine to form various species THMs. The reaction between free chlorine and bromide ions produces hypobromous acid. The incorporation of ammonia leads to the formation of chloramines, bromamines, and bromochloramine. All these halogens may react with HA or other precursors to form THMs (Buffle *et al.*, 2004; Zhang *et al.*, 2005). Combined effects of different levels of DOC, ammonia concentrations on formation and distribution of THMs species in six water samples A–F are presented in Fig. 6. Due to the relatively low DOC levels in water types A, B, E and F, the formation of THMs is quite low. Higher levels of THMs would be expected in water types C and D with high DOC. It was revealed that the concentrations of

THMs formation observed at 5.8 mg/L of DOC concentration was much higher than that at 2 mg/L of DOC concentration. Compared water samples A to B (or C to D) at constant DOC concentration and ammonia concentrations, increasing pH value enhanced THMs and resulted in a shift toward the formation of chlorinated species.

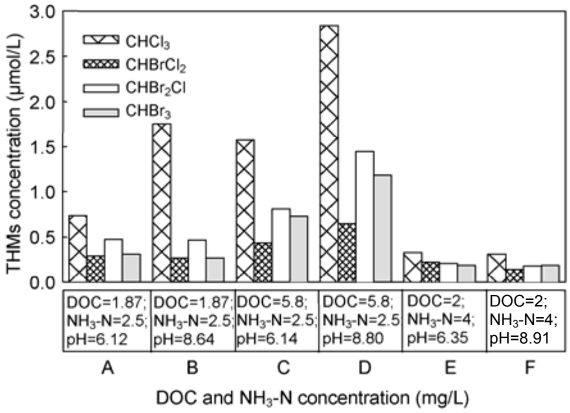

Fig. 6 Effect of different levels of DOC and ammonia concentrations on formation and distribution of THMs species

Reaction conditions: Br^-=1.62 mg/L; Cl_2 dose=20 mg/L; reaction time=48 h; temperature=21 °C

Water of types E and F have high levels of ammonia at constant DOC concentration and pH, and the formation of THMs was found to sharply decrease but have a higher BIF value. The results could be explained by competition kinetics of free chlorine reacting with bromide and ammonia at different pH. In the presence of ammonia, the formation of THMs-Br and THMs-Cl is inhibited due to chloramine formation (Karpel Vel Leitner *et al.*, 1998). It was thus concluded that compared with increasing pH value, high DOC concentration favors to enhance the THMs formation, and ammonia would reduce THMs formation.

3.6 Development of THMs-Br formation model

Numerous predictive models for THMs formation have been developed in the past three decades (Sadiq and Rodriguez, 2004; Chowdhury *et al.*, 2009). The presence of bromide ions in water samples make reactions more complex and have different pathways to form various THMs species (Buffle *et al.*, 2004). However, research on prediction of THMs-Br was rarely reported. To identify the importance of different operational and water quality parameters, especially in various bromide concentration conditions in controlling the formation of THMs-Br, it is necessary to develop the predictive model for THMs-Br. According to the results in effect factors analysis, bromide concentration, DOC, ammonia concentration, pH value and reaction time were the main factors. Therefore, the effect of temperature on THMs-Br formation could be ignored in this investigation. An empirical model was developed after collecting experimental data from chlorination experiments with water samples collected from the filtered Songhua river water (SWTP, at Harbin in China) which were added to potassium bromide and combined with a solution of HA.

A multiple linear regression THMs-Br model was analyzed:

$$C_{\text{THMs-Br}} = a \cdot C_{\text{Br}^-}^{b_1} \cdot C_{\text{DOC}}^{b_2} \cdot C_{\text{NH}_3\text{-N}}^{b_3} \cdot \text{pH}^{b_4} \cdot t^{b_5}. \quad (2)$$

The results of parameters for the regression coefficients for predictive THMs-Br model are shown in Table 2.

Table 2 Regression coefficients for predictive THMs-Br model

Parameter	Experimental range	Coefficient regression (R^2)	a ($\times10^{-3}$)	
Br^- (μg/L)	8–1000	b_1 (0.35)	a_{Br^-}	58.22
DOC (mg/L)	0.48–5.00	b_2 (0.27)	a_{DOC}	25.11
NH_3-N (mg/L)	0.14–2.58	b_3 (−0.32)	$a_{\text{NH}_3\text{-N}}$	30.79
pH	5.12–9.37	b_4 (0.23)	a_{pH}	39.01
React. time (h)	0–72	b_5 (0.13)	$a_{\text{React.}}$	80.89
			$\bar{a}$	46.81

The values of b_1, b_2, b_4 and b_5 are always positive, which indicates that increasing initial bromide concentration, DOC, pH value and reaction time increases THMs-Br formation. Alternatively, NH_3-N produces negative coefficients, which suggests that increasing ammonia concentration decreases THMs-Br formation.

The relationships between the actual values and predicted values are shown in Fig. 7 and the high correlation coefficient (R^2) shows a good predictive value for THMs-Br.

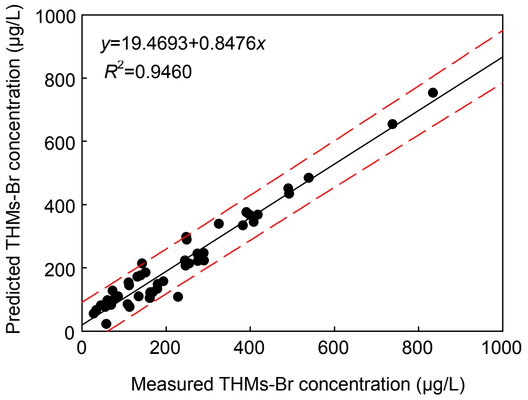

Fig. 7 Linear regression and 95% confidence intervals for measured and predicted THMs-Br

4 Conclusion

The results showed that reaction time and Br^- concentrations exerted dominant effects on the formation of THMs during the chlorination. Moreover, there exist high correlations between the BIF and Br^-/Cl_2 consumption ratio. Different bromide concentration exerted different trends of BIF when reaction time, pH and ammonia concentration were considered. No correlations between BIF and TTHM formations were found at constant DOC, pH value, Br^-/DOC ratio, and bromide concentration. High Br^-/DOC and Br^-/Cl_2 favor the formation of THMs-Br over THMs-Cl. DOC and ammonia concentration incorporation factors were considered and it reveals that compared with increasing pH value, high DOC concentration favor to enhance the TTHM formation, and ammonia would reduce the TTHM formation.

The predictive model of THMs-Br formation was established in terms of bromide concentration, DOC, ammonia concentration, pH and reaction time by performing regression analysis on experimental data, $C_{\text{THMs-Br}}=0.047(C_{\text{Br}^-})^{0.35}\cdot(C_{\text{DOC}})^{0.27}\cdot(C_{\text{NH}_3\text{-N}})^{-0.32}\cdot(\text{pH})^{0.23}\cdot(t)^{0.13}$. And high correlation coefficient R^2 of the predictive model indicates simple model with very good predictive ability. It is beneficial to use this model in determining strategies aimed at decreasing THMs-Br concentrations in water treatment plant, which is reducing the potential risk.

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