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Supplementary Materials

Formation of brominated-haloacetamides from trihalomethanes during zero valent iron reduction and subsequent booster chlorination in drinking water distribution

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Bromine utilization factors (BUF) calculation.

Bromine utilization factors (BUF) is an index to indicate the percentage of bromide utilized in forming Br-DBPs during booster chlorination. To identify the Br^- utilized in the formation of various Br-DBPs (i.e., Br-THMs and Br-HAMs during chlorination process in this study, BUF was calculated in this study according to Eqs. (1) and (2).

$$\text{BUF (THMs)} = \frac{3[\text{TBM}] + 2[\text{DBCM}] + [\text{BDCM}]}{[\text{Br}^-]} \quad (1)$$

$$\text{BUF (HAMs)} = \frac{3[\text{TBAM}] + 2[\text{DBCAM}] + [\text{BDCAM}] + [BCAM]}{[\text{Br}^-]} \quad (2)$$

where all concentrations were on a molar basis and $[Br^-]$ was detected in the beginning of the chlorination mentioned in this part.

For BUF-THMs, the residual TBM and DBM, the reduction products, were not considered. This was because DBM could not react with chlorine to form the Br-THMs, which was verified by a DBM chlorination experiment (Fig. SM3). As shown in Fig. SM3, the DBM concentration was stable in the presence of 5 mg/L of chlorine and no BDCM, DBCM or TBM was detectable.

Figure SM1. Chlorination of DBM and TBM. pH = 7.0; Cl_2 dose = 5.0 mg/L; T = 25 ± 0.2 °C.

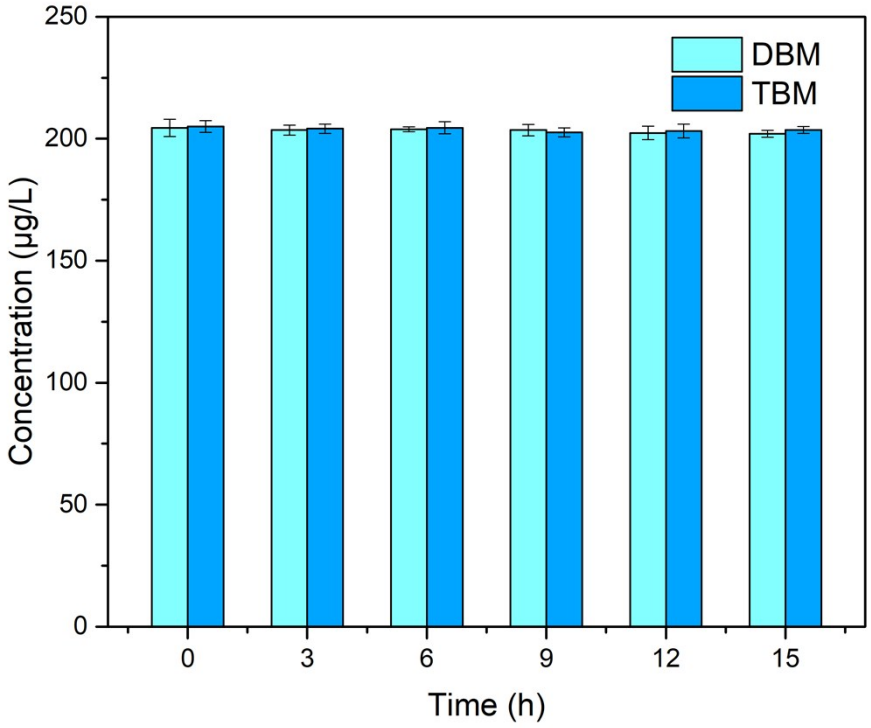
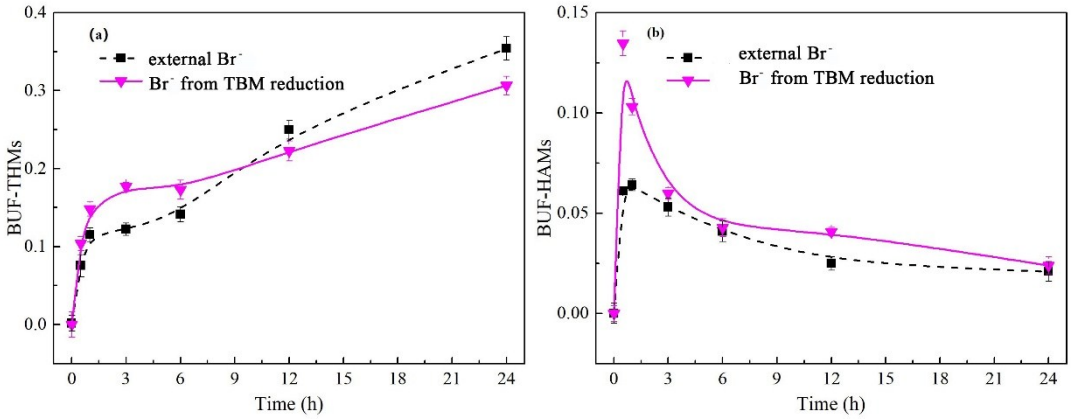
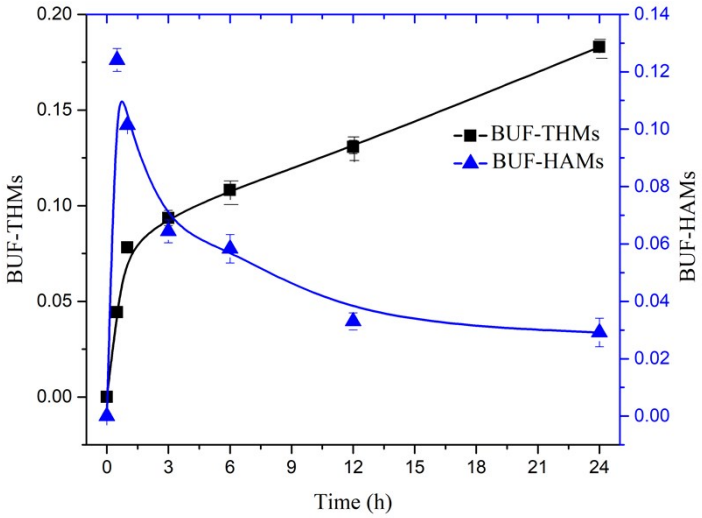


Figure SM2. The BUF of THMs and HAMs under two experimental situations. Br- from TBM reduction represents tap water containing Br- from TBM reduction by ZVI; external Br- represents tap water containing external bromide (spiked in); Figure 5a, BUF for THMs; Figure 5b, BUF for HAMs. pH = 7.07; ZVI dose = 5 g/L; T = 25±0.2 °C.



As shown in Fig SM2, the BUF for THMs increased with time and there was more Br^- utilization in TBM reduction water than in the water with external bromide addition within the first 9 h and then it became opposite. The BUF for HAMs also increased first and then deceased with time in two conditions (Fig SM2b). This was because the rapidly formed HAMs reacted with free chlorine and degraded subsequently and/or underwent hydrolysis. Previous study [1] pointed out that the BUF exhibited the downward trend with increasing Br^- levels in a study which compared the formation of HAMs in seven raw waters. In this study, the initial Br^- concentration of TBM was 117.6 µg/L, respectively. The results showed that BUF for both HAMs and THMs increased with decreasing Br^- levels, which indicated that the Br^- was more difficult to be utilized into DBPs with decreasing its levels.

Figure SM3. The BUF of THMs and HAMs under mixed THMs experimental situation. pH = 7.07; ZVI dose = 5.0 g/L; T = 25 ± 0.2 °C.



Calculation results of BUF-THMs and BUF-HAMs were both illustrated in Fig SM3. After chlorine addition, BUF-THMs exhibited an increasing trend and finally reached 0.18 in 24 h, BUF-HAMs decreased from 0.12 to 0.03 after a sharp increase in the first 0.5 h, which both followed the trends shown in Fig SM2a and Fig SM2b. Compared with Fig. 5, BUF-THMs and BUF-HAMs in this test are lower due to the lower initial Br^- concentration.

Table SM1. Water quality characteristics of the two waters included in this study.

Paraments	Tap water	Prepared HA water
pH	7.07	7.21
Cl^-(mg/L)	21.0	0.13
Br^-(μg/L)	37	<10
DOC (mg/L)	1.94	2.01
$SUVA_{254}$	1.07	7.43
Residual Chlorine (mg/L)	0.01	-

SUVA254 = specific ultraviolet absorbance at 254 nm

Table SM2. R2 and rate in different TBM reduction by ZVI conditions.

different condition		K_0	R^2
different ZVI dosages	1.0 g/L	0.0272	0.987
	5.0 g/L	0.1679	0.969
	10.0 g/L	0.2249	0.993
different pH	pH 6.0	0.2879	0.9762
	pH 7.0	0.1492	0.976
	pH 8.0	0.1228	0.98
different water types	Control	0.1686	0.9702
	HA	0.0632	0.9827
	tap water	0.2374	0.9859
different anions	Control	0.1553	0.9808
	5μM SO_4^{2-}	0.1621	0.988
	10μM SO_4^{2-}	0.1958	0.996
	5 μM HCO_3^-	0.238	0.995
	10 μM HCO_3^-	0.2665	0.9937

Table SM3. Blank control results of the tap water ZVI reduction and chlorination. (ppb)

Time(h)	-12	-11.5	-11	-9	-3	0	0.5	1	3	6	12	24
DBP												
TCM	0.53	0.43	0.42	0.21	0.02	0.21	1.34	1.20	0.85	0.62	0.32	0.33
TBM	-	-	-	-	-	-	-	-	-	-	-	-
BDCM	0.01	-	-	-	-	-	-	-	-	-	-	0.03
DBCM	-	-	-	-	-	-	-	-	-	-	-	-
BCAM	-	-	-	-	-	-	0.03	-	-	-	-	0.01
TBAM	-	-	-	-	-	-	-	-	-	-	-	-
DBCAM	0.01	-	-	-	-	-	-	-	-	-	-	-
BDCAM	-	-	-	-	-	-	0.02	-	-	-	-	-

Table SM4. The $\%C_{1/2X}$ and $genotoxic\ \ potency_X$ values of each DBP. [2]

DBP	$\%C_{1/2X}$ (M)	$genotoxic\ \ potency_X$ (M)
TCM	0.00962	0.01
TBM	0.00396	0.01
DBM	0.00396	0.01
BDCM	0.0115	0.01
DBCM	0.00536	0.01
BCAM	0.0000171	0.000583
TBAM	0.00000314	0.0000325
DBCAM	0.00000475	0.0000694
BDCAM	0.00000868	0.000146

Reference

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