Using prechloramination to control trihalomethanes formation in River Huang water with high bromide

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Abstract: An effective technology in controlling trihalomethanes (THMs) formation in the case of large amounts of bromide presenting was proposed, and the water of River Huang seriously polluted by bromide in winter in Tianjin City was studied. The THMs formation characteristics during prechloramination using preformed chloramines and converted chloramines were studied through jar tests. Results show that, in prechloramination process, the formation of THMs by preformed chloramines is very few, while that by converted chloramines is a little higher. And the formation of THMs, especially Br^- substituted THMs, increases with the increase of time and Cl_2:N ratio as well as the decrease of pH. The result obtained in a pilot plant shows that compared with prechlorination, the prechloramination process can efficiently control the formation of THMs, especially the Br^- substituted species. With equal chlorine dosage, the prechloramination can maintain a larger chlorine residue which offers a larger CT value than prechlorination.

Key words: prechloramination; trihalomethanes; bromide; pilot plant; chemical security
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Prechlorination has a good effect in enhanced coagulation, algal removal and disinfection, but for the DBPs concern, it is being canceled or changed to ozonation and other processes in many countries. For the economy sense, it is still widely used in most developing countries such as China [1,2].

Chloramines are widely used as disinfectant all over the world[3]. Recent years, most of the studies such as the chloramine chemistry, controlling disinfection byproducts (DBPs), disinfection abilities and control microbial stability in distribution system are all well studied, but the prechloramination process is neglected [4-9].

Consider for the characteristics of raw water and treatment process of the majority of water plants in China, prechloramination and its efficiencies in removal of pollutants are been investigated. For the raw water of northern China, the result shows that the Br^- causes a large amount of THMFP especially Br^- substituted THMs which have a greater toxicity formation. In order to estimate the ability of prechloramination in controlling DBPs formation of raw water rich in bromide, the THMs formation characteristics were studied through jar tests and compared with prechlorination in pilot plant. The results demonstrated that the prechloramination can efficiently control the formation of THMs in raw water polluted by bromide.

1 Materials and Methods

1.1 Materials

In all cases, reagent grade chemicals were used without further purification. Stock chlorine solutions were prepared by diluting sodium hypochlorite into chlorine-demand-free water to a concentration of about 2.00 g/L, and then standardized by iodometric method. Ammonia chloride solutions were prepared by dissolving ammonia chloride powder which was baked for 2 h at 100 ℃ in chlorine-demand-free water to a concentration of 1.00 g/L (calculated as N). Preformed chloramines was prepared by mixing stock chlorine solution with ammonia solution at a certain Cl_2:N ratio at pH 8.0, and then stirred for 20 min. Buffers used in this study were mixtures of KH_2PO_4-NaOH, KH_2PO_4-$Na_2B_4O_7$ and $Na_2B_4O_7$-NaOH to obtain pH values in the ranges of 6.0-7.0, 8.0-9.0 and 9.0-10.0, respectively.

1.2 Methods

1.2.1 Jar tests

Followed the sample was adjusted to the pH needed by HNO_3 or NaOH (if necessary), 2.0 mL buffer was added. For the test of converted chloramines, ammonia was dosed. Fill the incubation bottle

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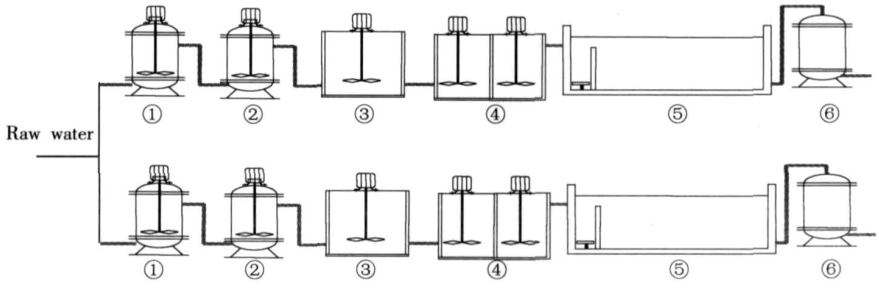
three quarters full with buffered water sample, dose with preformed chloramines or chlorine, cap bottle and invert twice. Fill to top with buffered water sample and cap headspace-free. Invert 10 times. The bottle was incubated in dark at 20.0 ℃ for a certain time. After incubation, measure chlorine residue and pH, and sample for THMs. The sample for THMs was quenched by 0.1 mL $Na_2S_2O_3$ (50 g/L). THMs were analyzed by headspace method using a gas chromatograph equipped with an electrolytic conductivity detector (Agilent 6890N GC, U. S. A.). Chlorine residue was analyzed by FAS-DPD method. TOC was analyzed according to USEPA method 5310 C[2]. The THMs formation potential was analyzed using Uniform Formation Conditions (UFC) test for the result of the method has a perfect according to practical condition [10].

1.2.2 Pilot plant experiments

The pilot plant is build up by two parallel system with a design flow of 120 m^3/d composed by two preoxidation reactor with a each detention time of 10 min, a mechanical mixer with a detention time of 1 min, a two stage mechanical flocculating tank with a total detention time of 18 min, then a dissolved air flotation (DAF) tank with a detention time of 15 min with a reflux ration of 7%, and at last a dual media filter with a filter velocity of 8 m/h (Fig. 1). At the experimental period, the parameters of two systems were keeping the same, and the coagulant used was $FeCl_3$ with a dosage of 11.2 mg/L at the inlet of mixer. One of the systems was dosed with 0.32 mg/L ammonia followed by 2.0 mg/L chlorine while the other only dosed chlorine at the inlet of preoxidation reactor. Ammonia stock solution was made up by dilute aqua ammonia in tap water and calibrated before using. Chlorine stock solution was prepared by dissolving chlorine gas in tap water and calibrated by iodometric method before employing. All of the chemical agents used in pilot plant were dosed by metering pump (P046 Liquid Metronics LMI Milton Roy, MA, U. S. A.). After a stabilization time of a few days, chlorine residue, TOC and THMs was sampled at the outlet of preoxidation tank, DAF and filter.



①Preoxidation reactor; ②Preoxidation reactor; ③Mixing tank; ④Flocculation tank; ⑤Flotation tank; ⑥ Filter

Fig. 1 The flow chart of pilot plant

2 Results and Discussion

2.1 The Characteristics of Raw Water

The UFCTHMs was designated as the THMs formation potential tested by UFC method[10]. As shown in Fig. 2, UFCTHMs of raw water went along up from Nov. 2004 to Mar. 2005, reached 282.4 μg/L, as compared with FEB. 2005 and Nov. 2004, increased by 30.2% and 107.2%, respectively, while the UV_{254} and TOC (not showed in the article) had no so distinct changes. At the aspect of THMs species illustrated in Fig. 3, the increases of THMs formation are all due to the increase of Br^- substituted THMs while the chloroform theatrically greatly decreases. For the limitation of detection, the bromide concentration in the raw water was not detected. But compared with the works of other investigator [11], and the condition of the region near Bohai Sea, it was concluded that the pollution of bromide was the main reason of the great increase of THMs.

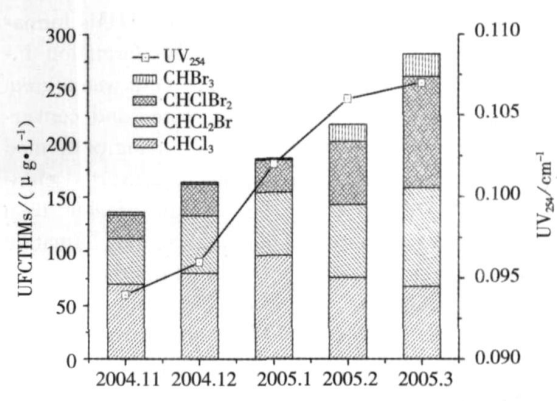


Fig. 2 Variation of organic matters and UFCTHMs in raw water

The contradiction occurred: prechlorination would cause a large amount of THMs formation, but without prechlorination process it is very difficult to achieve the effective removal of organics and disinfection. Aim at this contradiction, the prechloramination process is been studied in this paper with both jar test and pilot plant examination.

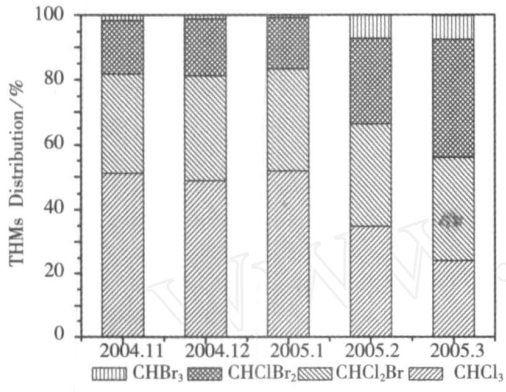


Fig. 3 The variation of UFCTHMs species in raw water

All of the experiments were performed in Mar. 2005, and the representative characteristics of raw water are low temperature, low turbidity, rich in humic substances, high bromide concentrationwhich are the main precursors of chlorinated byproducts[11-12]. The main parameters are given in Tab. 1.

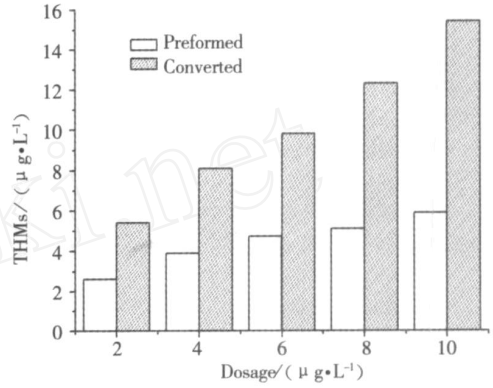
Tab. 1 The typical parameter of raw water

Parameter	Turbidity NTU	UV_{254} cm^{-1}	TOC $mg \cdot L^{-1}$	Alkalinity $mg \cdot L^{-1}$	pH	NH_3-N $mg \cdot L^{-1}$
Average	7.11	0.107	4.6	179	7.84	0.08

2.2 Jar Test

2.2.1 The effect of chloramines dosage on THMs formation

The effects of chloramines dosage on THMs formation were shown in Fig. 4. The THMs formation increased with chloramines dosage, but there was a great difference between preformed chloramines and converted chloramines: the increase of THMs using preformed chloramines was slower than that using converted chloramines. At condition of the dosage greater than 6.0 mg/L using preformed chloramines, the formation stabilized at 6 μg/L with no distinct increase. This demonstrated that the preformed chloramines caused only a micro lever amount of THMs which was consistent with other investigators[13]. Differently from the preformed chloramines, the THMs formation increased along with the converted chloramines dosage, and had a good linearity with it. But for the two kinds of chloramines at the dosage that most utilities usually used, the THMs formation were all less than 10 μg/L, much lower than the standard of USEPA and WHO. This also demonstrates the advancement of prechloramination in controlling the DBPs formation in water which abundant in bromide.

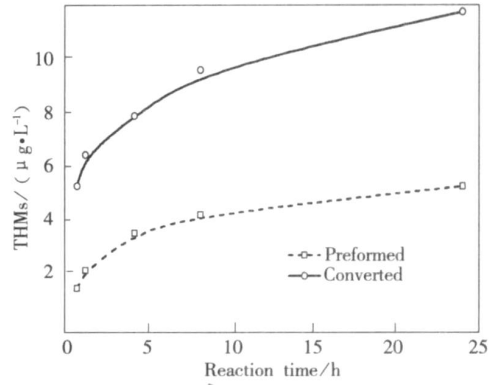


(Incubation conditions: pH, 8.0 ±0.2; temperature, 20 ℃; Cl_2 : N = 4 :1; time, 24 h)

Fig. 4 The effect of chloramines dosage on THMs formation

2.2.2 The effect of reaction time on THMs formation

As revealed in Fig. 5, the formation of THMs increase with incubation time using either preformed or converted chloramines. For the two dose modes, at the initial period of chloramines dosed, the formation of THMs was very fast, but with the time extends, the formation velocity decreased. For preformed chloramines, the THMs formation at 30 min, 1 h and 8 h accounted 25%, 38.4% and 78.8% for which at 24 h, respectively. The formation of THMs from converted chloramines was higher at initial period, the formation



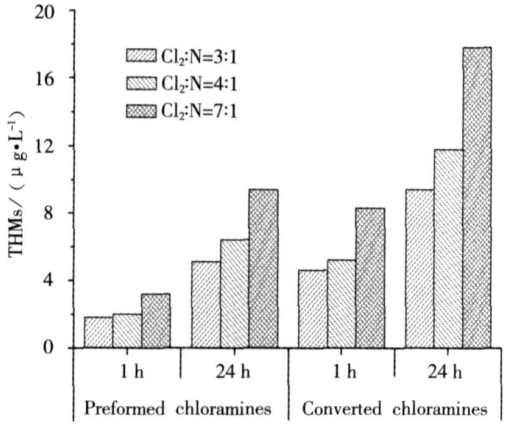
(Incubation conditions: pH, 8.0 ±0.2; temperature, 20 ℃; Cl_2 : N = 4 :1; chloramines/chlorine dosage, 8 mg/L)

Fig. 5 The effect of reaction time on THMs formation

at 30 min and 1 h accounted 44.1% and 54.2%, respectively. But the absolute value of 24 h THMs formation for two kinds of chloramines are all less than 15 μg/L, demonstrates that extends of contact time of prechloramination to enhance the treatment will not cause a great formation of THMs.

2.2.3 The effect of Cl_2:N on THMs formation

Fig. 6 illuminated that the increase of Cl_2:N causes an increase of THMs formation for both preformed and converted chloramines, and as the time extended, the effect of Cl_2:N on the formation of THMs became obvious. Moreover, the effect of Cl_2:N ratio on the formation of converted chloramines was greater than preformed chloramines. As chlorine chemistry[4] shows, chloramines instability, the hydrolyze and decomposition velocity increases with Cl_2:N, which will induce the greater formation of THMs. Whatever while Cl_2:N ratio between 3∶1 - 7∶1, the formation of THMs in 24 h only increased 4 - 8.0 μg/L with no instinct effect on total yield.



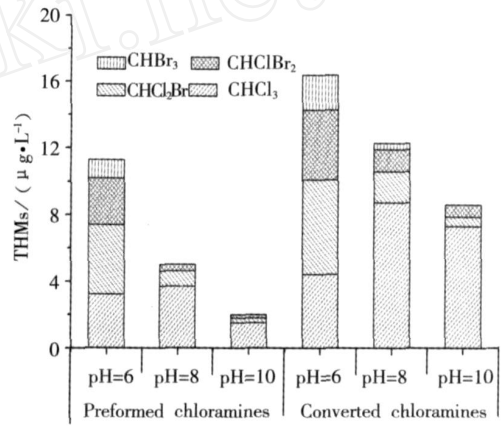
(Incubation conditions: pH, 8.0 ±0.2; temperature, 20 ℃; chloramines/chlorine dosage, 8 mg/L)

Fig. 6 The effect of Cl_2:N ratio on THMs formation

2.2.4 The effect of pH on THMs formation

As Fig. 7 shown, the formation of THMs decreased with increasing of pH. At pH 6.0, the THMs formed by preformed and converted chloramines were 10.2 μg/L and 16.4 μg/L, respectively. But at pH 8.0, the THMs yielding decreased to 5.0 μg/L and 12.3 μg/L, respectively. As obviously shown in Fig. 7, the decreasing was due the much more little formation of Br^- substituted species. And at pH 10.0, there was almost no formation of Br^- substituted species, and the THMs formations were decreased to 2.1 μg/L and 8.6 μg/L, respectively.

Many investigations[14] pointed out that the increase in pH could enhance the basic catalyzed hydrolyze step in the formation of THMs, and induce the greater yielding. For chloramines[15], the hypochlorite and dichloramine hydrolyzed and decomposed by chloramines are the main reason for the formation of THMs. But these hydrolyzation and decomposition processes are acidic catalyzed. With increase of pH, the concentration of hypochlorite and dichloramine decreased which cause little formation of THMs. Meanwhile, with bromide present, the increase of hypochlorite and dichloramine could oxidize Br^- to form hypobromous acid and bromamine, this bromine agents have a better substitute ability and cause a greater formation of THMs.



(Incubation conditions: Cl_2:N = 4∶1; temperature, 20 ℃; chloramines/chlorine dosage, 8 mg/L)

Fig. 7 The effect of pH on the formation of THMs

2.2.5 The effect of Br^- on THMs formation

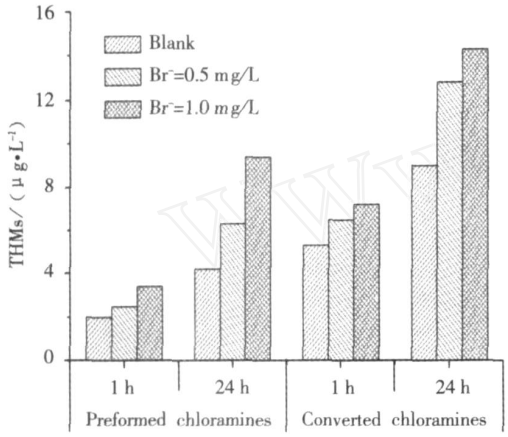
In order to test the ability of prechloramination in controlling THMs at the condition of even more bromide present, 0.5 mg/L and 1.0 mg/L bromide was dosed to raw water. The results were shown in Fig. 8: there was an increase of THMs formation when bromide either 0.5 mg/L or 1 mg/L was dosed to increase the bromide concentration, but the absolute formation amount are all less than 15 μg/L which showed the ability of prechloramination on controlling THMs formation.

2.3 Pilot Plant Experiments

Based on the jar tests, the ability of prechloramination on controlling THMs formation are examined on pilot plant. Although the preformed chloramines is even more effective than converted chloramines, but for the difficulty in preparation of great volume of preformed chloramines, the converted chloramines was employed as mentioned above.

Fig. 9 shows the average value of a great amount of data obtained during the operation. Apparently, at the equivalent chlorine dosage of 2.0 mg/L, the THMs formation using prechloramination is much more less

than that using prechlorination. At the prechloramination process, the THMs formation had no distinct increase after Preoxidation Reactor 1, and it can be estimated that the THMs formation would not increase obviously in the following disinfection process using chloramines. But for prechlorination process, the formation of THMs goes up along with the stream, and in the following disinfection process, the THMs could be formed continuously.



(Incubation conditions: Cl_2 :N = 4 :1; temperature, 20 ℃; chloramines/chlorine dosage, 8 mg/L; pH = 8.0)

Fig. 8 The effect of Br^- on the formation of THMs

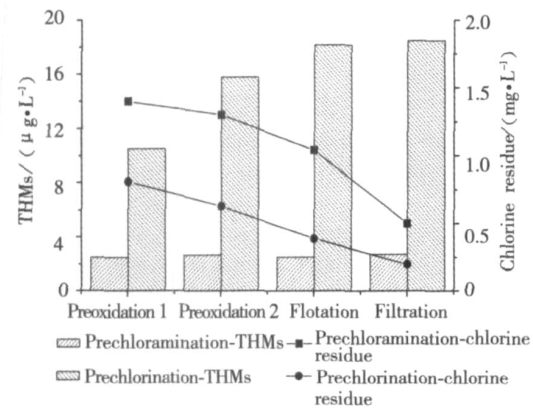


Fig. 9 The THMs formation and chlorine residue at the pilot plant process

2.4 Theory Analysis

The results of jar tests and pilot plant experiments demonstrated the advancement of prechloramination process in controlling THMs formation, especially in the water which abundant in bromide.

The following reactions occur as chlorine being dosed in water:

$$HOCl + NOM \xrightarrow{K_1} THMs \qquad (1)$$
$$K_1 = ?$$

$$HOCl + Br^- \xrightarrow{K_2} HOBr + Cl^- \qquad (2)$$
$$K_2 = 1.55 \times 10^3\ (mol \cdot L^{-1})^{-1} \cdot s^{-1}$$

$$HOCl + NH_3 \xrightarrow{K_3} NH_2Cl + H_2O \qquad (3)$$
$$K_3 = 4.2 \times 10^6\ (mol \cdot L^{-1})^{-1} \cdot s^{-1}$$

Although K_1 is unknown, many investigations[15-16] indicate that K_1 is much smaller than K_2 and K_3. While chlorine is dosed in water containing bromide, it react with bromide to form hypobromous acid first. Compared with hypochlorous species, the hypobromous species are more reactive in the formation of DBPs. Researches pointed out that chloramines do react with bromide to form bromamine, but the process is much slower than the reaction between chlorine and bromide. Also compared with hypobromous species, the bromamine yields little DBPs. At the condtion of converted chloramines was used, which is said that dose ammonia followed by chlorine as mentioned above, chlorine reacts both ammonia and bromide to form chloramine and hypobromous acid. But as illustrated in the above reactions, the reaction rate K_3 between chlorine and ammonia to form chloramines is much larger than K_2 between chlorine and bromide. It is said that in the excess of ammonia, there will be very few or no hypobromous acid formed, which cause the controlling of THMs formation.

3 Conclusions

1) The seasonal great increase of THMs is concluded to be caused by the pollution of bromide.

2) As indicated by jar tests, the increase in chloramines dosage, reaction time, Cl_2 :N, bromide concentration and decrease in pH could made the increase in THMs formation.

3) The preformed chloramines has a more advanced ability in controlling THMs formation as compared with converted chloramines, but the difficulty in prepare it restricted its use.

4) As demonstrated by the pilot plant experiments, the prechloramination process has a excellent effect on controlling THMs formation in River Huang water with high bromide, provide more chlorine residue at equivalent available chlorine dosage as compared with prechlorination process.

References:

[1] Edward A B, Geogrge P F, George C B. Disinfection Alternatives for Safe Drinking Water. New York: Van Nostrand Reinhold, 1992: 81 - 96.

[2] Seidal C J, Mcguire M J, Summers R S, *et al*. Have utilities switched to chloramines. J Am Water Works Assoc, 2005, 97(10): 87 - 97.

[3] Jafvert C T, Valentine R L. Reaction scheme for the chlorination of ammoniacal water. Environmental Science and

Technology, 1994, 26 (3): 577 - 586.
[4] Vikesland P J, Ozekin K, Valentine R L. Monochloramine decay in model and distribution system waters. Water Research, 2001, 35 (7): 1766 - 1776.
[5] Diehl A C, Speitel G E, Symons J K M K, *et al*. DBP formation during chloramination. Journal American Water Works Assocociation, 2000, 92 (6): 76 - 90.
[6] Qi Yinan, Shang Chii. Formation of haloacetic acids during monochloramination. Water Research, 2004, 38 (16): 2374 - 2382.
[7] Goel S, Bouwer E. Factors influencing inactivation of Klebsiella pneumoniae by chlorine and chloramines. Water Research, 2004, 38 (22): 301 - 308.
[8] Matthew A L, Mariñas B J. Inactivation of Bacillus subtilis spores with ozone and monochloramine. Water Research, 2003, 37 (4): 833 - 844.
[9] Norton C D, Lechevallier M W. Chloramination: Its effect on distribution system water quality. Journal American Water Works Assocociation, 1997, 89 (7): 66 - 77.
[10] Summers R S, Hooper S M, Shukairy H M, *et al*. Douglas Owe. Assessing DBP yield: Uniform formation conditions. American Water Works Association Journal, 1996, 88 (6): 80 - 93.
[11] Chang E E, Lin Y P, Chiang P C. Effects of bromide on the formation of THMs and HAAs. Chemosphere, 2001, 43 (8): 1029 - 1034.
[12] Singer P C. Control of disinfection by-products in drinking water. Journal of Environmetnal Engineering, 1994, 120 (4): 727 - 736.
[13] Carlson M, Hardy D. Controlling DBPs with monochloramine. Journal American Water Works Assocociation, 1998, 90 (2): 95 - 106.
[14] Stevens A A, Moore L A, Miltner R J. Formation and control of non-trihalomethane disinfection by-products. Journal American Water Works Assocociation, 1989, 81 (8): 54 - 60.
[15] Haag W R. Formation of N-bromo-nchloramines in chlorinated saline waters. Jolley R, editors. Water Chlorination: Chemistry, Environmental Impacts and Health Effects. Ann Arbor, Mich: Ann Arbor Science Publishers, 1980.
[16] Rook J J. Possible pathways for the formation of chlorinated degradation products during chlorination of humic acids and resorcinol. Jolley R, editors. Water Chlorination: Chemistry, Environmental Impact and Health Effects. Ann Arbor, Mich: Ann Arbor Science Publishers, 1980.