Desalination and Water Treatment 6 (2009) 1–4
www.deswater.com

Characterization of NOM and THM formation potential in reservoir source water

Liu Zhi-sheng[a*], Yin Jun[b], Liu Li[c], Yu Yu-juan[b]

[a]*School of Municipal and Environmental Engineering, Harbin Institute of Technology, 202 Haihe Road, Harbin 150090, PR China*
Tel. 0451-86282104; Fax: 0451-86282100; 86283006; email: lzs008@sohu.com
[b]*Department of Environmental Engineering, Jilin Architectural and Civil Engineering Institute, 1129 Hongqi Street, Changchun 130021, PR China*
[c]*Changchun Water (Group) Co., Ltd., 919 Dajing Road, Changchun 130041, PR China*

Received 30 July 2007; Accepted 14 September 2007

ABSTRACT

Resin adsorption technique with XAD-8 and XAD-4 was used to characterize the raw water from the Erlong reservoir in Jilin province, China. The NOM chemical composition sequences of the four organic fractions in the raw water, from high to low, are fulvic acid (FA) fraction, hydrophilic non-acid (HPINA) fraction, hydrophilic acid fraction(HPIA) fraction, and humic acid (HA) fraction. The experimental results show that FA is the main precursor of THMFP among the four organic fractions. However, HA or hydrophobic acid exhibits the highest chlorination activity in forming THMs. It is also found that the value of FI/DOC or SUVA and the specific THMFP have better positive correlation. Compared with former results, a part of these findings are different from some reports. It is implied that certain source water has a unique nature of NOM and DBPs.

Keywords: Natural organic matter; Disinfection by-products; THMFP; Chlorination activity; Fraction

1. Introduction

Reservoirs are the main sources of drinking water for many cities which are far from rivers. Natural organic matter (NOM), derived both from natural degradation of some organic substances within the ecological systems and from human activities, affects significantly many aspects of water treatment, including the performance of unit processes, application of disinfectants, and biological stability. During the disinfection process with chlorine, NOM could potentially be converted to potentially harmful disinfection by-products (DBPs). Owing to the physical/chemical properties of organic species in each specific location, their ability to form DBPs might be different [1]. The maximum contamination levels of trihalomethanes (THMs), as determined by the World Health Organization, is less than 80 µg/L. A new Water Quality Standards for Urban Water Supply regulates that chloroform is under a maximum contaminant level of 60 µg/L, was issued by the Ministry of Construction, PR China, in February 2005. Since the discovery of THMs in drinking water, studies have been directed towards methods of controlling and investigating their formation. The former approach advanced benefits of removing THM precursor and chlorination characterization.

It is necessary to understand the characteristics of reservoir source water, including organic fraction, DBPs precursors, UV absorbance, and so on, for selecting the effective water purification processes. Since the variety of NOM affects the treatability of organic matter and DBPs, the determination of NOM in source water will assist in the enhancement of removal efficiency. The objective of

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*Corresponding author.

Presented at IWA Efficient 2007, May 20–23, 2007, Jeju, Korea.

this study was to investigate the mass distribution of NOM fraction and their relationship with trihalomethanes formation potential (THMFP), and report the experience for the control of DBPs in full-scale treatment.

2. Materials and methods

2.1. Sample preparations

The raw water samples were collected from the Erlong reservoir, which provides about 70% of the drinking water for a certain city, in Jilin province, China. All samples were prepared by filtering through a 0.45 μm cellulose filter to obtain the DOM. Filtered water samples were stored in a refrigerator with temperature controlled at 4°C before chlorination and fractionation.

2.2. Fractionation

The resin adsorption technique was employed to characterize NOM availably [2–4]. In this work, the NOM in the raw water was extracted with an XAD-8 and XAD-4 resin and separated into four fractions: humic acid fraction (HA), fulvic acid fraction (FA), hydrophilic acid fraction (HPIA) and hydrophilic non-acid fraction (HPINA). Glass columns were packed with preconditioned XAD-8 or XAD-4, according to10 of the ratio of height of resin to diameter. The extraction resins were cleaned with methanol and aether, respectively.

The experimental fractionation scheme of NOM is shown in Fig. 1. Filtered raw water was first adjusted to pH 2 using 0.1 N HCl, and drawn to pass through the XAD-8 and XAD-4 resin column with a flow rate of 10 ml/min. The effluent from XAD-4 resin column was the HPINA. The XAD-4 resin column was washed out with HPIA by eluting by 0.1 N NaOH. The XAD-8 resin column was washed out with hydrophobic acid fraction by 0.1 N NaOH. The hydrophobic acid fraction was adjusted to pH 1, then supernatant fluid, that is, FA was obtained by centrifugation. Residual fraction dissolved by 0.1 N NaOH, then HA, was achieved with vacuum anhydration.

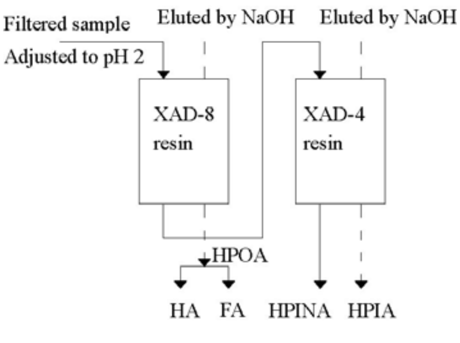

Fig. 1. Flow scheme of NOM fraction with resin technique.

2.3. THM formation potential

THMFP were determined using the uniform formation conditions (UFC) [5]. For the UFC, water is chlorinated and incubated at a pH of 8.0±0.2, with a temperature controlled at 20±1.0 , for 24±1 h. Multiple incubations were prepared with different initial chlorine concentrations. Chlorine incubations were conducted in 100 ml colormetric cylinder under the condition of encapsulation. At the end of the incubation period, the chlorine residuals were tested using a DPD colorimetric method for free chlorine. The parallel sample with a chlorine residual of 1.0+0.4 mg Cl_2/L was identified, quenched using sodium thiosulfate, preserved in the original colormetric cylinder, then prepared to measure the THM. For quality control of the experimental results, the THMFP test was performed in triplicate to minimize errors from the experimental procedure.

2.4. Analytical methods

The concentration of dissolved organic carbon (DOC) was analyzed from all water samples using a Shimadzu TOC-VOPN analyzer (Kyoto, Japan), after filtering through a 0.45 μm membrane. At least two replications of each measurement were carried out and more replications were executed in the cases where the variation between each measurement exceeded 5%. Absorbance of ultraviolet light at a wavelength of 254 nm (UV_{254}) was measured with a Shimadzu UV-1700, UV-VIS spectrophotometer with a 1 cm quartz cell. The absorbance was measured in duplicate with a coefficient of variation less than 2%. All organic fraction samples were adjusted to pH 7 by NaOH and H_2SO_4 prior to the measure of DOC and UV_{254}. Specific ultraviolet absorbance (SUVA) was calculated subsequently as the ratio between UV_{254} and DOC of the same water sample. The fluorescence intensity (FI) was determined using a fluorescence spectrophotometer (Hitachi, F-2000) at an excitation wavelength of 315 nm and an emission wavelength of 417 nm. THMs ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$) were measured by a purge and trap/Shimadzu GC-2100 gas chromatograph with an electron capture detector .

All standard solutions were prepared in deionized water (Milli-Q plus, Millipore, Molsheim, France).

3. Results and discussion

3.1. Characteristics of raw water

The distribution of different fraction of NOM is illustrated in Fig. 2. Raw water with 10.05 mg/L of DOC is typical eutrophication source water with 35.4 μg/L of *chl-a* concentration. The DOC mass distribution sequences of

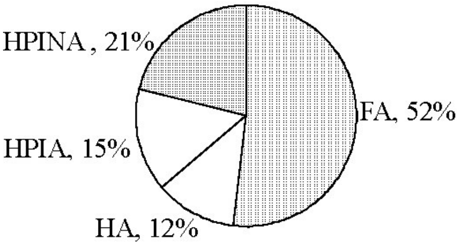

Fig. 2. Percentage distribution of NOM fractions.

the four organic fraction in the raw water, from high to low, were FA fraction, HPINA fraction, HPIA fraction, and HA fraction. It can be seen that the FA fraction of 52% was the major component in the raw water sample. In particular, hydrophobic acid fraction, namely FA fraction plus HA fraction, constituted as much as 64% of the total organic content. These results were inconsistent with the reported data from some literature, which shows the organic matter fractions were different from different raw waters.

3.2. THMFP

The THMFP of each organic fraction is shown in Fig. 3. In this study, the total THMFP was defined as the ratio between THMFP from each organic fraction and volume of the water sample. This was given an overall view of how THMs were formed in the water sample. The THMFP of FA fraction, HPINA fraction, HPIA fraction, and HA fraction was 181.7 µg/L, 19.8 µg/L, 48.2 µg/L and 54.7 µg/L, respectively. This implied that the sequence of total THMFP was different from the DOC mass distribution sequence. The main precursor of THMFP was found to be FA, simply because of its larger quantity. The HA substances has higher molecule weight in the NOM, while other fractions lower [6]. Thus, it is concluded that lower molecule weight organic matters was the main content in the raw water. The potential reason is that the ratio of small molecules to large molecules rose as eutrophication sharpened and continued [7].

The specific THMFP was the ratio between THMFP and DOC of each organic fraction. This facilitated the analysis of the reactivity of each organic fraction on the formation of THMs. As shown in Fig. 4, the specific THMFP of FA fraction, HPINA fraction, HPIA fraction, and HA fraction was 34.8 µg/mg, 9.4 µg/mg, 31.9 µg/mg and 45.4 µg/mg, respectively. It can be seen that HA was the most inactive organic precursors of THMs. It should be mentioned that, although organic fractions with larger quantity could potentially lead to more THMs formed during the chlorination, the reactivity of such organic fractions might not follow the same trend. In terms of the hydrophobic acid, the total specific THMFP of HA and FA was 80.2 µg/mg, and had the 66% of percentage. This was found to be same as other reports, which demonstrated that hydrophobic acid fraction was the greatest precursor for DBPs, particularly THMs [8].

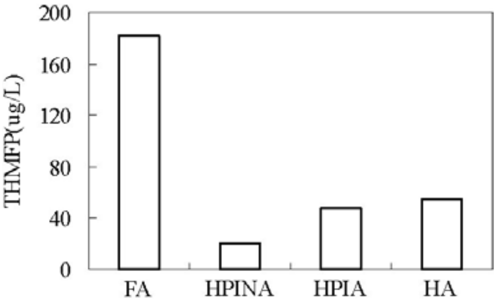

Fig. 3. THMFP obtained from each fraction.

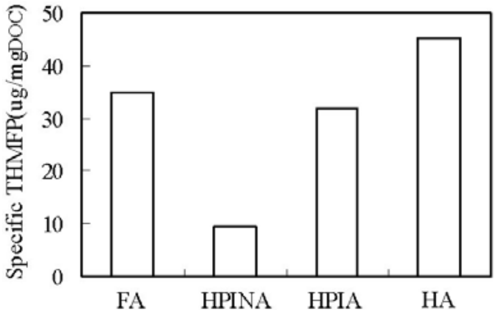

Fig. 4. Specific THMFP of each fraction.

3.3. Chlorination velocity

Fig. 5 shows the THMs formation quantity of each fraction as function of time, under the consistent condition of 6.0 mg/L DOC and initial chlorine concentration 20 mg/L. The fastest reactive velocity of HA with chlorine than others was observed. In all, maximal THMs formation time is 30 min. At a time of 15 min, the formation of HA has reached 95% of 30 min, while FA, HPIA and HPINA reached 90%, 75% and 72%, respectively. This also meant that HA and FA exhibited the highest chlorination activity in forming THMs and hydrophilic fraction including HPIA and HPINA was quite inactive in forming THMs in the chlorination process. But, the most active HPIA fraction was indicated [1]. This was possibly due to the differences in the nature of HPIA from the different water sources.

3.4. THMFP and water quality parameters

Compared to the specific THMFP, the values of SUVA and FI/DOC from each organic fraction were investigated, and results are shown in Fig. 6. The value sequences of SUVA and FI/DOC of the four organic fractions in the raw water were identical, and from high to low, were HA fraction, FA fraction, HPIA fraction and

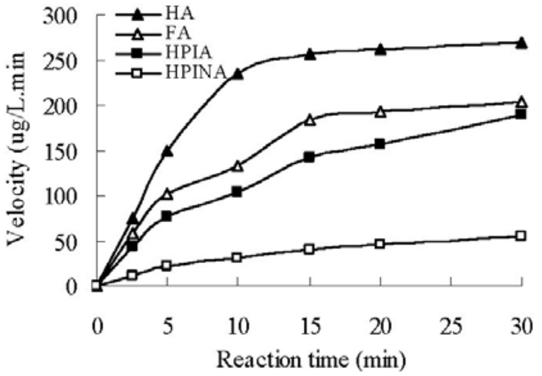

Fig. 5. THMs formation velocity of each fraction.

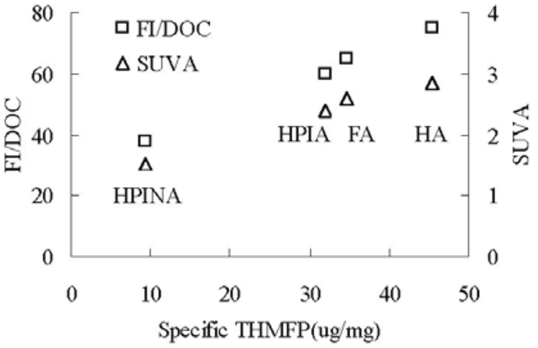

Fig. 6. Relation of specific THMs of each fraction and SUVA and FI/DOC.

HPINA fraction. This result corresponded well the order of the specific THMFP and chlorination activity. Analytical results indicated that the level of FI/DOC obtained from each organic fraction was proportional to the specific THMFP (R^2=0.9925), and that correlation coefficient of SUVA and the specific THMFP was 0.9868. This meant that chlorination activity increased as the values of SUVA and FI/DOC increased. Surrogate parameter of FI/DOC was better than SUVA slightly.

As shown in Fig. 6, the HA had the maximum FI/DOC and SUVA. Generally, the benzene ring and the double bonds of C=O, C=N and N=O can absorb UV at 254 nm, and the conjugated double bonds in the benzene compounds of organics can emit fluorescence after excited by UV [9,10]. The humic acids contain many aromatic compounds. Both the UV_{254} and FI methods are highly sensitive in qualitatively and quantitatively measuring the humic acids.

4. Conclusions

A raw water sample from a reservoir was examined for chemical composition, THMFP, DOC, FI, and UV_{254}. It was observed that the FA fraction is the dominant organic fraction in this water source. The main precursor of THMFP is found to be FA, simply because of its greater quantity. However, according to the specific THMFP and formation velocity obtained, HA or hydrophobic acid including HA and FA exhibit the highest chlorination activity in forming THMs. The experimental results show that FI/DOC or SUVA and the specific THMFP has better positive correlation. As can be observed from the above results, this finding is different from some reports. This implies that certain source water has a unique nature of NOM and DBPs. The information obtained from this work can be further employed in the design of the control techniques and management strategies for water treatment plants [11]. For example, the choice of coagulation or a disinfection technique might be applied to maximize dissolved organic matter selective removal and minimize DBPs formation.

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