Disinfection byproduct precursor removal by enhanced coagulation and their distribution in chemical fractions

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Abstract

Raw water from the Songhua River was treated by four types of coagulants, ferric chloride (FeCl_3), aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), polyaluminum chloride (PACl) and composite polyaluminum (HPAC), in order to remove dissolved organic matter (DOM). Considering the disinfection byproduct (DBP) precursor treatability, DOM was divided into five chemical fractions based on resin adsorption. Trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAFP) were measured for each fraction. The results showed that hydrophobic acids (HoA), hydrophilic matter (HiM) and hydrophobic neutral (HoN) were the dominant fractions. Although both HoN and HoA were the main THM precursors, the contribution for THMFP changed after coagulation. Additionally, HoA and HiM were the main HAA precursors, while the contribution of HoN to HAAFP significantly increased after coagulation. HoM was more easily removed than HiM, no matter which coagulant was used, especially under enhanced coagulation conditions. DOC removal was highest for enhanced coagulation using FeCl_3 while DBPFP was lowest using PACl. This could indicate that not all DOC fractions contained the precursors of DBPs. Reduction of THMFP and HAAFP by PACl under enhanced coagulation could reach 51% and 59% respectively.

Key words: trihalomethanes; haloacetic acids; dissolved organic matter; chemical fractionation; enhanced coagulation

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Introduction

As a conventional approach, coagulation plays an important role in water treatment. But traditional coagulation, which aims at turbidity removal, cannot now effectively remove the increasing levels of organic matter to protect drinking water security, especially in view of the rising concern of disinfection byproducts (DBPs). In the disinfection process, dissolved organic matter (DOM) can react with chlorine, leading to the formation of halogenated DBPs that have potential adverse effects on human health (Plewa et al., 2010; Richardson et al., 2007, 2008). As reported, reduction in natural organic matter (NOM) before disinfection can minimize the formation of DBPs, it is thus very important to increase the removal of precursors of DBPs in drinking water treatment plants. According to the Disinfectants/DBP (D/DBP) Rule of 1998 proposed by the US Environmental Protection Agency (US EPA), enhanced coagulation aimed at maximized total organic carbon removal is the best available technology to reduce DBP precursors (US EPA, 1998).

NOM is a complex mixture of various compounds with different chemical properties. To understand its removal in water treatment, a fractionation procedure was developed previously (Leenheer, 1981; Leenheer and Croué, 2003). This method separates NOM into several components according to their chemical properties (hydrophilicity-hydrophobicity). Based on this method, the behaviors of different NOM fractions have been investigated (Chow et al., 2005; Hua and Reckhow, 2007; Kitis et al., 2002; Krasner et al., 1996; Liang and Singer, 2003; Matilainen et al., 2011; Panyapinyopol et al., 2005). The results showed that the hydrophilic fractions of NOM are composed mostly of aliphatic carbon and nitrogen compounds (such as carbohydrates, sugars, and amino acids), while hydrophobic NOM primarily consists of humic and fulvic acids and is rich in aromatic carbon, phenolic structures and conjugated double bonds (Krasner et al., 1996). The hydrophobic compounds of NOM are the most important precursors for DBP formation and hydrophilic compounds may play a significant role in the formation of new compounds (Kitis et al., 2002; Liang and Singer, 2003).

Many other researchers have studied the features of

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DOM by enhanced coagulation and achieved some important results (Chang et al., 2004; Fabris et al., 2003; Marhaba and Pipada, 2000; Sharp et al., 2006; Soh et al., 2008; Yan et al., 2009). For example, Fabris et al. (2003) compared the impact of different coagulants on the removal of DOM in two reservoir waters and concluded that ferric chloride was better than alum under enhanced coagulation conditions. These studies mainly concentrated on total removal of DOM by coagulation rather than the specific removal of the fractional DOM characteristics. Soh et al. (2008) assessed the removal capacities of different fractions for three alum dosages, low (50 mg/L), operational (100 mg/L) and high (200 mg/L). The results indicated that NOM that cannot be removed by coagulation had the potential to enhance DBP formation. However, the study only detected DOC removal, not DBPs themselves. Clearly coagulation may change the properties of NOM, resulting in formation of different DBPs during subsequent chlorination or chloramination, which requires more exploration.

In this study, four different coagulants, ferric chloride (FeCl_3), aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), polyaluminum chloride (PACl) and composite polyaluminum (HPAC), were selected to study NOM treatability using the resin fractionation technique. The aim was to determine the possibility of removal of each fraction by enhanced coagulation and explore the features of DBP formation from each fraction. This included several aspects: (1) DBP formation potential of DOM in raw water and the residual water after coagulation. (2) The removal features of each fraction by conventional coagulation and enhanced coagulation. (3) The different capabilities of four coagulants in removing DBP precursors in each NOM fraction.

1 Materials and methods

1.1 Water sources

Raw water was collected from the Songhua River, which is the major drinking water source in the city of Harbin, Northeast China. The water sample was collected from raw water for a local water treatment plant in October 2008. The main water quality parameters were as follows: turbidity 20 NTU, alkalinity 75 mg CaCO_3/L , pH 8.0, DOC 4.1 mg/L, UV_{254} 0.123 cm^{-1} , and SUVA $3.0 \text{ L}/(\text{cm}\cdot\text{mg})$.

The water was alkaline and low alkalinity, which was suitable for drinking water. Although the value of DOC was relatively high compared with other source waters in China (Liu et al., 2011; Zhang et al., 2011), it was still lower than Norwegian and Australian source waters (Fabris et al., 2008).

Additionally, three-dimensional excitation-emission matrix fluorescence spectra and fluorescence intensity of DOM was studied, as shown in Fig. 1. The spectra revealed two main fluorophores: the humic acid-like fluorophore (A) and fulvic acid-like fluorophore (C)

Fig. 1 Fluorescence spectroscopy of DOM in raw water. A: humic acid-like fluorophore; C: fulvic acid-like fluorophore

(Coble, 1996). According to the results of McKnight (2001), the ratio of the emission intensity at a wavelength of 450 nm to that at 500 nm ($I_{450}/I_{500} = 35.2/21.5 = 1.6$), obtained with an excitation of 370 nm, may reflect both terrestrial and microbial inputs in the Songhua River. According to the linear regression equation (McKnight et al., 2001): $y = -0.027x + 2.1$, $r^2 = 0.85$, the raw water DOM should have 18% aromatic content.

1.2 Chemicals and materials

FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ were analytical grade. PACl (OH/Al, molar ratio: 2.4) was prepared by a base titration method carried out at room temperature (APHA, 1998). HPAC was produced by Beijing Wanshui Water Cleaning Agent Co., China, using the technique developed in our laboratory. It was prepared from PACl with high Al_{13} content and other polymeric additives including active silica. Both PACl and HPAC contained 10% Al_2O_3 .

THMs consisting of four species: chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (BF) were purchased from AccuStandard, with purity above 98%; HAAs consisting of eight species: dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), chlorodibromoacetic acid (CDBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA) and internal standard 1,2-dibromopropane were also purchased from AccuStandard, with purity above 96%; methanol, methyl-tert-butyl ether (MTBE) and hexane were HPLC grade; analytical grade anhydrous sodium sulfite was heated at 450°C for 3 hr; acidic methanol (10%) was prepared daily; water was ultrapure ($18.2 \text{ }\Omega\cdot\text{cm}$); stock solutions of chlorine ($\text{NaClO} > 9\%$) were periodically standardized with N,N-Diethyl-p-phenylenediamine spectrophotometry.

1.3 Jar tests and dosages

Jar tests were performed with 800 mL raw water, and a programmable jar testing apparatus was used with the following procedure: 30 sec of rapid mixing at 250 r/min

followed by addition of coagulant, 2 min of rapid mixing at 250 r/min, 15 min of flocculation at 40 r/min and 30 min of settling. After settling was completed, samples were collected (1 cm below water surface) and measured for turbidity (2100P, Hach, USA). Samples were filtered through a 0.45 μm cellulose acetate membrane for DOC analyses (TOC-VCPH, Shimadzu, Japan).

According to the curves of turbidity and DOC reductions with coagulant dosing, the baseline coagulation point (BC, dosage optimized for turbidity removal, residual turbidity < 1 NTU) and the enhanced coagulation point (EC, dosage optimized for DOC removal, DOC reduction was less than 0.1 mg/L with dosage increased by 0.1 mmol/L as Al^{3+} or Fe^{3+}) were determined. In order to facilitate comparison, chemical dosages were expressed as molar concentration of Fe or Al and the dosages at BC and EC are listed in **Table 1**. Here, the baseline jar tests served as a point of comparison to the enhanced coagulation conditions.

Table 1 Dosages of four coagulants at BC and EC (unit: mmol/L)

Coagulant	FeCl_3	$\text{Al}_2(\text{SO}_4)_3$	PACl	HPAC
BC	0.1	0.1	0.04	0.04
EC	0.4	0.3	0.3	0.3

1.4 Chemical fractionation

In the resin modified fractionation technique (Wei et al., 2006, 2008), non-ionic resins (Amberlite XAD-8 and XAD-4) were used and DOM in both raw water and the water after coagulation (BC and EC) were divided into five fractions: hydrophobic bases (HoB), hydrophobic neutral (HoN), hydrophobic acids (HoA), weakly hydrophobic acids (wHoA) and hydrophilic matter (HiM). The steps were as follows: Step 1, water samples were directed to an XAD-8 packed column which was then backwashed with 0.1 mol/L H_3PO_4 . The effluent was HoB and the fraction absorbed by the resin was HoN. Step 2, the first effluent from the XAD-8 column was adjusted to pH 2 by H_3PO_4 and added onto this XAD-8 resin column again. The fraction absorbed by the resin was HoA. Step 3, the second effluent from the XAD-8 column was passed through an XAD-4 resin and the fraction adsorbed by this resin was wHoA. The final effluent from the XAD-4 was HiM. The parameters of each fraction (except HoB, which was calculated based on the mass balance) were determined by

the organic carbon concentration difference between the influent and the effluent from each resin column.

1.5 Disinfection byproduct formation potential

Chlorination DBP tests were carried out in accordance with standard methods 5710B (APHA et al., 2002) and 552.3 (US EPA, 2003). The pH of the samples was kept at 7.0 ± 0.2 with phosphate buffer solution and then the stock chlorine solution was added. All the samples were kept at 25°C in the dark. At the end of the 7 days incubation period, samples had remaining residual chlorine of 3–5 mg Cl_2/L . Finally, sodium sulfite solution was added to quench residual chlorine. THMs and HAAs were measured immediately using gas chromatography (Agilent 6890N) with an electron capture detector and a capillary column (HP-5: 30 m $\times$ 320 μm $\times$ 0.25 μm).

The temperature program was (1) THMs: detector, 250°C ; injector, 200°C ; initial column temperature 35°C for 4 min, then increased to 260°C by $20^\circ\text{C}/\text{min}$, held 4 min; (2) HAAs: detector, 250°C ; injector, 250°C ; initial column temperature 35°C for 4 min, then increased to 70°C by $2^\circ\text{C}/\text{min}$. Injection volume was 1 μL for both.

1.6 Fluorescence spectroscopy

A fluorescence spectrophotometer (model F-4500, Hitachi, Japan) was used in our study. Three-dimensional spectra were obtained by measuring the emission spectra in the range from 280 to 550 nm repeatedly at the excitation wavelengths from 220 to 400 nm. A 1-cm path length quartz cell was used. Blanks of ultra-pure water were included in the correction of inner filtering and Raman scattering of the fluorescence spectra.

2 Results and discussion

2.1 Characteristics of the DOM fractions in raw water

DOC and DBPFP of each fraction in raw water were measured and are displayed in **Table S1** and **Fig. 2**. Both HAAFP and specific-HAAFP were about twice THMFP and specific-THMFP. This reflected the fact that the risk of HAAFP in raw water was greater than that of THMFP. After chemical fractionation, the HoA and the HiM were the dominant fractions as DOC masses and HoA was richer than HiM. The percentage of hydrophobic matter (HoM), as the sum of HoB, HoN, HoA and wHoA together, was 71%. According to the results summarized by Chow et al.

Fig. 2 Fractional mass distribution of DOC, THMFP and HAAFP in raw water.

(2005), this latter value was consistent with other studies in that HoM is usually the largest fraction (the range was 23%–78%). In these five fractions, THMFP ranged from 1% to 48% and HAAFP from 3% to 41%. HoM generated both more THMs (93%) and HAAs (67%), while HiM only generated less THMs (7%) and HAAs (30%). The order for THMs was HoA > HoN > HiM > wHoA > HoB and the order for HAAs was HoA > HiM > wHoA > HoN > HoB. It was worth noting that the specific-HAAFP of wHoA was the highest (Fig. 3 and Table S1). The specific-THMFP of HoN and HoA was greater than the specific-HAAFP. By contrast, wHoA and HiM had higher specific-HAAFP than THMFP. This further demonstrated that DBPFP was closely related to characteristics of DOM.

2.2 DOC removal of each fraction

As shown in Fig. 4, the residual DOC concentration decreased by almost 20% at EC compared to that at BC. According to the USEPA D/DBP Rule of 1998, for raw water with the alkalinity 75 mg CaCO₃/L, DOC removal by enhanced coagulation should be more than 35%. Here, these four types of coagulants achieved the requirement. Notably, the removal by FeCl₃ at EC reached 57%. The DOM removal efficiencies for the four types of coagulants at EC were in the order of FeCl₃ > HPAC ≈ Al₂(SO₄)₃ > PACl. The result is consistent with the finding that alum-based coagulants show better performance in turbidity removal than ferric coagulants while ferric coagulants were better in removing NOM (Fabris et al., 2003; Matilainen et al., 2010). For Al-based coagulants, HPAC was prepared to enhance the charge neutralization and adsorption-bridging ability of PACl, therefore the DOM removal efficiency by HPAC was higher than PACl.

Although HoA and HiM were still the two main fractions after coagulation, the distribution changed. The content of HoA decreased at both BC and EC, while the content of HiM was only decreased significantly at EC. For example, the removal of HoA ranged from 38% to 67% at EC and HiM ranged from 5% to 37% at EC. Also, the content of wHoA in some samples rose after coagulation. This illustrated that HoM (such as HoA and

Fig. 3 Specific-DBPFP (DBP formation per mg of DOC) of each fraction in raw water.

Fig. 4 DOC distribution of each fraction in treated water at BC and EC.

HoN) is more easily removed than HiM by coagulation. This can be explained by the mechanisms of charge neutralization and adsorption. HoM have a significantly higher charge density than HiM (Edzwald, 1993; Sharp et al., 2006), and HoM includes more high molecular weight DOM. The two aspects are beneficial to the performance of coagulants. Additionally, the residual concentration of HiM by both PACl and HPAC was lower than that of FeCl₃ and Al₂(SO₄)₃. The results indicated that the two Al-based polymeric coagulants, which enhanced the amounts of highly-charged, moderate-molar-mass hydrolysis species (especially Al₁₃) at EC, had advantages in removing HiM.

2.3 DBPFP removal of each fraction

Figure 5 presents the DBPFPs of different fractions in raw water and the water after coagulation. Similarly to the DOC removal, both THMFP and HAAFP decreased after coagulation and their removal at EC was almost 20% more than that at BC. The removal performance for THM and HAA precursors by PACl at EC was the best

Fig. 5 DBPFP distribution of each fraction in treated water at BC and EC. (a) THMFP, (b) HAAFP.

of the four types of coagulants. The residual THMFP and HAAFP concentration decreased by 40 $\mu\text{g/L}$ and 193 $\mu\text{g/L}$ from EC to BC respectively. In addition, THM precursors decreased slightly compared to HAA precursors at BC. This further reflects the fact that conventional coagulation (aimed at turbidity removal) is inefficient in removing DBP precursors, especially HAA precursors. Enhanced coagulation should be used to reduce DBPFP.

The DBPFP distribution of each fraction after coagulation was different from that in the raw water. Although HoA and HoN were still THM precursors, the proportion of HoA became higher than that of HoN after coagulation. This can be explained by the fact that HoN, some of which is THM precursors, is more easily removed by coagulation than other fractions.

HoA, the largest HAA precursor in raw water, became the third largest after coagulation. HoN became the largest HAA precursor, and HiM was the second. This was opposite to THM precursors. Although HoA, HoN and HiM were all the main HAA precursors, HoN should generate HAAs more easily than HoA, and it did so after coagulation. Perhaps this could contribute to the part competition between HoN and HoA. The two fractions were obtained by the resin adsorption method based on DOM chemical properties (hydrophilicity-hydrophobicity). It is inevitable that each fraction will include different size and molecular weight DOM. Both HoN and HoA could include two parts: as THM precursors, HoN was more easily removed than HoA; while, as HAA precursors, HoA was more easily removed than HoN. Of course, there may be another reason which needs further research. Additionally, HiM, which was hard to remove by coagulation, was still the main source of HAA precursors.

2.4 DBPFP removal of DBPs species

Three species of THM formation potential were detected (CF, DCBM, and DBCM, but not BF). The results are shown in Fig. 6a. The order of THMFP for the three species was CF > DCBM > DBCM in all the samples and the percentages were 85%, 14% and 1% respectively. This result was consistent with other studies (Deng et al., 2008; Golfinopoulos and Nikolaou, 2005). A conclusion can be drawn that the formation mechanism of THM species in the water after coagulation is the same as that in the raw water. The reductions in CF, DCBM and DBCM formation potentials were about 50%, 50% and 60% respectively at EC. There was no significant difference in the amount and species of THMs removed at EC for the four types of coagulants. This illustrated that the four coagulants had a limited capability to remove THMFP.

As shown in Fig. 6b, all eight HAAs were detected. It was found that the proportion of each species was similar in raw water and the water after coagulation. TCAA had the highest proportion (56%) in all samples, followed by BDCAA (15%) and DCAA (13%). The other five species

Fig. 6 DBPFP distributions of DBP species in treated water at BC and EC. (a) THMFP, (b) HAAFP.

had considerably lower concentrations. The removal of HAA species was slightly lower than that of THM species, except for the case of PACI as coagulant. The removals for DCAA, TCAA and BDCAA at EC were 50%, 65% and 60% respectively.

2.5 Comparison of THMFP and HAAFP at BC and EC

Figure 7 presents comparisons between THMFP and HAAFP after treatment by coagulation. The ratio in all samples was below 1. It implied that, as in raw water, the risk of HAA formation was higher than that of THM formation after coagulation. The ratio after coagulation became smaller than that in raw water, except for PACI treatment at EC, and the ratio at EC was greater than that at BC. This indicated that THM precursors (wHoA, HiM) were preferentially removed by coagulation compared to HAA precursors, and more HAA precursors (wHoA, HiM) could be removed only after removal of more THM precursors. In other words, the risk of THM formation was more easily decreased by coagulation than that of HAA formation. PACI was expected to have an advantage in reducing of

Fig. 7 Ratio of THMFP to HAAFP without fractionation in treated water at BC and EC. The dashed line represents THMFP/HAAFP in raw water.

Fig. 8 Relationship between the percentage of THMFP and HAAFP. The legend circled represents the percentage in raw water. The diagonal line is the isoline meaning THMFP% equals HAAFP%.

the risk of HAA formation.

Figure 8 shows the relationship between the percentage of THMFP and HAAFP. Apparently, HoA generated more THMs (under the isoline) and HiM generated more HAAs (above the isoline). HoM (in the top right corner) was more reactive in forming both THMs and HAAs than HiM fractions (in the bottom left corner). It is worth noting that the position of some points changed after coagulation. For HoM and HiM, the percent at EC was greater than that at BC. This suggested that EC can be used to further reduce the risk of DBP formation in the actual water treatment process. On the one hand, although both HoM and HiM were all largely removed at EC, the rest of HoM still had higher THMFP and the rest of HiM had higher HAAFP. On the other hand, the points for HoB&N after coagulation appeared above the isoline, different from the case for raw water where it appeared under the isoline. This illustrated that chemical property (hydrophilicity-hydrophobicity) of NOM changed after coagulation. In order to further reduce the risk of DBP formation, the use of water treatment technology that removes more DBP precursors needs to be strengthened, including enhanced coagulation.

3 Conclusions

Characteristics of raw water in the Songhua River were studied. Humic acid-like and fulvic acid-like materials were the two main DOM components. According to chemical fraction, it can be found that HoA and HiM were the dominant fractions. HoN and HoA were the main THM precursors, while HoA and HiM were the main HAA precursors. In raw water and the water after coagulation, CF, as the main THM species, was more than 85%, followed by DCBM, DBCM and BF. TCAA was the main HAA species followed by DCAA and BDCAA. The risk of HAA formation was higher than that of THM formation

in all samples. The removal of DBPFP at EC was higher than that at BC by almost 20%. The removal by PACl at EC was the highest, and it could reach 51% for THMFP and 59% for HAAFP. For each fraction, the amount and the distribution of DBPFP at EC differed significantly. The THMFP of HoA was much larger than that of HoN, while HAAFP of HoN became the largest. Three fractions, HoA, HoN, and HiM, should be preferentially removed to control DBPFP. For raw water like that of the Songhua River, PACl should be recommended as the most suitable coagulant.

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Supporting materials

Supplementary data associated with this article can be found in the online version.

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