



Changes in different organic matter fractions during conventional treatment and advanced treatment

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Received 15 March 2010; revised 29 July 2010; accepted 03 September 2010

Abstract

XAD-8 resin isolation of organic matter in water was used to divide organic matter into the hydrophobic and hydrophilic fractions. A pilot plant was used to investigate the change in both fractions during conventional and advanced treatment processes. The treatment of hydrophobic organics (HPO), rather than hydrophilic organics (HPI), should carry greater emphasis due to HPO's higher trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAFP). The removal of hydrophobic matter and its transmission into hydrophilic matter reduced ultimate DBP yield during the disinfection process. The results showed that sand filtration, ozonation, and biological activated carbon (BAC) filtration had distinct influences on the removal of both organic fractions. Additionally, the combination of processes changed the organic fraction proportions present during treatment. The use of ozonation and BAC maximized organic matter removal efficiency, especially for the hydrophobic fraction. In sum, the combination of pre-ozonation, conventional treatment, and O₃-BAC removed 48% of dissolved organic carbon (DOC), 60% of HPO, 30% of HPI, 63% of THMFP, and 85% of HAAFP. The use of conventional treatment and O₃-BAC without pre-ozonation had a comparable performance, removing 51% of DOC, 56% of HPO, 45% of HPI, 61% of THMFP, and 72% of HAAFP. The effectiveness of this analysis method indicated that resin isolation and fractionation should be standardized as an applicable test to help assess water treatment process efficiency.

Key words: organic matter; hydrophobic; hydrophilic; polarity; drinking water treatment

DOI: 10.1016/S1001-0742(10)60423-8

Citation: Chen C, Zhang X J, Zhu L X, He W J, Han H D, 2011. Changes in different organic matter fractions during conventional treatment and advanced treatment using resin isolation. *Journal of Environmental Sciences*, 23(4): 582–586

Introduction

Organic matter in source water has gained increasing attention worldwide. Even in well-protected source water, natural organic matter (NOM) greatly complicates and decreases the effectiveness of many treatment processes, including the performance of unit processes (i.e., oxidation, coagulation, and adsorption), the application of disinfectants, and biological stability. In addition, humic substances, a component of NOM, are strong disinfection byproduct (DBP) precursors (Singer, 1999) and directly correlate the formation of DBPs (Liu and Qi, 2010).

High organic matter concentration severely affects water quality and public health in China, particularly in relation to odor and taste. The pre-chlorination process commonly used in China produces a high concentration of DBPs (Zhou et al., 2004). The high concentration of organic materials also results in the regrowth of bacteria in distribution systems and the deterioration of biostability (Lu and Zhang, 2005). Together with pathogen inactivation, organic matter removal is one of the most important

research areas for water treatment in China.

Numerous studies have investigated organic matter removal effectiveness of different water treatment processes. Jacangelo et al. (1995) concluded that enhanced coagulation, granular activated carbon (GAC) adsorption, and membrane filtration (nanofiltration) were effective processes for NOM removal. Consequently, these processes have been considered the best available technology (BAT) for disinfection byproduct (DBP) control, as documented in the D/DBP rules. Owen et al. (1995) discussed characteristics and treatability of seven source waters, recommending enhanced coagulation, GAC, and pre-ozonation to improve NOM removal. Xie and Zhou (2002) reported that biological activated carbon (BAC) was more efficient in removing haloacetic acid (HAAs) than autoclaved GAC due to HAAs biodegradation by microbes. Chen et al. (2007) also discussed unit process efficiency and calculated total efficiency of different process combinations to select the most appropriate treatment process. Currently, investigations are being conducted to explore the components and characteristics of organic matter to determine its behavior in water and how to effectively

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remove it during treatment. Understanding the components and characteristics of organic matter will help guide the operation of water purification systems and the development of future treatment processes.

Methods were developed to ascertain basic characteristics of organic matter due to its complex components and structure. Fractionation with resins is used to divide organic matter into its constituents based on physical-chemical characteristics. Fractionation with specific resins was first developed by Leenheer (1981), who divided organic matter into six fractions with XAD-8, AG-MP-50, and Duolite A-7 resins. Malcolm and McCarthy (1992) used XAD-8 and XAD-4 resins to divide organic matter into hydrophobic, hydrophilic, and transphilic fractions which was also followed by others (Leenheer and Croue, 2003; Sharp et al. 2006). Recently, there have been some derivations of and modifications to these two basic procedures. With resins of different polarity, electric charge, and rinsing solvent, adsorbed organic matter is typically divided into hydrophilic (HPI) and hydrophobic (HPO) organic fractions. More in-depth classification is possible using other resins.

Molecular weight fractionation is another popular method to determine NOM change using high-performance size exclusion chromatography (HPSEC) (Matilainen et al., 2002) or ultra-filtration membranes (Kitis et al., 2002). Additionally, the recently developed polarity rapid assessment method (PRAM) utilizes solid-phase extraction cartridges with different sorbents to illustrate the composition of DOM present (Rosario-Ortiz et al., 2007).

This article reports the behavior of organic matter and removal mechanisms by different processes. In this study, one-step resin isolation with XAD-8 resin was chosen to fractionate organic matter into its HPO and HPI components (Galapate et al., 1999). This method was specifically selected as HPO and HPI division is theorized to represent the main constituents of organic matter in water treatment. Furthermore, greater fractionation is thought to be too complex to be utilized extensively by WTPs and also a possible source of error (Chen et al., 2008). Traditional processes, such as coagulation, sedimentation, filtration, and disinfection, and advanced treatment, were assessed by the resin fractionation method. Although DAX and DEAE resin is increasingly favored over XAD-8 resin (Peuravuori et al., 2002), we selected it for this investigation for comparison with previous studies.

1 Materials and methods

1.1 Source water and pilot plant

A modular pilot plant was established for this study and was operated continuously for two years by Tianjin Waterworks Group Co., Ltd., China. The plant had a total flux of 5 m³/hr and included reactors for pre-oxidation, coagulation, sedimentation, air floatation, filtration, ozonation, GAC filtration, and disinfection. The description and parameters of each unit process are shown in Table 1. After one year of operation, resin fractionation assays were conducted in autumn with the process combination: Pre-O₃ + coagulation-air floatation (C&AF) + filtration (FLTR) + O₃-BAC (Test 1) and in spring with the process combination: C&AF + FLTR1 + GAC; or C&AF + FLTR2 + O₃-BAC (Test 2).

1.2 Water quality parameters and analytical methods

Several water quality parameters, including dissolved organic carbon (DOC), UV absorbance at 254 nm (UV₂₅₄), and the formation potential of THMs and HAAs (THMFP, HAAFP) were chosen to assess the organic matter removal efficiency of different combinations of water treatment processes. All analytical methods were conducted according to standard methods of Ministry of Health PRC (2006) or the Standard Methods for the Examination of Water and Wastewater (APHA et al., 1995).

1.3 Isolation and fractionation of DOC

The analytical procedure for preparative dissolved organic carbon (DOC) fractionation followed Leenheer (1981). Amberlite XAD-8 resin was purified by Soxhlet extraction before isolation. After the resin was cleaned, it was packed into a separate glass column for further isolation. During the isolation process, 60 L of raw water was firstly filtered with 0.45 μm membranes to remove suspended solid and particles. The raw water was then pumped through the resin columns. Organic matter adsorbed on the resin was designated as HPO and in the leakage solution as HPI. The initial concentration of each DOC fraction was determined by a Shimadzu TOC-5000 analyzer (Japan). The contributions of the DOC fractions to DBP precursors were determined as THMFP and HAAFP.

Table 1 Process description and parameters

Process	Parameter	Note
Pre-O ₃ (PreO ₃)	1.0 mg/L addition	AZONIA ozonizer with air source
Coagulation air-floatation (C&AF)	Coagulant: FeCl ₃ 17–25 mg/L; back flow rate: 10%	Aid: Na ₂ SiO ₃ 5–9 mg/L
Filtration (FLTR)	Sand and anthracite dual media; Speed: 10 m/hr; period: 18–24 hr	Anthracite: <i>d</i> 1.0–1.2 mm, <i>H</i> 600 mm; Sand: <i>d</i> 0.5–1.0 mm, <i>H</i> 400 mm
Mid-O ₃ (O ₃)	2.5 mg/L addition	AZONIA ozonizer with air source
Granular activated carbon (GAC)	CJ15 granular activated carbon; speed: 4 m/hr; period: 7–10 days	GAC: Φ1.5 mm × 5 mm, <i>H</i> 1500 mm
Biological activated carbon (BAC)	CJ15 granular activated carbon; speed: 4 m/hr; period: 7–10 days	GAC: Φ1.5 mm × 5 mm, <i>H</i> 1500 mm; inoculated with bacteria and operated for 3 months

2 Results and discussion

2.1 Characteristics of organics removal in unit processes

Each unit process had different characteristics concerning organics removal. As illustrated in Fig. 1, the two organic matter fractions changed during the sequential use of pre-ozonation, conventional treatment, and advanced treatment with O₃-BAC. In total, the combination of these processes removed 48% of DOC, 60% of HPO, 30% of HPI, 63% of THMFP, and 85% of HAAFP.

PreO₃ has the remarkable ability to transform HPO into HPI as it oxidizes organic matter and produces byproducts containing –OH and –COOH groups, which increases HPI and decreases HPO concentrations. The PreO₃ process alone caused a 22% decrease in HPO and a 17% increase in HPI; however, this method caused only minimal distinct mineralization of DOC (7%) with a limited dosage of 1 mg/L. Both THMFP and HAAFP were greatly reduced by PreO₃ (23% and 16%, respectively).

The C&AF processes subsequent to PreO₃, however, exhibited little selectivity for the removal of hydrophobic or hydrophilic organics, with HPO and HPI removal efficiencies only 12% and 10% individually. Additionally, results indicate that although filtration insignificantly affected hydrophobic matter concentration (4% decrease), it caused a more considerable decrease in hydrophilic organics (14%). This greater decrease was attributed to biological activity in the filter. In addition, THMFP and HAAFP were reduced by 20% and 18% by these conventional processes.

The O₃-BAC advanced treatment has been applied increasingly in China in recent years to improve organic matter removal efficiency (Chen et al., 2007). Compared with pre-ozonation, the performance of mid-ozonation was very different. The decrease rate of HPO after mid-ozonation was 12%, much lower than the 22% decrease from pre-ozonation. It is interesting to note that there was no change in HPI concentration after this process. We hypothesized that the easy-oxidized constituents of organic matter were largely transformed into HPI by pre-ozonation and consequently, less remained for mid-ozonation, even at higher dosages of 2.5 mg/L. The final BAC filtration lowered the concentrations of both fractions by 29%

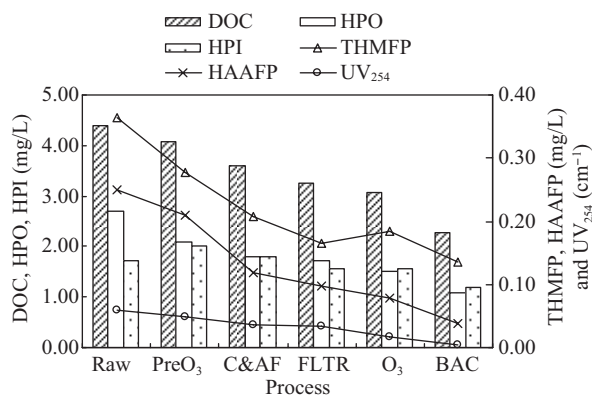


Fig. 1 Dynamics of different fractions and DBP precursors during pre-ozonation with conventional and advanced treatment processes.

(HPO) and 23% (HPI) individually after ozonation. The hydrophilic fraction was more easily biodegraded by microorganisms in the carbon filter, while the hydrophobic fraction was more easily adsorbed onto the surface of the activated carbon. Thus, the combination of O₃ and BAC maximized organic matter removal efficiency, especially for hydrophobic matter. In addition, THMFP and HAAFP were greatly decreased after the O₃-BAC process combination, 18% and 61% respectively.

The dynamics of organic matter polarity during conventional and advanced treatment processes tests are shown in Fig. 2. In total, the conventional treatment and O₃-BAC process removed 51% of DOC, 56% of HPO, 45% of HPI, 61% of THMFP, and 72% of HAAFP, similar to the results from the previous test in Fig. 1. As indicated by the results, pre-ozonation was not necessary when mid-O₃ was also applied.

Without the organic matter consumption by pre-ozonation, coagulation and air-floatation processes demonstrated much higher removal efficiencies for both HPO and HPI at 35% and 26% individually. It is interesting to note that the use of filtration increased HPO concentration by 6% due to organic matter accumulation in the filter and eventually, desorption. Microbiological degradation clearly affected HPI concentration, as evidenced by an 8% decrease. The parallel filtration and O₃-BAC processes demonstrated slightly higher organic matter removal efficacy than filtration and use of GAC. The advantage of BAC over GAC was evidenced by its more effective removal of HPI, THMFP and HAAFP.

2.2 Correlation between precursors and organic matter

As illustrated in Fig. 3, hydrophobic matter concentration had a close linear relationship with THM and HAA formation potentials, as confirmed by high *R*² values. Thus, hydrophobic matter should be the main focus of organics control in water treatment. The high correlation between HPO concentration and THM and HAA formation potential (Fig. 3a, 3b) indicates that HPO are the strongest precursor of THMs and HAAs. These results reinforce the findings of a previous study (Chen et al., 2008) in

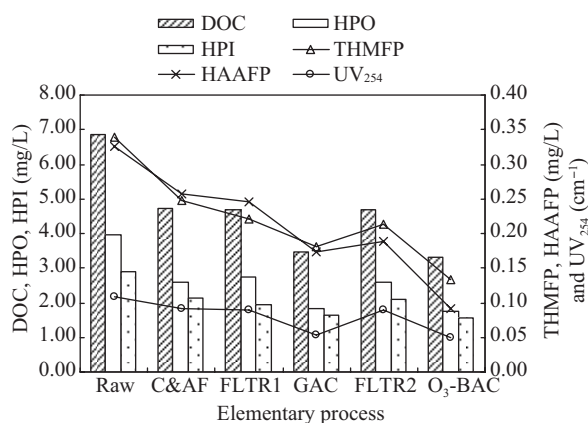


Fig. 2 Dynamics of different organic fractions and DBP precursors during conventional and advanced treatment using GAC adsorption or O₃-BAC.

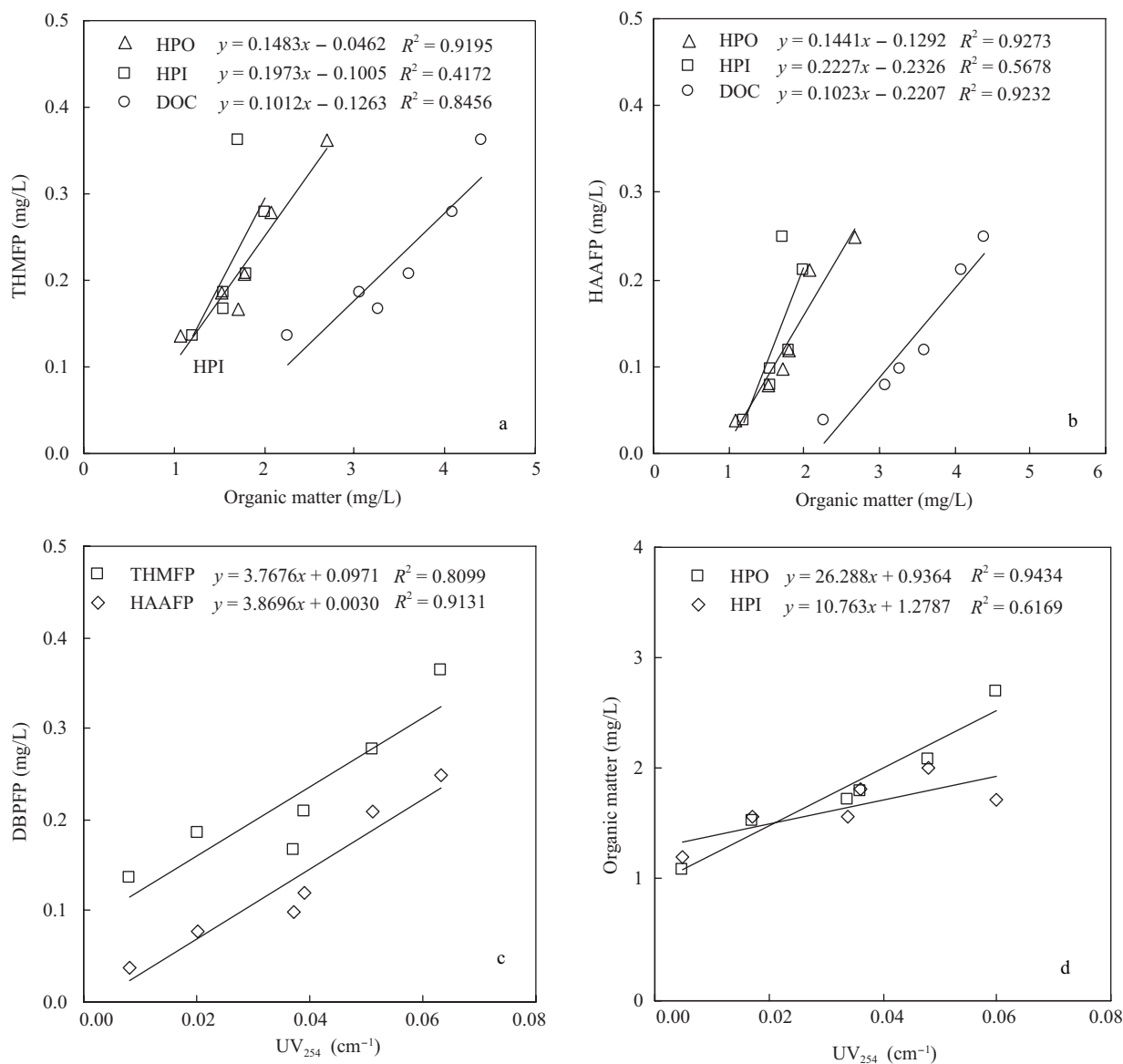


Fig. 3 Correlation between organic matter, UV₂₅₄, THMFP, and HAAFP (data obtained in Test 1, 2004, autumn).

which THMFP and HAAFP were determined for each organic fraction after resin isolation, with HPO determined a stronger precursor than HPI.

The well-known surrogate index of DBP precursors, UV₂₅₄, also closely correlates to THMFP and HAAFP. Concerning the best-fit curves for UV₂₅₄ and the DBP formation potentials, HPO had a much closer linear relationship with UV₂₅₄ ($R^2 = 0.9439$) than did HPI ($R^2 = 0.6169$). Additionally, DOC had a higher R^2 for DBPFP, which may be attributed to a high HPO concentration in all organic matter and high DBP yield of HPO.

Results from Test 1 were dissimilar to those obtained in Test 2 (Table 2). In Test 2, HPI had a marginally higher R^2 value than HPO and all fractions were more closely correlated to DBPFP than those from Test 1. By combining the data acquired from both tests, it was possible to understand seasonal variation in the correlation between organic matter concentration and precursor formation potential. The R^2 value for combined data was much lower than those for the two separate tests, indicating that organic matter

characteristics in raw water were seasonally dependent, which must be taken into account during analysis.

As demonstrated by our results, organic matter complexity, including polarity, charge density, molecular weight, and morphology, varies with the monsoonal climate in northern China. Consequently, this variation greatly influences the operation of water treatment plants located there. Autochthonous NOM, which originates from algae and other aquatic microorganisms, is a greater factor in summer and autumn. Allochthonous NOM, which originates from runoff and vegetative debris, is influenced by precipitation and vegetation. Further research on regression analysis of NOM and water quality parameters should take climate into account.

3 Conclusions

The use of resin isolation and fractionation of organic matter in water increases general understanding of NOM removal mechanisms under different water treatment

Table 2 Correlation between organic matter, UV₂₅₄, THMFP and HAAFP

Test	Time	Dependent variables	Independent variables							
			HPO		HPI		DOC		UV ₂₅₄	
			Equation	R ²	Equation	R ²	Equation	R ²	Equation	R ²
Test 1	Autumn	THMFP	0.1483x - 0.0462	0.9195	0.1973x - 0.1005	0.4172	0.1012x - 0.1263	0.8456	3.7676x + 0.0971	0.8099
		HAAFP	0.1441x - 0.1292	0.9273	0.2227x - 0.2326	0.5678	0.1023x - 0.2207	0.9232	3.8696x + 0.003	0.9131
		HPO							26.288x + 0.9364	0.9434
		HPI							10.763x + 1.2787	0.6169
Test 2	Spring	THMFP	0.0834x + 0.0081	0.9239	0.1428x - 0.0697	0.9416	0.0531x - 0.0228	0.9390	2.6989x + 0.0065	0.8288
		HAAFP	0.1503x - 0.0944	0.7693	0.0911x - 0.0211	0.8136	0.0573x - 0.0513	0.8044	3.1347x - 0.0378	0.8246
		HPO							31.634x + 0.039	0.8569
		HPI							18.245x + 0.585	0.8207
Total		THMFP	0.0757x + 0.0568	0.6204	0.1171x + 0.007	0.4621	0.0478x + 0.0299	0.5818	1.3242x + 0.1476	0.335
		HAAFP	0.1075x - 0.063	0.8675	0.1761x - 0.1517	0.7246	0.0692x - 0.1065	0.8450	2.4556x + 0.0334	0.7984
		HPO							21.782x + 0.9577	0.8364
		HPI							11.429x + 1.1943	0.7400

processes and guides the selection of best available technology. Resin isolation and fractionation should be standardized as an operational test to be used in water treatment plants.

Rather than HPI, treatment should concentrate on the removal of HPO as its concentration had a much higher linear relationship with THM and HAA formation potentials. This close correlation showed that HPO matter was the strongest precursor of THMs and HAAs and its removal and transmission into hydrophilic matter reduced the actual THM and HAA yield by post-disinfection.

Each unit process had different organic removal effectiveness. Filtration, ozonation, and BAC filtration distinctly influenced organic fractions removal. The combination of O₃ and BAC maximized organic matter removal efficiency, especially for hydrophobic organics.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 50708050) and the National Water Special Program of China (No. 2008ZX07420-005).

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