The influence of novel disinfection strategies in the removal of humic substances

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Abstract

Conventional drinking water production includes coagulation-flocculation, settling followed by sand filtration and chlorine disinfection. In order to avoid algae proliferation, pre and intermediate chlorination is usually effected. During these previous oxidation steps, water contains higher loads of organics; thus formation of chlorinated disinfection by products (DBP), such as trihalomethanes (THM), is favored. The nascent chlorine, ozone and chlorine dioxide combination generated in "CETOLAR" system presents greater oxidative power (synergy) than conventional chlorine. By the sum of oxidizers' power, this "CETOLAR" system confers greater capacity of disinfection and it is possible, with a smaller dosage, to eradicate the pathogenic germs and avoid the presence of resistant germs. However, very little is known about its effect over natural organic matter (NOM). The present paper studies the effect of such a pioneering oxidation strategy on the content, nature and reactivity to form THMs of NOM.

Keywords: Drinking water; Nascent chlorine; Humic substances, Trihalomethanes

1. Introduction

The increasing concern originated by the widespread presence of disinfection by products (DBPs) in chlorinated drinking water has driven the need of studying new treatment technologies. It is well known that chlorine reacts with natural organic matter (NOM) to form DBPs. Surface waters tend to have a significant content of humic material which is commonly rich in hydrophobic groups. Trihalomethane (THM) production capability of NOM is commonly related to dihydroxybenzene type structures [1]. When water contains higher loads of organics the formation of chlorinated DBPs, such trihalomethanes (THMs) and haloacetic acids (HAAs), is favoured [2].

Other oxidants such ozone and chlorine dioxide have been proposed as alternative oxidants in order to reduce DBPs formation. Nascent chlorine is generated in situ by electrolysis of brine. In this reaction chlorine is produced as primary reaction. Ozone and chlorine dioxide are produced as secondary reaction. This mixed oxidants system has proved to enhance bacterial removal efficiencies [3]. Ozone has a greater

disinfection effectiveness than other oxidizers whereas chlorine dioxide is a powerful oxidizer and germicidal agent which does not react with ammonia. Furthermore, it remains in its molecular form in the pH range typically found in natural waters.

The present paper presents results of the use of this alternative oxidation strategy when used in conjunction with conventional treatment. The selected water treatment plant (WTP) uses nascent chlorine as primary and secondary oxidant. Treatment includes preoxidation, coagulation-flocculation, intermediate oxidation, sand filtration and disinfection.

2. Analytical methods

pH measurements were carried out with a Crison (GLP-22) pH-meter. UV absorbance measurements were carried out in a Helios-γ (TermoSpectronic) spectrophotometer with one centimetre optical path lengths. Humic substances concentration was measured by two different procedures. First, by using two non-ionic macroporous resins in series; amberlite DAX-8 and supelite XAD-4 [4]. And second by using a weak ionic exchange resin (DEAE) [5,6]. THMs and HAA were determined by Gas Chromatography (GC)/Electron Capture Detector (ECD). For the analysis of HAA method EPA 552.3 was used. NOM characterisation was achieved by separation into hydrophobic acid (HPOA-DAX8), transphilic acid (TPHI), hydrophilic acid (HPIA-XAD4) using XAD resins. DEAE resin was used to obtain the so called HPOA-DEAE and HPIA-DEAE fractions. THM formation capability, defined as the THM formation potential (THMFP), of each fraction was studied by different standarized chlorination tests ($THMFP_{3h}$, $THMFP_{15h}$, $THMFP_F$, SDSTHMFP).

3. Results and discussion

THMs precursor content of raw water, measured as $THMFP_F$ was 367 µgTHM/L, high enough to exceed maximum contaminant level of 100 µg/L established by European Directive. SUVA value (2.4 L/mg m) denotes low to moderate aromaticity of NOM in sample. Based on UVA_{254nm} and $THMFP_F$ measurements, DEAE absorbs 72% and 92% of raw water values, respectively. Whereas, the sum of DAX8 and XAD4 extracts accounts for 57% and 77% of raw water $THMFP_F$ and UV absorbance, respectively. It is noteworthy the contribution of non-humic material to $THMFP_F$. Its contribution strongly varies depending on the used absorbent. DEAE extract accounts for most of the THMFP (for all chlorination times and conditions). Lab scale chlorination reaction test showed that within first 24 hours of reaction 85% of THM production stems from substances extractable with DEAE. DAX extracts showed less reactivity with chlorine. THM production profile of DAX8 extracts accounts for 50% of the THM formed during source water chlorination.

WTP removes up to 70% of UVA, reflecting a high reduction in aromatic structures. DOC progressively decreased throughout treatment; 1.9, 1.3 and 1.2 mg/L for raw, settled and filtered water, respectively. However, $THMFP_F$ reduction is minimal. Its

value descends from 113 µgTHM/L in raw water to 105 µgTHM/L at outlet stream. The variation in distribution of hydrophobic and hydrophilic fractions in NOM throughout the plant was determined depending on the $THMFP_F$ of the extracted NOM fractions as shown in Figure 1.
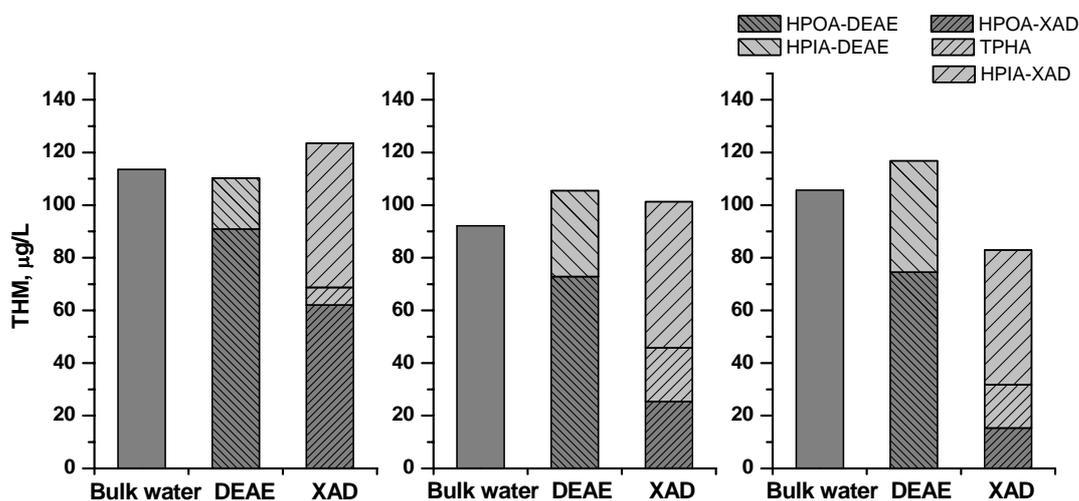

Figure 1. Contribution of NOM fractions to $THMFP_F$ along full scale WTP.

Both hydrophilic fractions (HPI-DEAE and HPI-XAD) showed similar behavior. HPI-DEAE contribution significantly increased along WTP, while HPI-XAD remained at same level. For the latest, hydrophobic substances conversion into transphilic was observed as deduced from HPO-DAX decline and increase of TPHI fraction. Similar results (not shown) were obtained when $THMFP_{3h}$, simulated plant ($THMFP_{15h}$) and simulated distribution system (SDSTHMFP) chlorination tests were applied. Ozone application is known to destroy NOM aromaticity. The ozone present in nascent chlorine system is effective in reducing hydrophobic substances while hydrophilic and neutral fractions are unaltered. This fact gains special relevance on view of the high THM formation capability shown by hydrophilic fraction.

Coagulation-flocculation was the most effective step in $THMFP_F$ removal. However, HPI fractions were not removed. In order to optimise operational conditions 96 Jar-test experiments have been systematically carried out. Independent variables were pH, coagulant type and dosage, mixing rate and water alkalinity-hardness. The latest was modified by addition of $CaCl_2$ and $NaHCO_3$ to raw water to increase alkalinity from 48.5 to 145.2 mgCaCO₃/L. Multivariable general linear models were used to explain the variance in $THMFP_F$, UVA and DOC removal. Results are summarised in Table 1. For example, for raw water, when coagulation was performed with 20 mg/L alum the average efficiency for the removal of UV absorbance was 47.1%. This is significantly different from that attained by using 40 or 60 mg/L alum. On the contrary, no statistically significant difference exists (55.3%, 55.6%) in the average removal efficiency of UV when either 40 or 60 mg/L alum is added.

Table 1. Post hoc analysis (p<0.05) for different datasets. Independent variables: AH-alkalinity and hardness, TC-type of coagulant, DC-dose of coagulant, pH. Dependent variables: percent removal for $THMFP_F$, UV_{254} and DOC. A) Raw water (RW), B) Alkalinity modified water (AMW).

A)

			$RE_{THMFP.}$ (%)				$RE_{UV.}$ (%)				$RE_{DOC.}$ (%)		
			Subgroup				Subgroup				Subgroup		
Alum	Dose	N	1	2	3	4	1	2	3	4	1	2	3
	20	8	29.3				47.1				15.7		
	40	8		40.4				55.3			17.5		
	60	8			45.8			55.6			14.1		
	pH												
	5.0	6	24.2				28.3				7.5	7.5	
	6.0	6				53.6				70.6			31.3
	7.0	6			44.3				60.6			19.1	
	8.0	6		32.0				51.2			5.3		
PACl	Dose	N											
	20	8	34.0				51.8				14.3		
	40	8		53.7*					69.3		18.0		
	60	8	49.9					64.7			11.5		
	pH												
	5.0	6	24.8				39.3				3.9		
	6.0	6		55.3				68.4				20.6	
	7.0	6		52.2				72.0				26.1	
	8.0	6		51.1				67.9			7.7		

B)

			$RE_{THMFP.}$ (%)			$RE_{UV,}$ (%)			$RE_{DOC.}$ (%)		
			Subgroup			Subgroup			Subgroup		
Alum	Dose	N	1	2	3	1	2	3	1	2	3
	20	8	18.3			39.3			1.0		
	40	8		32.1*			52.3			6.4	
	60	8	22.4					56.0*	0.1		
	pH										
	5.0	6			34.9		51.0		3.3		
	6.0	6			35.8			59.9	5.9		
	7.0	6		19.8			46.6		0.7		
	8.0	6	6.7			39.2			0.0		
PACl	Dose	N									
	20	8	35.7			37.2			0.4		
	40	8			60.9		57.0*			9.0	
	60	8		51.4		44.3					16.6
	pH										
	5.0	6	50.2			53.2				11.6	
	6.0	6	54.0			48.5				13.5	
	7.0	6	48.4			43.8			8.0	8.0	
	8.0	6	44.7			39.1			1.5		

Post hoc analysis showed that coagulation with 40 mg/L polyaluminium chloride (PACl) at pH 6 was the most effective treatment. Under these conditions process performance, in terms of DOC, THMFP and UV absorbance removal, doubled compared to that achieved in WTP (Table 2). Molecular weight distribution (MWD) studies (not shown) confirmed that higher molecular weight molecules (>10,000 Da) were preferably removed. Thus, lower MW and more hydrophilic molecules turned into main DBP source during disinfection.

Table 2. Removal efficiency (percent value, %) under optimum coagulation-flocculation-settling conditions deduced from data summarised in Table 1. Operational conditions: MI in r.p.m., DC in mg/L.

Source water	Optimum CFS conditions				Attained removal efficiencies			
	TC	MI	DC	pH	THMFP$_{15h}$	THMFP$_F$	UV$_{254}$	DOC
RW	PACl	80	40	6.0	72.7	64.2	59.7	30.92
RW	SA	80	40	6.0	61.5	56.0	73.5	34.8
AMW	PACl	80	40	6.0	59.2	78.4	57.6	10.1
AMW	SA	80	40	5.0	65.1	50.3	57.0	20.2
WTP[*]	PACl	-	20	7.9	32.4	27.5	55.0	28.8

* measured values in the full scale WTP.

In conclusion, the use of strong oxidants such ozone and chlorine dioxide affect the nature of NOM and therefore its treatability by conventional drinking water production systems. Enhancing the current coagulation flocculation process at Plant conditions would require pH adjustment to more acidic conditions. PACl used as coagulant worked best at dissimilar pH values for the removal of DOC, UV absorbance, and THM precursors. Monitoring NOM character by measuring the HPI fraction will allow operators to better control coagulant dose and pH to minimize DBP production. Sand filtration in WTP was not effective in removing THM precursors. Even more, sand-filtering increased THM formation capability of water. The use of advanced treatment technologies such activated carbon, either powdered or granulated, could aid in removing lower molecular weight organics formed during oxidation by nascent chlorine.

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