The formation and control of disinfection by-products using chlorine dioxide

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Abstract

In this study, chlorine dioxide (ClO_2) was used as an alternative disinfectant with vanillic acid, *p*-hydroxybenzoic acid, and humic acid as the organic precursors in a natural aquatic environment. The primary disinfection by-products (DBPs) formed were trihalomethanes (THMs) and haloacetic acids (HAAs). Under neutral conditions (pH = 7) for vanillic acid, more total haloacetic acids (THAAs) than total trihalomethanes (TTHMs) were found, with a substantial increase during the later stages of the reaction. In the case of *p*-hydroxybenzoic acid, the amount of THAAs produced was minimal. Raising the concentration of ClO_2 was not favorable for the control of THAAs in low concentrations of vanillic acid. ClO_2 could reduce the total amount of TTHMs and THAAs for higher concentration of vanillic acid. It was found that the humic acid treatment dosage was not significant. Under alkaline conditions (pH = 9), the control of TTHMs and THAAs for the treatment of vanillic acid was better and more economical, however, an appreciable amount of inorganic by-products were observed. Under the same alkaline condition, the control of THAA for the treatment of *p*-hydroxybenzoic acid was not beneficial and for the treatment of humic acid was not significant. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Recently municipal drinking water has become highly contaminated by human activity, requiring increased chlorination, which leads to the formation of harmful chlorine by-products, such as trihalomethanes (THMs) and haloacetic acids (HAAs). Since the detection of trihalomethanes in the 1970s by the US Environmental Protection Agency in the New Orleans La., USA, waterworks, the use of chlorine in water disinfection has been proven leading to the formation of disinfection by-products (DBPs) (Bellar et al., 1974; Rook, 1974; Oliver, 1983; Koch and Krasner, 1989; Peters et al., 1990). These compounds are produced by chemical reactions between organic compounds and the applied chlorine. These DBPs are potentially carcinogenic and teratologic substances (National Cancer Institute, 1976; Bull and Kopfler, 1991; Craun et al., 1994). Their presence in drinking water has given rise to health concerns, which have translated into regulations in several countries. This problem triggered the search for an alternative disinfectant (AWWA, 1986; Myer, 1990; White, 1992) to prevent or reduce the possibility of DBPs formation in disinfected water (Krasner et al., 1989; Arora et al., 1990). Chlorine dioxide (ClO_2) was

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investigated, as one of the promising disinfectants as a substitute for chlorine (Lykins and Griese, 1986; Narkis, 1995) for the following reasons. It is a strong disinfectant that is effective over a wide pH range (White, 1992). ClO_2 can eliminate bad odors (White, 1992; Edwards and Amirtharajah, 1993) iron and manganese in untreated water (Aieta and Berg, 1986; White, 1992). It is very successful in killing bacteria and especially most efficient in deactivating viruses. A smaller dosage and less reaction time are required for ClO_2 to produce the same disinfection effects as chlorine. The ClO_2 manufacturing system is also easy to install, operate and maintain. Because of these characteristics, ClO_2 was investigated as one of the promising substitute disinfectants for chlorine. The National Research Council (NRC, 1980) reported on the use of ClO_2 as an alternative disinfectant.

In this investigation, ClO_2 was used to treat a simulated water system containing humic acid, vanillic acid and *p*-hydroxybenzoic acid, which have been detected in natural bodies of water (Yamada and Somiya, 1979) and were found as organic precursors in the chlorination disinfection process (Rice, 1980). Our purpose was to study the disinfection effects of ClO_2 in respect to the control of disinfection by-product formation for its potential use in municipal water supplies. This provides the theoretical base for using ClO_2 as a disinfectant in waterworks in Taiwan.

2. Materials and methods

2.1. Procedure

In this DBP study, 5 ml of phosphate buffer solution, the proper amount of ClO_2, and organic precursors (humic acid, vanillic acid, *p*-hydroxybenzoic acid) under controlled parameters, were added to each BOD bottle reactor with de-ionized water and kept at 20°C in an incubator. This mixture was sampled at different time intervals over a total of 7 days. Three bottles were collected for analysis. The samples were immediately analyzed for ClO_2 residual concentration. A 10 mL portion from the 0.2 μm filtrate was collected to analyze the inorganic DBPs (Cl^-, ClO_2^-, Br^- and ClO_3^-) using ion chromatography (DIONEX, series 4500, column AS-12A, 4 mm (10–12), P/N 46034). In the remaining samples, 1 g of $Na_2S_2O_3$ was added to terminate the reaction. One portion of the sample was used to determine the amount of dissolved organic carbon (DOC) and UV absorption analysis.

The THMs sample was prepared in a 40 ml brown glass bottle (with a Teflon ring and screw-on cap) with 100 mg of NH_4Cl as the preservative. Water was then added to the above solution to fill the bottle. Samples were capped with Teflon-lined seals, returned to the

Table 1
The parameters in DBPs experiment

Parameter		Unit
Organic acids	5, 10, 20	mg-DOC/L
pH	$7 \pm 0.5, 9 \pm 0.5$	unit
Temperature	20	°C
ClO_2	15, 30	mg-ClO_2/L
Reaction time	0–168	h
Analysis	DOC, ClO_2, ClO_2^-, ClO_3^-, Cl^-, THMs, UV_{254}	

laboratory in a cooler and stored in a cold room until they were analyzed. The analytical methods followed the EPA 524.2. Samples were adjusted to pH 4.5 in the field and extracted with normal pentane, containing dibromomethane and 1,2-dibromoproane as the internal standards. The THMs were analyzed using a HP5890II plus gas chromatograph equipped with an electron capture detector (GC–ECD), a one-column injector and a J&W DB-5 capillary column. The HAAs water samples were prepared by adding 150 mL NH_4Cl per 100 ml of the sample with the pH adjusted to below 0.5. Samples were extracted with methy-tert-butylether (MTBE) esterized using diazomethane and analyzed using GC–ECD based on EPA standard 552.2 (see Table 1).

2.2. Quality control

All samples were collected in duplicate with control samples included for all-target analytes. All DBPs methods incorporated surrogate internal standards and quantification was based on response factors established by multi-level calibration with fortified samples analyzed under identical conditions. For the THMs, raw water samples (matrix spikes; $n = 11$) were analyzed at a fortification level of 5 μg/L (chloroform = 25 μg/L). The overall recovery was $98.3 \pm 2.7\%$. The HAAs method precision was estimated at ±20%. The mean recovery of HAAs was typically >92% as estimated from the recovery of the added MBBA internal standard. DBPs identified by GC–ECD were confirmed by GC–MS.

3. Results and discussion

3.1. Effect of organic acid species

3.1.1. Low dosage of ClO_2 for treating low DOC in neutral solution

By comparing the unit consumption of ClO_2 by DOC, TTHMs and THAAs in Table 2, the amount of decomposition products from the large molecular, humic acid, was much greater than that from vanillic acid and *p*-hydroxybenzoic acid. A possible reason is that the

humic acids' various functional groups, such as hydroxyl group (R–OH), carbonyl (–CO), carboxyl (–COOH), phenolic and quinoid groups react easily with ClO_2.

3.1.2. Low dosage ClO_2 for treating of high DOC in neutral solution

In Table 3, the unit consumption of ClO_2 for DOC was greater in the case of *p*-hydroxybenzoic acid than with vanillic acid. The formation of TTHMs and THAAs was reversed, indicating an increase for vanillic acid and the decomposition products from *p*-hydroxybenzoic acid reacting easily with ClO_2. The unit con-

sumption of ClO_2 per unit of DOC in humic acid was much greater in the case of vanillic acid, however the amounts of TTHMs and THAAs were much less than that in vanillic acid. This indicates that more ClO_2 is required to break down its large structure. TTHMs reformed after 16 h of reaction in vanillic acid, indicating that TTHMs can be controlled through reaction time.

3.1.3. High dosage of ClO_2 for treating high DOC in neutral solution

In Table 4, The consumption of ClO_2 was greatest for humic acid and the removal ratio of DOC was the

Table 2
Treatment of organic acids with ClO_2 (DOC = 5.0 mg/L, ClO_2 = 15.0 mg/L, pH = 7)

	Vanillic acid	*p*-Hydroxy benzoic acid	Humic acid
ClO_2/DOC[a]	3.9	4.9	4.7
THM, μg/L	2.0	2.6	3.1
TTHMs/DOC[b]	0.91	1.95	1.47
THAAs, μg/L	2.8	4.4	16.0
THAAs/DOC[c]	1.28	3.31	7.53
Major products[d]	$CHCl_3$ and TCAA		

[a] ClO_2 consumed/DOC removal.
[b] Final amount of TTHMs/DOC removal.
[c] Final amount of THAAs/DOC removal.
[d] Major products of TTHMs and THAAs.

Table 3
Treatment of organic acids with ClO_2 (DOC = 10.0 mg/L, ClO_2 = 15.0 mg/L, pH = 7)

	Vanillic acid	*p*-Hydroxybenzoic acid	Humic acid
ClO_2/DOC[a]	1.60	2.05	1.89
TTHMs, μg/L	4.8	3.7	2.8
TTHMs/DOC[b]	0.76	1.00	0.62
THAAs, μg/L	69.2	4.1	27.1
THAAs/DOC[c]	11.06	1.10	6.11
Major products[d]	$CHCl_3$ and TCAA		

[a] ClO_2 consumed/DOC removal.
[b] Final amount of TTHMs/DOC removal.
[c] Final amount of THAAs/DOC removal.
[d] Major products of TTHMs and THAAs.

Table 4
Treatment of organic acids with ClO_2 (DOC = 10.0 mg/L ClO_2 = 30.0 mg/L, pH = 7)

	Vanillic acid	*p*-Hydroxybenzoic acid	Humic acid
ClO_2/DOC[a]	1.74	2.22	7.84
TTHMs, μg/L	4.4	3.6	3.9
TTHMs/DOC[b]	0.65	0.51	1.79
THAAs, μg/L	48.0	2.3	37.1
THAAs/DOC[c]	7.03	0.33	17.11
Major products[d]	$CHCl_3$ and DCAA		

[a] ClO_2 consumed/DOC removal.
[b] Final amount of TTHMs/DOC removal.
[c] Final amount of THAAs/DOC removal.
[d] Major products of TTHMs and THAAs.

least. This suggested that humic acid has a larger structure than the others acids and it cannot be destroyed easily. The production of THAAs was greater in the case of p-hydroxybenzoic acid. This could be attributed to the reaction of its functional groups on the structure or its middle products with ClO_2. By considering the structures of vanillic acid and p-hydroxybenzoic acid, the presence of activating group, o-methoxy group ($–OCH_3$) in vanillic acid renders it to be more active in reaction with ClO_2 than p-hydroxybenzoic acid under this condition. In addition, the low concentration of TTHMs and THAAs from p-hydroxybenzoic acid favors the control of by-product formation.

3.1.4. Low dosage of ClO_2 for treating high DOC in alkaline solution

In an alkaline solution, the consumption of ClO_2 by the three organic acids and the production of TTHMs were similar, as shown in Table 5. In the formation of THAAs, vanillic acid produced a greater amount than the other two acids, and with a different trend, which indicates the difficulty in controlling THAAs formation.

3.2. Influence of ClO_2 dosages

3.2.1. Various dosages of ClO_2 in treating low DOC in neutral solution

The formation of THAAs from vanillic acid was faster and with greater amounts under a high dosage of ClO_2. This shows unfavorable control of THAAs formation using vanillic acid. In the case of p-hydroxybenzoic acid, there was a high residual concentration of ClO_2. Increasing the ClO_2 dosage increased the formation of TTHMs and THAAs. The residual percentage of humic acid with a high dosage of ClO_2 was lowered, but the residual percentage of DOC was higher, indicating the increased decomposition of the humic acid molecular structure by the stronger oxidizing power of ClO_2 at higher doses. Further reaction under these conditions produced more intermediates without removing the DOC.

3.2.2. Various dosages of ClO_2 for treating high DOC in neutral solution

Under this condition, a higher dosage of ClO_2 favored the oxidation reaction in this system. The final consumption of ClO_2 at a higher dosage was greater

Table 5
Treatment of organic acids with ClO_2 (DOC = 10.0 mg/L, ClO_2 = 15.0 mg/L, pH = 9)

	Vanillic acid	p-Hydroxybenzoic acid	Humic acid
ClO_2/DOC[a]	1.22	1.29	2.50
TTHMs, µg/L	3.0	2.5	2.6
TTHMs/DOC[b]	0.44	0.36	0.74
THAAs, µg/L	46.7	7.9	26.2
THAAs/DOC[c]	6.3	1.1	7.6
Major products[d]	$CHCl_3$ and DCAA		

[a] ClO_2 consumed/DOC removal.
[b] Final amount of TTHMs/DOC removal.
[c] Final amount of THAAs/DOC removal.
[d] Major products of TTHMs and THAAs.

Table 6
Effect of increasing ClO_2 on treatment

	DOC, mg/L	DOC removal, %	ClO_2 consumed, %	TTHMs, µg/L	THAAs, µg/L	Major product of HAAs
Vanillic acid	5.0	Increased	Reduced	Reduced	Increased	TCAA
	10.0	Increased	_[b]	_[a,b]	Reduced	_[c]
p-hydroxy benzoic acid	5.0	Increased	Reduced	Increased	Increased	TCAA
	10.0	Increased	Reduced	_[b]	_[a,d]	_[c]
Humic acid	5.0	Reduced	Increased	Reduced	_[b]	TCAA
	10.0	Increased	_[a]	Reduced	Reduced	_[c]

[a] Different trends of formation.
[b] Insignificant effect.
[c] TCAA as the major product at low dosage, DCAA as the major product at high dosage.
[d] Higher than which at low dosage in the former stage, lower in the later stage.

Table 7
Effect of ClO_2 treatment in alkaline solution ($ClO_2 = 15.0$ mg/L, DOC $= 10.0$ mg/L, pH $= 9$)

	DOC removal	ClO_2 consumed	TTHMs formed	THAAs formed	Major product of HAAs
Vanillic acid	$-^b$	Increased	Reduced[a]	Reduced	DCAA[c]
p-Hydroxybenzoic acid	Increased	$-^b$	Reduced	Increased[a]	DCAA[c]
Humic acid	Reduced	$-^b$	Reduced	$-^b$	DCAA[c]

[a] Different trends of formation in neutral and alkaline solutions.
[b] Insignificant effect.
[c] TCAA as the major product in neutral solution.

than that at a lower dosage. The removal percentage for DOC and concentration of chlorate anion were much higher. To a lesser extent, the concentrations of chlorite and chloride anions were also higher.

Table 6 summarizes the results, indicating that increased dosages of ClO_2 increase the DOC removal percentage, decrease the ClO_2 consumption and the formation of TTHMs. The major product from a low concentration of organic acid solution was TCAA, but not DCAA, and the situation was reversed for higher acid concentration.

3.2.3. Low dosage of ClO_2 for treating high DOC under different pH values

Using either a phosphate or boric acid buffer solution with vanillic acid with ClO_2 to control the treatment pH, the resulting for DOC removal was better in an alkaline solution than in a neutral solution. The formation of TTHMs and THAAs was substantially reduced with an almost equal quantity of ClO_2. However, the formation of chlorite and chlorate anions was much higher than with a lower dosage. The alkaline solution did not control the formation of THAAs from p-hydroxybenzoic acid. With regard to ClO_2 consumption, DOC removal, formation of TTHMs and THAAs, there was little difference for humic acid reactions in alkaline or neutral solutions.

Table 7 shows that the pH influence was more pronounced for TTHMs in the case of vanillic acid. The production of THAAs from p-hydroxybenzoic acid was more pronounced and concentrated. For humic acid, pH provided almost no influence on the formation of TTHMs and THAAs.

4. Conclusions and suggestions

Under the conditions of pH 7 and 9, DOC between 5 and 10 mg/L and a chlorine dioxide dosage between 15 and 30 mg/L (higher dosage than the normal operation conditions (0.1–1 mg ClO_2/L) to simulate the dosage after a rainstorm). The formation of TTHMs was

around 1.2–10.2 μg/L and THAAs, 2.3–69.2 μg/L from the ClO_2 reactions with vanillic acid, p-hydroxybenzoic acid and humic acid in water. According to the experimental results, ClO_2 is a recommendable alternative disinfectant.

Compared with the control factors for DBPs formation, overall, there was no relationship between pH and ClO_2/DOC, but the result indicate that higher pH is favorable for the removal of humic acid with large molecular weight. Lower pH was favorable to the removal of vanillic acid and p-hydroxybenzoic acid with small molecular weight. Otherwise in the formation of DBPs, lower pH reduced TTHMs production, but increased the HAAs and TOX production. Increased ClO_2 dosage increased the ratio of DOC removal and TTHMs, THAAs all increased. It was suggested that a higher ClO_2 dosage increased the chance of reaction with activating groups (–OH, –OCH$_3$) on the structure of the organic precursors.

In the study of influence by organic precursors, the concentration of organic acids and the ratio of DOC removal were increased at higher organic concentrations. The formation of TTHMs and THAAs, which were transformed from unit DOC consumption (TTHMs/DOC, THAAs/DOC), was also increased. The possible reason is that ClO_2 only breaks down large molecular structures into smaller structures. The above phenomenon is encouraging in humic acid reactions. According to these experiment observations, the reaction occurred fast during the initial 24 h and a certain level of DBPs was obtained. After 24 h, the greater the reaction time, the greater the production, but the level of increase was not great. This phenomenon will supply some operational options at the water treatment facilities.

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