Reduction of Low-MW Model Compounds by Ozonation and O_3/UV Processes

E. E. Chang[1]; P. C. Chiang[2]; and I. Shu Li[3]

Abstract: In this investigation, the low-molecular-weight organic matters, such as resorcinol, phloroglucinol, and *p*-hydroxybenzoic acid, were selected as organic precursors during the ozonation and chlorination processes. The research work focused on evaluating the effects of hydroxyl radical and ozone molecule on the reduction of organic precursors and disinfection by-products (DBP) formation, and assessing the carcinogenic risk with respect to DBP formation potentials between ozonation and O_3/UV processes. The two-stages ozone decomposition model, $[O_3]=[O_3]_0\{Fe^{-K_1\cdot t}+(1-F)e^{-K_2\cdot t}\}$, was developed throughout this investigation. In addition, a linear correlation between alkalinity and hydroxyl radical was found in the course of ozonation process. The destruction of organic precursors by hydroxyl radical exhibits better performance than that by ozone. According to the risk assessment on the ozonation process, water samples treated by the O_3/UV and O_3 (pH 5) process exhibit the lower risk. Therefore, both the O_3/UV and ozonation processes with proper operation can reduce the organic precursors, thereby providing safe drinking water.

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CE Database subject headings: Risk management; Ozonization; Organic matter; Chlorination.

Introduction

In conventional water treatment, the use of chlorine for disinfection is quite popular in the world. Residual chlorine in the finished water is essential to ensure the safe drinking water without microorganism contaminants in the water distribution system. However, chlorine reacts with natural organic matters (NOMs) in water generating disinfection by-products (DBP). Among these DBP, trihalomethanes (THM) and haloacetic acids (HAA) are commonly found and investigated, which have been confirmed to be carcinogenic to human beings.

The dominant organic precursors of THM formation in the water environment would be aquatic NOMs, mainly consist of humic substance (Boyce and Hornig 1983; Rook 1976). However, aquatic humic substances are complicated by its uncertain chemical structure. Many studies have focused on the reaction of chlorine with simple organic species in humic substance. It had been reported that aliphatic carboxylic, hydroxybenzoic acid, phenol, and pyrrole nitrogen derivatives were the main functional groups observed in the model compounds such as resorcinol, phloroglucinol, and *p*-hydroxybenzoic acid (Richardson et al. 1999; Boyce and Hornig 1983). Moreover, these simple organic matters are characterized as low-molecule DBP precursors, which are not effectively removed by the traditional water treatment processes (Chang et al. 2005).

In order to reduce the THM and HAA formation in the chlorination process, ozonation process could be introduced prior to the chlorination process for the purpose of reducing DBP precursors. Recently, ozone and other advanced oxidation processes (AOP), such as O_3/UV process, have been investigated to reduce total organic carbon (TOC) concentration and trihalomethane formation potential (THMFP) in source water (Amirsaedari et al. 2000; Chin and Bérubé 2005). Ozonation process is caused by its autocatalytic self-decomposition and other complex reactions including direct (ozone) and indirect (hydroxyl radical) ozone reactions, which are affected by different pH levels (Westerhoff et al. 1998; Daniel et al. 1999; von Gunten 2003). At high pH, ozone reacts with hydroxyl ions (OH^-) as a catalyst and yields many kinds of free radical such as $\cdot OH$, $O_2^-\cdot$, and $HO_2^-\cdot$, etc., which is also called the indirect ozonation. However, there are inhibitors including *tert*-butanol, *p*-chlorobenzoate, carbonate, and bicarbonate ions, which would limit and inhibit the hydroxyl radical formation resulted in reducing the performance of ozonation (Jans and Hoigne 1998; Fernando 2004). The mechanism of hydroxyl radical formation in the O_3/UV process can be expressed as follows (Mirat and Vasistas 1987):

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + h\nu \rightarrow 2(\cdot OH)$$

On the other hand, many studies were also conducted to investigate the disinfection by-products formation during the ozonation process including aldehyde, ketones, ketoaldehydes, carboxylic acids, also acids, keto acids, hydroxyl acids, esters, and alkanes (Miltner et al. 1992; Schechter and Singer 1995; Richardson et al. 1999). Among these by-products, aldehyde is mostly concerned and investigated because of its harmful and carcinogenic to human beings.

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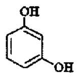
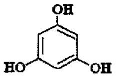
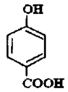
Table 1. Summary of the Physical/Chemical Properties for Organic Compounds

Organic Compounds	Resorcinol	Phloroglucinol	*p*-hydroxybenzoic acid
Molecular Formula	$C_6H_6O_2$	$C_6H_6O_3$	$C_7H_6O_3$
Molecular Weight	110.11	126.11	138.12
Structure			
Boiling Point (°C)	280	-	211
Melting Point (°C)	177	218.5	214.5
Density/Specific Gravity	1.27	1.46	1.44
Dissociation Constants	pK = 9.30	pK = 8.45	pK = 4.54
Octanol Water Partition Coefficient	$pK_{ow} = 0.80$	$pK_{ow} = 0.16$	$pK_{ow} = 1.58$
pH	5.2	-	2.4
Solubility	0.717 g/L	10.6 g/L	5 g/L
Vapor Density (air = 1)	3.79	4.3	4.8
Vapor Pressure (mmHg)	4.89×10^{-4}	1.6×10^{-4}	8.2×10^{-5}
Produced Company	ACROS	ACROS	ACROS

Reference: U.S. National Library of Medicine. http://toxnet.nim.nih.gov

Therefore, the objectives of this research were intended to (1) determine the hydroxyl radical formation in ozone and O_3/UV processes, (2) evaluate the effects of hydroxyl radical and ozone molecule on the reduction of organic precursor and the removal of DBP formation concentration, (3) understand the inhibition of alkalinity on indirect ozonation process and (4) assess the difference and carcinogenic risk in DBP formation during chlorination process followed by the ozonation or O_3/UV processes. In this investigation, the low-molecular weight organic matters, such as resorcinol, phloroglucinol, and *p*-hydroxybenzoic acid, were selected as organic precursors with high DBP formation potential during the ozonation and chlorination processes.

Materials and Methods

Sample Preparation

The characteristics of the selected model compounds including resorcinol (R), phloroglucinol (P), and *p*-hydroxybenzoic acid (PHBA) are listed in Table 1. The experimental synthetic water was composed of TOC 3.0±0.3 mg/L for R, P, and PHBA and were prepared with de-ionized water (Milli-Q SP). All chemicals for experimental analysis were prepared with de ionized water (Milli-Q SP).

Experimental Procedures

A glass reactor with an operation volume 5.0 L and free space 0.5 L was employed for ozonation process shown in Fig. 1. It was equipped with a water jacket to maintain a constant temperature, 25 °C. Ozone was generated by bubbling oxygen in an ozone generator (Model SG-01A, Sumitomo, Tokyo, Japan).

In the ozonation experiments, ozonated water was first prepared. Five liters of water was placed in the reactor and controlled at 25 °C. Ozone gas was then introduced into the water through a bubble diffuser at bottom of the reactor for 2 h until reaching an equilibrium concentration. The saturated ozone concentration in aqueous solution is approximately 18 mg/L. By adding the selected compounds of alkalinity and different pH levels changes the experimental conditions (pH 5, 7, and 9) and maintains 40 min reaction time to determine TOC, UV_{254}, and aldehyde concentration. An additive of alkalinity in ozonation is prepared by $NaHCO_3$ at 60 mg/L as $CaCO_3$. In the preliminary test, the selected compounds is substituted for blank water in the experiment and takes sample with specific reaction time until 40 min to determine concentration of alkalinity, dissolved ozone, hydroxyl radical, and hydrogen peroxide.

Chlorination process is to evaluate the chlorine demand and

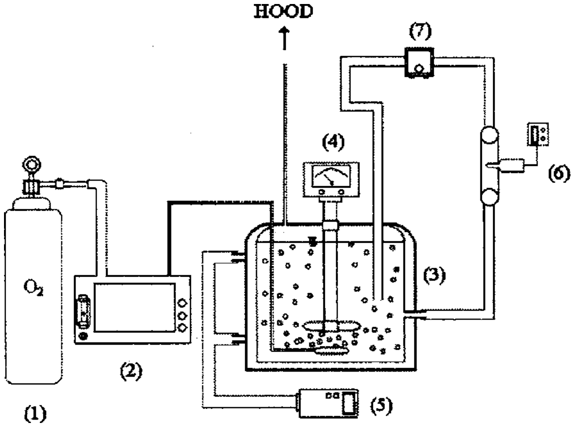


Fig. 1. Experimental apparatus of the ozone batch reactor: (1) oxygen cylinder; (2) ozone generator; (3) batch reactor; (4) 6-bladed-disk turbine; (5) thermostat; (6) pH meter; (7) pump

chlorination by-products formation in the chlorination followed by the ozonation process. A 7 days chlorine demand study was introduced by 10 mg/L chlorine dose to determine the chlorine consumption, THMFP, and chlorinated haloacetic acid formation potential. Throughout these chlorination experiments, all samples were chlorinated by 13% free chlorine (sodium hypochlorite) stock solution and add phosphate buffer (pH 7.0). Samples were chlorinated in 300 mL glass bottle and kept headspace free in the dark at room temperature (25±2°C) until 168 h.

Analytical Methods

Dissolved ozone concentrations were determined by the indigo method (method 4500-O_3, Standard Method, 19th Ed.). The TOC analysis (O. I. Analytical) was done by the UV-persulfate technique using the infrared carbon dioxide analyzer and calibrated with the potassium hydrogen phthalate standard. The UV_{254} were analyzed by UV-visible spectrophotometer (UV-1601, SHIMADZU) after filtering through a 0.45 μm filter. The determination of hydrogen peroxide was performed by a spectrophotometric method using N,N-diethyl-*p*-phenylene-diamine (Bader et al. 1988). The hydroxyl free radical is analyzed by a fluorometric method (Karin and Stefan 2002). Chlorine concentration was determined by DPD titration methods. All analyses, unless otherwise noted, were performed according to the 19th Ed. of the standard method.

Aldehyde including formaldehyde, acetaldehyde, glyoxal, and methyl glyoxal were derivatized to the corresponded oximes by *o*-(2,3,4,5,6 penta-fluorobenzyl)-hydroxylamine, which were microextracted with hexane and then analyzed in a GC/ECD system (Trace GC). THMs were analyzed in a GC/ECD system with purge and trap injection (HP 6890 series). The column in GC is a fused silica capillary column (Method 6232, Standard Method, 19th Ed.). HAAs were determined by a liquid-liquid extraction procedure (extracting with methyl tert-butyl ether) in a GC/ECD system, in accordance with USEPA Methods 552.2.

Results and Discussion

This study of ozonation and O_3/UV processes is divided into two phases. The preliminary test was performed to investigate the effects of hydroxyl radical and alkalinity on ozonation. Further, this study was focused on ozonation (O_3/UV) of organic precursors and ozonation by-products formation.

Ozonation Process at Different pH Levels

In a batch reactor, ozonation mechanism changes at different pH levels. At pH 5 (acidic condition), ozone self-decomposition reaction is the predominant reaction. This reaction mechanism may be described by the first-order model (Slawomir et al. 1999) shown in the following equation, and is called direct reaction:

$$-r_{O_3} = \frac{d[O_3]}{dt} = K_D[O_3] \tag{1}$$

At pH 7 (neutral condition) and pH 9 (basic condition), ozone decomposes rapidly to form hydroxyl radical, and is called indirect reaction.

In Fig. 2, it was observed that ozone decomposition rate increases with increasing pH. There are more hydroxyl ions (OH^-) at high pH, which promotes ozone decomposition reaction to form hydroxyl radical (Staehelin and Hoigné 1982). At pH 5, ozone self-decomposition reaction results in high ozone concentration. Further, the highest ozone decomposition rate is at pH 9 and the order of ozone decomposition rate at different pH levels is $O_3(\text{pH } 9) > O_3(\text{pH } 7) > O_3(\text{pH } 5)$.

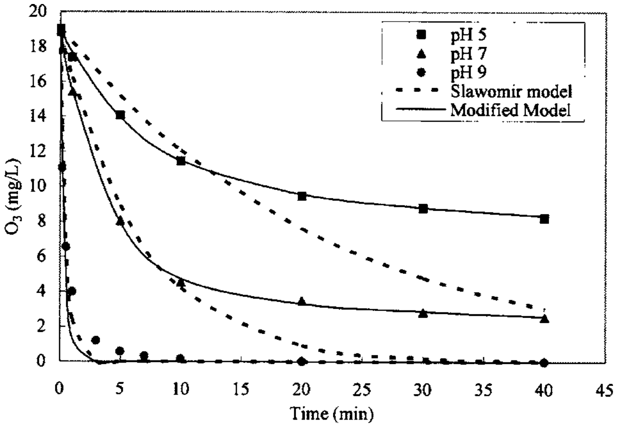


Fig. 2. Ozone decomposition and predictive decay model at different pH levels

As shown in Fig. 2, the ozone decomposition reaction may be divided into two stages at pH 5, 7, and 9. Ozone decomposes fast in the first stage (rapid reaction), but the decomposition curve trends smoothly in the second stage (slow reaction). According to the Slawomir and co-workers study (1999), the theory of ozone decomposition reaction follows the first-order model, but the simple kinetics equation [Eq. (1)] does not completely describe the ozone decomposition in the both stages. The kinetic constants of the both stages are obviously different as indicated by the slope of the curve shown in Fig. 2. The designation K_1 and K_2 represents the kinetics constants for the rapid and slow reactions in this study, respectively. In order to mathematically model the experimental data of ozone decomposition reaction in two stages, the ozone decomposition reaction was modified as

$$[O_3] = [O_3]_0\{Fe^{-K_1 t} + (1 - F)e^{-K_2 t}\} \tag{2}$$

where $[O_3]$=ozone concentration at time t (mg/L); $[O_3]_0$=initial ozone concentration; F=fraction of the ozone consumption attributed to rapid reaction; K_1=first-order rate constant for the rapid reaction (min^{-1}); and K_2=first-order rate constant for the slow reaction (min^{-1}). The parameters F, K_1, and K_2 were determined by nonlinear regression software (SYSTAT 5.01). Because the almost ozone decomposes in the rapid reaction at pH 9, the difference between rapid and slow reactions is insignificant. Therefore, the fraction of the ozone consumption attributed to the rapid reaction, F, at pH 9 is equal to 1, which indicates that there is only K_1 rate constant existed in the modified model.

The kinetic constants for these two stages at pH 5, 7, and 9 are listed in Table 2. The higher correlation coefficients (R^2) shown in Table 2 indicate that Eq. (2) expresses the ozone decomposition reaction very well. Because the ozone consumption lacks the slow

Table 2. Ozone Decomposition Constant for Parallel First-Order Reaction at Different pH Levels

pH	F	K_1	K_2	R^2
5	0.534	0.005	0.158	0.999
7	0.787	0.256	0.011	0.999
9	1	2.643	–	0.963

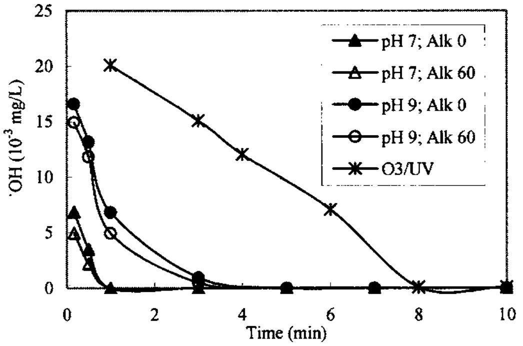


Fig. 3. Difference in hydroxyl radical between ozonation and O_3/UV processes

reaction at pH 9, the modified model based on rapid and slow reactions shows the worse correlation coefficient (R^2) than that at pH 7. Fig. 2 also presents the ozone decomposition reaction and predictive data at different pH levels, in which the dashed lines and solid lines denote the predictive data determined by the Slawomir model and modified model, respectively. As shown in Table 2, the value of K_1 increases with increasing pH value, which indicates ozone molecules decompose more rapidly in the beginning at high pH level than that at low pH level. Besides, the fraction of the ozone consumption attributed to rapid reaction, F, also increases with increasing pH value. The slow reaction rate shown in Fig. 2 varies smoothly, but the value of K_2 also increases with increasing pH.

The formation concentration of hydroxyl radical at pH 7 and 9 is shown in Fig. 3. According to Fig. 3, hydroxyl radical formation is more significant at pH 9 than pH 7, which indicates that more hydroxyl ions (OH^-) would promote more hydroxyl radical formation, and also affect ozone decomposition rate. High pH increases the ozone decomposition rate as well as the hydroxyl radical formation.

Fig. 4 presents linear correlation between ozone and hydroxyl radical concentration at pH 7 and 9 at different ozonation time. As the high OH^- concentration at pH 9 decomposes ozone completely to form more hydroxyl radical, the residual ozone concentration shown in the y intercept (O_3) is close to 0. However, the occurrence of less hydroxyl radical formation and high ozone concentration at pH 7 resulted in producing a residual ozone concentration of 15 mg/L as shown in the y intercept (O_3). The above evidence suggests that the main oxidants in ozonation at pH 7 are both ozone molecules and hydroxyl radicals.

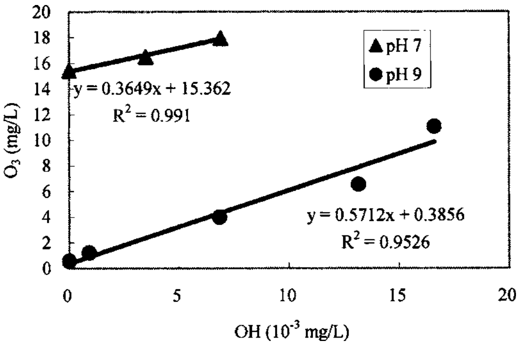


Fig. 4. Relationship between ozone and hydroxyl radical concentration at pH 7 and 9 in the ozonation process

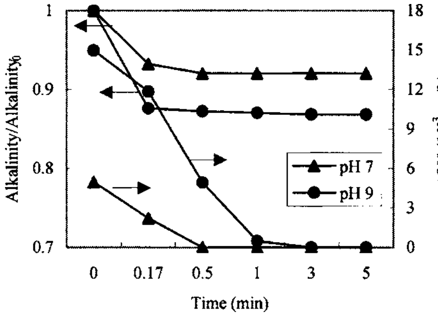


Fig. 5. Correlation of residual alkalinity ratio and hydroxyl radical concentration during the ozonation process

Effect of Alkalinity on Ozonation

To simulate nature water quality in this experiment, alkalinity is prepared by adding $NaHCO_3$ at 60 mg/L as $CaCO_3$. Correlation of the residual alkalinity ratio and hydroxyl radical concentration during the ozonation process was shown in Fig. 5. The [alkalinity/alkalinity$_0$] represents the ratio between the residual alkalinity and the initial alkalinity. Alkalinity at pH 7 and 9 decreases rapidly in the beginning and remains constant afterwards. It was reported that the hydroxyl radical reacts with carbonate and bicarbonate ions to lead to the alkalinity decrease at pH 7 and 9. The reducing degree of alkalinity has a strong correlation with the presence of hydroxyl radical concentration, i.e., pH 9 > pH 7. In Fig. 5, alkalinity concentration decreases as hydroxyl radical increases, and remains constant once the hydroxyl radical disappears. Therefore, the hydroxyl radical is one of the most important chemical elements affecting the alkalinity concentration during the ozonation process. Further evidence of the effect of alkalinity on ozonation is illustrated in Fig. 6, which presents the relationship between hydroxyl radical exposure and alkalinity reduction. In this study, the exposure represents the multiplication between reactant (·OH) concentration and reaction time. The high exposure (10^{-3} mg/L min) of hydroxyl radical leads to low alkalinity ratio, which is expressed by the empirical formula: $Y = -0.0006X + 0.8786$ (X = hydroxyl radical exposure and Y = alkalinity/alkalinity$_0$) as shown in Fig. 6. Based on the empirical formula, the hydroxyl radical exposure during the ozonation process could be easily interpreted by the reduction of alkalinity.

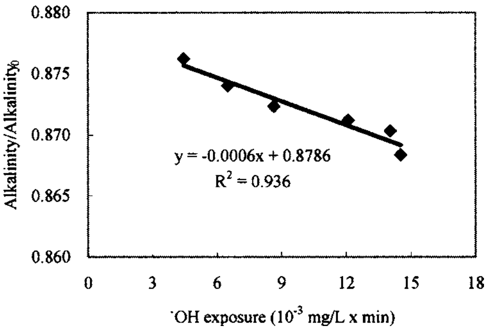


Fig. 6. Correlation between hydroxyl radical exposure and residual alkalinity ratio at pH 9

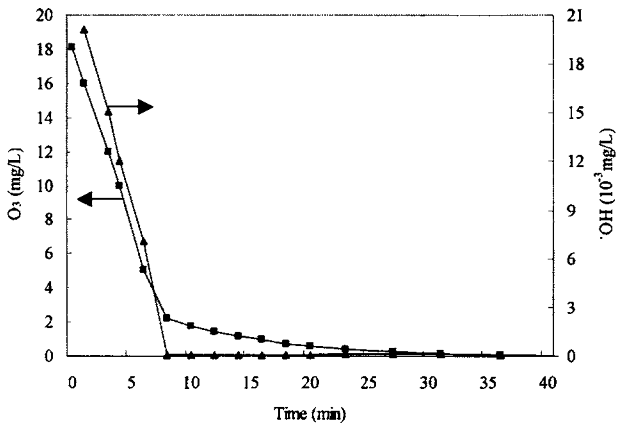


Fig. 7. Measured concentration of dissolved ozone and hydroxyl radical during the O_3/UV process

O_3 /UV Process

The photolysis of aqueous ozone (O_3/UV process), called the AOPs is commonly used in water and wastewater treatment plants. Fig. 7 shows the measured concentration of dissolved ozone and hydroxyl radical during the ozonation and O_3/UV processes. The O_3/UV process is operated at 30 W (UV light intensity). With increasing illumination time by UV light, the ozone concentration decreases rapidly and forms more hydroxyl radical in a batch reaction.

The difference in hydroxyl radical formation between indirect ozone process and O_3/UV process was clearly shown in Fig. 3. The hydroxyl radical formation concentration in O_3/UV process is about 0.02 mg/L at 1 min reaction which is much higher than that at pH 9 (0.007 mg/L). Moreover, the order of hydroxyl radical formation concentration is $\cdot OH(O_3/UV) > \cdot OH(pH\ 9) > \cdot OH(pH\ 7)$, and the effect of alkalinity on hydroxyl radical formation is not significant once the pH value is held constant. Table 3 summaries the experimental data for the ozone, hydroxyl radical, and hydrogen peroxide concentration in the ozonation and O_3/UV processes.

Ozonation of Organic Precursors

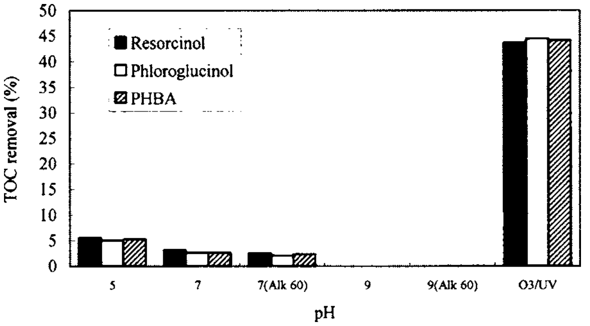


Fig. 8. Removal of TOC at various levels of pH and alkalinity for three model compounds treated by the ozonation and O_3/UV processes

Fig. 8 presents the results of TOC removal efficiency in the ozonation and O_3/UV processes. The removal efficiency of TOC in the batch ozonation is below 6%. This evidence suggests that the electrophilic character of ozone could only oxidize and destroy a small amount of the aromatic structure and unsaturated bond of organic matter without mineralizing the organic carbon to form carbon dioxide as well as the destruction by hydroxyl radical. Therefore, the reduction of these organic precursors in the ozonation process is very limited. The removal efficiency of TOC for three model compounds was found to be over 40% in the O_3/UV process, which suggests that the higher hydroxyl radical exposures (O_3/UV) could effectively reduce the TOC concentration. The effect of alkalinity on removal of TOC was presented in Fig. 8 which indicates that the natural inhibitor (alkalinity) could be negligible because of the insignificant removal efficiency of TOC in ozonation.

Table 3. Summary Experimental Data for Ozonation and O_3/UV Process

	Ozonation					O_3/UV
	Alkalinity=0[a]			Alkalinity=60[a]		
Item	pH 5	pH 7	pH 9	pH 7	pH 9	pH 5
Ozone exposure (mg/L min)	425.4	194.2	154.7	17.8	5.3	97.5
OH exposure (10^{-3} mg/L min)	0	2.6	0.9	18.7	14.5	77.9
H_2O_2[b] (μm) (Maximum concentration)	14.1	1.1	–	1.4	–	–

[a] Unit of alkalinity=mg/L as $CaCO_3$.

[b] Analysis method (Bader et al. 1988).

Organic compounds with aromatic structures or conjugated double bonds would absorb light in the ultraviolet wavelength range, commonly 254 nm (UV_{254}). SUVA is defined as a ratio between the ultraviolet absorbance (UV_{254}) and the concentration of TOC in water, i.e., UV_{254} (m^{-1})/TOC (mg/L). The change of the value of SUVA is shown in Fig. 9. The most aromatic structure and conjugated double bonds are destroyed by ozone and hydroxyl radical resulting in the high UV_{254} decrease, which results in the low value of SUVA. According to a study by Edzwald and Van (1990), when the value of SUVA is smaller than 2, the composition in the sample is mostly nonhumics, low hydrophilic materials, and low molecular weight. In other words, the sample contains relatively small amount of aromatic moieties. Therefore, the lower SUVA after the ozonation and O_3/UV processes indicates that ozone and hydroxyl radical can effectively destroy the aromatic structure and also reduce chlorinated by-products formation potential (Rook 1976). As shown in Fig. 9, the difference of SUVA for the three model compounds is insignificant, because of their similar benzene structure, to which the attack of ozone fol-

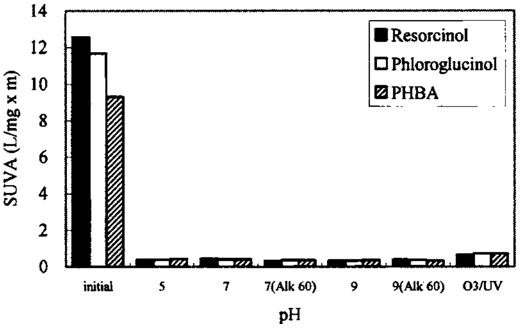


Fig. 9. SUVA measured at various levels of pH and alkalinity for model compounds treated by the ozonation and O_3/UV processes

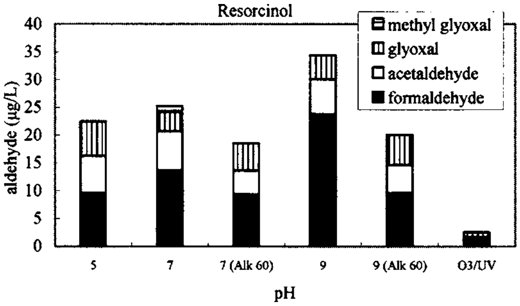


Fig. 10. Formation of aldehyde for resorcinol at various levels of pH and alkalinity treated by the ozonation and O_3/UV processes

lowing Crigee mechanism and the nonselective reactivity of hydroxyl radical result in having similar TOC and UV_{254} removal.

Formation of Ozonation By-Products

According to a study by Glaze (1986), the ozonation by-products include aliphatic aldehyde, hydrogen peroxide, organic peroxide, and saturated carboxylic acid. Among them, aldehyde is the most concerned because of its harmful to human health. Aldehyde consists of formaldehyde, acetaldehyde, glyoxal, and methyl glyoxal that are commonly found and investigated in ozonation process. Fig. 10 shows the formation of the ozonation by-product (aldehyde) for resorcinol at different levels of pH and alkalinity treated by the ozonation and O_3/UV processes. In this study, the principal aldehyde formation is formaldehyde, especially at high pH. For instance, at pH 9 the ratio of formaldehyde in aldehyde formation is up to 70%, whereas at pH 7 is 50%, and pH 5 is 39% in resorcinol. This formation suggests that hydroxyl radical (formed at pH 9) could destroy organic compound and generate shorter chain by-products such as formaldehyde than ozone molecule (formed at pH 5). In general, the order of the aldehyde formation concentration is $O_3(\text{pH } 9) > O_3(\text{pH } 7) > O_3(\text{pH } 5)$. Similar observations for phloroglucinol and *p*-hydroxybenzoic acid were also found in this study.

As shown in Fig. 10, the addition of alkalinity would decrease the aldehyde concentration in the indirect ozone process. The phenomenon conforms to the above-mentioned findings, which states that alkalinity could reduce hydroxyl radical concentration to inhibit oxidation reaction and result in less aldehyde formation. In the O_3/UV process, the higher hydroxyl radical exposure reduces TOC by 40% and further oxidization results in lowering aldehyde concentration to 2 μg/L. In summary, the order of aldehyde formation with respect to the ozonation process is $O_3(\text{pH } 9; \text{Alk}=0) > O_3(\text{pH } 9; \text{Alk}=60) > O_3(\text{pH } 7; \text{Alk}=0) > O_3(\text{pH } 7; \text{Alk}=60) > O_3(\text{pH } 5) > O_3/UV$. It was thus concluded that the ozone and hydroxyl radical could break the aromatic structure and destroy organic precursors in the ozonation process.

Formation of Chlorination By-Products

Among the chlorine demands for these three model compounds, resorcinol is the lowest. It could be explained that the two activating –OH groups in resorcinol are situated at vicinal position to stabilize the transition state of the reaction through the donation of electron density. Therefore, the electrophilic addition and substitution reactions by chlorine easily occurs, which leads to low chlorine demand (Boyce and Hornig 1983). However, the symmetric structure for phloroglucinol flanked with three –OH groups may form a resonance-stabilized intermediate, which could confine the hydrolysis and decarboxylation with C-C bond cleavage on the aromatic structure and result in more chlorine demand (Chang et al. 2006). For *p*-hydroxybenzoic acid, the moderately deactivating group (–COOH) would lower the electron density on aromatic structure, but not for the symmetric structure such as phloroglucinol. Therefore, the order of chlorine demand is strictly depended upon the physical and chemical property of the model compounds and followed by $P > \text{PHBA} > R$. In this investigation, the destruction of organic precursors by hydroxyl radical results in the higher chlorine consumption than ozone molecular during the chlorination process, and the inhibition of alkalinity would increase the chlorine consumption. The detailed experimental data are listed in Table 4.

Table 4. Comparisons of Chlorine Consumption, Specific DBP, and DBP Yield Coefficient for Three Model Compounds

	Ozonation					O_3/UV
	Alkalinity=0			Alkalinity=60		
Organic	pH 5	pH 7	pH 9	pH 7	pH 9	pH 5
			Chlorine consumption ($\text{mg Cl}_2/\text{mg C}$)[a]			
R	2.0	1.5	1.3	1.6	1.3	5.2
P	2.0	1.5	1.3	1.6	1.3	5.1
PHBA	2.0	1.5	1.2	1.6	1.3	5.2
			Specific DBP (μg DBP/mg C)[b]			
R	23.6	98.6	220	88.5	154	7.3
P	18.2	98	232	85	170	7.2
PHBA	22.3	107	247	91.9	165	10.7
			D ($\mu\text{g DBP}/\text{mg Cl}_2$)[c]			
R	12.4	64.1	173.9	53.4	115	1.4
P	8.8	63.3	190	52.2	130	1.4
PHBA	11.2	69.7	201	56.3	124	2.1

[a] Chlorine consumption ($\text{mg Cl}_2/\text{mg C}$)=chlorine consumption after 168 residual TOC (mg/L) after ozonation.

[b] Specific DBPEP: DBPFP (μg/L)/residual TOC (mg/L) after ozonation.

[c] *D*=DBPEP (μg/L)/Cl_2 demand (mg/L) after 168 h.

Table 5. Carcinogenic Risk for THM, HAA, and Aldehyde in Different Treatment Processes

Organics		Carcinogenic risk					
		Ozonation					O_3/UV
		Alkalinity=0			Alkalinity=60		
		pH 5	pH 7	pH 9	pH 7	pH 9	pH 5
R	THM	7×10^{-7}	4×10^{-6}	1×10^{-5}	3×10^{-6}	8×10^{-6}	6×10^{-7}
	HAA	2×10^{-7}	1×10^{-6}	1×10^{-5}	9×10^{-7}	5×10^{-6}	6×10^{-9}
	Aldehyde	3×10^{-6}	7×10^{-6}	1×10^{-5}	5×10^{-6}	6×10^{-6}	7×10^{-7}
	Risk	4×10^{-6}	1×10^{-5}	3×10^{-5}	9×10^{-6}	2×10^{-5}	1×10^{-6}
P	THM	1×10^{-7}	3×10^{-6}	2×10^{-5}	2×10^{-6}	1×10^{-5}	4×10^{-7}
	HAA	2×10^{-7}	1×10^{-6}	1×10^{-5}	9×10^{-7}	5×10^{-6}	6×10^{-9}
	Aldehede	6×10^{-6}	7×10^{-6}	9×10^{-6}	5×10^{-6}	5×10^{-6}	5×10^{-7}
	Risk	6×10^{-6}	1×10^{-5}	4×10^{-5}	8×10^{-6}	2×10^{-5}	1×10^{-6}
PHBA	THM	1×10^{-6}	3×10^{-6}	2×10^{-5}	2×10^{-6}	8×10^{-6}	6×10^{-7}
	HAA	3×10^{-7}	3×10^{-6}	1×10^{-5}	2×10^{-6}	6×10^{-6}	3×10^{-8}
	Aldehyde	6×10^{-6}	7×10^{-6}	1×10^{-5}	5×10^{-6}	5×10^{-6}	5×10^{-7}
	Risk	7×10^{-6}	1×10^{-5}	4×10^{-5}	9×10^{-5}	2×10^{-5}	1×10^{-6}

Note: Source=USEPA (2005).

Chlorination of natural organic matter results in the formation of various chlorination DBP. Among all DBP, the THM and HAA are considered as the principal disinfection by-products which cause public health concerns for safe drinking water. The comparison of specific DBP formation potentials and DBP yield coefficient (D) between the ozonation and O_3/UV processes are also shown in Table 4. As mentioned earlier, the ozone and hydroxyl radical could change the properties in the three model compounds by destroying the aromatic structure, which leads to more reduction of chlorine demand and DBPFP. In the O_3/UV process, the 40% TOC reduction performed by the hydroxyl radical would also enhance the reduction of DBPFP. Therefore, the reduction of DBPFP by the O_3/UV process is much higher than that by the ozonation process. The relationship between DBP formation and chlorine demand could be evaluated by the DBP yield coefficient (D). Table 4 shows the values of D in different processes. The order of D is similar to the order of DBPFP as O_3/UV system $\ll$ ozonation.

Risk Assessment between Ozonation and O_3/UV Process

In this study, it was found that ozonation of organic precursors is successful in reducing the chlorination by products, especially at pH 5 for the ozonation and the O_3/UV processes. However, it is noted that there are other DBPs such as aldehyde would be occurred in the course of ozonation. Therefore, it is required to have a further risk assessment to determine if the ozonation process is appropriate based on the carcinogenic DBPs concerns. The THMs, HAAs, and aldehyde are considered carcinogenic substances by USEPA and its carcinogenic risk can be determined by the following equation:

$$\text{carcinogenic risk} = \text{CDI} \times \text{SF} \tag{3}$$

Where chronic daily intake is the quantity of ingestion (mg/kg day), and slope factor is the carcinogenic slope factor $(\text{mg/kg day})^{-1}$. The value of CDI is calculated based on the assumption that one person drinks 2L of water per day, with an average weight of 70 kg. The value of SF is varied with different carcinogenic substances, which represents the slope of diagram of dose-response relationship. According to toxicity data of DBP and aldehyde proposed by USEPA, the value of SF is 4.4×10^{-3} for chloroform, 4×10^{-3} for HAA, and 0.08 for formaldehyde. The final carcinogenic risk is assumed to be the sum of these three carcinogenic substances and listed in Table 5.

According to Table 5, the lowest carcinogenic risk is in the O_3/UV process and the order of carcinogenic risk is $O_3/UV \ll O_3(\text{pH } 5) < O_3(\text{pH } 7; \text{Alk}=60) < O_3(\text{pH } 7; \text{Alk}=0) < O_3(\text{pH } 9; \text{Alk}=60) < O_3(\text{pH } 9; \text{Alk}=0)$. Therefore, both the ozonation with proper operation and O_3/UV processes can reduce the organic precursors and provide safer drinking water. Further, the O_3/UV process is considered as the appropriate treatment technology for reducing DBPs and aldehyde formation under the conditions operated in this investigation.

Conclusions

The ozone decomposition mechanism changes at different pH levels. There are more hydroxyl ions (OH^-) at high pH, which promotes ozone decomposition reaction to form hydroxyl radical. A modified ozonation decomposition model, $[O_3]=[O_3]_0\{Fe^{-K_1 \cdot t} + (1-F)e^{-K_2 \cdot t}\}$, is developed in this investigation. The model can predict the ozone decomposition reaction more accurately than that by the first order model (Slawomir et al. 1999).

The fluorescence method was introduced to analyze hydroxyl radical level in the indirect ozone process and O_3/UV processes. It was observed that the amount of hydroxyl radical exposure in the O_3/UV process was much higher than in the indirect ozone process. In the presence of alkalinity, the inhibition is significant and the linear correlation between alkalinity and hydroxyl radical exposure was revealed which might have insight into the effect of alkalinity on inhibition of hydroxyl radical. Consequently, more reduction of TOC and DBP in the O_3/UV process would be observed.

In ozonation, the chlorine demand increases with decreasing pH and increasing alkalinity. It is concluded that hydroxyl radical can more strongly destroy the organic precursors resulted in reducing chlorine consumption than ozone molecule. Moreover, the destruction of organic precursors by hydroxyl radical exhibits higher DBP formation potential than that by ozone molecule, and the inhibition of alkalinity in hydroxyl radical results in less DBP formation. In the ozonation process, the aldehyde concentration increases with increasing pH, which indicates that the hydroxyl radical increases both chlorination by-products and aldehyde formation. According to the risk assessment in ozonation process, water samples treated by the O_3/UV and O_3 (pH 5) process exhibit the lower risk. Therefore, both the ozonation and O_3/UV processes with proper operation can reduce the organic precursors thereby providing the safe drinking water.

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Notation

The following symbols are used in this paper:

F = fraction of the ozone consumption attributed to rapid reaction;
K_1 = first-order rate constant for the rapid reaction;
K_2 = first-order rate constant for the slow reaction;
$[O_3]$ = ozone concentration at time t; and
$[O_3]_0$ = initial ozone concentration.

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