A predictive model of chlorination by-products formation in the ozonation/chlorination processes

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Abstract - **The objective of this investigation is performed to evaluate the effects of the ozone and hydroxyl radical on the chlorination by-products formation (CBPs) in the ozonation (O_3/UV)/chlorination processes. The model compounds including resorcinol, phloroglucinol, and *p*-hydroxylbenzoic acid were selected as low molecular weight and high CBPs formation potential in this investigation. The results of this study reveal that the destruction of organic precursors by hydroxyl radical exhibits higher CBP formation than that by ozone. However, the high hydroxyl radical formation (O_3/UV process) would show the least CBP formation. The developed model could be successfully in predicting the chlorine decay and CBPs formation in the ozonation/chlorination processes. With this development, the model would simulate and minimize the CBPs formation in chlorination process.**

Index Terms - ozone, hydroxyl radical, chlorination by-products, ozonation, O_3/UV process

INTRODUCTION

Ozone is an attractive disinfectant, which can destroy highly resistant pathogenic microorganisms such as *Cryptoporidium parvum oocysts* in the water treatment plant [1], [2]. Once ozone is applied in water treatment, it can not only carry out self-decomposition reaction, but also react rapidly with the organic matters. This reaction is known to produce secondary oxidants, such as the hydroxyl radical, a much more powerful and indiscriminate oxidant than ozone [3], [4]. This is beneficial as the non-selective characteristic of hydroxyl radical to oxidize a broad range of organic compounds [5]. Some systems based on the generation of highly reactive and oxidizing free radical, such as hydroxyl radical, have experimental an increasing interest due to their high oxidant power, which is named advanced oxidation processes (AOPs) [6], [7] Among them, the oxidation by several agents such as ozone, UV radiation, Fenton reagent, photo-catalysis, etc. has been extensively used with success [8]. AOPs have been paid a high attention as promising technologies for degrading toxic and hazardous organic matters [9].

In the reaction of ozone with natural organic matters (NOMs), the ozone molecule acts as an electrophilic agent because of its negative charge on one of the terminal oxygen atoms, which attacks one nucleophilic position of aromatic compounds [10], [11]. The different substituting groups in the aromatic molecule would strongly affect the reactivity of the aromatic structure with ozone. Thus, the different groups activate or deactivate the aromatic ring for electrophilic substitution reaction. Generally, the activating groups (-OH) promote the substitution of hydrogen atoms from their ortho- and pata- positions, but the deactivating groups (-COOH) promote the substitution in the meta- positions [12].

Trihalomethanes (THMs) and haloacetic acids (HAAs) are typical DBPs generated during the chlorination process [13], [14], [15]. The distribution and concentration of DBPs would depend on water quality parameters and operating conditions including pH, temperature, relative concentration of chlorine, bromide concentration, reaction time, and the NOM concentration and nature [16], [17].

Chlorination of organic matters can be divided into two stages: rapid and slow reactions [18]. Hass and Karra (1984) [19] proposed a model parallel first-order reaction to evaluate the chlorine decay. By assuming the CBPs formation proportional to the chlorine demand, the predictive model would be proposed as follows: [20]

$$C(t) = C_0\{ f \cdot e^{-K_R \cdot t} + (1-f) \cdot e^{-K_s \cdot t} \} \quad (1)$$

$$DBP = D \cdot C_0 \cdot \{1 - f \cdot e^{-K_R \cdot t} - (1-f) \cdot e^{-K_S \cdot t} \} \quad (2)$$

However, several studies reported that the above-mentioned THMs kinetics model was not in agreement with their experiments because of the $THMFP_i$ (initial THMFP corresponded to fast reacting THMs precursors) and $THMFP_f$ (final THMFP) showing different kinetics for the formation of THMs [21], [22]. Therefore, the predictive model which is modified as the parallel first-order (slow reaction) and second-order (rapid reaction) reactions were proposed [23].

$$C(t) = [-K_R \cdot t \cdot (-n+1) + f \cdot {C_0}^{-n+1}]^{\frac{1}{-n+1}} + [-K_S \cdot t \cdot (-m+1) + f \cdot {C_0}^{-m+1}]^{\frac{1}{-m+1}} \quad (3)$$

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$$CBPs = E\{fC_0 \cdot \left[1 - \frac{1}{fC_0 k_R t + 1}\right]\}^n + F\{(1-f)C_0\left[1 - e^{-k_s t}\right]\}^m \qquad (4)$$

in which $C(t)$ is the chlorine concentration at any time t (mg/L), C_0 is the initial chlorine concentration (dose), f is the fraction of the chlorine demand attributed to rapid reactions, k_R is the rate constant for rapid reactions, and k_S is the rate constant for slow reactions. The value n and m are determined by the best fit as compared with the suggested reaction orders. E and F are the CBPs yield coefficients from the rapid and slow chlorine consumed, respectively.

The recently proposed DBPs predictive model are listed in Table I.

TABLE I
SUMMARY OF DBPS PREDICTIVE MODEL

Reference	Model
[21]	[TTHM] = $A\left(C_1 - \left(\frac{C_1(1-K)}{1-Ke^{-ut}}\right)\right)$; A=0.71, K=0.78, M=0.42
[24]	[TTHM] = 13.5 Ln (Ch-a)-14.5 (pH)+230 (Br^-)-140 $(Br^-)^2$-25.3 (S) + 110.6 (Sp)-6.6 (T Sp)+1.48 (T D)
[25]	[TTHM] = $0.00412(DOC)^{1.10}\,(D)^{0.152}\,(Br)^{0.068}\,(T)^{0.61}\,(pH)^{1.60}\,(t)^{0.260}$
[26]	$[TTHM]_{Field} = 1.392\,(DOC)^{1.092}\,(pH)^{0.531}\,(T)^{0.255}$ $[TTHM]_{Laboratory} = 0.044\,(DOC)^{1.030}\,(t)^{0.262}\,(pH)^{1.149}\,(D)^{0.277}\,(T)^{0.968}$
[27]	[DBPs] = $A_i\left(C_1 - \left(\frac{C_1(1-K)}{1-Ke^{-ut}}\right)\right)$; M=0.70, K=0.95
[28]	[TTHM] = -0.26 (Ch-a) + 1.57 (pH) + 28.74 (Br^-) - 66.72 $(Br^-)^2$- 43.63 (S) + 1.13 (Sp) + 2.62 (T S) - 0.72 (T D)
[29]	[HAAs] = Linear regression in function of various THM species
[30]	[TTHM]&[HAAs] = Single linear and non-linear regression models for water of each utility (in function of water temperature, TOC, chlorine dose and contact time)
[20]	[TTHM] = $\alpha_1 D\left\{1 - fe^{(-K_R \cdot t)} - (1-f)e^{(-K_s \cdot t)}\right\}$
[23]	$CBPs = E\{fC_0 \cdot \left[1 - \frac{1}{fC_0 k_R t + 1}\right]\}^n + F\{(1-f)C_0\left[1 - e^{-k_s t}\right]\}^m$

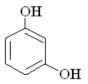
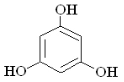
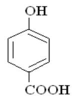
Therefore, the objectives of this research were intended to (1) assess the chlorine decay and chlorination by-products formation and (2) develop the predictive chlorination by-products formation model during chlorination process followed by the ozonation (O_3/UV) processes.

MATERIAL AND METHODS

Sample Preparation

The selected organic model compounds in the investigation are including resorcinol (R), phloroglucinol (P), and *p*-hydroxybenzoic acid (PHBA). The molecular weight and structure of these three organic compounds are listed in Table II. The synthetic sample concentration used in the study was for R, P and PHBA composed of total organic carbon (TOC) 3.0 ± 0.3 mg/L by de-ionized water (Milli-Q SP). All chemicals used for the experimental analysis were prepared with deionized water (Milli-Q SP).

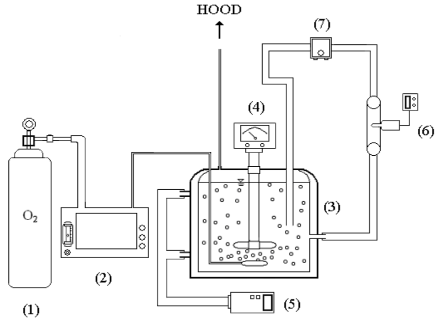
TABLE II
SUMMARY OF MOLECULAR WEIGHT AND STRUCTURE FOR ORGANIC COMPOUNDS

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			

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

Experimental Procedures

In the experiment, a glass reactor consists of an operation volume (5.0 L) and free space (0.5 L) shown in Figure 1 It was equipped with a thermostat to maintain a constant temperature, 25 °C and with a 6-bladed-disk turbine to improve the magnitude of mixing. Ozone was generated by bubbling oxygen into an ozone generator (model SG-01A, Sumitomo, Tokyo, Japan).



(1) Oxygen cylinder; (2) Ozone generator; (3) Batch reactor; (4) 6-bladed-disk turbine; (5) Thermostat; (6) pH meter; (7) Pump

FIGURE 1
THE EXPERIMENTAL APPARATUS OF THE OZONE BATCH REACTOR

Five liters blank water was placed in a 25 °C bath, and ozone gas was introduced to the water through a bubble diffuser bottom of the reactor for 2 hours until reaching an equilibrium concentration. The saturated ozone concentration in aqueous solution is about 18 mg/L at 25 °C. An additive of alkalinity in the ozonation process is prepared by $NaHCO_3$ at 60 mg/L as $CaCO_3$. Putting the selected model compounds in the reactor and perform the process forty minutes. Afterwards, the ozonated samples prepared to proceed to the following chlorination process.

Based on the procedure in Standard Methods for the Examination of Water and Wastewater (Iodometric Method I-4500B) [31], chlorination of selected model compounds was implemented by aqueous 13% free chlorine (sodium hypochlorite) stock solution and add phosphate buffer (pH 7.0). A seven-days chlorination study was introduced by 10mg/L chlorine dose to determine the chlorine consumption, trihalomethane formation potential (THMFP), and haloacetic acid formation potential (HAAFP) in this investigation. Sample were chlorinated in 300 mL glass bottle and kept headspace free in the dark at room temperature (25±2 °C) until 168 hours. The sample were collected after 1, 3, 6, 24, 48, and 168 hours contact time.

Analytical Methods

Chlorine concentration was measured by DPD (N,N-diethyl-p- phenylene-diamine) titration methods. All analyses, unless otherwise noted, were performed according to the 19th edition of the standard method [31].

THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) were analyzed by combining a purge and trap injection, and a GC/ECD system (HP 6890 series). The column in GC is a fused silica capillary column (method 6232, standard method 19th edition). For the determination of HAAs (chloroacetic acid, dichloroacrtic acid, and trichloroacetic acid), a liquid-liquid extraction procedure (extracting with methyl tert-butyl ether, MtBE) considered as a pretreatment and analyzed by GC/ECD system (HP 5890II series), in accordance with USEPA method 552.2.

RESULTS AND DISCUSSION

Chlorine Demand and Chlorine Decay Model

In this investigation, these three model compounds were first pretreated by the ozonation and O_3/UV processes and then followed by the general procedures to determine the chlorine demand in the chlorination process [32].

I. Chlorine Demand

Figure 2 presents the measured residual chlorine concentration as the plots for resorcinol, phloroglucinol, and p-hydroxybenzoic acid at various reaction times during the chlorination process. The chlorine demand was increased as the increasing chlorine contact time. The chlorine consumption rate was fast in the first 6 hours (rapid reaction) and then the rate gradually reduced (slow reaction).

As shown in Figure 2, the chlorine consumption was increased with decreasing pH. The model compounds selectively destroyed by ozone molecule to form more complex hydrocarbon compounds than by hydroxyl radical, so the complex compounds would then proceed to the addition, substitution and oxidation reactions by chlorine and result in more chlorine demand. In the presence of alkalinity, hydroxyl radical oxidation reaction would be inhibited, which causes the higher chlorine demand than that of without alkalinity in the indirect ozone process.

Figure 2 also presents the chlorine consumption of three model compounds after the O_3/UV process which is greatly different from that of the ozonation process. The phenomenon indicates that the high hydroxyl radical formation in the O_3/UV process [32] would oxidize the organic precursors more completely and further transfer hydroxyl radical electrons to the carbon ions of reactants with an electrophilic character. These specific carbon ions would enhance the addition and substitution reactions by chlorine. Therefore, the chlorine consumption in the O_3/UV system is much higher than that of the ozonation process and the order of chlorine consumption is O_3/UV > O_3 (pH 5) > O_3 (pH 7; Alk=60) > O_3 (pH 7; Alk=0) > O_3 (pH 9; Alk=60) > O_3 (pH 9; Alk=0).

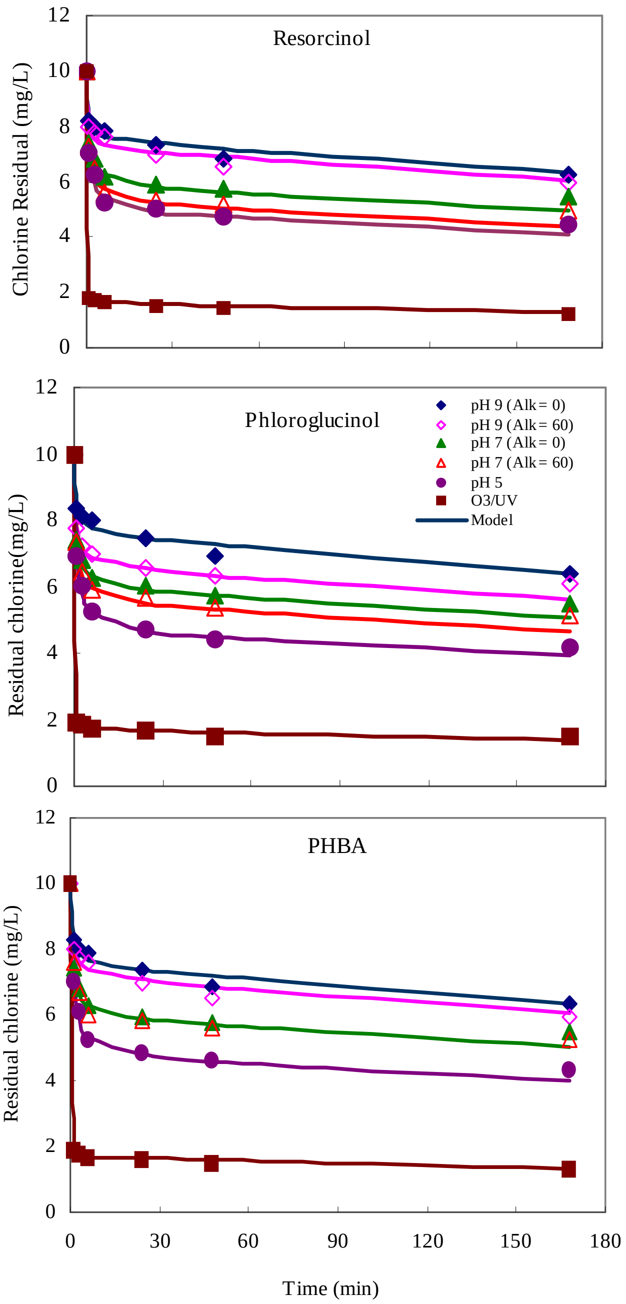


FIGURE 2

THE MEASURED RESIDUAL CHLORINE CONCENTRATION FOR RESORCINOL, PHLOROGLUCINOL, AND *P*-HYDROXYBENZOIC ACID AT VARIOUS REACTION TIMES

In this investigation, the resorcinol and phloroglucinol with 2-OH and 3-OH phenolic groups under the attacks of ozone and hydroxyl radical would lead to ring cleavage and the formation of organic precursors such as formic acid, C_2-C_6 dicarboxylic acid, and aldehyde [33], [34]. Since the similar products were generated by the ozonation process, one would expect to observe the difference on chlorine demand for resorcinol and phloroglucinol is insignificant. The difference in chlorine demand between *p*-hydroxybenzoic acid and resorcinol (or phloroglucinol) is also insignificant, which indicates that the higher oxidative ability of ozone and hydroxyl radical could lead to ring cleavage of the different structure and formation of by-products similar to resorcinol and phloroglucinol. This hypothesis can be further confirmed by analyzing the data via the analysis of variance (ANOVA) — F test method as shown in Table III, which indicates that the difference in chlorine demand among the three model compounds is insignificant. The result of F test among the three compounds is 0.0035, which is lower than the $F_{critical}$ (2, 12) = 2.8068.

TABLE III
ANALYSIS OF VARIANCE (ANOVA) — F TEST FOR CHLORINE DEMAND AND CBPS FORMATION

Chlorine demand					
Variance source	Square sum	Freedom degree	Square mean	F-ratio	F(2,12)
Between	0.0044	2	0.0022	0.0035	2.8068
Within	7.502	12	0.6251		
Sum	7.5064	14	-		
CBPs formation					
Variance source	Square sum	Freedom degree	Square mean	F-ratio	F(2,12)
Between	2308.624	2	1154.312	0.020	2.8068
Within	695105.251	12	57733.052		
Sum	697413.875	14	-		

II Chlorine Decay Model

The chlorine decay model was determined as the second order in the rapid reaction and the first order in the slow reaction and expressed as follows:

$$C(t)=C_0\{[\frac{f}{f\cdot C_0\cdot K_R\cdot t+1}]+(1-f)\cdot e^{-K_s\cdot t}\} \qquad (5)$$

The chlorine decay constants in combination of the three model compounds for parallel first and second order reaction in the ozonation (O_3/UV)/chlorination process are listed in Table 2. In the ozonation/chlorination processes, the rate constants for rapid reaction (K_R) are higher than those of the slow reaction (K_S) for these compounds, which suggests that the reaction proceeds rapidly at the beginning as K_R, and is followed by a slow reaction afterwards as K_S. Comparison of K_R values at the different pH levels, the K_R values increase with increasing pH, which indicate that the samples destroyed by hydroxyl radical result in a faster chlorine decay rate than that by the ozone molecule. However, in the presence of alkalinity, the oxidation capability was inhibited and resulted in the decreases of the K_R values. However, the predicted value of K_R and K_S in the O_3/UV process is different from that of the ozonation process. The value of K_R (0.001) is much smaller than K_S (3.878~3.931) for three model compounds. In summary, the magnitude of K_R in the ozonation and O_3/UV processes is followed by the sequence as: O_3 (pH 9; Alk=0) > O_3 (pH 9; Alk=60) > O_3 (pH 7; Alk=0) > O_3 (pH 7; Alk=60) > O_3 (pH 5)>> O_3/UV.

At high pH level, the lower chlorine demand exhibits the lower *f* value in the ozonation (O_3/UV)/chlorination processes as shown in Table IV. In the presence of alkalinity, the occurrence of inhibition would increase the *f* value. Therefore, the order of *f* is strictly as follows: O_3 (pH 5) > O_3 (pH 7; Alk=60) > O_3 (pH 7; Alk=0) > O_3 (pH 9; Alk=60) > O_3 (pH 9; Alk=0) >> O_3/UV. Figure 2 shows the observed and predictive residual chlorine concentrations for resorcinol, phloroglucinol and *p*-hydroxybenzoic acid at various reaction times, respectively. As shown in Figure 2 and Table IV, the low deviation and high correlation coefficient indicates that the predictive model could estimate the chlorine decay in the ozonation (O_3/UV) / chlorination processes successfully.

TABLE IV
PARAMETERS OF CHLORINE DECAY AND CBPS FORMATION MODELS FOR COMBINATION OF R, P AND PHBA

Parameter	Ozonation					O_3/UV
	Alkalinity = 0			Alkalinity = 60		
	pH 5	pH 7	pH 9	pH 7	pH 9	
Chlorine decay model						
K_R	0.224	0.377	0.744	0.285	0.609	0.001
K_S	0.001	0.001	0.001	0.001	0.001	3.922
f	0.528	0.409	0.246	0.455	0.301	0.171
R^2	0.993	0.996	0.975	0.989	0.969	0.999
CBPs formation model						
E	0.52	5.50	61.54	3.20	22.41	20.03
F	67.43	243.63	293.93	257.16	292.33	0.42
R^2	0.94	0.95	0.99	0.94	0.96	0.97

Chlorination by-products (CBPs) formation and Predictive Model

I Chlorination by-products (CBPs) Formation

The THMs and HAAs are considered as the principal CBPs formation in the chlorination process (Stuart et al., 1999). The CBPs formation concentration curves (the sum of THMs and HAAs) for resorcinol, phloroglucinol, and *p*-hydroxybenzoic at various time were shown in Figure 4. The CBPs formation concentration raises with increasing chlorine consumption and contact time. At different pH levels and alkalinity in the ozonation (O_3/UV) and chlorination processes, the order of CBPs concentration is as follows: O_3 (pH 9; Alk=0) > O_3 (pH 9; Alk=60) > O_3 (pH 7; Alk=0) □O_3 (pH 7; Alk=60) >> O_3 (pH 5) > O_3/UV process.

In the presence of alkalinity, the inhibition reaction exhibits less CBPs formation at pH 7 and 9. Since the hydroxyl radical is the predominant oxidant at pH 9, the occurrence of alkalinity inhibition affects the CBPs reduction more significant at pH 9 than at pH 7. In O_3/UV process, the higher chlorine consumption and lower CBPs formation are found simultaneously due to its high TOC reduction.

The comparisons of CBPs formation potential with these three organic precursors are corresponded to the chlorine consumption for three model compounds. The similar benzene structure observed in these three model compounds shows the insignificant difference in CBPs formation during the ozonation (O_3/UV)/ chlorination process. The above evidence can be validated further by analyzing the experimental data presented via the analysis of variance (ANOVA) — F test method and shown in Table III. The order of specific CBPFP and *D* is O_3 (pH 9; Alk=0) > O_3 (pH 9; Alk=60) > O_3 (pH 7; Alk=0) > O_3 (pH 7; Alk=60) > O_3 (pH 5) > O_3/UV process.

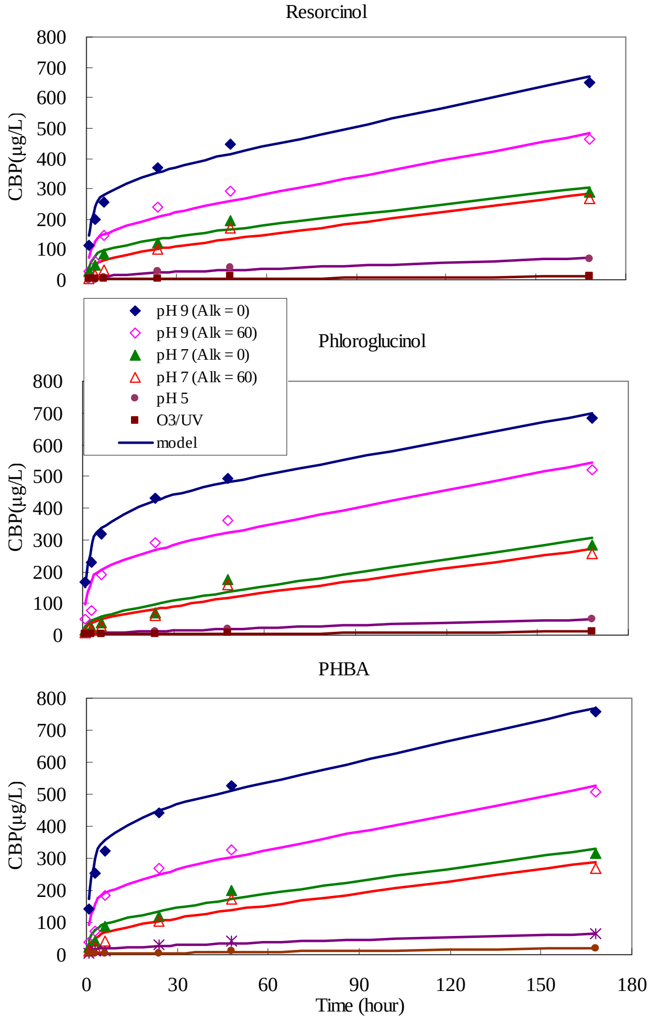


FIGURE 4

COMPARISON BETWEEN THE MEASURED AND PREDICTIVE CBPs FORMATION CONCENTRATION FOR RESORCINOL, PHLOROGLUCINOL, AND *P*-HYDROXYBENZOIC ACID IN THE PREDICTIVE MODEL.

II Predictive Model

The CBPs predictive model developed by Gang (2003) was based on the assumption that the CBPs formation is proportional to chlorine demand. However, in this investigation, a generalized model was proposed by assuming that the CBPs formation are a function of chlorine consumption with respect to the rapid and slow reaction with n and m order, respectively as follows:

$$CBP = E\{f \cdot C_0 \cdot [1 - \frac{1}{f \cdot C_0 \cdot K_R \cdot t + 1}]\}^n + F\{(1-f) \cdot C_0 \cdot [1 - e^{-K_s \cdot t}]\}^m \quad (4)$$

In Equation 4, the n and m are varied with the selected model compounds. According to the experimental data performed in this investigation, it was observed that the CBPs formation is the second order to chlorine consumption in the rapid reaction and the first order to chlorine consumption in the slow reaction. As a result, the predictive model for CBPs formation can be expressed as follows (*n=2*, *m=1*):

$$CBP = E\{f \cdot C_0 \cdot [1 - \frac{1}{f \cdot C_0 \cdot K_R \cdot t + 1}]\}^2 + F\{(1-f) \cdot C_0 \cdot [1 - e^{-K_s \cdot t}]\}^1 \quad (6)$$

Table II lists the parameters of the CBPs predictive model for combination of resorcinol, phloroglucinol and *p*-hydroxylbenzoic, which indicates that the high correlation coefficient (R^2) between the measured and predicted data. In Table 2, the E and F represent the CBPs yield coefficients in the rapid and slow reactions, respectively. For the CBPs formation, it was observed that E and F increase with increasing pH, which confirms that high CBPs formation due to its high THMs yield coefficients. Since F is much higher than E in the processes, it implies that the major species of CBPs are formed in the rapid reaction during the chlorination process. However, in the presence of alkalinity, the inhibition reduces CBPs formation and lowers the yield coefficient. In the O_3/UV process, the predicted parameters of E and F are different from those in the ozonation process, i.e., the E is much higher than F, which indicates that major species of CBPs are formed in the rapid reaction in chlorination process.

The higher correlation coefficients (R^2) associated with the experimental data for three model compounds indicates that the parallel first and second order CBPs formation models can will express the behavior of low-MW organic precursor in the ozonation (O_3/UV) / chlorination process. Figure 4 presents the observed CBPs formation concentrations and the predictive curve from the model for resorcinol, phloroglucinol and *p*-hydroxybenzoic acid, in which the dotted lines and solid lines are the observed and predictive data, respectively.

CONCLUSIONS

The less hydroxyl radical formation in ozonation process causes the negative effect in reducing the CBPs formation at pH 7 and 9. However, the large amount of hydroxyl radical formed in O_3/UV process could decrease the CBPs formation significantly. Moreover, in the presence of alkalinity, the inhibition in hydroxyl radical would increase the chlorine consumption and decrease the CBPs formation.

The proposed chlorine decay model based on the parallel first-order and second-order reactions in chlorine consumption can fit the chlorine decay quite well. Moreover, in the CBPs predictive model, the assumption of the CBPs formation corresponded to the second order to chlorine consumption in the rapid reaction and the first order to that in the slow reaction (n=2, m=1) as well as chlorine decay model also exhibits the high correlation coefficient. Therefore, the proposed generalized model could be used to estimate the CBPs formation in chlorination process.

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