Modeling Chlorine Decay in Surface Water

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ABSTRACT. Chlorination is the most widely practiced form of disinfection in the US. However, there is concern that the disinfection by-products (DBPs) formed during chlorination might be carcinogenic. Because of this increasing concern in water supply systems, there is a need for models that can be used to predict chlorine residuals and optimize the disinfection practices. This paper presents a chlorine decay model based on the possible chlorine decay mechanisms. To evaluate this model, four raw surface and alum treated waters (Chester, Garden City, Maysville, and Lake Vandalia) were used. The chlorine residual at the end of the study period was maintained at the same concentration to avoid effects of chlorine concentration difference. Results show that this model predicts the chlorine residual extremely well, consistently yielding correlation coefficients greater than 0.98. Alum treatment substantially increased the fraction of rapidly reacting functional groups by 24% and decreased the specific chlorine demand (SCD) by an average of 14.4%. Therefore, alum coagulation processes may preferentially remove natural organic matter (NOM) having a slower reaction rate (with chlorine), higher specific chlorine demand, and higher chlorinated DBPs production.

Keywords: alum coagulation, chlorine decay, chlorine residual, modeling, parallel first-order model, regression, surface water

1. Introduction

The primary objective of drinking water treatment is to provide water that is safe from disease causing pathogenic organisms. Thus, treated drinking water should be disinfected and a disinfectant residual should be maintained in the distribution system to protect it from recontamination. In the United States, chlorine has been used as a disinfectant since 1908 and it is still being used for this purpose. Its popularity arises from its high oxidation potential, relatively low cost, high disinfection efficiency, and ease of use. Disadvantages of free chlorine use relate to the fact that it can react rapidly with natural organic matter (NOM) in water by oxidation, addition and substitution reactions to form disinfection by-products (DBPs), some of which are of concern from health risk point of view. The goal of maintaining a proper chlorine level for controlling microorganisms while minimizing DBPs formation is forcing utilities to closely examine and optimize their disinfection practices (Gang et al., 2002). Although chlorine is still the most commonly used water disinfectant, its reaction kinetics is not predictable to a large extent. A reliable model could be used to better predict the chlorine decay and DBP formation in water treatment and distribution systems. Modeling chlorine decay is difficult because of the fast initial reaction with inorganic components and NOM. Many attempts have been made to predict chlorine decay in water (Dugan et al., 1995;

Vasconcelos et al., 1995; Koechling, 1998; Fang, et al., 1999; Gang et al., 2003). Single first order models cannot describe the entire chlorine decay (Isabel et al., 2000). In order to develop a model to predict the short-term and long-term consumption of chlorine, Qualls and Johnson (1983) considered two reactions in parallel: one that was almost complete within 30 seconds, and another that continued for at least 5 minutes (the duration of their experiments). Jadas-Hecart et al. (1992) also used an initial phase of immediate chlorine consumption during the first 4 hours and a second slow consumption phase after 4 hours for the long-term chlorine decay model. Haas and Karra (1984) proposed a parallel first order chlorine decay model in wastewater system to deal with the initial and long-term chlorine consumption. Vasconcelos et al. (1995) tested four kinetic models to describe the chlorine decay in drinking water distribution systems: (1) a first-order expression, (2) an nth-order equation, (3) limited first-order kinetics, and (4) a parallel first-order decay rate. However, the chlorine residuals in most of the above decay models were different at the end of the study period (sometime zero). Because the initial chlorine concentrations in these studies were based on the total organic carbon (TOC) or total dissolved carbon (DOC) concentration of the water samples, the type of NOM present in water samples could be different, which made the results of these studies not comparable. Even the water that has the same initial TOC concentration can have different chlorine residuals after a certain time period. The rate of chlorine decay is chlorine concentration (initial and residual)

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dependent (Summers et al*.,* 1996; Fang et al., 1997; Isabel et al., 2000), so it is difficult to compare the kinetic behavior between water samples if the chlorine residuals are different. In the study reported herein, the chlorine residual at the end of the study period was controlled to the same level in order to avoid the difficulty stated above. The chlorine dose used in our study was selected to yield a 120-hour residual of 1.0 ± 0.4 mg/L free chlorine. It was determined by preliminary chlorine demand experiments (120 hours). This selection to keep the chlorine residual at this level is reasonable, as valid in most drinking water distribution systems. A proper chlorine level is required to control the microorganism re-growth. The specific goals of the research presented herein were: (1) to propose chlorine reaction mechanisms and deduce a parallel first order model for chlorine decay reaction; (2) to investigate the chlorine decay in raw and alum treated waters when the chlorine residual is constant at the end of the study period; (3) to assess the impact of alum treatment on chlorine decay; and (4) to model the chlorine decay in raw and alum treated waters using the parallel first-order reaction model.

2. Model Development

2.1. Chlorine Decay Mechanisms

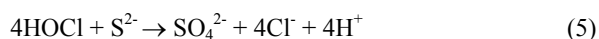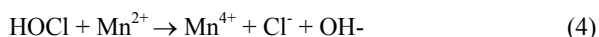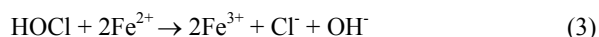When chlorine gas is added to water, rapid hydrolysis forms hydrochloric (HCl) and hypochlorous acid (HOCl) as shown:

$$Cl_2 + H_2O \Leftrightarrow HCl + HOCl \tag{1}$$

At pH values above 4.4, essentially no molecular chlorine remains in aqueous solution. HOCl is a weak acid with a pK_a of 7.5 (25°C), which further hydrolyzes to yield a hydronium ion (H_3O^+) and a hypochlorite ion (OCl^-) according to the following equation:

$$HOCl + H_2O \Leftrightarrow H_3O^+ + OCl^- \tag{2}$$

With increasing pH, at a given temperature, the fraction of the anionic species increases.

Chlorine added to water disappears by numerous pathways. In general, four kinds of reactions lead to the disappearance of chlorine: (1) oxidation; (2) addition; (3) substitution; and (4) catalyzed or light decomposition. When oxidation of a substance by HOCl occurs, the Cl^+ radical accepts two electrons from the substance being oxidized to become a chloride ion (Cl^-). The following equations are common chlorine oxidation reactions occurring in waters:

$$HOCl + 2Fe^{2+} \rightarrow 2Fe^{3+} + Cl^- + OH^- \tag{3}$$

$$HOCl + Mn^{2+} \rightarrow Mn^{4+} + Cl^- + OH- \tag{4}$$

$$4HOCl + S^{2-} \rightarrow SO_4^{2-} + 4Cl^- + 4H^+ \tag{5}$$

$$HOCl + Br^- \rightarrow HOBr + Cl^- \tag{6}$$

$$3HOCl + 2NH_3 \rightarrow N_2 + 3Cl^- + 3H_2O + 3H^+ \tag{7}$$

$$R\text{-}CHO + HOCl \rightarrow R\text{-}COOH + Cl^- + H^+ \tag{8}$$

Equations (3) to (7) are the reactions of HOCl with inorganic water constituents, which cause the immediate chlorine residual consumption. Equations (8) and (9) are the reactions between HOCl and the function groups that exist in the NOM molecules in water. All of the above reactions do not produce chlorinated DBPs, as they only consume the chlorine residuals.

$$\tag{9}$$
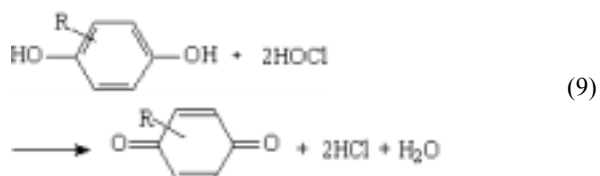
In addition and substitution reactions, chlorine is added or substituted into the NOM molecular structure to form chlorinated organic intermediates, which might further decompose to form many of the DBPs (van Hoof, 1992). Addition reactions with free chlorine could be significant in waters containing highly unsaturated plant pigments. However, they are slow reactions unless the double bonds are activated by substituent groups (Brezonik, 1994). In equation 10, R_1, R_2, R_3, and R_4 are substituent groups that activate the double bounds.

$$\tag{10}$$
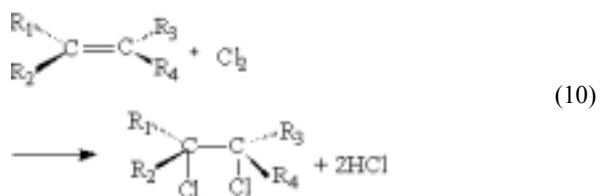
Substitution reactions involving chlorine are usually electrophilic (Brezonik, 1994) substitution (Equation 11).

$$\tag{11}$$
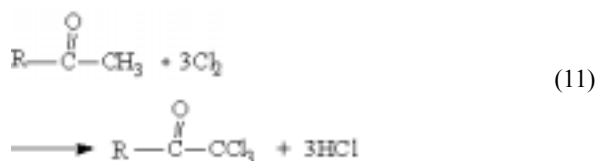
Hypochlorite ion decomposition in basic solution is a slow process (Gordon and Bubnis, 2000). The decomposition of OCl^- involves chlorite ion (ClO_2^-) as an intermediate in the following reaction (Adam and Gordon, 1999):

$$3OCl^- \rightarrow ClO_3^- + 2Cl^- \tag{12}$$

The decomposition of hypochlorious acid (HOCl) at pH 5 to 9 proceeds according to the following reaction stoichiometry (Adam et al. 1992):

$$2HOCl + OCl^- \rightarrow ClO_3^- + 2H^+ + 2Cl^- \qquad (13)$$

The other way for hypochlorite decomposition is the formation of O_2 (Lister and Petterson, 1962). The decomposition may be catalyzed by transition-metal ions such as Ni(II), Cu(II), and Fe(III) (Gordon and Bubnis, 2000).

$$OCl^- + OCl^- \xrightarrow{\text{transition-metal or UV}} O_2 + 2Cl^- \quad (14)$$
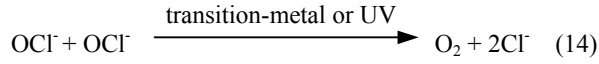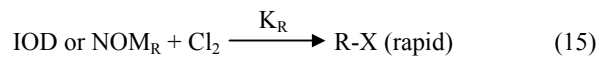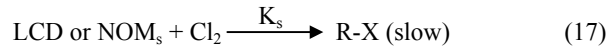
2.2. Model Development

A mathematical model was developed based on the above chlorine decay mechanisms to investigate chlorine decay in natural waters based on the following assumptions (Gang et al., 2002):

(1) In the presence of inorganic demand (IOD), chlorine follows a rapid first order decay when it reacts with these inorganic compounds (equations 3 to 7, 14).

(2) Two distinct types of reactive functionalities exist in NOM resulting in two parallel first order reactions. One NOM_R functionality, possibly attributed to aldehyde and phenolic hydroxyl groups, results in a very rapid rate of chlorine consumption (equations 8, 9). The other NOM_S functionality is less reactive, such as expected for activated double bonds and methyl groups, and results in a slow, long-term chlorine consumption (equations 10, 11).

(3) The other long-term chlorine demand (LCD) (12 and 13) follows slow first order decay.

(4) A fixed proportion of the chlorine follows rapid first order decay while the remaining proportion decays at slower first order rate for specific water.

The chemical reactions and corresponding kinetic equations for the consumption of chlorine by NOM are as follows:

$$\text{IOD or } NOM_R + Cl_2 \xrightarrow{K_R} R\text{-}X \text{ (rapid)} \qquad (15)$$

$$\frac{dC_R}{dt} = -k_R C \qquad (16)$$

$$\text{LCD or } NOM_s + Cl_2 \xrightarrow{K_s} R\text{-}X \text{ (slow)} \qquad (17)$$

$$\frac{dC_S}{dt} = -k_S C \qquad (18)$$

Integrating the above rate equations with $C_{R0} = fC_0$ and $C_{S0} = (1-f)C_0$, the chlorine concentration over time is:

$$C(t) = C_0 \left\{ f e^{-k_R t} + (1-f) e^{-k_S t} \right\} \qquad (19)$$

where

$C(t)$ is the chlorine concentration at any time t, (mg/L);
C_0 is the initial chlorine concentration (dose) to give the chlorine residual of approximately 1 mg/L after five days of reaction;
C_{R0} is the initial chlorine concentration participating in the rapid reaction (mg/L);
C_{S0} is the initial chlorine concentration participating in the slow reaction (mg/L);
f is the fraction of the chlorine decay attributed to rapid reactions (dimensionless);
k_R is the first-order rate constant for rapid reactions (h^{-1});
k_S is the first-order rate constant for slow reactions (h^{-1}).

3. Material and Methods

Three of the surface water samples (Garden City, Maysville, and Lake Vandalia) were from small lakes in rural Missouri agricultural watersheds and the fourth was from the Mississippi River at Chester, IL south of the Missouri River confluence. The characteristics of the water samples are listed in Table 1. In Table 1, CWR and CWT represent Chester Raw Water and alum treated Chester water, respectively; GWR and GWT represent Garden City Raw Water and alum treated Garden City water, respectively; MWR and MWT represent Maysville Lake Raw Water and alum treated Maysville Lake water, respectively; LWR and LWT represent Lake Vandalia Raw Water and alum treated Lake Vandalia water. Alum coagulated waters at a dose of 60 mg/L alum were prepared from these waters using a Phipps and Bird jar test apparatus. Rapid mixing was at 200 rpm for 1 minute; flocculation was at 40 rpm for 30 minutes; settling was for 30 minutes; followed by filtration using a 1.0-μm glass fiber filter. The filtrate from each jar was used for the chlorine decay studies.

The sodium hypochlorite dosing solution was made from a 13% free chlorine (sodium hypochlorite) stock solution and buffered to pH 8.0 using a borate buffer (Summers et al., 1996). Prior to chlorination, the strength of the dosing solution was measured three times to ensure accuracy. The average of the three analyses was used to calculate the dosing solution volume required for obtaining the desired chlorine dose in the test reactor. Chlorination was carried out at pH 8.0 (± 0.2) (Summers et al., 1996). Appropriate amounts from a concentrated sodium hypochlorite dosing solution (1 to 3 g/L) were added to the water samples to obtain the desired disinfectant doses. A blank was prepared using the same amount of deionized ultra filtered water (DIUF, obtained from Fisher Scientific) chlorinated under the same conditions as the samples. This blank was used as a reference to establish the initial chlorine concentration.

A 120-hour chlorine demand preliminary study was performed using a series of three chlorine dosages based on Cl$_2$:DOC ratios of 1.2:1, 1.8:1, and 2.5:1 to determine the chlorine demand (120 hours) of the water samples (Summers et al., 1996).

Samples were chlorinated in two gallon glass bottles and then carefully transferred into 150 ml amber glass bottles with Teflon-lined caps (making sure no air bubbles

passed through the sample during the bottle filling operation, or were trapped in the sample when the bottle was sealed). A separate bottle was used for each reaction time investigated. Until analyzed, the samples were kept headspace free in the dark at room temperature (25°C). Chlorine residual, UV adsorption were measured at different times for each bottle. Chlorine concentration was measured by DPD colorimetric method (EPA approved HACH 8021) using HACH DR/2000 spectrophotometer. Ultra violet absorbance at 254 nm (UV_{254}) was conducted with a CARY 50 spectrophotometer with a 1-cm quartz cell. The specific ultraviolet absorbance (SUVA) was calculated as UVA*100/DOC (unit of L·m/mg). DOC concentrations were measured using a Dohrman Phoenix 8000 TOC analyzer. Potassium hydrogen phthalate was used as an external standard.

The parameters f (the fraction of the chlorine demand attributed to rapid reactions), k_R (the first-order rate constant for rapid reactions, h^{-1}), and k_S (the first-order rate constant for slow reactions, h^{-1}) were determined from the collected chlorine decay data using nonlinear regression software (SigmaPlot Version 5.0, SPSS).

4. Results and Discussion

4.1. Chlorine Decay in Different Surface Waters

Figures 1 and 2 show the chlorine decay data of the raw and alum treated water samples, respectively. From these figures it can be seen that the chlorine residual decreased with time. Chlorine decay was quite fast at the beginning for all the water samples. It was apparent from the shape of the chlorine residual curves that rapid and slow reactions were taking place. It was difficult to make a conclusion about the chlorine decay kinetics, since the chlorine dosed varied from 3.62 mg/L to 12.20 mg/L. In order to more clearly illustrate the initial chlorine decay kinetics, and to minimize the variability in the initial chlorine dose, the results were plotted on a normalized semi-log scale in Figures 3 and 4, where the concentrations were expressed as C/C_0. Comparing the results in Figure 3 it can be seen that the chlorine decay kinetics were generally similar under the experimental conditions for all raw waters, although the DOC characteristics were different. The DOC concentrations in these waters varied from 3.99 to 9.89 mg/L (Table 1). After 15 minutes, all water samples had a residual of about 80 to 85% of the initial dose; after 8 hours, the residuals were reduced to about 60% of the initial dose. Similar results were observed from alum treated waters in Figure 4, but there were some differences in the kinetics between these water samples. For example, chlorine decay exhibits approximately 25 percent faster in Maysville (MWT) water than in Garden City water (GWT). After 15 minutes, all water samples had a residual of about 80% of the initial dose; after 8 hours, the residuals were reduced to about 45 to 60% of the initial dose. As expected, these

results varied from other researcher's (Isabel et al., 2000) conclusions, because chlorine residual concentrations in this study were constant at the end of study period.
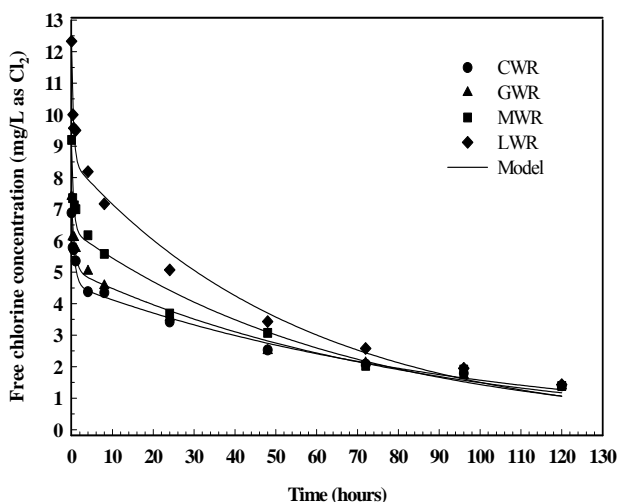

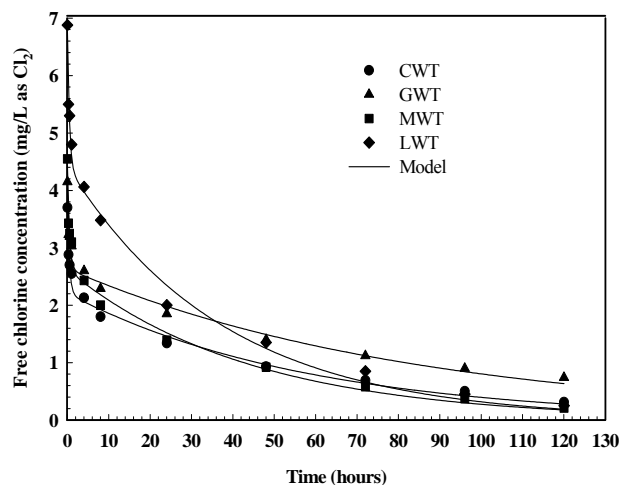**Figure 1.** Chlorine decay data of raw waters and fitted to the parallel first-order reaction model.

Figure 2. Chlorine decay data of alum treated waters and fitted to the parallel first-order reaction model.

4.2. Chlorine Decay Parameters

The three-parameter parallel first-order reaction model (equation 19) was used to fit the chlorine decay data of the raw and alum treated waters. The results are shown in Figures 1 and 2. The lines in these figures are the modeling results. The model fitted the chlorine data well, yielding correlation coefficients of about 0.98. The reaction constants and other parameters are shown in Table 2.
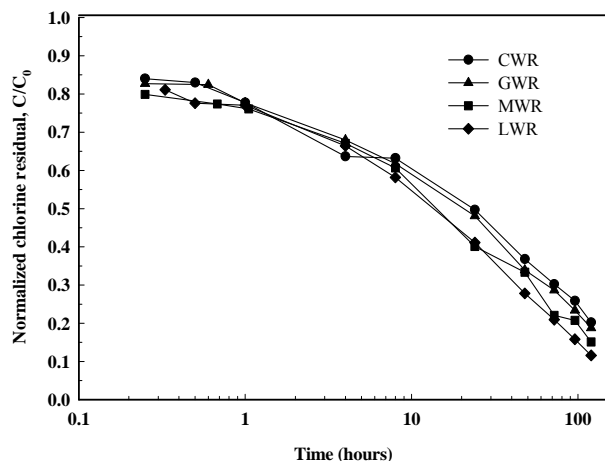
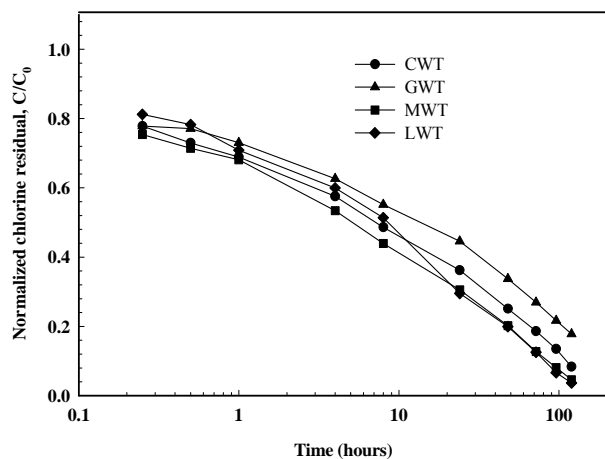**Figure 3.** Dose normalized Chlorine decay curves of raw waters.

Figure 4. Dose normalized chlorine decay curves of Alum treated waters.

Values of k_R for raw surface waters ranged from 1.25 to 2.06 h^{-1} and k_S ranged from 0.011 to 0.017 h^{-1}. The k_R was about 100 to 200 times larger than k_S for all raw surface water samples. Values of k_R for treated waters ranged from 1.91 to 2.21 h^{-1} and k_S ranged from 0.012 to 0.026. The k_R was about 80 to 160 times larger than k_S for all treated water samples. The f values (the fraction of the chlorine decay attributed to rapid reactions) of the raw waters ranged from 0.29 to 0.30, which meant that about 30% of chlorine was used up by the rapid first order decay reaction in the raw waters (CWR, GWR, MWR, and LWR). The f values of the alum treated waters range from 0.34 to 0.41. The average f value of the treated waters was about 0.35, which meant that about 35% of the chlorine was consumed by the rapid first order reaction. Vasconcelos et al. (1995) reported that the k_R was sometimes larger than k_S in some water samples, while in others k_R was smaller than k_S and f value changed from 0.36 to 1.0 for different water samples. This could be due to variable chlorine residual concentrations of water

samples at the end of their study. Another possible reason could be the different characteristics of the water samples, because surface and well waters were used in their study.

4.3. Effects of Alum Coagulation on Chlorine Decay

From Table 1 it can be seen that alum coagulation reduced the DOC by 35.5 %, the UV_{254} by 60 %, chlorine demands (120hrs) by 38.6%, and SUVA by 40% on the average, suggesting that alum treatment preferentially removed higher UV absorbing organics.

The decay constants (k_R and k_S) and f values of the raw waters were compared to that of the treated waters in Table 2. On average k_R increased 32.3%, while k_S increased 44% after alum coagulation treatment. All f values of the treated waters were higher than those of the raw waters. This suggested that more chlorine followed the rapid first order decay in the treated waters compared to the raw waters. Alum treatment substantially increased the fraction of rapidly reacting functional groups for all treated waters with f increase averaging 24% after treatment. These results suggest that the alum treatment removed a large portion of the slowly reacting organics. Sinha (1999) reported that larger molecular weight NOMs are preferentially removed by coagulation as compared with the small molecular weight NOMs. Therefore the slowly reacting organics may be attributed to high molecular weight DOC. In Table 2 average specific chlorine demand (SCD) [defined as the ratio of the chlorine demand (mg/L) to the concentration of DOC (mg-C/L)] of the treated waters was 1.15; while in the raw waters it was 1.34. All the SCD of the treated waters were lower than the raw waters. Alum treatment decreased the specific chlorine demand (SCD) of the water by an average of 14.4%. Therefore, alum coagulation processes may preferentially remove more NOM, which has higher specific chlorine demands, and hence may have higher chlorinated DBPs production.
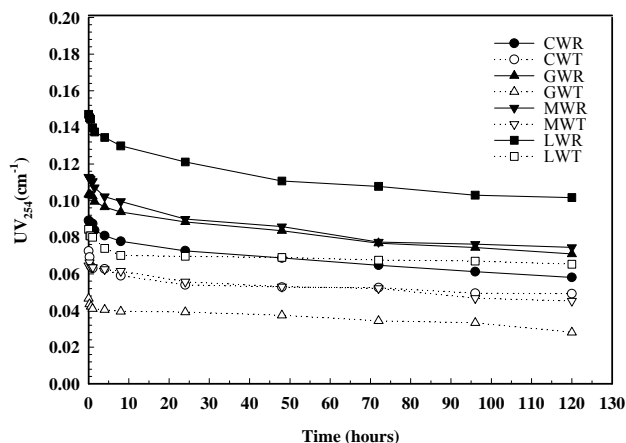

Figure 5. Comparison of UV_{254} changes with time for raw and treated winter waters.

Table 1. Characteristics of the Raw and Alum Treated Water Samples[*]

Water sources		DOC (mg/L)	DOC change (%)	C_0 (mg Cl₂/L)	Chlorine demand change (%)	UV_{254} (cm⁻¹)	UV_{254} change (%)	SUVA (L · m/mg)	SUVA change (%)
Mississippi River (Chester)	Raw (CWR[**])	3.99	-22.6	6.68	-38.3	0.1096	-52.7	2.75	-39.0
	Tretd (CWT)	3.09		3.62		0.0518		1.68	
Garden City	Raw (GWR)	4.40	-36.4	7.16	-43.3	0.1045	-72.8	2.38	-57.3
	Tretd (GWT)	2.80		4.03		0.0284		1.01	
Maysville Lake	Raw (MWR)	5.66	-32.0	8.95	-44.4	0.1346	-65.6	2.38	-49.4
	Tretd (MWT)	3.85		4.43		0.0463		1.20	
Lake Vandalia	Raw (LWR)	9.89	-41.7	12.20	-40.2	0.1574	-58.0	1.60	-28.0
	Tretd (LWT)	5.77		6.67		0.0661		1.15	
Average			-35.5		-38.6		-59.8		-39.9

[*]Water samples were collected in Dec, 1999

[**]CWR: Chester Raw Water; CWT: Alum treated Chester water; GWR: Garden City Raw Water; GWT: Alum treated Garden City water; MWR: Maysville Lake Raw Water; MWT: Alum treated Maysville Lake water; LWR: Lake Vandalia Raw Water; LWT: Alum treated Lake Vandalia water.

Table 2. Chlorine Decay Constants and Fitting Parameters of Raw and Alum Treated Waters

Water sources		k_R (h⁻¹)	Change (%)	K_S (h⁻¹)	Change (%)	f	Change (%)	SCD	SCD Change (%)	R^2
Chester	CWR[*]	1.25	77.3	0.011	61.7	0.32	23.7	1.38	-20.3	0.991
	CWT	2.21		0.017		0.39		1.10		0.991
Garden City	GWR	1.30	46.8	0.011	9.0	0.30	18.0	1.37	-10.8	0.987
	GWT	1.91		0.012		0.35		1.22		0.985
Maysville	MWR	1.92	4.19	0.015	52.7	0.29	39.9	1.38	-18.3	0.979
	MWT	2.00		0.023		0.41		1.13		0.989
Lake Vandalia	LWR	2.06	1.0	0.017	52.6	0.30	14.9	1.10	-8.1	0.990
	LWT	2.08		0.026		0.35		1.13		0.994
Average			32.3		44.0		24.0		-14.4	0.988

[*]CWR: Chester Raw Water; CWT: Alum treated Chester water; GWR: Garden City Raw Water; GWT: Alum treated Garden City water; MWR: Maysville Lake Raw Water; MWT: Alum treated Maysville Lake water; LWR: Lake Vandalia Raw Water; LWT: Alum treated Lake Vandalia water.

4.4. Alum Coagulation Effects on UV_{254} Values

Figure 5 illustrates the UV_{254} changes with time after chlorination of raw and alum treatment water samples. UV_{254} decreased with time for both raw and alum treated water samples, especially at the beginning of the reaction period. UV_{254} is a measurement of unsaturated bonds in the DOC. After the addition reaction, a portion of the unsaturated bonds became saturated, and the UV_{254} values decreased with time. This conclusion is consistent with the results reported by Li and his co-workers (1998) that the chlorination of potable water altered and/or destroyed chromophores in NOM, causing UV_{254} of the solution to decrease. Change in UV_{254} upon chlorination may be due to alteration/removal of the function groups of the aromatic rings rather than cleavage of the rings. These alternations may change the electron distribution around the multiple aromatic rings making up the high molecular weight NOM, affecting the UV_{254}. Most of the UV_{254} related NOM were not degraded, because of the stability of the benzyl or phenyl rings. Thus, only a small change in UV_{254} was seen with extensive chlorination.

UV_{254} declined rapidly while the rapid reaction dominated the chlorine demand and slowly thereafter. Thus, UV_{254} contributes mostly to the rapid reaction and very little to the slower reaction. For treated water, very little change in UV_{254} occurs after the initial decline. The overall decline in UV_{254} is about 15% in 120 h. UV_{254} may be a misleading DPB formation surrogate or model parameter for alum treated waters, because only a small portion of UV_{254} was affected by the chlorination reaction. The UV_{254} values of the treated water samples were smaller than those of the raw water samples at a specific time due to the removal of the DOC by the alum coagulation.

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