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Occurrence of disinfectant by-products during the sequential disinfection process

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ABSTRACT

Sequential disinfection is considered a viable treatment option for the effective inactivation of pathogenic micro-organisms such as oocysts of protozoan parasites (e.g. *Cryptosporidium parvum* etc.) and spores of vegetative bacteria (e.g. *Bacillus subtilis* and *Bacillus anthracis*) that cannot be treated by the single-step application of chlorine-based disinfectants and for viruses (e.g. *Adenovirus*) that cannot be easily treated by the single-step application of UV irradiation. The aim of this research was to investigate the inactivation of *B. subtilis* spore and formation of disinfection by-products (DBPs) during sequential disinfection using a combination of chlorine dioxide and chlorine (ClO_2/HOCl) or UV and chlorine (UV/HOCl) sequential disinfection. *B. subtilis* spores have been widely used as an indicator micro-organism for *C. parvum* oocysts. Trihalomethanes (THMs) and haloacetic acids have been used as indicator for DBPs. This study evaluates the effect of operating parameters (e.g. chemical dose, contact time, organic matters, and pH) on the synergistic inactivation of *B. subtilis* spores and formation properties of DBPs. The synergistic effect of inactivation of *B. subtilis* spores and control of DBPs were shown when chlorine dioxide was used as the primary disinfectant and chlorine as the secondary disinfect. Almost no synergistic effect was observed when the UV irradiation treatment was followed by chlorine reaction. In contrast to ClO_2/HOCl sequential disinfection, THMs were increased when UV was used as the primary disinfectant and chlorine as the secondary disinfect. UV/HOCl sequential disinfection increased chlorine demand about 13.6%. This result might be attributed to the change of DOM structure by UV irradiation which might affect the chlorine demand, and resulted in increase of THMs formation in the UV/HOCl sequential disinfection.

Keywords: Sequential disinfection; Disinfectant by-products(DBPs); Chlorine dioxide; UV; Chlorine

1. Introduction

When the rate of used chlorine is increased to control chlorine-resistant pathogenic micro-organisms during the purification treatment process, the risk of the formation of disinfectant by-products, such as trihalomethanes (THMs) and haloacetic acids (HAAs), also increase. Thus, a substitutive disinfectant technology that can supplement the insufficient CT value rate

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and simultaneously optimize the removal of micro-organisms during the conventional treatment processes must be used. The substitutive disinfectant technology must have low risk of disinfectant by-products while having a strong enough CT value to inactivate the protozoans. Even if such a substitutive disinfectant is used, however, an additional chlorinated disinfectant with a high residual concentration must also be used to control micro-organisms in the distribution system. As a result, ozone, chlorine dioxide, and UV must be used as the pre-disinfectants to perfectly remove chlorine-resistant pathogenic micro-organisms that are difficult to control with chlorination alone; chlorination must be used as the post-disinfectants to continually provide microbiologically safe water in the distribution system after the pre-disinfection process. The pre- and post-disinfection processes are collectively called the sequential disinfection process [1]. In a sequential disinfection scheme, a strong primary disinfectant is first applied to achieve a portion of the target inactivation level followed by the secondary disinfectant to attain further inactivation and to provide residual disinfection for water distribution. When disinfectants are applied consecutively, it is often found that the overall inactivation level achieved is greater than the sum of the inactivation levels achieved when each disinfectant is applied independently. The representative sequential disinfection technologies include the free chlorine after ozone reaction (O_3/HOCl), free chlorine after chlorine dioxide (ClO_2/HOCl), and free chlorine after ultraviolet reaction (UV/HOCl). For instance, the sequential application of ozone (or ozone/H_2O_2) followed by free chlorine was shown to achieve a higher level of inactivation of *B. subtilis* spores than the sum of the inactivation level achieved with individual ozone and free chlorine application [2]. The synergistic effect of sequential disinfection on micro-organism inactivation has been verified, but there are few studies on the changes in the productive characteristics of the disinfectant by-products at same conditions. Accordingly, this study was conducted to evaluate the inactivation of *B. subtilis* spores and formation characteristics of disinfection by-products (DBPs) during sequential disinfection using ClO_2/HOCl and UV/HOCl. Especially, this study focuses on the effect of operating parameters (e.g. chemical dose, contact time, organic matters, and pH) on the synergistic inactivation of *B. subtilis* spores and formation of DBPs.

2. Materials and methods

A sequential application of chlorine dioxide or UV as a primary disinfectant followed by free chlorine as secondary, residual disinfectant was performed to evaluate the synergistic inactivation of *B. subtilis* spores and the productive characteristics of the disinfectant by-products. The sequential disinfection experiments were performed by first applying chlorine dioxide and UV as the primary disinfectant and then free chlorine as the secondary disinfectant. *B. subtilis* spores have been widely used as an indicator micro-organism for *C. parvum* oocysts. THMs and HAAs have been used as indicator for DBPs in this study. Grade chemicals were used for all the reagents in the experiments. 12 N H_2SO_4 (Showa Co., Japan) and 25% $NaClO_2$ (Aldrich Co.) were used to form chlorine dioxide [3]. The collimated-beam UV system was used for the UV disinfection. Four low-pressure UV lamps [Germicidal Lamp (253.7 nm, 4 W, Philips Co.)] were used as the sources of light, and their vertical illumination was adjusted. The Pyrex Deep Petri-dish (50 mL, 6 × 3 cm) was used as the reactor in the UV disinfection, and was agitated using a magnetic stirrer. A UV 253.7 Detector (UVX radiometer, UVP Co.) was used to measure the light intensity, and was set at 0.1–0.4 mW/cm^2 by adjusting the distance between the reactor and the lamp [4,5]. The pH of a phosphoric acid buffer solution was used as the control pH; 1,000 mg/L of a stock solution was made by diluting concentrated sodium hypochlorite (10–13%, Aldrich Co.) as the chlorinated disinfectant. The TOC analyzer (Shimadzu TOC-5000A, Japan) was used to analyze the DOC, and the chlorine concentration was colored with a DPD (*N*,*N*-dimethyl-p-phenylenediamine) indicator and then analyzed at 530 nm using the UV/Vis spectrophotometer (DR/4000, HACH Co.). THMs were pretreated with the Standard Method 6232B (liquid–liquid extraction method) and analyzed with GC/ECD. J&W Scientific DB 624 (30 m × 0.53 mm ID × 3 μm) was used as the column and analyzed at 5–170℃/min, with an oven temperature of 35℃ (2 min) set in the split mode [6]. HAAs were pre-treated with the EPA Method 552.3 and analyzed with GC/ECD. The J&W Scientific DB 5 column was used and analyzed at 4–90℃ (5 min) and 10–200℃ (1 min) with an oven temperature of 4–80℃ (5 min) in the split mode [7]. A platinum pool of a refrigerated *B. subtilis* sp. (ATCC 6633) solution was inoculated into nutrient broth (Difco Co., USA), then incubated at 37° C and spread on 1/10 nutrient agar for 5–6 days. The induced sporulation was collected to clean the suspended liquid in the PBS, and then was heat treated for 15 min at 80℃ for use in the experiment. A precise amount was quantified with the spread plate method [6].

3. Results and discussion

3.1. *Inactivation of* B. subtilis *spores*

Fig. 1 shows the decrease in the viability of *B. subtilis* spores vs. CT (i.e. the product of time-averaged disinfectant concentration, C, and contact time) during the chlorine dioxide as a primary disinfectant followed by free chlorine as a secondary. The ClO_2/HOCl reaction showed an obvious increase of *B. subtilis* inactivation according to the change in the CT value at the pH of 5.6 and 8.2. This reaction showed a satisfactory above 5 log level in 30 mg/L min of HOCl CT, if the CT level of 40 mg/L min was satisfied using chlorine dioxide for the pre-treatment. Similarly, at a pH of 8.2, the level of HOCl CT declined by around 55% from 400 to 180 mg/L min, if 40 mg/L min chlorine dioxide CT was satisfied to remove 3 log.

Fig. 2 shows the decrease in the viability of *B. subtilis* spores during the UV as a primary disinfectant followed by free chlorine as a secondary. *B. subtilis* spores inactivation at above 25 mJ/cm^2 was increased in UV/HOCl than in HOCl alone with a pH of 5.6, which also showed 3 log at 50 mg/L min. Almost no synergistic effect was seen in this reaction.

Table 1 summarizes synergistic effects quantified using percent synergistic effect in sequential disinfection previously defined as "additional log inactivation achieved via sequential disinfectant application compared to individual application"[2]. Percent synergistic effects for ClO_2/HOCl sequential disinfection for *B. subtilis* spores were 175 and 130% at pre-chlorine dioxide 5 mg/L min, respectively. As shown in Table 1, UV/HOCl reaction showed the absence of synergistic effect at UV 10 mJ/cm^2 condition.

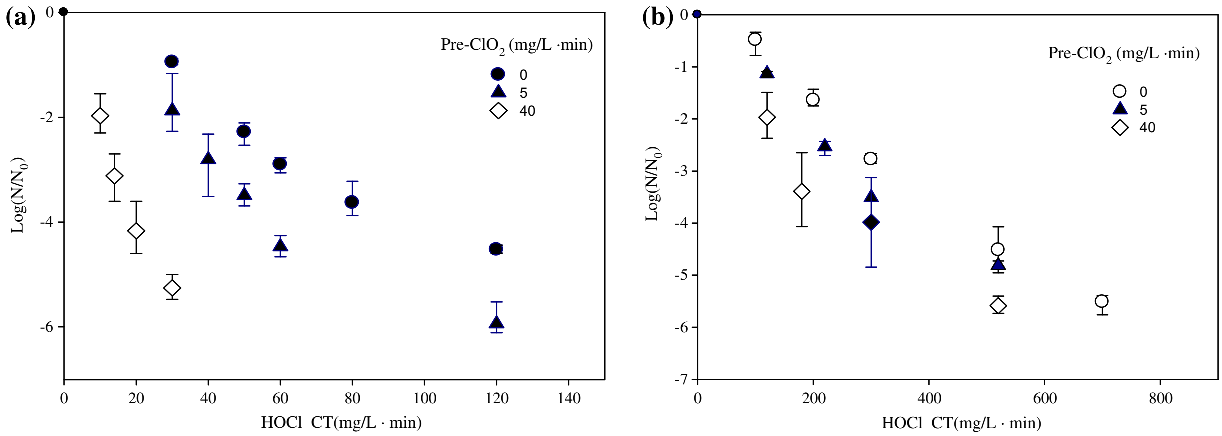

Fig. 1. Inactivation of *B. subtilis* sp. through sequential application of free chlorine after chlorine dioxide at pH of (a) 5.6 and (b) 8.2 and at 20°C.

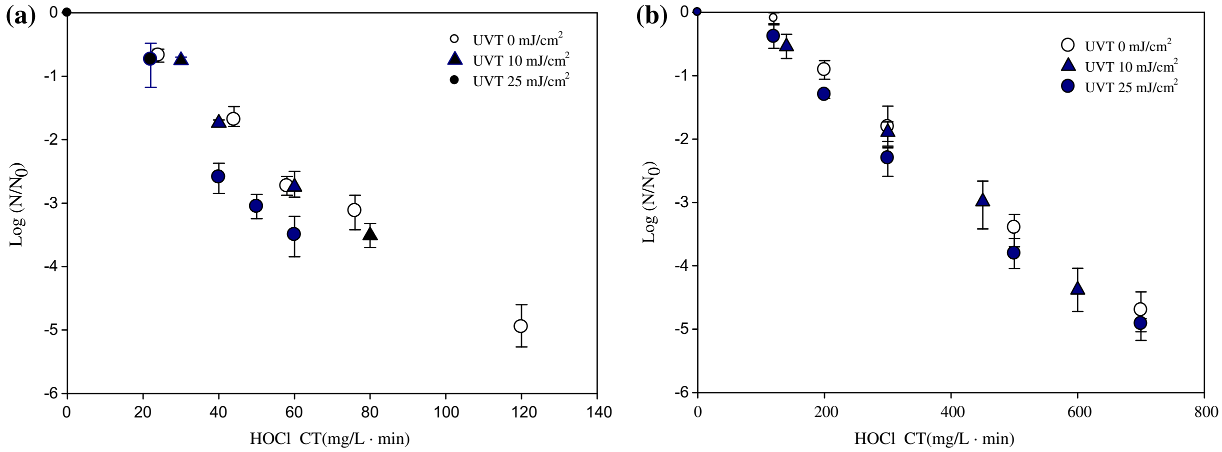

Fig. 2. Inactivation of *B. subtilis* sp. through sequential application of free chlorine after UV at pH of (a) 5.6 and (b) 8.2 and at 20°C.

Table 1
Percent synergy effect of *B. subtilis* spores inactivation in ClO_2/HOCl and UV/HOCl sequential disinfection

	HOCl	ClO_2/HOCl Pre-chlorine dioxide (mg/L min)		UV/HOCl Pre-UV(mJ/cm^2)	
		5	40	10	25
pH 5.6	2 log	3.5 log	7 log	2 log	3 log
pH 8.6	2 log	2.6 log	4 log	2 log	2 log

3.2. THMs formation in ClO_2/HOCl sequential disinfection

This study comparatively examined the properties of THMs formation characteristics by changing the conditions, including the pH, temperature, reaction time, and DOC, in the sequential disinfection of ClO_2/HOCl reaction and HOCl alone. The experimental conditions were changed within the following ranges: DOC concentration, 1.27–5.18 mg/L; pH, 5–9; temperature, 10–20℃; chlorine dioxide concentration, 1.2–5 mg/L; chlorine concentration, 0.7–5.4 mg/L; and reaction time, 0–12 h. The quenching reagent, $Na_2S_2O_3$, was used to remove the remaining disinfectants. Fig. 3 shows the results of the THMs formation at each hour by changing chlorine dioxide concentration in ClO_2/HOCl sequential disinfection. Experimental conditions were DOC of 1.27 mg/L, a pH of 7, a temperature of 20℃, and a ClO_2 concentration was increased from 1.2 to 5 mg/L. The ClO_2 reaction time was set at 10 min, and a 2 mg/L free chlorine concentration was sequentially injected. The quantity of THMs will increase as the reaction time increases, but will not drastically change as the chlorine dioxide concentration increases in range of 1.2–2 mg/L or 3.5–5 mg/L. The results of the experiment showed a bigger reduction in the THMs formation in ClO_2/HOCl reaction than HOCl alone, and a decrease in the THMs formation with a higher concentration of chlorine dioxide.

Fig. 4 shows the results of the comparison of the THMs formation that were formed in ClO_2/HOCl and HOCl reaction at same condition for the 2 log *Giardia* inactivation, respectively. After 5 mg/L of ClO_2 as the primary disinfectant was injected to ClO_2/HOCl reactor and then, 1.5 mg/L of the free chlorine as the secondary disinfectant was injected. The sum of the HOCl CT level became 60 mg/L min. For the same condition with the HOCl alone, CT value with HOCl reaction alone was kept at 420 mg/L min. The results

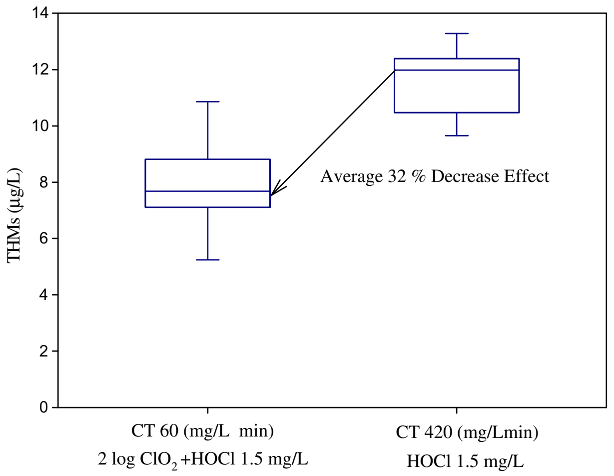

Fig. 4. THMs formation in ClO_2/HOCl and HOCl, under the CT conditions that satisfied 2 log *Giardia* inactivation (DOC 1.27 mg/L, pH 7, temperature 20℃).

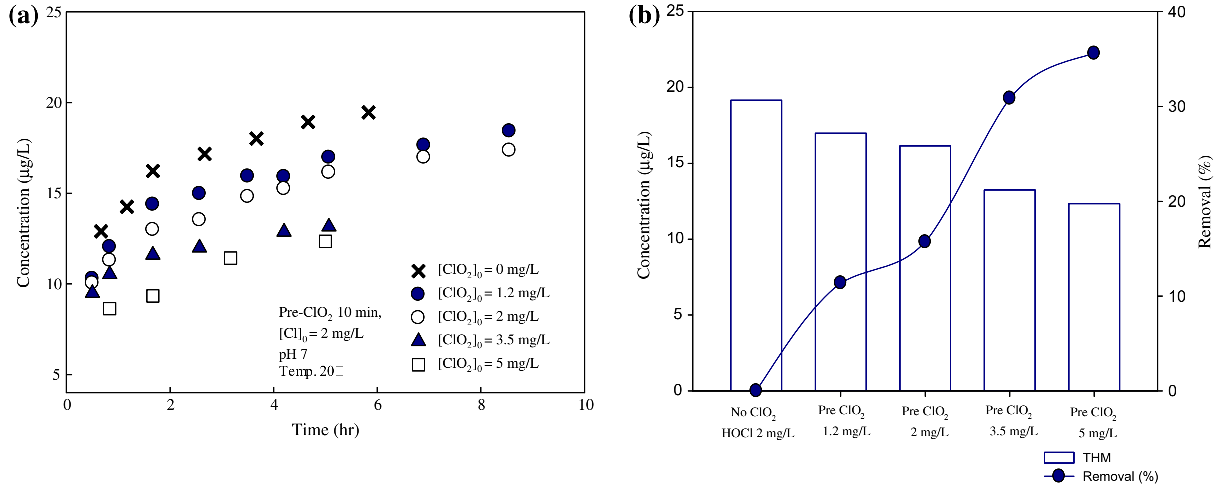

Fig. 3. THMs formation in ClO_2/HOCl (a) THMs formation at the reaction time of 0–12 h and (b) THMs formation at the reaction time of 5 h based on the ClO_2 concentration.

showed 32% lower THMs formation in ClO_2/HOCl than in HOCl reaction alone. The possible cause is that ClO_2 as the primary disinfectant reacted directly with DBPs precursors.

Fig. 5 shows the results of the comparison of the THMs formation in ClO_2/HOCl with that in HOCl reaction by changing the DOC concentration. The DOC was changed from 1.27 to 3.32 and 5.18 mg/L, and the pH was set at 7; the temperature, at 20˚C; the ClO_2 concentration, at 5 mg/L; and the reaction time, at 10 min, to conduct the experiment by changing the reaction time and the HOCl concentration. The results of the experiment showed an increase in the THMs formation with a higher DOC concentration, and the THMs formation was approximately 28.3% lower in ClO_2/HOCl than in HOCl, with the a DOC concentration of 5.18 mg/L and a CT of 600 mg/L min, particularly as the DOC concentration increased.

3.3. *Effect of different NOMs on THMs formation in ClO_2/HOCl*

In this study, the properties of disinfectant by-product formation in sequential disinfection were observed by using raw water from P water purification plant, humic acid (Aldrich Chemicals, USA) (Cat. No. H1675-2), Suwannee River humic acid standard II (Cat. No. 2S101H), and natural organic matter (NOM) (RO Isolation) [International Humic Substances Society (IHSS) (Cat. No. 1R101N), USA] [8]. All samples were filtered through a 0.45 μm cellulose acetate membrane filter. The DOC level of the Aldrich humic acid, Suwannee River humic acid, and NOM samples was 1.6 mg/L, and the UV_{254} were 0.159, 0.122, and 0.129 cm^{-1}, respectively, with an alkalinity of approximately 30 mg/L as $CaCO_3$. The raw water at P purification plant had a DOC level of 1.6 mg/L, a 0.024 cm^{-1} UV_{254}, an alkalinity of 50 mg/L as $CaCO_3$, and 1 NTU turbidity. In the ClO_2/HOCl reaction, the ClO_2 was set at 2 mg/L; the reaction time, at 1 h; and the chlorine injection rate, at 5 mg/L, to observe the changes with the reaction times of 2–168 h at a temperature of 20˚C. For the UV/HOCl reaction, the UV dose was set at 60 mJ/cm^2, with the chlorine dose of 5 mg/L, to observe the changes with the reaction times of 2–168 h. The quenching reagent, $Na_2S_2O_3$, was also used to remove the residual. The results of the THMs formation based on the type of organic matter in ClO_2/HOCl reaction and HOCl are shown in Fig. 6. The concentration of THMs in both processes constantly increased until reaction time of up to 168 h, and the THMs formation showed a greater decrease in ClO_2/HOCl reaction than HOCl alone, even with different organic matter. The reduction in the THMs formation seemed to have been greatest in the Suwanne River NOM.

Fig. 7 shows the combined results of the comparison of the formation of THMs in ClO_2/HOCl reaction with that in HOCl alone at 168 h. The reduction effect of the THMs formation was seen in all the conditions of the organic matter in ClO_2/HOCl reaction, and a 20 μg/L reduction in the THMs formation was seen in the raw water, based on the changing properties of the organic matter. Also, a reduction rate of 20–100 μg/L was seen in each type of organic matter. Accordingly, the changing properties of the organic matter in ClO_2/HOCl reaction significantly affected the potential for THMs formation, and led to the conclusion that the analysis of the properties of the organic matter of raw water must be prioritized to minimize THMs formation, if this process is implemented in actual sites.

Fig. 8 shows the results of the comparison of the formation of HAAs in ClO_2/HOCl sequential disinfec-

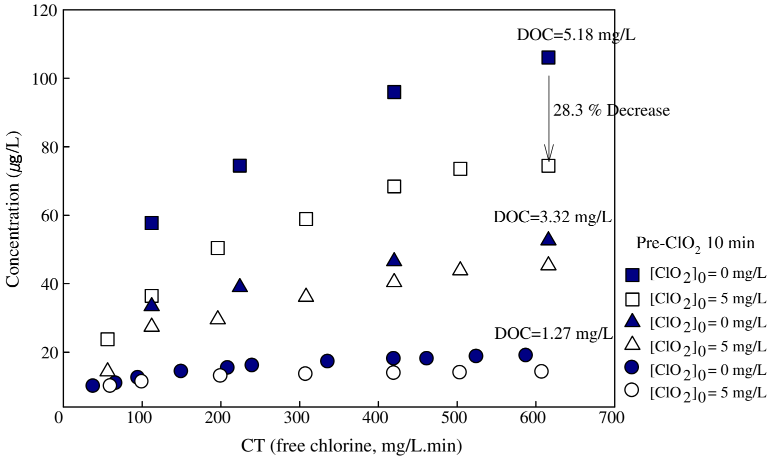

Fig. 5. Comparison of the THMs formation according to the DOC concentration in ClO_2/HOCl and HOCl.

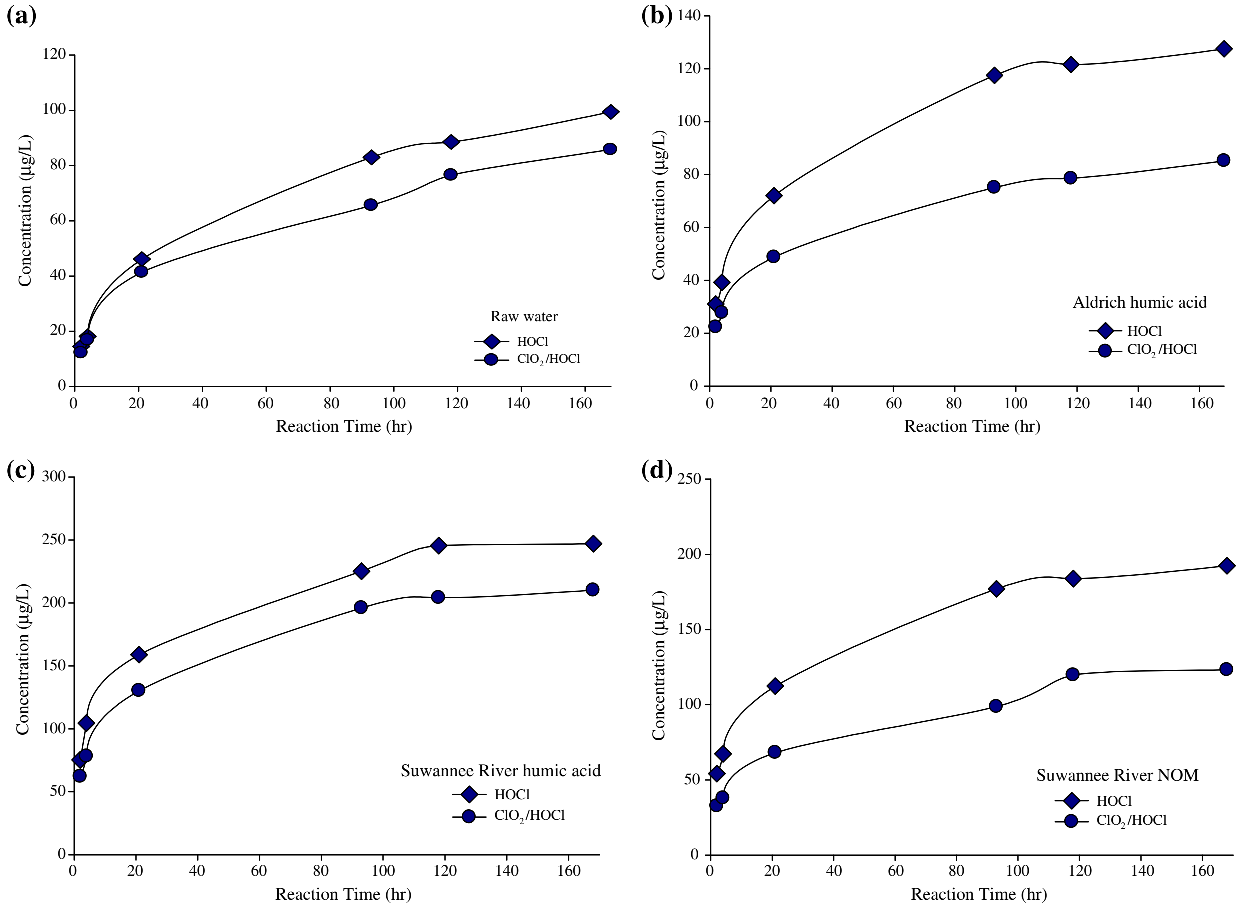

Fig. 6. THMs formation in the ClO_2/HOCl of the selected organic waters.

tion and HOCl disinfection alone at same condition in Fig. 7. The formation of HAAs was the lowest in raw water from P water purification plant and the highest in the Suwanne River humic acid in both the ClO_2/HOCl and HOCl.

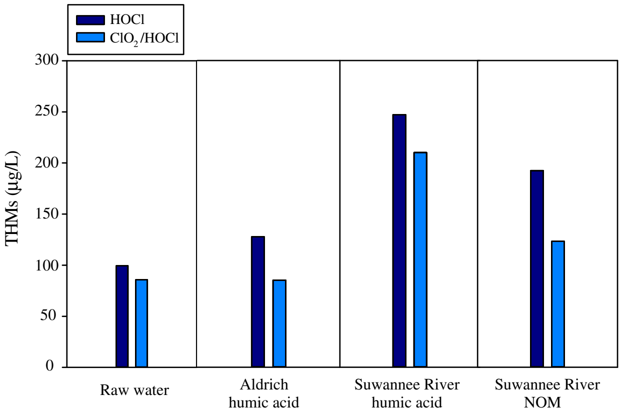

Fig. 7. THMs formation from ClO_2/HOCl and HOCl in four different organic waters.

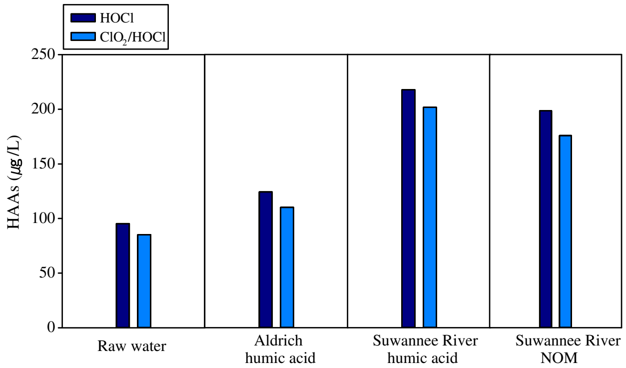

Fig. 8. HAAs formation from the ClO_2/HOCl and HOCl in four different organic waters.

3.4. Effect of different NOMs on THMs formation in UV/HOCl sequential disinfection

A 4 W low-pressure sterilizing UV lamp was used in the UV/HOCl reaction, and the UV strength was measured with a UVX radiometer, with the HOCl concentration set at 5 mg/L. Fig. 9 shows the results

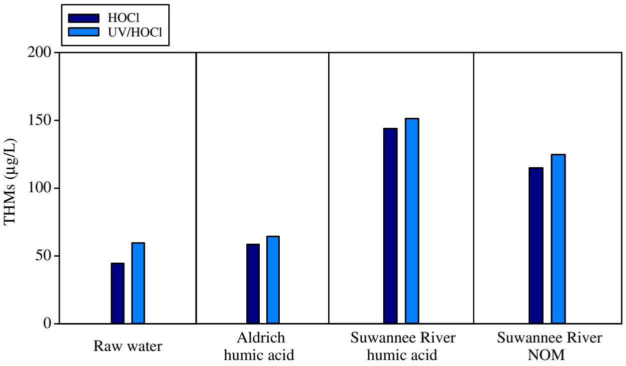

Fig. 9. THMs formation from the UV/HOCl and HOCl in four different organic waters.

of the THMs formation that reacted with chlorine at 168 h for each type of organic matter in the UV/HOCl reaction and HOCl. The results also showed the highest THMs formation in the Suwanne River humic acid after 168 h, among the four organic matters, and a greater increase in the THMs formation in the UV/HOCl reaction than in HOCl. Furthermore, the greatest increase in the THMs formation was seen in the UV/HOCl reaction than HOCl alone, after 168 h in the P water purification plant sample, at approximately 25.2%. In contrast to ClO_2/HOCl sequential disinfection, THMs were increased when UV was used as the primary disinfectant and chlorine as the secondary disinfect. UV/HOCl reaction increased chlorine demand about 13.6%, this caused the increment of THMs formation. Many researchers also have reported that UV irradiation can modify DOM structure and increase biodegradability [8,9]. This result is attributed to the change of DOM structure by UV irradiation which might affect the chlorine demand, and result in increase of THMs formation in UV/HOCl reaction.

4. Conclusions

A sequential application of chlorine dioxide or UV as a primary disinfectant followed by free chlorine as secondary, residual disinfectant was performed to evaluate the synergistic inactivation of *B. subtilis* spores and the productive characteristics of the disinfectant by-products. ClO_2/HOCl sequential disinfection showed a more efficient synergistic effect, in comparison with the *B. subtilis* spores inactivation, as well as lower THMs and HAAs formation than UV/HOCl and HOCl alone. Percent synergistic effects for ClO_2/HOCl sequential disinfection for *B. subtilis* spores were 175 and 130% at pH of 5.6 and 8.2, respectively. UV/HOCl reaction showed the absence of synergistic effect. ClO_2/HOCl sequential disinfection showed about 20% decrease in the THMs formation than HOCl reaction alone, and the reduction effect was seen as greater with a higher DOC concentration. In contrast to ClO_2/HOCl, the THMs formation increased in the UV/HOCl reaction. UV/HOCl sequential disinfection increased chlorine demand about 13.6%. This result might be attributed to the change of DOM structure by UV irradiation which might affect the chlorine demand, and result in increase of THMs formation in the UV/HOCl reaction. Low pressure UV irradiation generally cannot mineralize DOM, but might change chemical structure and characteristics of DOM.

Acknowledgements

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