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Simultaneous Control of Microorganisms and Disinfection By-products by Sequential Chlorination[1]

CHAO CHEN[*], XIAO-JIAN ZHANG[*], WEN-JIE HE[#], AND HONG-DA HAN[#]

[*]*Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China;* [#]*Tianjin Water Works (Group) Co. Ltd., Tianjin 300040, China*

Objective To introduce a new sequential chlorination disinfection process in which short-term free chlorine and chloramine are sequentially added. **Methods** Pilot tests of this sequential chlorination were carried out in a drinking water plant. **Results** The sequential chlorination disinfection process had the same or better efficiency on microbe (including virus) inactivation compared with the free chlorine disinfection process. There seemed to be some synergetic disinfection effect between free chlorine and monochloramine because they attacked different targets. The sequential chlorination disinfection process resulted in 35.7%-77.0% TTHM formation and 36.6%-54.8% THAA5 formation less than the free chlorination process. The poorer the water quality was, the more advantage the sequential chlorination disinfection had over the free chlorination. **Conclusion** This process takes advantages of free chlorine's quick inactivation of microorganisms and chloramine's low disinfection by-product (DBP) yield and long-term residual effect, allowing simultaneous control of microbes and DBPs in an effective and economic way.

Key words: Disinfection; Free chlorine; Chloramine; Disinfection by-products; Microorganisms

INTRODUCTION

There are three kinds of traditional chlorine disinfection processes. Free chlorine disinfection has the advantage of being highly efficient in microorganism inactivation and the disadvantage of having a high yield of disinfection by-products (DBPs) and a faster decay in the distribution systems. Some water plants add free chlorine in the influent of the clear well and add ammonia in the effluent of it. By this means, the residual chlorine in a network can be retained and the chlorine odor can be avoided. But this method leads to the formation of a considerable amount of DBPs in the clear well because the retention time is usually as long as 120 minutes. An alternative method of chlorine disinfection is chloramine disinfection, in which free chlorine and ammonia are added simultaneously and chemical chloramines are used for disinfection. Chloramine disinfection is characterized by a low DBP yield and slow inactivation of microorganisms[1-2].

We developed a new sequential chlorination process using short-term free chlorine plus chloramine disinfection process in order to achieve the integrative control of microorganisms and DBPs. In this process, free chlorine is added first. After a short period, no more than 15 minutes' free chlorine disinfection, ammonia is added and transformed into chloramines, usually in the form of monochloramine[3].

The sequential disinfection process takes advantage of free chlorine's quick inactivation of microorganisms and chloramine's low DBP yield and long-term retention. Free chlorine kills bacteria and viruses quickly. The disinfectant at normal concentrations brings about rather good microbe inactivation in five to fifteen minutes, and only a small amount of DBPs is formed in the short term. Chloramine disinfection has steady inactivation performance but it takes a much longer time than free chlorine. It also has a lower DBP yield[4]. By integrating these two disinfectants, the primary short-term free chlorine disinfection can avoid high DBP yields, and the subsequent chloramine disinfection results in excellent inactivation and low DBP formation. By this means, both microbes and DBPs can be effectively and economically controlled[5].

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Biographical note of the first author: Chao CHEN, male, born in 1977, Ph. D., majoring in theory and technology of water and wastewater disinfection. Tel: 86-10-62781779. E-mail: chen_water@tsinghua.edu.cn

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MATERIAL AND METHODS

Raw Water

Pilot tests were carried out at a water plant of the Tianjin Water Works Company. The raw water was the same as the plant influent. Since the raw water was stored in a reservoir for a long period, the quality was worsened. Table 1 shows the water quality in April 2004.

Water Treatment Processes

Two series of processes in the pilot plant are shown in Fig. 1 below.

The disinfection processes are shown in Fig. 2.

TABLE 1

Quality of Raw Water in April 2004

Indices	Maximum	Minimum	Average
Turbidity (NTU)	13.5	4.6	8.06
TOC	5.70	5.10	5.30
COD_{Mn}	6.45	4.60	5.62
UV_{254} (/cm)	0.140	0.108	0.081
NH_3-N (mg/L)	0.27	0.14	0.21
Alkalinity (mg/L)	348	194	260
TBC (CFU/mL)	700	170	335
TCC (CFU/100 mL)	900	52	294
FCC (CFU/100 mL)	140	0	45

Note. TOC= total organic carbon; COD_{Mn}=chemical oxygen demand with $KMnO_4$ method; TBC=total bacteria count; TCC=total coliform count; FCC=fecal coliform count.

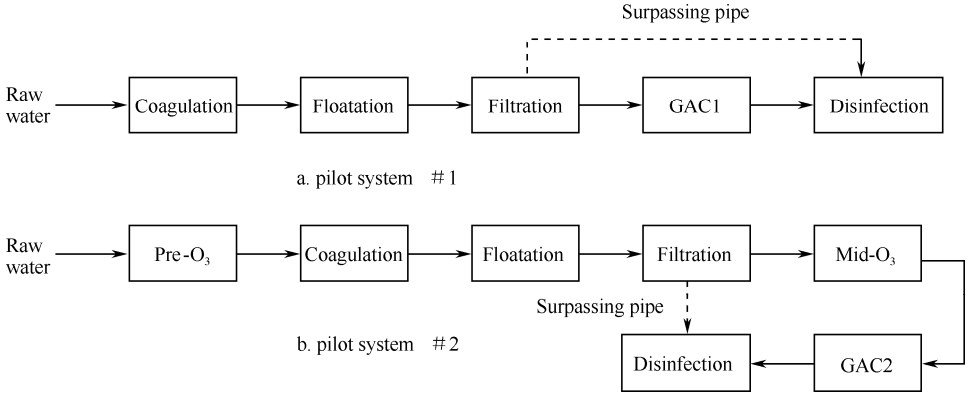

FIG.1. Processes of pilot system.

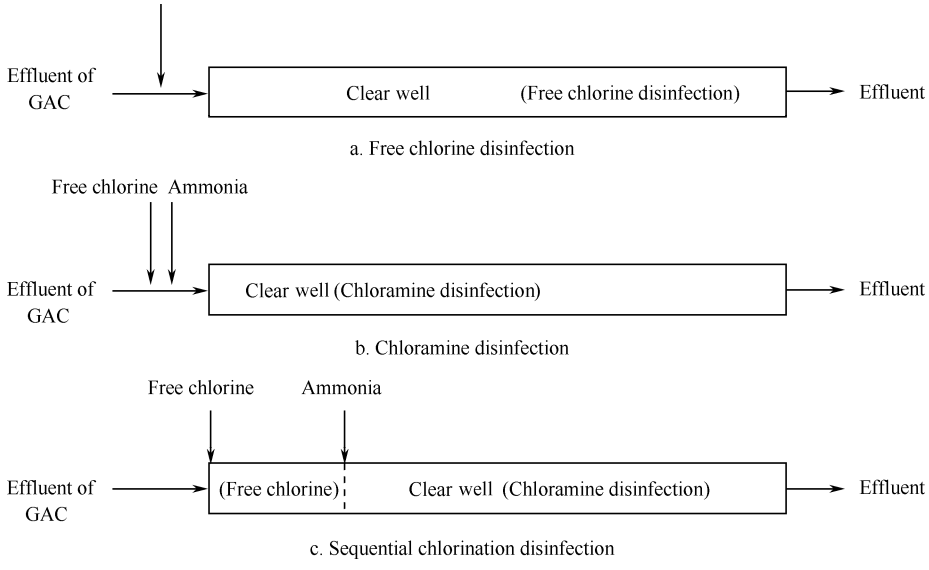

FIG. 2. Different disinfection processes.

Free chlorine disinfection, chloramines disinfection and sequential chlorination disinfection were adopted in this study. These three disinfection processes could be added to each process by surpassing pipes. The stock free chlorine solution was carried by pipe from the water plant and stored in a tank. The chlorine concentration was about 600 to 1000 mg/L. After titration, a controlled amount of chlorine was pumped into the clear well by a metric pump. The ammonia solution was diluted to 200 mg/L, titrated and also pumped accurately. The ratio of chlorine to ammonia in the latter two disinfection processes was 4:1. The dosage was adjusted to 1.0-1.5 mg/L of chlorine for 120 minutes in order to maintain the residual chlorine in the networks.

The pilot clearing pools were two stainless steel tanks. Each had a volume of 2.5 m^3 and 120 min hydraulic retention time (HRT), and the flux was 1.25 m^3/h. Each pool had a chlorine valve at the influent point, with 0 min HRT. Three ammonia valves were set at 5, 10, 15 minutes' for HRT. The valve with 10 min HRT was chosen to add the ammonia for sequential chlorination according to the laboratory results. There were 6 sampling valves with the HRT set at 5, 10, 15, 30, 60, and 120 minutes.

Analytical Methods

All the analytical methods followed the Chinese standard methods and the APHA standard methods for the examination of water and wastewater[6-7].

Free chlorine, NH_2Cl, and $NHCl_2$ residual concentrations were determined by the DPD-ferrous titrimetric method, method 4500-Cl F[7]. The NH_3-N concentration was measured by spectrophotometry. The pH of the water was measured with an Orion 410A pH meter.

The total bacteria count was determined by the traditional nutrient-agar culture with 24-hour incubation at 37℃. The number of total coliform groups was determined by the Chinese standard total coliform membrane filter procedure, which was the same as APHA method 9222 B except for some changes of the culture media. Since China has not set a heterotrophic plate count (HPC) standard, the HPC was determined by method 9215 B with 9-day incubation at 20℃[7].

The GAC effluent of system #2 was used to test the ability of disinfectants to inactivate viruses in cooperation with the PLA Medical Science Institute. The effluent was separated into control group, free chlorination group, and sequential chlorination group, each having a volume of 10 liters. Standard viruses of poliovirus Ⅰ and coliphage f_2 were added to each group. At the beginning of the test, disinfectants were added to the latter two groups, the pilot test parameters and requirements were followed, and 1.0-1.5 mg/L of effluent chlorine was retained for 120 minutes. After 20-minute disinfection, a sample of each group was taken to assay the coliphage f_2 since the poliovirus test was complex. After 120-minute disinfection, the residual chlorine in the whole 10 liters was quenched and the surviving viruses were enriched. Then, the concentrations of the viruses in each group were determined.

THMs were measured by head-space gas chromatography[8]. HAAs were measured by micro-extraction at pH 0.5 with methyl tertiary butyl ether and methylation with acidic methanol[9]. The five HAAs regulated by China and USA were measured by gas chromatography. A Shimadzu GC-17A gas chromatographer with an electron capture detector and SPB-1701 capillary column was used.

UV absorbance at 254 nm is an excellent surrogate parameter for estimating the raw water concentration of THM or other DBP precursors[10]. These concentrations were determined according to APHA method 5910 B. Water was filtered by 0.45 μm membrane and its UV absorbance at 254 nm was measured with a Shimadzu UV-1650PC spectrophotometer.

DATA AND RESULTS

Inactivation of Microorganism

Bacteria To directly compare the inactivation efficiency of sequential chlorination with free chlorination, the effluent of pilot system #2 was used as raw water. We tested the changes of chlorine residue, total bacteria count, HPC, and total coliform count in the water with hydraulic retention time. The results are listed in Table 2.

According to these pre-experiment results, 3 mg/L chlorine was added in free chlorination disinfection test. 2.5 mg/L chlorine was added to sequential chlorination test, with 0.5 mg/L ammonia added 10 minutes later to transform free chlorine into monochloramine. Thus, the 120-minute effluent chlorine residues in the two tanks were obtained at 1.0-1.5 mg/L. As shown from the residual chlorine data, the residual chlorine decayed slower when being transformed into monochloramine. As a result, the dosage of disinfectant could be reduced, and the accessory expense of ammonia was counteracted by the saving of chlorine.

Both disinfection processes had the same effect on the indices of total bacteria count, HPC, and total

TABLE 2

Control of Hygienic Indices by Disinfection Processes

	HRT (min)	0	5	10	15	30	60	120
Free Chlorination Disinfection	Chlorine Residue (mg/L)	3.00	2.55	2.26	2.18	1.98	1.66	1.44
	TBC (CFU/mL)	350	20	0	0	0	0	0
	HPC (CFU/mL)	6900	30	0	2	0	6	2
	TCC (CFU/L)	650	25	0	0	0	0	0
Sequential Chlorination Disinfection	Chlorine Residue (mg/L)	2.5	1.91	1.75	1.65	1.60	1.36	1.23
	TBC (CFU/mL)	350	20	2	1	1	0	0
	HPC (CFU/mL)	6900	6	0	6	0	0	0
	TCC (CFU/L)	650	55	10	10	0	0	0

coliform count. There was no bacterium or coliform detected in the 120-minute effluent for either system, which met the water quality standards of China. Moreover, the HPC was only 2 CFU/mL for free chlorine disinfection and that of sequential chlorination was zero, which was far below US standards.

However, there were some differences between the two processes. Free chlorine disinfection killed microorganisms faster than sequential chlorination disinfection. After 10-minute exposure, no bacterium or coliform was detected in the water. The results of HPC showed a fluctuant increase with time and there were still heterotrophic bacteria present in the final effluent, indicating that there might be some mechanism causing bacterial conglomeration or restoration. The results of repeated experiments confirmed the existence of this phenomenon.

Sequential chlorination had a fairly slower inactivation because of the transformation of disinfectant and smaller dosage. But its activation efficiency was steady. No heterotrophic bacteria or coliform were detected in the effluent after 60- and 120-minute effluence. The sequential chlorination process had better inactivation efficiency than the free chlorination process. Although the advantage was not remarkable since only a small number of bacteria were presented in the pilot test, the laboratory work before pilot test gave more clear evidence. Moreover, it seemed that there was a synergetic disinfection effect between free chorine and monochloramine. Kouame and Charles also reported the synergy of free chlorine and monochloramine when simultaneously added[11].

Viruses In cooperation with the PLA Medical Science Institute, the second system was used to test the efficiency of virus inactivation. After 20-minute disinfection, a sample was taken from each group to detect the coliphage f_2. After 120-minute disinfection, the residual chlorine in the whole 10 liters was titrated and quenched, and the surviving viruses were enriched. Then the concentrations of the viruses in each group were determined. The results are shown in Table 3.

TABLE 3

Virus Inactivation Results

Groups	Coliphage f_2				Poliovirus Ⅰ	
	20 Minutes' Inactivation (pfu/10 L)	Rate (%)	120 Minutes' Inactivation (pfu/10 L)	Rate (%)	120 Minutes' Inactivation (pfu/10 L)	Rate (%)
Control	3.76×10^6	——	3.05×10^6	——	7.96×10^7	——
Free Chlorination	0	>99.9999	0	>99.9999	0	>99.99999
Sequential Chlorination	0	>99.9999	0	>99.9999	0	>99.99999

The results showed no difference between the free chlorination and sequential chlorination processes. After 120-minute disinfection, no coliphage f_2 or poliovirus was detected in 10 liters of water and the inactivation rate was higher than 99.9999%. After 20-minute disinfection, no coliphage f_2 was detected in the water and the inactivation rate was higher than 99.9999%.

Control of Disinfection By-products

Two indicators could influence DBP formation. One is the disinfection process, the other is the

precursor concentration or the water treatment process before disinfection. Three disinfection processes were compared for their DBP formation: free chlorination, chloramination, and sequential chlorination. Effluents of three processes combinations were used in the comparison: filtration 1 effluent, GAC 1 effluent, and GAC 2 effluent. Thus, a 3*3 matrix was formed (Fig. 3).

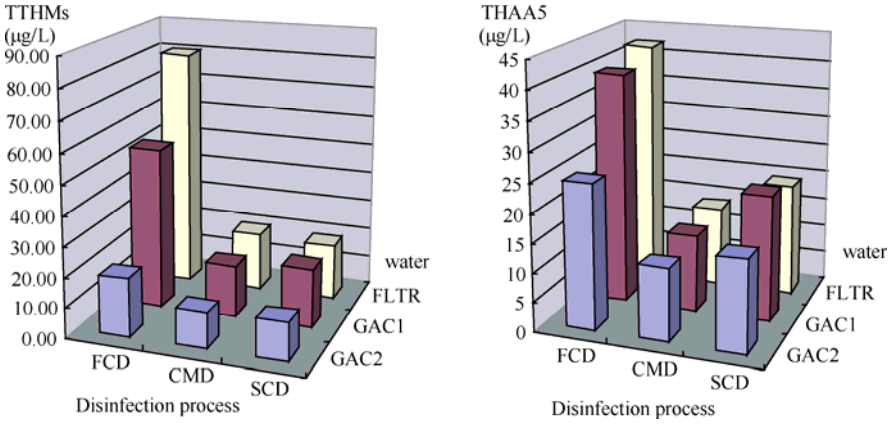

FIG. 3. Comparison of DBP formation[a]. [a]FCD-free chlorination disinfection, CMD-chloramination disinfection, SCD-safe chloriantion disinfection, FLTR-filtration #1 effluent, UV_{254}=0.105; GAC1-GAC #1 effluent, UV_{254}=0.074; GAC2-GAC #2 effluent, UV_{254}=0.040.

As far as disinfection processes were concerned, the highest TTHM and THAA5 concentrations were produced in free chlorination with three kinds of water. The sequential chlorination process produced much less particular DBPs than free chlorination and almost the same as chloramination disinfection. For example, the disinfection with filtration #1 effluent was carried out to simulate the conventional treatment. Free chlorination produced 80.37 μg/L TTHM and 42.06 μg/L THAA5, respectively. Chloramination produced 19.40 μg/L and 13.80 μg/L of particular DBPs, respectively. The sequential chlorination process produced 18.51 μg/L and 19.25 μg/L of particular DBPS, respectively. The TTHM yield in free chlorination even exceeded the US standard in D/DBP rule stage 2. Therefore, it was necessary to limit the usage of free chlorination, especially in conditions of poor water quality. The yields of two DBPs in sequential chlorination were 77.0% and 54.2% lower than those in the free chlorination process, showing that sequential chlorination might have great advantages over free chlorination.

Moreover, the water treatment process had an effect on DBP formation and advantages of sequential chlorination over free chlorination. UV_{254} is a good index of DBP precursors. The higher the UV_{254} value was, the more the THMs and HAAs were produced in each disinfection. The UV_{254} value of GAC #2, GAC #1, filtration #1 was the lowest at 0.040 cm^{-1}, moderate at 0.074 cm^{-1}, and the highest at 0.105 cm^{-1}, respectively. When GAC #2 effluent was used, the reduction rate of TTHM and THAA5 in sequential chlorination over free chlorination was 35.7% and 36.9%, respectively. When GAC #1 effluent was used, the reduction rate was 63.2% and 45.5%, respectively. When filtration #1 effluent was used, the rate was as high as 77.0% and 54.2%, respectively.

Generally, the sequential chlorination process could produce 35.7%-77.0% TTHM formation and 36.9%-54.2% THAA5 formation less than the free chlorination process. It could effectively control excess DBP formation. Moreover, the poorer the water quality was, the more advantage the sequential chlorination disinfection had.

DISCUSSION

Inactivation of Microorganisms

Bacteria Generally, the Ct value of microorganism inactivation by free chlorine is less than 1% of that of monochloramine. Thus, free chlorine plus monochloramine disinfection is less efficient than free chlorine disinfection. However, the results showed that the sequential chlorination process was more efficient, suggesting that there is a synergetic disinfection effect between free chlorine and monochloramine.

As a strong oxidant and disinfectant, free chlorine affects many vital functions of microorganisms[12]. A principal mode of bacterial destruction by free chlorine is disruption of the integrity of cell

membrane[13]. This action severely impairs cellular respiration, membrane permeability and essential metabolic functions. Although the general mechanism by which chloramines destroy bacteria and viruses has been postulated to be similar to that of free chlorine, differences may result from the distinct chemical properties of the two disinfectants[13]. Firstly, chloramines can also destroy the membrane, enhance the membrane permeability, and affect bacteria respiration. Secondly, they irreversibly harm the cell metabolism. The structure of hemin is chemically modified by both hypochlorous acid and monochloramine, indicating that hemin destruction is largely responsible for bacterial inactivation by monochloramine because the original hemin structure can not be restored by reducing compounds. Finally, monochloramine can also inactivate bacterial cells by damaging the nucleic acid.

The proposed short-term free chlorine plus chloramine disinfection process is somewhat more efficient than free chlorination disinfection process. This may be attributed to the synergetic effect of free chlorine and monochloramine. We believe that the short-term free chlorine process can inactivate the majority of microorganisms and destroy cell membranes of the residual microorganisms. Since monochloramine is neutral, it can easily be diffused to approach germs. As the physiological barrier is damaged, the membrane permeability is enhanced, and the enzyme system controlling the transport and discharge of materials is destroyed. Thus, monochloramine can easily enter the interior, damage the nucleic acids and kill the bacteria. However, this supposition was not confirmed in this research due to the limited experimental equipment.

Viruses Some researchers have studied the mechanism behind virus inactivation by chlorine and monochloramine[12]. Chang[14] proposed that virus inactivation by free chlorine is related to the denaturalization of the capsid. Fujioka[15] also drew the conclusion that the poliovirus inactivation mechanism by monochloramine is mainly related to capsid damage. However, Olivieri[16] believes that the first target of the free chlorine or monochloramine on coliphage f_2 is located on the RNA. Shin and Sobvey[17] carried out an experiment on virus inactivation by monochloramine and found that the monochloramine first attacks the virus capsid.

Since viral infectivity is related to the external capsid and envelope, viruses lacking capsid may lose their infectivity and eventually die. However, the capsid may be reloaded on the viruses and the infectivity can be prevented in certain situations. PCR can clarify whether the disinfectant attacks the virus capsid and destroys the nucleic acids, and is widely used in determining the inactivation of microorganisms.

The sequential chlorination process can inactivate the virus as the free chlorination disinfection process. The inactivation might be a synergetic effect of free chlorine and monochloramine. Since free chlorine has a high oxidation potential, it could attack and destroy the capsid, thus helping the monochloramine penetration into the interior of the virus, eventually damaging the nucleic acid.

Control of Disinfection By-products

The classic THM formation reaction of chlorine and fulvic acid is regarded as a chlorine-substituted reaction, in which chlorine reacts with the organic matter containing methyl ketone or hydroxyl benzene in the catalysis of OH^-[18]. Tests have proven that free chlorine produces DBPs at a very high rate, but monochloramine produces DBPs much more slowly, indicating that monochloramine first hydrolyzes into hypochlorous acid and then reacts with the precursors. Since the hydrolyzing reaction of monochloramine is slow, DBPs are formed much more slowly.

$$NH_2Cl+H_2O \xleftrightarrow{K1} HOCl+NH_3 \quad k_1=3.5\times10^{-5}\ mol^{-1}\cdot L\cdot s^{-1} \tag{1}$$

$$HOCl+precursor \leftrightarrow THMs+HAAs \tag{2}$$

There are three kinds of materials in the sequential chlorination system: free chlorine, ammonia, and precursors. Free chlorine first reacts with the ammonia very quickly and entirely. At normal temperatures and pH and at a Cl_2/N ratio of 4:1, the residual chlorine exists in the form of monochloramine in the water. Thus, the DBP formation reaction is slowed down and the DBPs can be controlled.

In conclusion, the sequential chlorination is as efficient as free chlorine disinfection. There is no difference between free chlorine disinfection and sequential chlorination disinfection in the inactivation of viruses. The sequential chlorination process can effectively control DBP formation.

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