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Reflection on Kinetic Models to the Chlorine Disinfection for Drinking Water Production

Yoon-jin Lee* and Sang-ho Nam

Department of Environmental Engineering, College of Engineering,
Konkuk University, Seoul 143-701, South Korea

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Experiments for the characterization of inactivation were performed in a series of batch processes with the total coliform used as a general indicator organism based on the chlorine residuals as a disinfectant. The water samples were taken from the outlet of a settling basin in a conventional surface water treatment system that is provided with the raw water drawn from the mid-stream of the Han River. The inactivation of total coliform was experimentally analyzed for the dose of disinfectant, contact time, filtration and mixing intensity. The curves obtained from a series of batch processes were shaped with a general tailing-off and biphasic mode of inactivation, i.e. a sharp loss of bacterial viability within 15 min followed by an extended phase. In order to observe the effect of carry-over suspended solids on chlorine consumption and disinfection efficiency, the water samples were filtered, prior to inoculation with coliforms, with membranes of both 2.5 μm and 11.0 μm pore size, and with a sand filter of 1.0 mm in effective size and of 1.4 in uniformity coefficient. As far as the disinfection efficiency is concerned, there were no significant differences. The parameters estimated by the models of Chick-Watson, Hom and Selleck from our experimental data obtained within 120 min are: $\log(N/N_0)=-0.16CT$ with $n=1$, $\log(N/N_0)=-0.71C^{0.87}T$ with $n\neq 1$ for the Chick-Watson model, $\log(N/N_0)=-1.87C^{0.47}T^{0.36}$ for the Hom model, $\log(N/N_0)=-2.13\log(1+CT/0.11)$ for the Selleck model. It is notable that among the models reviewed with regard to the experimental data obtained, the Selleck model appeared to most closely resemble the total coliform survival curve.

Key words: disinfection, total coliform, chlorine, model, parameters

Chlorine has long been used as the most effective disinfectant against water-borne pathogenic organisms because of its many advantages (White, 1992; Gerald, 1997). Coliform bacteria are historically the conventional indicator organisms to demonstrate and measure whether drinking water has been adequately treated at the source to protect people from contamination. Chlorine is most often used in spite of the fact that newly emerging pathogenic protozoa such as *Giardia* cysts and *Cryptosporidium* oocysts are fairly resistant to the normally used dose of chlorine (Bitton, 1994; EPA, 1991).

The effectiveness of disinfection is influenced by such factors as detention time, disinfectant dosage, pH, temperature, the presence of reducing substances and mixing intensity (Donald *et al.*, 1979). It is generally accepted that the time required for the disinfection process is inversely proportional to the concentration of the disinfectant residual. Mixing has been shown to be an important parameter in all disinfection systems. White (1974) found that all treatment plants exhibiting good disinfection systems had good mixing in common. Camp and Stein (1943) first proposed the use of the velocity gradient *G*, as a measure for mixing.

Disinfection kinetic models are the basis for assessing the disinfection performance and the design of contactor systems (Trussell and Chao, 1977). Over the years, a number of kinetic models have been proposed for the formulation of disinfection design criteria. Model adequacy is dependent upon the robustness of the underlying inactivation rate law if the model accounts for the disappearance of the chemical disinfectant during the contact time.

This study was carried out to review experimentally the limited kinetic models applied frequently for potable water disinfection with regard to the dosage of disinfectant, contact time, prefiltration and mixing intensity.

Materials and Methods

Sample preparation and laboratory materials

In this study, the samples were taken from a water treatment plant having a nominal capacity of 1,450,000 m^3/

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* To whom correspondence should be addressed.
(Tel) 82-02-447-8367; (Fax) 82-02-447-8367
(E-mail) yjlee@konkuk.ac.kr

Table 1. Characteristics of water samples

Parameter	Condition
pH	7.2
Temperature (°C)	22.0
DO (mg/l)	8.2
TOC (mg/l)	2.54
NH_3-N (mg/l)	0.09
Turbidity (NTU)	1.2
HPC (cfu/ml)	10
Total coliform (number/100 ml)	ND

Table 2. Summary of design configurations for sand filter

Item	Conditions
Diameter (m)	0.05
Height (m)	1.2
Sand layer (m)	1
Flow rate (m^3/d)	0.44
Linear velocity (m/h)	9.35
Empty bed contact time (min)	7.69

day, supplied with Han River water; the treatment train consists of coagulation, sedimentation, filtration and chlorination. Samples were collected at the point of filter inlet. The characteristics of samples used are described in Table 1. Water samples were collected aseptically with sterilized 1 liter Pyrex bottles which had been specially treated by acid-washing and baking at 300°C to remove carbon compounds. Appropriate volumes of sample were filtered through the sand columns in our laboratory. The design configurations for the sand filters are represented in Table 2. To find out the effects of suspended matter or turbidity-causing matter in different size on disinfection, the filtrations of target water samples were done with the filter paper of 2.5, 11 μm in pore size and the sand columns before chlorination.

Deionized laboratory water was obtained from an ultra pure water system (Pure up 700, Mirae Scientific) operated at a resistivity of at least 18 MΩcm. Phosphate buffer was prepared with disodium hydrogen orthophosphate ($Na_2HPO_4 \cdot 7H_2O$) and potassium dihydrogen orthophosphate (KH_2PO_4). Chlorine stock solutions of 15 mg/l were prepared daily with the sodium hypochlorite (NaOCl) solutions containing 15% available chlorine and oxidant-demand-free water.

Preparation for bacterial inoculums

The samples for preparing stock inoculums were collected from the sewer manhole adjacent to Konkuk University, which is located in the eastern part of Seoul. They were filtered through membrane filters (pore size: 11 μm). The filtrate of 10 ml were placed on m-Endo medium in a Petri dish and incubated for 24 h at 35± 1°C. The colonies were placed on the solution of nutrient broth and incubated at 25°C for 24 h. The coliform bacteria were isolated by centrifugation at 5×10^3 *G* for 5 min, washed twice and resuspended in the buffer solution free from chlorine demand at pH 7. The coliform bacteria isolated from the media were mixed by a vortex mixer. The fresh cell suspensions in the chlorine-demand-free solution were used in all experiments. The density of cells was between 2×10^6 and 8×10^8 cfu/100 ml in total coliforms.

Analytical methods

Experiments were performed at pH 7 at 20°C. Aliquots were withdrawn in accordance with the predetermined nine intervals up to 180 min. They were immediately dechlorinated by adding 0.2 ml of 3% sodium thiosulfate ($Na_2S_2O_3$). Free chlorine levels were determined by the DPD colorimetric method with a chemical chlorine kit (Hach Chemical). The pH was determined by a digital pH meter, which was standardized several times a day with pH 4, 7, 10 buffers.

Total coliforms were enumerated in accordance with a membrane filtration procedure in the US standard method 9222B (APHA *et al.*, 1995). The samples containing coliform bacteria were filtered through the Millipore membrane sterilized (0.45 μm in porosity). Each station in the filtration system was sterilized. A membrane was placed under sterile conditions on the apparatus. The aliquots of 1, 10 and 100 ml were filtered. The membranes were then placed on m-Endo agar medium in Petri dishes and incubated for 24 h at 35± 1°C. Results are expressed as coliform colony per 100 ml.

Results and Discussion

Filtration effect

The filtration effects on the disinfection were experimentally observed. We defined the disinfection effectiveness as the time required for a level of bacterial inactivation as measured by the log unit survival ratio (log N_t/N_0). The data presented in Fig. 1 were produced by chlorinating water in 1 liter bottles for 3 hr at pH 7, 20°C on the fixed

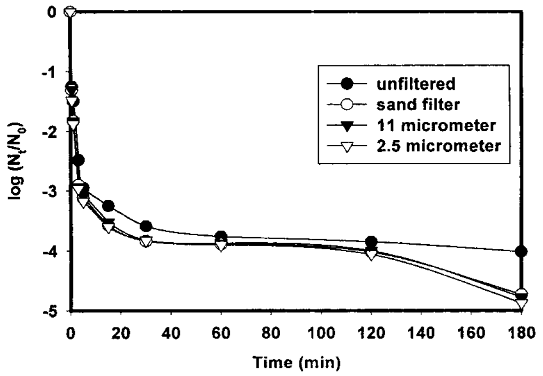

Fig. 1. Total coliform inactivation by chlorine in the filtered and unfiltered water.

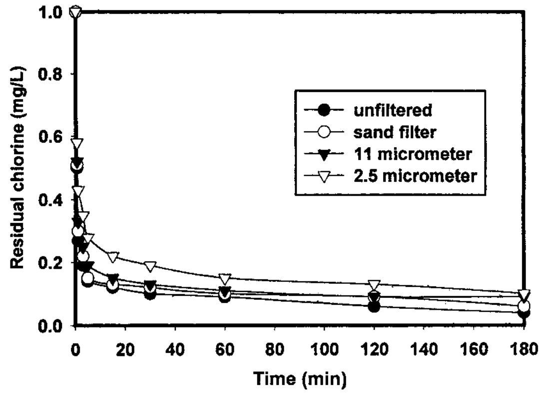

Fig. 2. Chlorine decay in the filtered and unfiltered water.

basis of 1 mg Cl$_2$/l.

The log survival ratio for 180 min was found to be 4.88 for the filtrate (2.5 μm), 4.78 for the filtrate (11 μm), 4.73 for the effluent from sand filter, and 4.01 for the unfiltered sample. The disinfection effectiveness of filtrates was better than that of the unfiltered sample. The findings for the filtrates suggest that the size of particulates to the magnitude encountered does not affect the disinfection effectiveness.

As shown in Fig. 2, the chlorine consumption was less for the filtered samples. It might be attributable to the removal of reductants such as chemically oxidizable organic matter, ammonium particles etc. in the suspended matter.

Effect of mixing velocity gradient

The effects of initial mixing on the disinfection of coliform bacteria were carefully observed. The results are shown in Fig. 3. The data were produced by chlorinating the water in the bottles of 1 liter equipped with paddles for 2 hr at pH 7 and 20°C. The chlorine dosage was fixed at 3 mg/l. The series of mixing intensities were at the G value of 0, 250, 500, 1000 and 1500/s.

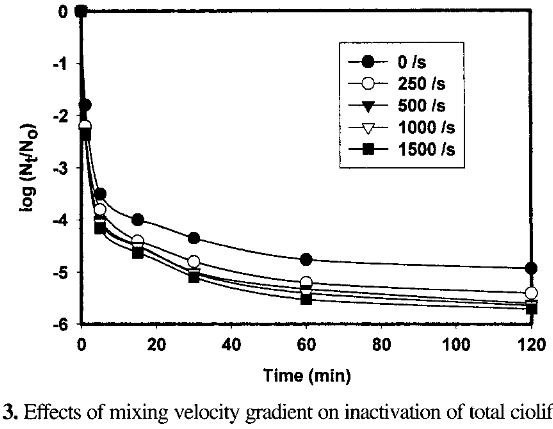

Fig. 3. Effects of mixing velocity gradient on inactivation of total cioliforms.

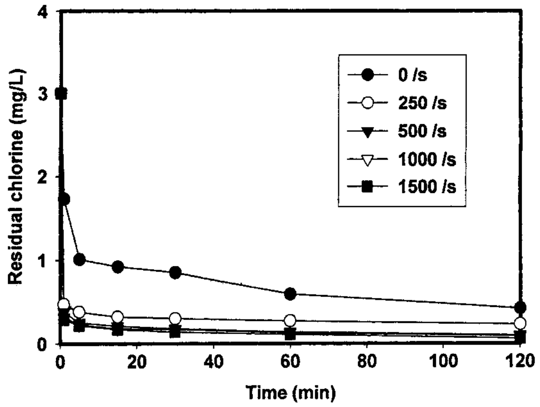

Fig. 4. Free chlorine residuals on mixing velocity gradient.

The curves indicate that the total coliform inactivation by chlorine was increased as the G value increased -4.93, -5.40, -5.60, -5.64, -5.71 log$_{10}$ reduction by 120 min. At the G value above 500/s, there was a little difference in disinfection effectiveness. White (1974) used to believe that the G value should be approximately 1,000/s for superior mixing. The results obtained from the experiments revealed that the acceptable values of G could be less than 1,000/s at the turbulence levels evaluated, but it should be noted that the G value at 1,500/s still gave better inactivation of the target indicator organism. It showed clearly that a rapid dispersion of chemical disinfectant to react on the microorganisms is a key influential factor in the disinfection process.

Effect of chlorine concentration

In the range of initial chlorine concentration from 0.1 to 3 mg/l as free chlorine, the curves shown in Fig. 5 are a typically biphasic mode with little inactivation occurring after a contact time of 15 min. The reduction of total coliform was performed at the chlorine concentrations of 0.1, 0.5, 1, 3 and 5 mg/l as free chlorine. The results obtained in the elapse of time are as follows:

After a contact time of 30 seconds, the inactivation of initial total coliform was in the order of 0.20, 0.91, 0.95, 1.00 and 1.05 log$_{10}$ reduction. After 15 min contact time,

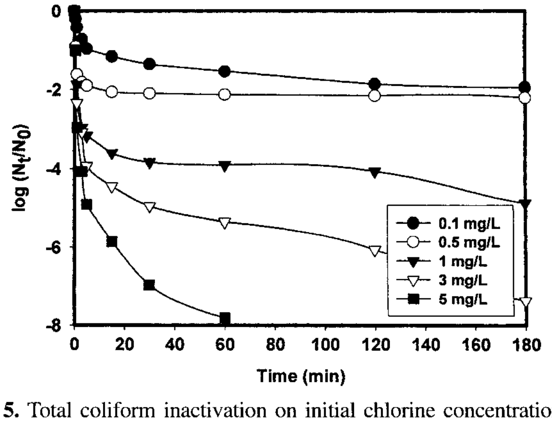

Fig. 5. Total coliform inactivation on initial chlorine concentration.

the inactivation was 1.16, 2.06, 3.60, 4.45 and 5.86 $\log_{10}$ reduction. After 120 min., the inactivation was 1.86, 2.15, 4.06 and 6.06 $\log_{10}$ assuming that the hydraulic retention time would be 120 min at minimum in clear wells. When the contact time was extended up to 180 min, the inactivation ratios of total coliform was 60, 93, 74 and 60% respectively. Most parts of the reaction on the indicator organism was achieved in 15 minutes when the chlorine concentration did not exceed 1 mg/l. For potable water disinfection in water filtration plants, this level of chlorine concentration is meaningful in a practical sense.

For the inactivation of 99.9% (3 log), the contact time required was 3.05, 3.00 and 1.00 min at a chlorine concentration of 1, 3 and 5 mg/l, respectively. For the 99.99% (4 log) inactivation, the contact time needed was 95.00, 5.40 and 2.75 min at a chlorine concentration of 1, 3 and 5 mg/l, respectively. It is notable that in cases of chlorine concentration levels of both 0.1 and 0.5 mg/l, the disinfection level required could not be achieved because the coliform reduction had 1.9 log and 2.2 log for 180 min on the basis of 99.9%. The higher initial concentration of chlorine as disinfectant, the better disinfection efficiency on coliforms. However, in some cases, the high concentration of chlorine in water in the presence of organic matter as precursor may form the THMs (trihalomethanes) that are cancer-causing chemicals.

In the process of inactivation of coliform bacteria, the chlorine concentration diminished about 50-72% within 5 min. Residuals persisted by 15 min as shown in Fig. 6. At a contact time of 120 minutes, the chlorine residuals were 0.04, 0.06, 0.13, 0.42 and 0.80 mg/l for the chlorine dose of 0.1, 0.5, 1, 3, 5 mg/l. In this context, the chlorine residual of 0.2 mg/l in distribution systems corresponds to the chlorine dose of 1.4 mg/l.

Disinfection kinetics

An essential feature of kinetic modeling is not only to simplify, but also to idealize, a complex phenomena of disinfection systems. With the data from these experiments described above, we attempted to determine the coefficients of selected models. The major precepts of disinfection kinetics were enunciated by Chick and recognized the close similarity between microbial inactivation by chemical disinfectants and chemical reactions (Chick, 1908).

$$\ln\frac{N}{N_0} = k^*t \tag{1}$$

where N = a number of microorganism at contact time t,
N_0 = a number of initial microorganism at contact time, t = 0
k^* = reaction rate constant,
t = contact time.

Watson (1908) proposed an empirical logarithmic function to relate the rate constant of inactivation, k to the disinfectant concentration C. In general, disinfection systems are designed by the Ct values derived from Chick-Watson kinetics based on the data obtained from laboratory inactivation studies.

$$k^* = kC^n \tag{2}$$

$$\log\frac{N}{N_0} = -kC^nt \tag{3}$$

where k = constant for a specific microorganism and set of conditions,
C = disinfectant concentration,
n = coefficient of dilution.

The Watson function, (3), is based on the assumption that microorganisms are genetically similar and of a single strain of synchronous development and the killing action would be a single-hit and single-site type. The assumptions are necessary in order to derive the Chick-Watson model based on a chemical reaction mechanism. In many cases, the n value for Chick-Watson law is close to 1.0 and hence a fixed value of the product of concentration and time (Ct product) results in a fixed degree of inactivation (AWWA, 1999). The inactivation degree on Ct value presented in Fig. 7 indicates the experimental results.

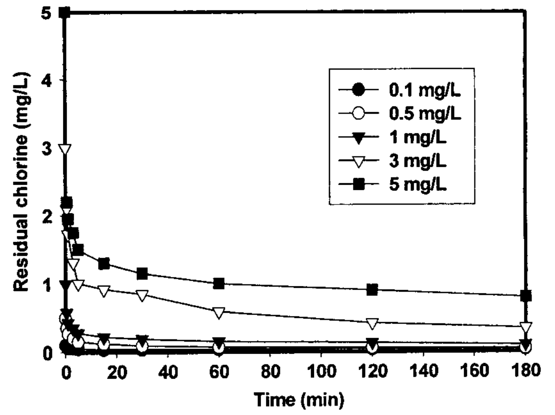

Fig. 6. Free chlorine residuals on chlorine dose.

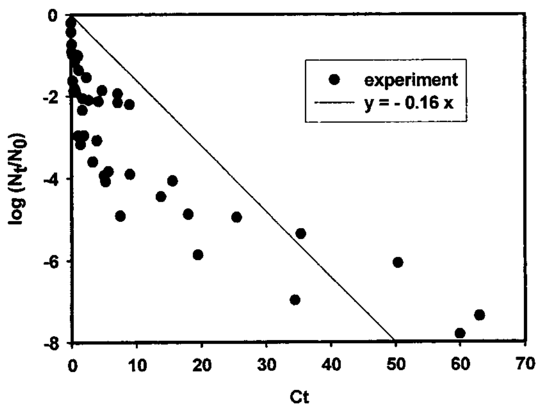

Fig. 7. Relationship between log survival ratio and and Ct.

As seen in eq. (3), our experiments found 0.16 for the value of k.

$$\log\frac{N}{N_0} = -0.16Ct \tag{4}$$

From the data in Fig. 5 and Fig. 6, the Chick-Watson model with $n \neq 1$ generates this equation (5) :

$$\log\frac{N}{N_0} = -0.71C^{0.87}t \tag{5}$$

Hom generalized empirically the Chick-Watson pseudo first-order rate law (Hass and Karra, 1984)

$$\frac{dN}{dt} = -kmNC^n t^{m-1} \tag{6}$$

Integration of Eq. (6) gives the empirical Hom model

$$\log\frac{N}{N_0} = -kC^n t^m \tag{7}$$

where N = number of coliform organisms per unit volume
N_0 = number of coliform organisms at initial time zero
n = coefficient of dillution
m = m order and n order reaction rate constant

From the experimental data, the constants of k, n and m are 1.87, 0.47, and 0.36 by means of multitiple linear regression as shown in Fig. 8 and equation (8).

$$\log\frac{N}{N_0} = -1.87C^{0.47}t^{0.36} \tag{8}$$

Depending upon the value of m, both shoulders and tailing may be depicted by Equation 7. For the case in which m is greater than unity, the survival curve displays an initial shoulder, while a tailing-off effect is produced when m is less than unity (Hass and Karra, 1984). In this case, the tailing inactivation curves ($m<1$) are shown in Fig. 5. Tailing inactivation curves may be explained either by a vitalistic hypothesis in which individuals in a population are not identical, and their inherent resistance is distributed in a permanent (time-independent) manner, or by a mechanistic concept (Cerf, 1977).

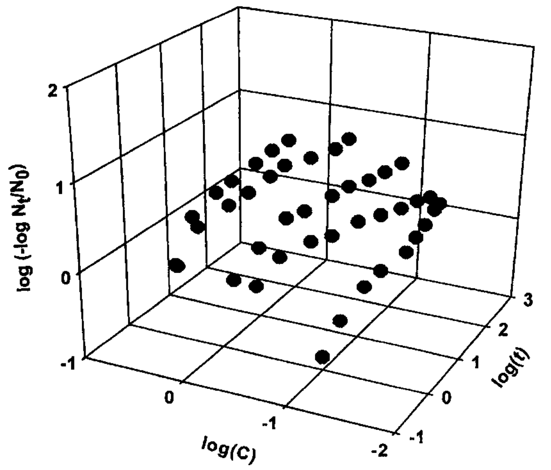

Fig. 8. A maximum likelihood approach to Chick-Watson Model.

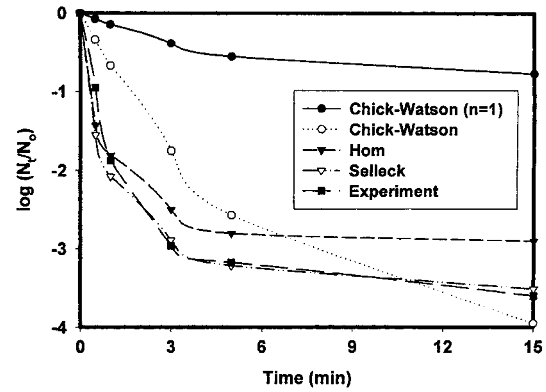

Fig. 9. Survival ratio of total coliforms with an initial chlorine of 1 mg/l.

The following rate law was proposed by Selleck (1978) to describe chlorine inactivation of coliform bacteria in wastewater effluent. Although the Selleck model was initially derived for chlorine inactivation of bacteria in wastewater, it is an empirical model and therefore applicable to any chemical disinfectant, organism and test water.

$$\log\frac{N}{N_0} = -n\log\left(1+\frac{Ct}{k}\right) \tag{9}$$

Values of k, n were 0.11, 2.13 when applied to the data by computation, yields

$$\log\frac{N}{N_0} = -2.13\log\left(1+\frac{Ct}{0.11}\right) \tag{10}$$

The survival ratio of coliform bacteria based on the selected models is illustrated in Fig. 9 with an initial chlorine concentration of 1mg/l, which had disappeared at the rate of 0.075 mg/l/min at pH 7 and 20°C in the beginning. The Chick-Watson model with n=1 significantly underestimates levels of inactivation compared to other fitting models. The Chick-Watson model with $n \neq 1$ is shown to overestimate the level of bacteria killed at contact times greater than 15 min. Among the models selected, the Selleck model best reflected the data produced from these experiments.

This study was performed to investigate experimentally the disinfection effects with chlorine on total coliforms in water and a maximum likelihood was used to estimate the key parameters for the limited kinetic models. The conclusions drawn from the study are as follows:

1. Among the models reviewed, it was found that the Selleck model best reflected the total coliform survival curve obtained with our experimental data.
2. Inactivation curves indicated a tailing-off mode of inactivation and characteristic biphasic mode.
3. Filtration of water samples with the membrane of 2.5

μm in pore size improved slightly disinfection efficiency, but no significant difference in disinfection efficiency was shown between the filtrates with a membrane of 11 μm in pore size and sand filter effluent.

4. For a complete mix of the chlorine solution, the intensity of initial mixing might not need to be as high as 1,000/s of *G* value. The *G* value above 500/s showed little difference in disinfection effectiveness.

5. Chick-Watson (n=1), Chick-Watson (n≠ 1), Hom and Selleck model parameters were estimated respectively as follows:

$\log(N/N_0)= -0.16CT$, $\log(N/N_0)= -0.71C^{0.87}T$, $\log(N/N_0) = -1.87C^{0.47}T^{0.36}$, $\log(N/N_0)= -2.13\log(1+CT/0.11)$.

Acknowledgment

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