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Impact of Water Quality Parameters on the Disinfection of Total Coliform with Chlorine Dioxide

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Abstract: This study investigated the inactivation of the total coliform, an indicator organism in chlorine dioxide, in order to assess the optimal disinfection procedure for drinking water treatment and distribution systems. This research focus on a number of factors, including the dosage of disinfectant, contact time, pH, temperature and DOC. Water samples were taken from the outlet of a settling basin at a conventional surface water treatment system. As the pH increased in the range of pH 6-9, the bactericidal effects of disinfectants decreased. Changes in levels of pH did not significantly after the disinfection effect of chlorine dioxide for total coliform. With an increase in temperature, there was a subsequent increase in the bactericidal effects of disinfectants. Thus, it is evident that a decrease in temperature will higher the CT values required to inactivate coliform for during the winter. DOC addition can also reduce total coliform inactivation. DOC is the most significant variable in total coliform inactivation with chlorine dioxide.

Keywords: total coliform, chlorine dioxide, water parameter, disinfection

Introduction

The process of disinfection has been implemented for many years as a means to control waterborne diseases.[1,2] To effectively control resistant pathogens in potable water, it is necessary to utilize effective disinfectants, and to uphold design techniques that are both cost-effective, and can protect public health without exposing them to insidious by-products of the disinfection process.[3,4]

Total coliform is used as primary indicators measuring water supply treatment effectiveness and the probability of public health risk. The primary goal of coliform monitoring is preventing the supply and distribution of water carrying certain pathogens capable of triggering infection, due to the presence of human or animal excrement.[5]

The presence of coliforms in the absence of contamination triggers false alarms regarding microbiological water quality. More importantly, the growth of coliform bacteria in potable water supplies could mask the presence of indicator organisms, which point towards a true breakdown in treatment barriers. However, appropriate study of factors that lead to the presence of coliform bacteria in portable water is still required.

While inactivation of pathogenic organisms is a primary function, disinfectants are also used as oxidants in drinking water treatment for various other functions. These oxidants are most often used for any of the following: the oxidation of reduced iron and manganese, destruction of taste and odor causing organic contaminants, elimination of color and the destruction of synthetic organic chemicals of public health concern.[6,7] Additionally, many of these oxidants aid in the process of coagulation and are employed as part of an overall program to control potentially harmful by-products of disinfection.

Chlorine dioxide has been cited one of the most effective means of controlling THMs.[8] The Ohio River water, which was treated with various combinations of chlorine dioxide and chlorine, typifies the accumulated results. That even small amounts of chlorine dioxide are sufficient to inhibit the formation of THMs by as much as 20% is a significant finding.[9] However, chlorine dioxide can be changed into chlorite and chlorate in water.[10] Toxicological studies of different animal species revealed that chlorite and chlorate could present hematological effects.[11]

This study aims to identify the inactivation of total

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coliform as the indicator organism when chlorine dioxide is used in portable water treatment and distribution systems. This study was conducted to evaluate potable water disinfection with regard to the dosage of disinfectants, contact time, pH, temperature and DOC.

Materials and Methods

Laboratory Materials and Sample Preparation

Samples used in this study were taken from a water treatment plant with a nominal capacity of 1,450,000 m^3/day, supplied with Han River water; the treatment process at the plant includes coagulation, sedimentation, filtration, and chlorination. Samples were collected from the entrance of the filter inlet. Table 1 describes the characteristics of the samples used in this study.

Water samples were collected aseptically using sterilized 1 *l* Pyrex bottles, which were specially treated by washing them in acid and baking them at 300°C to remove carbon compounds. Sand columns in our laboratory were used to filter the appropriate volumes of the sample. Table 2 presents the design configurations of the sand filter.

Table 1. Characteristics of water samples

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

Table 2. Design configurations for sand filter

Item	Conditions
Diameter (m)	0.05
Height (m)	1.2
Sand layer (m)	1
Q (m^3/d)	0.44
LV (m/h)	9.35
EBCT (min)	7.69

Chlorine dioxide was generated through acidification of a technical grade of sodium chlorite (Aldrich chemical). A schematic of the chlorine dioxide apparatus used for this study utilized a modified version of the one used in standard method 4500-ClO_2.[12] This procedure generated chlorine dioxide in the collecting bottle, which was immediately capped and stored in a dark room at 4°C. Stock chlorine dioxide solutions were generally kept for a maximum of 2 weeks.

Culture Conditions and Microorganisms

The samples used to prepare stock inoculums were obtained from a sewer manhole adjacent to K University, which is located in the eastern area of Seoul. They were filtered through 11 μm membrane filters. A 10 m*l* filtrate was placed on a M-endo medium in a petridish and incubated for 24 h at 35°C. The colonies formed were introduced on the solution of nutrient broth and incubated at 25°C for 24 hr. The coliform bacteria were isolated using centrifugation at 5×10^3 *G* for 5 min, then washed twice and resuspended in the buffer solution free from chlorine demand at a pH level of 7. The coliform bacteria isolated from the media were mixed using a vortex mixer. All experiments used the fresh cell suspensions in chlorine-demand-fee solution. The density of cells used varied between 2×10^6 and 8×10^8 cfu/100 m*l* in total coliform.

Methods of Analysis

The reactor vessel was soaked for at least 3 hours in a chlorine solution with a residual of 10mg/*l* or more by applying standard methods prior to each use. Subsequently, it was rinsed with milli-Q water, dried and then covered with aluminum foil to protect it from dust. All test tubes used in the sampling process or dilutions were treated by washing them in acid, and rininsing with Mili-Q water. Then, they were dried and autoclaved.

The experiment was planed to assess the effect of factors present in water, which influence the kinetics of disinfectant. Aliquots were withdrawn in accordance with the predetermined nine intervals up to 180 min. They were immediately dechlorinated by adding 0.2 m*l* sodium thiosulfate ($Na_2S_2O_3$) of 3%. The pH level was measured with a digital pH meter, which was standardized several times a day with pH 4, 7, 10 buffers.

Total coliform was enumerated in accordance with a membrane filtration procedure outlined by the US standard method 9222B.[12] The samples containing the coliform bacteria were filtered through the Millipore membrane sterilized to 0.45 μm in porosity. Every station in the filtration system was sterilized. A membrane was placed on the apparatus. Then, the aliquots of 1, 10 and 100 m*l* were filtered. Next, the membrane was placed on an agar M-endo medium in a petridish and incubated for 24 hr at 35°C(±1°C). Results are expressed as coliform colony per 100 m*l*.

Results and Discussion

Effect of Initial Chlorine Dioxide

Fig. 1 shows how total coliform inactivation varies depending on the level of initial chlorine dioxide when temperature was 20°C and pH was 7. The reaction of chlorine dioxide with organic substances in water after a period of 5 min was extremely violent, and it continued to react for 30 min proceeding.

The log survival ratio for 3 min was observed as −1.84, −3.42 and −4.98 for 0.5, 1 and 3 mg/*l* and The log survival ratio for 30 min was observed as −2.16, −3.91 and −5.52 for the 0.5, 1 and 3 mg/*l*. Thus, the inactivation ratios when time ranged from 3 min to 30 min were 67, 77 and 90%.

Fig. 2 illustrates how residual chlorine dioxide varies depending on initial chlorine dioxide when

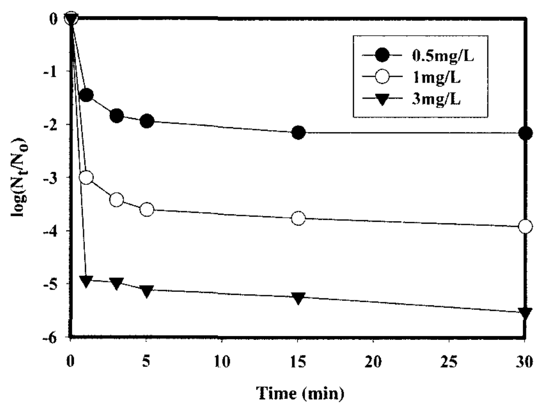

Fig. 1. Total coliform inactivation on initial chlorine dioxide concentration.

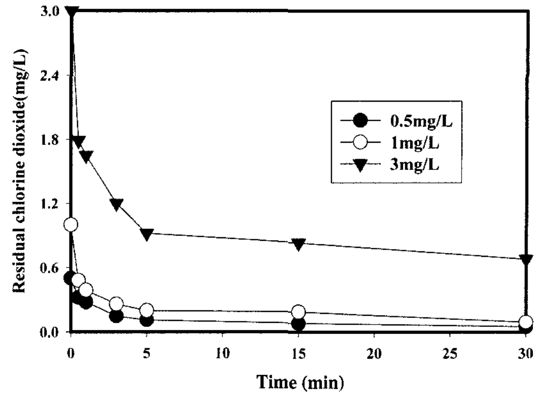

Fig. 2. Chlorine dioxide residuals on chlorine dioxide dose.

temperature was 20°C and pH was 7. After 1 min, the consumption of chlorine dioxide was very high, along with the inactivation of coliforms. When the initial concentrations of chlorine dioxide were 0.5, 1 and 3 mg/*l*, concentrations of chlorine dioxide remaining were 0.08, 0.19 and 0.83 mg/*l* after 15 min. Thus, the ratios of residual chlorine dioxide to initial chlorine dioxide were 16, 19 and 28%.

For the inactivation of 99.9%, 5 min of contact time were required for a chlorine concentration of 1 mg/*l*. For 99.99% inactivation, 30 min of contact time were required, and 1 min was required for chlorine concentrations of 1 and 3 mg/*l*, respectively. When chlorine concentration levels were 0.5 mg/*l*, it was not possible to achieve the disinfection level required because the coliform reduction was 2.15 log for 30 min on the basis of 99.9%. In summary, CT values of total coliform for *D* plant, for the dose of chlorine dioxide based on 99.9 and 99.99% were 1.0 and 3.6 mg·min/*l* of total coliform. For application of chlorine design based on coliforms to drinking surface water systems, CT values 2.3 times greater than those required to use chlorine dioxide must be obtained.

Effect of pH

Fig. 3 shows how the inactivation of coliforms varies, depending on the pH when chlorine dioxide was injected in levels of 3 mg/*l* at 20°C. Log survival ratio for 1 min was found to be −5.07, −4.92, −4.88 and −4.83 for 6, 7, 8 and 9. The log survival ratio after 30 min was determined to be

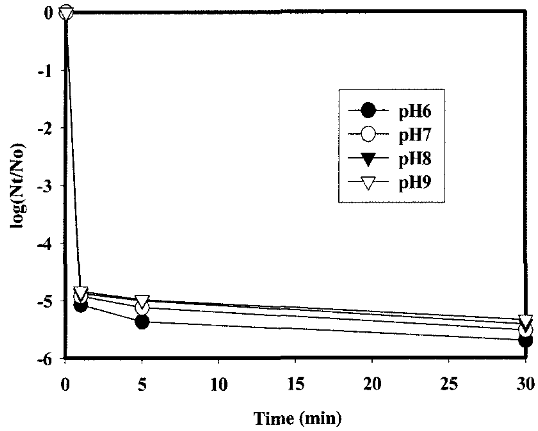

Fig. 3. Total coliform inactivation by chlorine dioxide on pH.

−5.70, −5.52, −5.42 and −5.34 for 6, 7, 8 and 9. Thus, it is evident that for the time period ranging from 1 min to 30 min, the ratios of the inactivation were 89, 90, and 91%. The majority of inactivation was achieved after 1 min with a dose of 3 mg as ClO_2/*l*.

This evidence indicates that the total coliform inactivation by chlorine dioxide was increased as the pH value decreased. This may result from the disproportionate reaction of chlorine dioxide, which converted chlorite and chlorate under basic conditions.

In this experiment, when the contact time for chlorine dioxide was 30 min and pH levels ranged from 6-9, chlorine dioxide exhibited inactivation effects within a relatively wider range of pH values. It has been reported that chlorine dioxide could achieve inactivation effects on *poliovirus-1*, *ECHO-11*, *coxsackie B*, *adenovirus-7*, *herpes simplex virus-1* and *mumps virus* when pH values range from 3-9 at 7 mg/*l*. However, as Jeong *et al.* (1993) reported, *E-coli* inactivation rate observed at pH 8.5 was higher than that at pH 7.

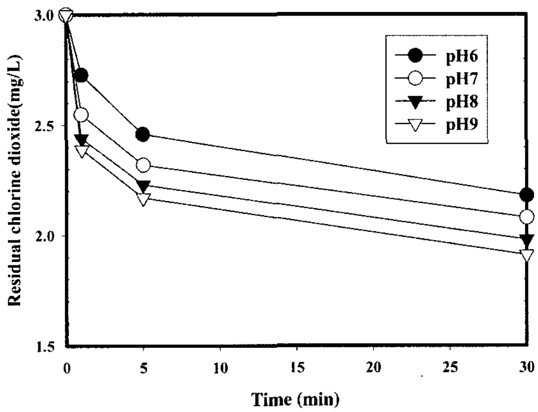

Fig. 4. Chlorine dioxide residuals on pH.

Fig. 4 illustrates the variation of chlorine dioxide that remained after coming into contact with coliforms at various pH values. When pH was 6, 7, 8 and 9 after 1min, the chlorine dioxide consumed after 1 min was 1.17, 1.35, 1.46 and 1.51 mg/*l*, and the chlorine dioxide consumed after 5 min was 1.94, 2.08, 2.17 and 2.23 mg/*l* for pH 6, 7, 8 and 9. Therefore, the ratios of chlorine dioxide consumed at 5 min to the final chlorine dioxide consumed were 65, 69, 72 and 74%.

As the following equation reveals, the oxidation-reduction reaction of chlorine dioxide in water resulted in the formation of chlorite ion

$$ClO_2 + e \rightarrow ClO_2^- \qquad (1)$$

Lee *et al.* (2001) demonstrated that the formation of chlorite tended to increase as the pH levels increased.[13] When pH was 4, 7 and 10 after 30 min, the ratios of chlorine dioxide consumed were 74, 77, 81 and 83%. This demonstrates that more chlorite was formed at higher levels of pH. In alkaline solution, at higher conversion ratios to by-products, the rate of chlorine dioxide decomposed was also relatively higher. It was reported that the activity of chlorine dioxide is dependant on pH,

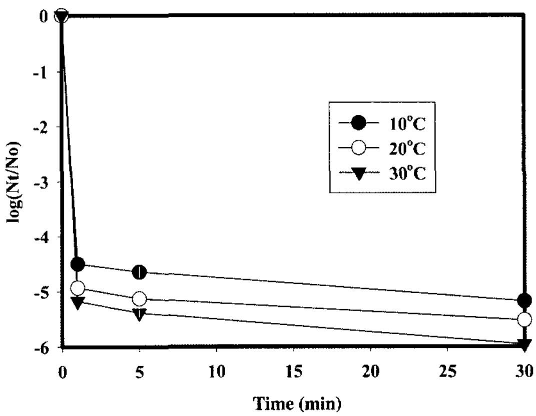

Fig. 5. Total coliform inactivation by chlorine dioxide on temperature.

since this controls the number of electrons.

Effects of Temperature

Fig. 5 demonstrates how inactivation varies, depending on temperature, when chlorine dioxide was injected in the amount of 3 mg/*l* at pH 7. As Arrhenius's equation highlights, the rate of chemical reaction is influenced by chemical temperature. The reaction rate formula can be implemented to express the relationship between required disinfection time and various temperatures to obtain a certain disinfection effect.

As temperature increased, the bactericidal effects of the disinfectants also increased. The log survival ratio for 1 min was determined to be –4.49, –4.93 and –5.17 for the 10, 20 and 30°C and the log survival ratio for 30 min was determined to be –4.64, –5.12 and –5.39 for 10, 20 and 30°C. This evidence suggests that the ratios for inactivation from 5 min to the final inactivation of 30 min were 70, 74 and 80%.

As temperature affects the rate of reaction, the amount chlorine dioxide consumed also increased at higher temperatures. The ratios of chlorine dioxide consumed to chlorine dioxide present were as follows: Chlorine dioxide consumed was 0.30, 0.45 and 0.63 mg/*l* at 1 min and chlorine dioxide consumed at 15 min was 0.74, 0.92 and 1.15 mg/*l* for 10, 20 and 30°C. Therefore, the ratios of chlorine dioxide consumed at 5 min to chlorine dioxide consumed at 30 min were 70, 74 and 80%.

Fig. 6 depicts the variation of chlorine dioxide remaining when subjected to coliforms at various temperatures. When temperature was 10, 20 and 30°C at 1 min, chlorine dioxide consumed at 1 min was 1.20, 1.35 and 1.53. Chlorine dioxide consumed at 5 min was 1.92, 2.08 and 2.32 mg/*l* for 10, 20 and 30°C. Chlorine dioxide consumed at 30 min was 1.92, 2.08 and 2.32 mg/*l* for 10, 20 and 30°C. The ratios of chlorine dioxide consumed at 15 min to final chlorine dioxide consumed were 71, 73 and 85%. This indicates that an high rate of chlorine dioxide consumption was achieved at high temperatures.

Effect of DOC

Fig. 7 illustrates the inactivation of chorine dioxide in the range of DOC from 2.54 to 7.54 mg/*l* when chorine dioxide was injected with 3 mg/*l*. After a contact time of 1 min, the inactivation was –4.93, –2.92, –0.48 log10 reduction when DOC

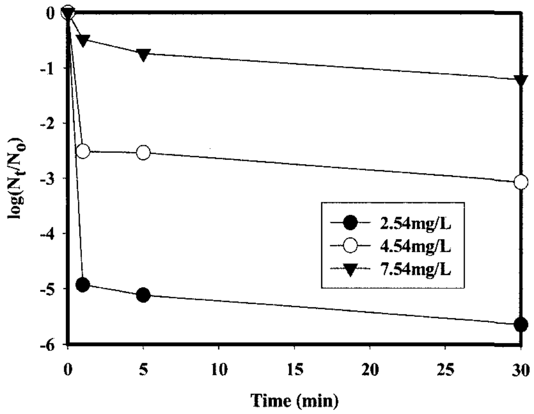

Fig. 7. Total coliform inactivation by chlorine dioxide on DOC.

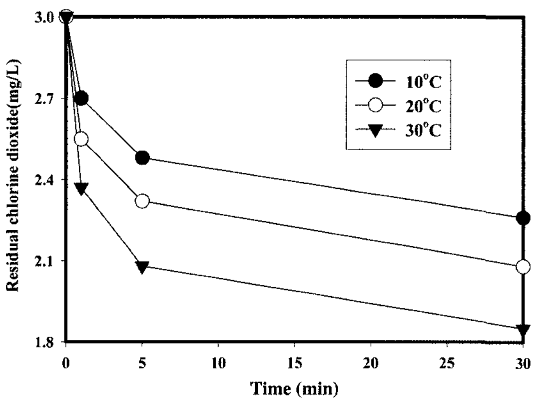

Fig. 6. Chlorine dioxide residuals on temp.

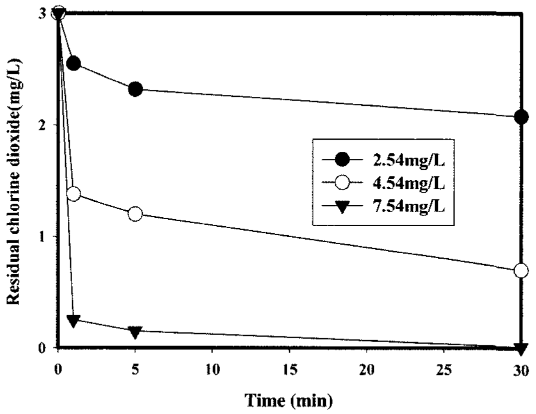

Fig. 8. Chlorine dioxide residuals on DOC.

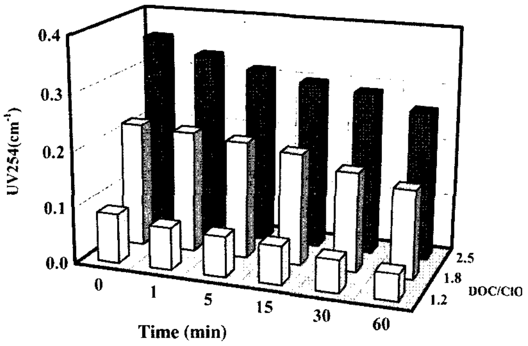

Fig. 9. Effect of chlorine dioxide/DOC ratio in UV_{254} reduction.

was 2.54, 4.54 and 7.54 mg/*l*. After 30 min contact time, the inactivation was −5.63, −3.06, −1.20 log10 reduction when DOC was 2.54, 4.54 and 7.54 mg/*l*.

The amount of chlorine dioxide consumed was 1.35, 2.02 and 2.75 at 1min, and the amount of chlorine dioxide consumed at 5 min was 2.08, 2.27 and 2.85 mg/*l* for 2.54, 4.54 and 7.54 mg DOC/*l*. Thus, the ratios of chlorine dioxide consumed at 5 min to final chlorine dioxide consumed were 69, 76 and 95%. This evidence reveals that chlorine dioxide was consumed easily when the amount of DOC in water was high. It reported that chlorine dioxide primarily reacts with organic compounds as an electron-transfer oxidant, which forms oxygenated products as diols, aldehydes, ketones and carboxylic acids.

As the concentration of DOC in water increased, chlorine dioxide maintained low values. After 30 min, the amount of chlorine dioxide consumed was 2.32, 2.64 and 2.99 mg/*l*, respectively. When chlorine dioxide reacts with organics, one of by-product is chlorite ion. This fact correlates with evidence presented by Jeong *et al.* Based on this result it is evident that DOC significantly affects chlorine dioxide inactivation kinetics.

The relationship presented is linear in the range between 2.54 and 7.54 mg/*l* DOC. Most types of water are included in this DOC range. The slope in the linear portion indicates that the decay rate increases by 0.16 min^{-1} per mg/*l* DOC for 5 min. Choi et al reported on the equation for DOC and chlorine dioxide as follows: $ClO_2(consumend) = 0.16DOC + 1.63$, R = 0.91.

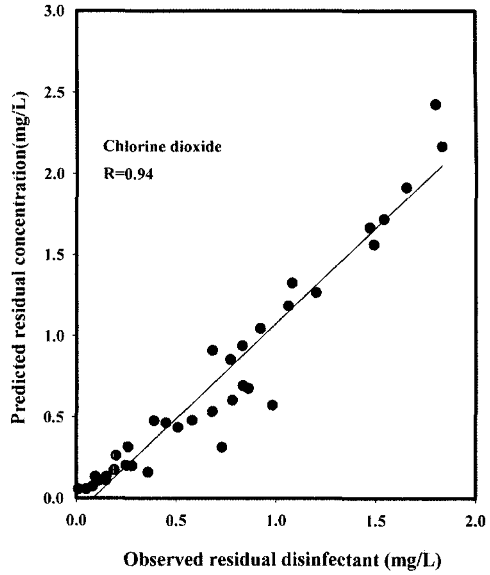

Fig. 10. Comparison of the predicted versus observed concentration of residual disinfectant.

Fig. 9 depicts UV absorbance at 254 nm for various dosages of chlorine dioxide and DOC. The ratios of DOC to chlorine dioxide were 1.2, 1.8, and 2.5. As the ratios of chlorine dioxide to DOC in water increased, the UV254 decrement increased. After 30 min, UV254 content had decreased to 34, 30 and 19% when the ratios of DOC to chlorine dioxide were 1.2, 1.8 and 2.5 mg/*l*. At 60 min, UV254 content was decreased as 47, 29, and 27% when the ratios of DOC to chlorine dioxide were 1.2, 1.8 and 2.5 mg/*l*. UV absorbance at 254 nm was decreased as the reaction time incresased. The ratios of UV254 at 60 min to an initial UV254 were 53, 71 and 73% when the ratios of free chlorine to DOC were 1.2, 1.8 and 2.5 mg/*l*.

Models for Predicting Inactivation of Total Coliform

Plot of predicted against observed total coliform reductions for chlorine dioxide is presented in Fig. 10. These models predicted the observed reductions reasonably well. The multiple correlation coefficients (R) for the chlorine dioxide was 0.93. To determine which factors are most influential in the process of disinfection with chlorine dioxide multiple regression analyses was conducted.

The result for total coliform with chlorine dioxide was:

$$\frac{N_t}{N_0} = (10)^{-1.65}(Residual\ chlorine\ dioxide)^{-2.53}$$
$$(Time)^{-1.39}(pH)^{-1.19}(Temp)^{-2.20}(DOC)^{3.74} \quad (2)$$

Absolute effect total coliform inactivation with chlorine dioxide was DOC > Residual chlorine dioxide > temp. > time > pH.

Conclusions

This research was to determine the inactivation of total coliform as the indicator organism with chlorine dioxide for drinking water treatment. This study was carried out to develop practical model for potable water disinfection with regard to the dosage of disinfectant, contact time, pH, temperature and DOC. The conclusions can be drawn from this research as follows:

CT values with the dose of chlorine dioxide for *D* plant that it was based on 99.9% was 1.00 mg·min/*l* of total coliform. CT values with the dose of chlorine dioxide that it was based on 99.99% were 2.60 mg·min/*l* of total coliform. The bactericidal effects of disinfectants decreased with pH increase in the range of pH 6-9. But, the influence of pH change on the killing effect of chlorine dioxide was not strong, The bactericidal effects of the disinfectants were increased as the temperature increase. This result shows that CT values required for coliform inactivation at winter season can lead to decreases by decrease in temperature. Absolute effect total coliform inactivation with chlorine dioxide appeared in the biggest order of DOC, Residual chlorine dioxide, temp., time and pH.

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