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Factors Affecting Chemical Disinfection of Drinking Water

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Abstract : This research sought to compare chlorine, chlorine dioxide and ozone as chemical disinfectants of drinking water, with inactivation of total coliform as the indicator. The inactivation of total coliform was tested against several variables, including the dose of disinfectant, contact time, pH, temperature and DOC. A series of batch processes were performed on water samples 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.

Injection of 1 mg/L of chlorine, chlorine dioxide and ozone resulted in nearly 2.4, 3.0 and 3.9 log inactivation, respectively, of total coliform at 5 min. To achieve 99.9 % the inactivation, the disinfectants were required in concentrations of 1.70, 1.00 and 0.60 mg/L for chlorine, chlorine dioxide and ozone, respectively. Bactericidal effects generally decreased as pH increased in the range of pH 6 to 9. The influence of pH change on the killing effect of chlorine dioxide was not strong, but that on ozone and free chlorine was sensitive. The activation energies of chlorine, chlorine dioxide and ozone were 36,053, 29,822 and 24,906 J/mol for coliforms with inactivation effects being shown in the lowest orders of these.

keywords : Chlorine, Chlorine Dioxide, Ozone, Disinfection, Factors, Drinking Water Treatment

1. INTRODUCTION

Disinfection has been used in the treatment of drinking water for many years to control waterborne diseases. Effective control of resistant pathogens in potable water requires not only the use of efficacious disinfectants but also optimal design criteria to cost-effectively protect public health while minimizing the risk of exposure to disinfection by-products (Geo, 1992).

Total coliform bacteria counts are used primarily to measures the effectiveness of water supply treatment effectiveness and the corresponding risk to public health risk. The chief aim of coliform monitoring is to prevent the supply and consumption of water that is contaminated by human or animal excrement. Such water could potentially contain pathogens capable of spreading infections throughout the community (Kramer et al., 1996).

Chlorine has long been recognized as the most effective disinfectant against waterborne pathogenic organisms (Gerald, 1997), and it is the primary disinfectant used for this purpose in Korea. Chlorine remains the most commonly used disinfectant despite the fact that newly emerging pathogenic protozoa such as *Giardia cysts* and *Cryptosporidium oocysts* are fairly resistant to the typical dose (Miller, D. G., 1992).

The safety of chlorine began to be questioned in 1974, when chlorination of drinking water was found to produce THMs (trihalomethanes), and the by-product of one of these, chloroform, was shown to increase the incidence of tumors (Johnson, J. D. and Jenson, J. N., 1986). In order to comply with the subsequent regulations on THMs, many drinking water utilities were forced to alter their treatment methods. The options available to these utilities are to use a disinfectant other than chlorine such as chlorine dioxide and ozone etc (Hopf, 1967).

Disinfecting with chlorine dioxide or ozone creates no THMs and fewer nonvolatile halogenated organic products than with chlorine. However, these disinfectants are active chemicals and react with aquatic organic substances to form yet other by-products. Interest is mounting for using chlorine dioxide and ozone to treat drinking water for taste, odor control, and oxidation of iron and manganese (Robert et al., 1990).

In 1990 reports by institute for environmental research in Yonsi University that chlorination of waters results in THM gave impetus to study directed toward using alternative disinfectants in Korea. In addition, Virus in tap

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water has been reported by Kim. Unfortunately, free chlorine the most common disinfectant used by water utilities in Korea are generally not effective for in activation virus when used as primary disinfectant.

The CT concept is a simple approach that was used to develop disinfection requirements under the water treatment rule. Independently of what the disinfection concentration and contact time are individually, if the product is the same, the same level of inactivation is achieved. The validity of the CT concept to represent the inactivation kinetics of total coliforms including by various disinfectants including free chlorine has been questioned recently (Hunt and Marinas, 1997). There is a need for a more comprehensive assessment of the validity of the CT concept before undertaking a more complex approach in the development of future disinfection requirements for drinking water disinfection.

This research presents a developed discussion that can be used to assess the applicability of various disinfectants to selecting an appropriate disinfection strategy for drinking water systems. The disinfection effects of chlorine, chlorine dioxide, and ozone with respect to the dosage of disinfectant, contact time, pH, temperature, and DOC were investigated.

2. MATERIALS AND METHODS

2.1. Sample Preparation

Samples were taken from a water treatment plant with a nominal capacity of 1,450,000 m^3/day of water from the Han River. This plant's treatment process includes coagulation, sedimentation, filtration, and chlorination. Water samples were collected at the point of the filter inlet. This was accomplished aseptically with sterilized 1L Pyrex bottles that had previously been treated by acid washing and baking at 300°C to remove all carbon compounds. Appropriate volumes of the sample were filtered through sand columns in the laboratory. Sample characteristics aredescribed in Table 1.

Table 1. Characteristics of water samples

Parameter	Condition
pH	7.2
Temperature(℃)	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/mL)	10
Total coliform (number/100mL)	ND

2.2. Microorganisms and Culture Conditions

The samples to be used for preparation of stock inocula were collected from the sewer manhole adjacent to *K* University, located in the eastern part of Seoul. They were filtered through 11 ㎛ membrane filters. The filtrate of 10mL was placed on M-endo medium in a Petri dish and incubated for 24 h at 35°C. The colonies that formed were placed on a solution of nutrient broth and incubated for 24 h at 25°C. The coliform bacteria were isolated by centrifugation at 5×10^3 *G* for 5 min, washed twice, and resuspended in buffer solution free from chlorine demand at pH 7. The coliform bacteria isolated from the media were mixed with a vortexer. The fresh cell suspensions in the chlorine-demand-free solution were used for all experiments. The density of total coliform was between 2×10^6 and 8×10^8 cfu/100mL.

2.3. Disinfection Procedure

The schematic diagram of experimental equipment is shown in Fig. 1. The reactors were covered with aluminum foil to prevent stray ultraviolet radiation from adversely affecting the disappearance rate of the oxidant. Experiments were conducted using 250 mL amber batch reactors. The reactors, test water, and microorganisms were slowly brought to the desired temperature using the incubator. The microorganisms were acclimated to the water bath for a minimum of 60 min. Vigorous agitation of the microorganisms was essential prior to addition of the oxidant. The concentration of the stock disinfectant solution was measured immediately before the experimental trial, and a volume of stock solution corresponding to the prescribed initial disinfectant dose was then added to the coliform-containing reactor using a pipette. This procedure was repeated for the control reactors as well. At the end of the contact time, remaining oxidants were neutralized using appropriate reducing agents. Finally, the reactor vessels were sampled and analyzed for surviving microorganisms.

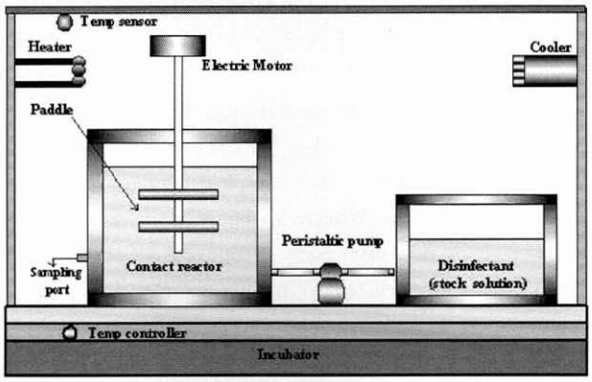

Fig. 1. Schematic of experimental apparatus.

2.4. Analytical Methods

Free chlorine stock solutions were prepared daily as needed using sodium hypochlorite solution (Sigma chemicals, 10 percent available) with oxidant demand free water to give a concentration ranging from 300 to 1,000 mg/L. Free chlorine levels were determined by the DPD colorimetric method with a chemical chlorine kit (Hach Chemical).

Chlorine dioxide was generated through acidification of technical grade sodium chlorite (Aldrich Chemical). A schematic of the chlorine dioxide apparatus used for this study, a modified version of that used in standard method 4500-ClO_2 (APHA et al., 1992). The concentration of the stock chlorine dioxide solution was determined with a UV-visible spectrophotometer. Absorbance readings were taken at 360 nm in a 1 cm cuvette. A molar absorptivity of 1250 $M^{-1}cm^{-1}$ at this wave length was used to calculate the corresponding concentrations of chlorine dioxide (Lee et al., 2001).

Ozone gas was generated using a water-cooled, corona discharge generator (Erwin sander) from extra dry oxygen feed gas. Oxygen carrier gas containing approximately 5 percent ozone was bubbled for a minimum of 20 min at 20°C through 400 mL of regent grade water in a 500 mL gas absorption flask. Ozone concentrations in the stock solution were approximately 20 mg/L. Ozone residual analyses were conducted by the standard colorimetric method (APHA et al, 1995). Indigo stock solution was prepared from potassium indigo trisulphonate-concentrated phosphoric acid and anhydrous monobasic sodium phosphate. Samples were analyzed at 600 nm with a UV spectrophotometer (UV-1601, Shimadzu).

Deionized laboratory water was obtained from an ultra pure water system (Pure Up 700, Mirae Scientific) operated at a resistivity of at least 18 ㏁/cm. Phosphate buffer was prepared with disodium hydrogen orthophosphate ($Na_2HPO_4 \cdot 7H_2O$) and potassium dihydrogen orthophosphate (KH_2PO_4). DOC levels controlled from humic acid. Humic material was purchases from Sigma Chemical Co. The preparation of humic material was performed according to Meier et al.

Total coliform was enumerated according to a membrane filtration procedure from the US standard method 9222B (APHA et al., 1995). The samples containing coliform bacteria were filtered through Millipore membrane sterilized to 0.45 ㎛ in porosity. Each component of the filtration system was also sterilized. A membrane was placed on the apparatus under sterile conditions, and aliquots of 1, 10, and 100 mL were filtered. The membrane was then placed on agar M-endo medium in a Petri dish and incubated for 24 hr at 35°C. Results are expressed as coliform colonies per 100 mL.

3. RESULTS AND DISCUSSION

3.1. Effect of Dosage of Disinfectant

Various doses of disinfectants were added to a given volume of bacteria-containing solution and reacted for 5 min at 20°C. The results are shown in Fig. 2. Chlorine, chlorine dioxide, and ozone all exhibited moderate killing effects on total coliform, and these killing effects gradually increased with the dose of disinfectant. At 5 min contact time and 1 mg/L disinfectant concentration, coliform was reduced by 2.42, 2.99, and 3.93 $\log_{10}$ with ozone, chlorine dioxide, and chlorine, respectively.

The killing effect of ozone was better than that of chlorine dioxide and chlorine. For example, if 99.9 % of the killing effect was attained, the required amount of ozone was about 0.6 mg/L, chlorine dioxide was about 1.0 mg/L, but for the chlorine, 1.7 mg/L was required. Under normal temperature and pressure, chlorine dioxide dissolves easily in water. Its solubility is five times that of chlorine gas. In contrast to the hydrolysis of chlorine gas in water, chlorine dioxide does not hydrolyze to any appreciable extent but rather remains in solution as a dissolved gas. Owing to its strong oxidizability and near 100 % existence in the molecular state, chlorine dioxide can penetrate the cell membrane of a bacterium easily. When this occurs, the semipermeable membrane and the permeable pressure are destroyed (Geo, 1992). However, Jeong et al. (1993) reported that the killing effect of *E-coli* with chlorine was similar than that with free chlorine.

As shown in Fig. 3, less ozone was required to attain the same bactericidal effect than for any other disinfectant.

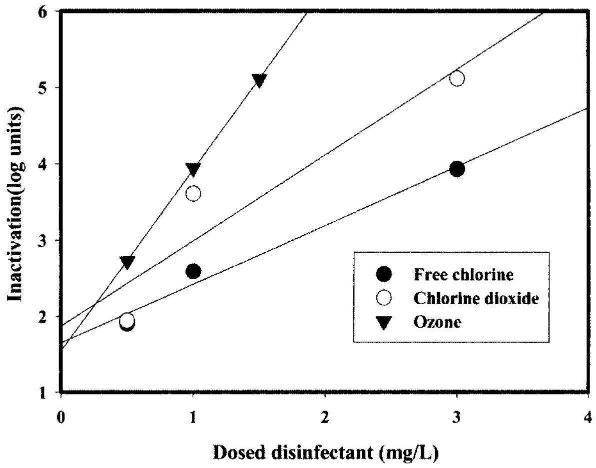

Fig. 2. Total coliform inactivation of free chlorine, chlorine dioxide and ozone dosages.

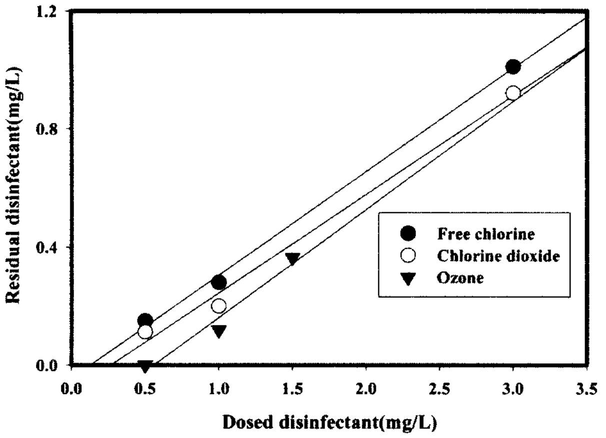

Fig. 3. Disinfectant residuals detected after 5 min of contact time as a function of the dosage.

To attain 99.9 % of total killing effect, the required amount of ozone was 0.6 mg/L, chlorine dioxide, 1.0 mg/L, and chlorine, 1.7 mg/L. These results may be attributable to the different mechanisms by which the disinfectants act. It is thought that ozone attacks proteins and unsaturated lipids in cell membranes, denatures enzymes, and damages genetic materials inside cells (Cho et al., 1989).

3.2. Effect of pH

In general, it is very meaningful fact to compare the killing effects at different pH values. Fig. 4 shows the impact of pH on the disinfection of total coliform and demonstrates increases in the killing effects with decreasing chlorination pH. In water treatment, HOCl and OCl^- coexist. Generally considering, HOCl plays a main role in bactericidal and disinfection function. The bactericidal efficiency of HOCl is nearly 80 times as high as that of OCl^- (Geo, 1992). The higher the pH is, the lower the ratio of HOCl and the weaker the activity is, and the poorer the disinfectant effects are. But, a recent publication, however, indicated that inactivation of *poliovirus I* was more effective at pH levels where the free chlorine was in the form of OCl^- rather than in the form of HOCl. Hypochlorite ion at pH 10 was found to be seven times more effective against *poliovirus I* than HOCl at pH 6 (Wickramanayake and Sproul, 1988).

As can be seen from the tests, the influence of pH change on killing effect of chlorine dioxide was not strong. In the range of pH 6-9, coliforms may be killed effectively by chlorine dioxide. Oxidation capacity of chlorine dioxide depends upon the acidity and basicity of the solution. The stronger the acidity of solution, the higher the oxidation capacity of chlorine dioxide. But at pH 9, chlorine dioxide lost a little the inactivation effects on the coliforms. This may be caused by the disproportionate reaction of chlorine dioxide under the basic condition. The pH impacts on inactivation efficiencies have been observed by other researchers. Junli (1997) observed that chlorine dioxide was unaffected by pH values between 6 and 10. Kristen et al (2000) reported the 20-30 % decrease in CT requirement to achieve *Cryptosporidium* inactivation efficiencies in the range of 90 to 99.9 % when pH was decreased from 10 to 6-8.

As the pH of solution is decreased, ozone becomes more stable. In the general case molecular ozone is the predominant oxidative agent. Farooq et al. (1977) determined that pH has a minimal effect on ozone inactivation kinetics when using a semi batch reactor with no decrease in the ozone residual. However, as observed by Labatiuk (Labatiuk et al., 1992), pH is a significant factor in a batch reactor assay with decreasing ozone residual. Wickramanayake et al., suggest that differences in membrane constituents can lead to variations in ozone permeability or pH sensitivity.

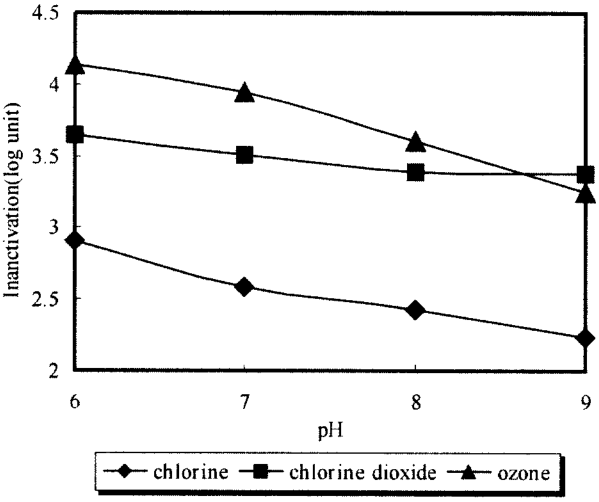

Fig. 4. Total coliform inactivation of free chlorine, chlorine dioxide and ozone at different pH value.
(Disinfectant dosage = 1 mg/L)

3.3. Effect of Temperature

The role of temperature in the inactivation of coliforms with chlorine, chlorine dioxide, and ozone is depicted in Fig. 5. All disinfectants demonstrated an increase in inactivation effect at higher temperatures. For a temperature rise of 10°C, for example, log survival ratio of coliforms inactivation with chlorine was increased by 0.2. The dependence of the inactivation rate constant on temperature was analyzed using the classical Arrhenius expression. From this, the difference between inactivation rate constants at high and low temperatures would be expected to be greater for ozone than for the other disifectants. A plot of rate

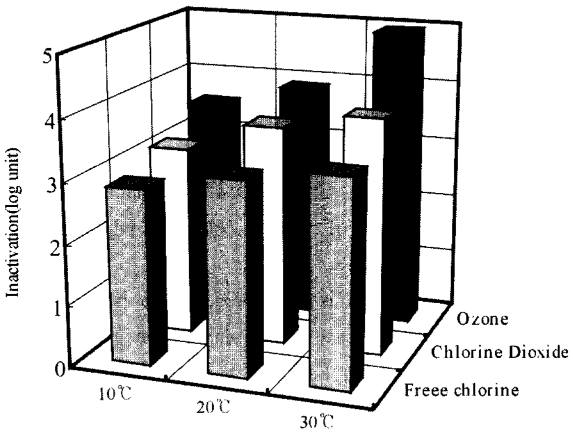

Fig. 5. Total coliform inactivation of free chlorine, chlorine dioxide and ozone at different temperature. (Disinfectant dosage = 1 mg/L)

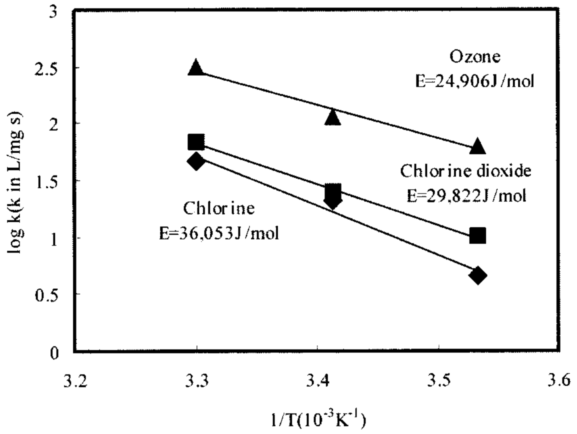

Fig. 6. Arrhenius plots for the inactivation rate constants.

constants according to the Arrehenius expression and the corresponding best-fit line are presented in Fig. 6.

The energies to inactivate coliforms at pH 7.0 in the temperature range 10 to 30°C for chlorine, chlorine dioxide, and ozone were 36,053, 29,822 and 24,906 J/mol, respectively. Because the inactivation energies of chlorine and chlorine dioxide were larger, one concludes that coliforms are killed more easily by ozone. The inactivation energies of chlorine and chlorine dioxide for killing *E. coli* have been reported as 34,580 and 19,000 J/mol (Junli, 1997), while that of ozone, 37,100 J/mol (Hunt and Marinas, 1997).

3.4. Effect of DOC

To examine the effect of DOC concentration on the inactivation of coliforms, chlorine, chlorine dioxide and ozone were injected at 1 mg/L disinfectant dose and DOC levels of 2.54 and 4.54 mg/L. If the DOC is raised by 1 mg/L, log survival ratio of coliforms inactivation with chlorine, chlorine dioxide and ozone can be decreased 0.16. 0.25 and 0.37.

DOC is significant to inactivation kinetics. Acha et al. (1984) reported that chlorine dioxide primarily reacts with organic compounds as an electron-transfer oxidant giving rise to the formation of oxygenated products (diols, aldehydes, ketones, and carboxylic acids). Chlorite ion is the by-product when chlorine dioxide reacts with organic molecules. Increased DOC concentration results in a decrease of inactivation with ozonation because more ozone and HO· are consumed. Ozonation of water containing DOC results in direct consumption of molecular ozone without the formation of byproducts because bonds within the organic molecules are cleaved and reproportioning of the electron charge from the ozone occurs (Rice et al., 1981).

To examine the effect of DOC concentration on the inactivation of coliforms, 1 mg/L of chlorine, chlorine dioxide, and ozone were injected at DOC levels of 2.54 and 4.54 mg/L. A 1 mg/L rise in DOC caused decreases of 0.16, 0.25, and 0.37 in log survival ratio of coliforms inactivation for chlorine, chlorine dioxide, and ozone.

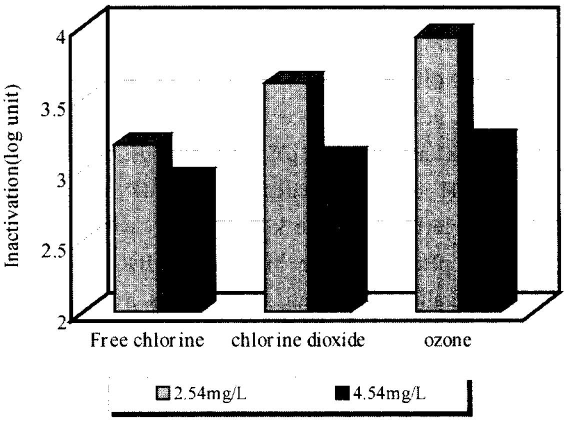

Fig. 7. Total coliform inactivation of free chlorine, chlorine dioxide and ozone at different DOC. (Disinfectant dosage = 1 mg/L).

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