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Evaluation of mixed oxidants generated by an electrochemical method

Kyunghyuk Lee*, Jaelim Lim, Doojin Lee, Seongsu Kim, Hyowon Ahn

K-water (Korea Water Resources Corporation), Shintanjinro 560, Yeonchuk-dong, Daedeok-gu, Daejeon, Korea 306-711
Tel. +82 42 870-7526; Fax. +82 42 870-7549; email: kh.lee@kwater.or.kr

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ABSTRACT

Mixed oxidants produced by means of an electrochemical method were evaluated to confirm the presence of oxidants other than free chlorine. Inactivation rate of *B. subtilis* spore on the mixed oxidants were similar with that on free chlorine. Activation energy of mixed oxidants and free chlorine for *B. subtilis* spore inactivation at pH 8.3 were determined as 30.8 $kJ \cdot mol^{-1}$ and 34.7 $kJ \cdot mol^{-1}$ respectively. UV absorption spectrum of both free chlorine and mixed oxidants were compared. Molar extinction coefficients of free chlorine and mixed oxidants at 292 nm, which is the maximum absorption wavelength of OCl^-, were 357 $M^{-1}\,cm^{-1}$ and 377 $M^{-1}\,cm^{-1}$, respectively. Disinfectant decay rate and formation rate of THM on sand filtration effluent at S WTP were compared. The disinfectant decay rate followed a first-order reaction for both mixed oxidants and chlorine. In order to evaluate the effect of secondary disinfection, the decay rate of chlorine followed by mixed oxidants was evaluated compared with chlorine secondary disinfection. The formation rate of THM on both mixed oxidants and chlorine show an insignificant difference. In consequence, most of the oxidants in mixed oxidants are hypochlorite.

Keywords: *B. subtilis*; Disinfectant; Inactivation; Mixed oxidants

1. Introduction

The most common disinfectant used for drinking in Korea water is chlorine. However, the chlorine process needs special care due to gas storage conditions. The chlorine process has special problems for operation and management in small community water supply systems and secondary chlorination (boosting chlorination) system in a drinking water supply where the system management is delicate. For the convenience of operation of the disinfection system, on-site disinfectant generation systems have been developed [1]. One of the disinfectant generation systems is the mixed oxidant generation system generated by the electrochemical method using a sodium chloride (NaCl) solution. The mixed oxidant systems are reportedly more effective for inactivation efficiency for microbes, reduce biofilm regrowth in the distribution system, and lower formation rate of disinfection by-products than free chlorine [2–4]. The system is currently operating widely for chlorine boosting stations in a multi-regional water supply, small community water treatment systems and distribution reservoirs in Korea. However, the mixed oxidants generation system has not been evaluated on the concentration and species of each oxidant in the mixed oxidants due to the lack of effective analytical methods [5]. Thus, there are still conflicts on the efficiency of mixed oxidants as disinfectant. The efficiency of the mixed oxidant system compared with free chlorine was investigated in this study.

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*Corresponding author.

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The mechanism of mixed oxidant generation is the electrochemical reaction of solute (NaCl) flow between anode and cathode plates. The formation of several oxidants in the electrochemical reaction was reported by Kaczur and Cawlfield [6]. The following oxidants are theoretically generated in cathode, and hydrogen gas and hydroxide ion are produced in anode by electrolysis [Eqs. (1)–(6)]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \quad (2)$$

$$HOCl + H_2O \rightarrow ClO_2 + 3H^+ + 3e^- \quad (3)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (4)$$

$$O_2 + H_2O \rightarrow O_3 + 2H^+ + 2e^- \quad (5)$$

$$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^- \quad (6)$$

The mixed oxidants produced from the system stored in the reservoir to feed appropriate dosages of oxidants into water.

2. Materials and methods

Disinfectants used in this study were hypochlorite (10%) and mixed oxidants electrochemically generated from saturated sodium chloride solution. The mixed oxidants are used for the experiment immediately as soon as generated from the system. The experiments were conducted in a 50 mL Pyrex petri dish. For the complete mixing of the solution during reaction time, a magnetic stirrer was employed. For the *B. subtilis* spore inactivation experiments, mixed oxidants and free chlorine were diluted so as to have an appropriate oxidant concentration as HOCl, using distilled water. The initial microbial population of 105 CFU was prepared with phosphate buffer saline.

B. subtilis (ATCC 6633) spores were prepared by the procedure described by Cho et al. [7]. The UV spectrum of the mixed oxidants was measured by a UV spectrophotometer (Varian, Carry 300, USA). The concentration of mixed oxidants and chlorine was measured by DPD methods using a DR 2000 (Hach, USA). The THM analysis during disinfectant decay was accomplished by GC–ECD using the liquid–liquid extraction method.

3. Results and discussion

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

In order to evaluate disinfection efficiency with mixed oxidants, the inactivation rate of *B. subtilis* spores were evaluated with mixed oxidants and free chlorine. The inactivation rate of *B. subtilis* spores is generally expressed as Eq. (7) [8]:

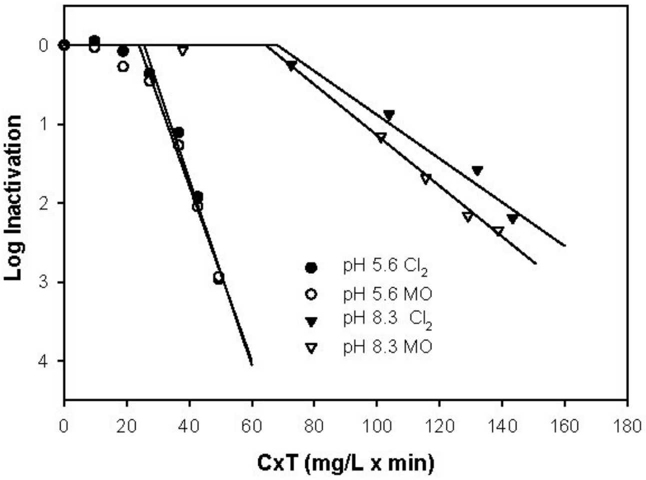

Fig. 1. Comparison of inactivation rate of *B. subtilis* spores by free chlorine and mixed oxidants (test water: distilled).

$$\log (N/N_0) = -k\,(CT - CT_{Lag}) \quad (7)$$

where N_0 is the initial cell population(CFU/mL), N the remaining cell population (CFU/mL) at time T, C the disinfectant concentration (mg/L), T the reaction time (min), and T_{Lag} is the lag time for inactivation (min).

Fig. 1. shows the inactivation rate of *B. subtilis* spores on the mixed oxidants and chlorine at pH 5.3 and pH 8.3, respectively. The inactivation rate of *B. subtilis* spores on hypochlorite at pH 5.6 was greater than that at pH 8.3 due to dissociation profile of hypochlorite(pKa =7.6 at 20°C). The inactivation rate on mixed oxidants was also increased as pH increased. Although the inactivation rates at pH 5.3 show insignificant different between free chlorine and mixed oxidants, inactivation rate at pH 8.3 on mixed oxidants was 1.7 times higher than that on free chlorine. This result follows the previous study by Son et al. [8]. It might be thought that the level of oxidants other than chlorine in the mixed oxidants did not have any measur-able disinfection ability for *B. subtilis* spores.

3.2. *Determination of activation energy for* B. subtilis *spore inactivation*

It is difficult to analyze the concentration of each component in mixed oxidants due to the technical problems for the chemical analysis. For the analysis of ozone and chlorine in the solution presence together, DPD reagent is oxidized by both oxidants instantaneously. It results that the one oxidant interfere the other oxidants for the quantitative analysis.

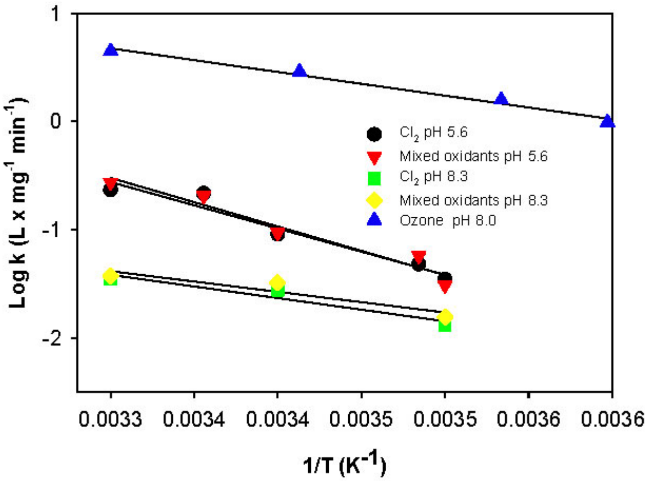

Fig. 2. Determination of activation energy for *B. subtilis* spore inactivation with free chlorine, ozone, and mixed oxidants.

The activation energy, which is a specific value of oxidants of *B. subtilis* spore inactivation with both chlorine and mixed oxidants, was determined based on the inactivation experiments. According to the Arrenius equation (8), activation energy of chlorine and mixed oxidants for inactivation of *B. subtilis* spores at pH 5.6 were 34.7 kJ mol^{-1} and 30.8 kJmol^{-1}, respectively. As shown in Fig. 2, activation energy at pH 8.3 also shows similar values for free chlorine and mixed oxidants as 74.4 kJ mol^{-1} and 78.9 kJ mol^{-1}, respectively. The activation energy of ozone for the inactivation of *B. subtilis* spores at pH 8.0 was determined by Gunten [9] as 42.1 kJ mol^{-1}.

$$\log K = \log A - \frac{E_a}{2.303} \times RT \tag{8}$$

where k is the rate constant (L/mol·min), A the collision frequency parameter (L/mol·min), E_a the activation energy (J mol^{-1}), R the ideal gas constant (8.314 Jmol^{-1}K^{-1}) and T the absolute temperature (K).

Activation energy for the mixed oxidants of *B. subtilis* spore inactivation show significantly different values with free chlorine if other oxidants such as ozone, chlorine dioxide, and hydrogen peroxide are present in the mixed oxidants. Although the activation energy for the mixed oxidants and ozone were slightly different, it is hard to explain the oxidant—except free chlorine—presence in the mixed oxidants due to the difference of inactivation rate results in the experimental deviation. However, the concentration of other oxidants other than free chlorine might be present at trace levels relative to the concentration of free chlorine.

3.3. UV absorption spectrum of mixed oxidants

In order to evaluate the UV absorption characteristics of mixed oxidants, the UV absorption spectrum (200–450 nm) was measured. The mixed oxidants were immediately measured by UV spectrophotometer as soon as it produced by the mixed oxidant generation system. UV absorption of mixed oxidants shows the same trend but slightly different absorbance with chlorine at pH 8.3. At pH 8.3, the UV molar extinction coefficients at 292, in which maximum peak of chlorine and mixed oxidants, were 356 M^{-1} cm^{-1}, 377 M^{-1} cm^{-1}, respectively. As shown in Table 1., Siddiqui [10] presents molar extinction coefficients and peak absorption wavelength of oxidants. The molar extinction coefficient of free chlorine at pH 8.0 shows a similar value with that from this study. Compared to free chlorine, the oxidants such as ozone, chlorine dioxide, and hydrogen peroxide have either different peak absorption wavelengths or relatively low molar extinction coefficients. This indicates that the major oxidant in the mixed oxidant is free chlorine.

Table 1
Peak absorption wavelengths and molar extinction coefficients of oxidants [10]

Oxidants	Peak absorption wavelength (nm)	Molar extinction coefficient (M^{-1} cm^{-1})
Ocl$^-$	292	419
O_3	258	3200
H_2O_2	240	40
ClO_2[a]	359.2	1210

[a] Jeong et al. [11].

3.4. Decay rate and THM formation rate of mixed oxidants

Evaluation of residual oxidant and formation of TMH, which is one of chlorine disinfection by-products, were performed in a sand filtration effluent at the Suji WTP, Korea. Initial concentration range of oxidants (chlorine, mixed oxidants) is approximately 0.8–1.0 mg/L.

The first-order decay rate of mixed oxidants and chlorine at pH 7.3 and temperature 20°C were 0.030 h^{-1} and 0.023 h^{-1}, respectively. Although the decay rate of mixed oxidants is higher than that of chlorine, there was statistically no difference (95% confidence interval) between mixed oxidants and chlorine.

The effect of the secondary disinfection process (boosting chlorination) was also investigated with chlorine and mixed oxidants (Fig. 3.) The decay rate of chlorine followed by either mixed oxidants or chlorine as secondary disinfectant was evaluated. The chlorine decay rate in the primary disinfection was 0.0248 h^{-1}. The decay rates of secondary disinfection by mixed oxidants and chlorine were decreased compared to that of primary disinfection due to the chlorine reaction with NOM which

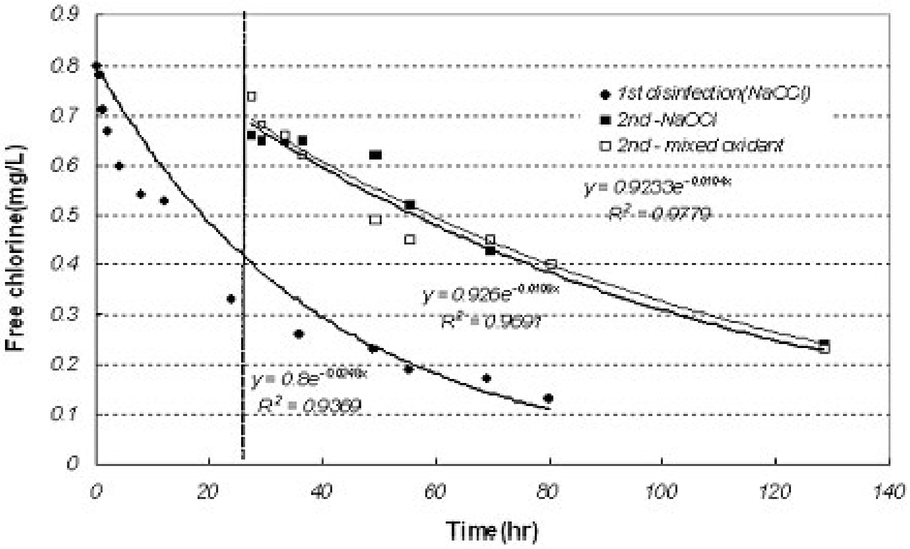

Fig. 3. Decay rate of mixed oxidants and free chlorine for secondary disinfection process. (Raw water: sand filtration effluent at the Suji WTP, Korea, phosphate buffer : pH 7.3, temp.: 20°C, DOC: mg/L).

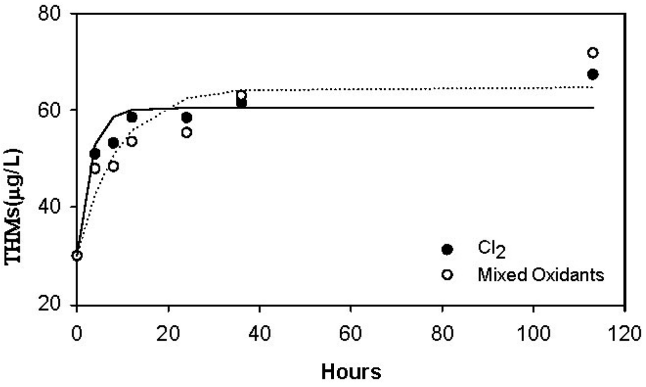

Fig. 4. Comparison of THMs formation on free chlorine and mixed oxidants on sand filtration effluent at the Suji WTP, Korea.

has fast reactivity take place in the primary disinfection process. Thus, decay rate of secondary disinfectants are decreased for both mixed oxidants and chlorine. The decay rate of secondary disinfectants as chlorine and mixed oxidants had insignificant difference.

For the formation of THM on mixed oxidants and chlorine, Fig. 4 shows that the THM formation rate on chlorine is higher than that on mixed oxidants at the initial reaction time which follows THM formation, Eq. (9), developed by American Water Works Association [12]:

$$THM(t) = Co + (FP - Co) \times \left[1 - \exp(-kt)\right] \tag{9}$$

where $THM(t)$ is the THM concentration at time t (h), Co the THM concentration (μg/L), FP is the ultimate concentration of THM formed (THM formation potential), and k is the first-order formation coefficient (h^{-1}). However, the formation of THM on both free chlorine and mixed oxidations is eventually similar. The THM formation potentials in the mixed oxidants and free chlorine calculated by the equation were determined as 61 μg/L and 65 μg/L, respectively.

4. Conclusions

The mixed oxidants electrochemically generated from sodium chloride are expected to be composed of several oxidants such as ozone, hydrogen peroxide, chlorine dioxide including free chlorine. However, due to the lack of analysis technique, it has not been investigated the composition and concentration of each oxidants in the mixed oxidants. The disinfection efficiency of mixed oxidants compared to free chlorine was evaluated on the inactivation of *B. subtilis* spores. The inactivation rates of *B. subtilis* on mixed oxidants were changed as free chlorine at various pH. The activation energy of mixed oxidants for *B. subtilis* inactivation also determined at pH as 30.8 kJ mol^{-1}, which is similar to free chlorine.

Based on the UV spectrum of mixed oxidants, molar extinction coefficient of mixed oxidants was determined at a maximum peak of OCl^- (292 nm) as 377 M^{-1} cm^{-1} at pH 8.3. The decay rate of mixed oxidants and the formation rate of THM on mixed oxidants were statistically no different, even for the secondary disinfection process. Consequently, the mixed oxidants theoretically may have oxidants other than free chlorine. However, the analytical results and disinfectant characteristic evaluated in this study could not determine any difference with free chlorine. The mixed oxidants may have trace amount of oxidants other than free chlorine and the major composition of mixed oxidants is chlorine free.

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