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Effects of Storage Conditions and pH on Chlorine Loss in Electrolyzed Oxidizing (EO) Water

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The chlorine loss of electrolyzed oxidizing (EO) water was examined during storage under different light, agitation, and packaging conditions. The chlorine loss of pH-adjusted EO water was also examined. Under open conditions, the chlorine loss through evaporation followed first-order kinetics. The rate of chlorine loss was increased about 5-fold with agitation, but it was not significantly affected by diffused light. Under closed conditions, the chlorine loss did not follow first-order kinetics, because the primary mechanism of chlorine loss may be self-decomposition of chlorine species rather than chlorine evaporation. The effect of diffused light was more significant compared to agitation after two months of storage under closed conditions. The chlorine loss of EO water and commercial chlorinated water decreased dramatically with the increase of pH from the acidic (pH 2.5) to the alkaline (pH 9.0) region.

KEYWORDS: Electrolyzed oxidizing water; chlorine; storage; agitation; diffused light; pH

INTRODUCTION

Electrolyzed oxidizing (EO) water recently has been introduced to food industries as a novel disinfecting agent (*1*−*4*). Its active bactericidal agent is believed to be hypochlorous acid (HOCl) formed by the hydrolysis of electrochemically produced chlorine gas (Cl_2) (*5*).

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (1)$$

Disinfection with EO water is more convenient than conventional chlorine disinfection because EO water can be generated on-site by simple electrolysis of a dilute salt solution. In addition, use of EO water reduces the cost and hazards associated with handling, transportation, and storage of concentrated chlorine solution (*6*).

One of the limitations of EO water is the reduction of its bactericidal activity with time, which is caused by chlorine loss (*7, 8*). It is known that the chlorine loss is due to the evaporation of dissolved chlorine gas and ensuing HOCl decomposition (eq 1). Several factors such as light, temperature, agitation, and packaging could affect the chlorine loss by influencing the dynamics of chlorine evaporation (*6, 9*). The pH of EO water could also affect the chlorine evaporation because the ratio of dissolved chlorine gas to HOCl in a solution is pH dependent (*6*).

The objective of this study was to examine the chlorine loss of EO water during storage under different light, agitation, and packaging conditions. The chlorine loss of pH-adjusted EO water was also evaluated.

MATERIALS AND METHODS

Analytical Measurements. The concentration of active chlorine was measured using an iodometric-method-based chlorine test kit (Hach Co., Ames, IA). The pH and oxidation−reduction potential (ORP) were measured using a pH/ORP meter (model Accumet 15, Fisher Scientific Co., Pittsburgh, PA). The ORP sensor had a platinum rod as a working electrode and a silver/silver chloride wire in saturated potassium chloride as a reference electrode.

Preparation of EO Water and Chlorinated Water. EO water was prepared by the electrolysis of 0.1% NaCl solution at 14 A and 7.4 V using a commercial EO water generator (model ROX-20TA, Hoshizaki Electric Inc., Aichi, Japan). The pH, ORP, and active chlorine concentration of EO water were 2.5−2.6, 1020−1120 mV, and 53−56 mg/L, respectively.

Chlorinated water was prepared by appropriately diluting saturated chlorinated water (Fisher Scientific Co., Pittsburgh, PA) with deionized water. The pH of the chlorinated water was adjusted to 2.3−2.4 using HCl. The final pH, ORP, and active chlorine concentration of the diluted chlorinated water were 2.5−2.6, 1020−1120 mV, and 53−56 mg/L, respectively.

Effect of Storage. The chlorine loss of EO water was tested under 8 storage conditions, which were combinations of open/closed,

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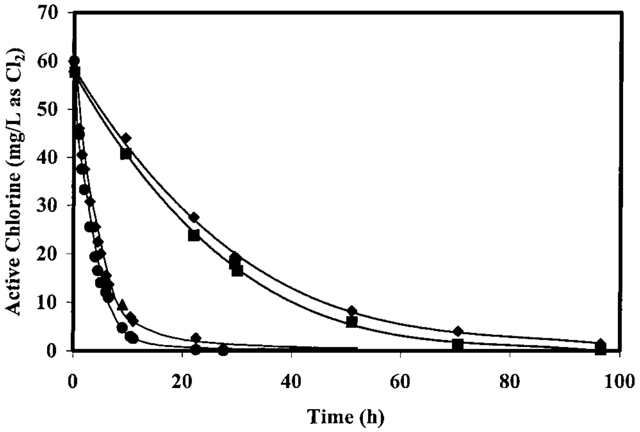

Figure 1. Active chlorine profile of EO water stored under open conditions at 25 ± 2 °C: (◆) open/nonagitated/dark, (■) open/nonagitated/diffused light, (▲) open/agitated/dark, and (●) open/agitated/diffused light.

agitated/nonagitated, and diffused light/dark conditions. EO water was poured into a glass jar (12.4 cm diam × 21.6 cm high) to a level of 1700 mL. For closed storage, the jar was sealed using a screw cap. For the agitated condition, a magnetic bar (0.8 cm diam × 3.8 cm long) was used to stir EO water at 250 rpm using a stir plate (Nuova SP 18425, Thermolyne, Dubuque, IA). For exposure to diffused light, a fluorescent light was used at 373 lux, which was within a normal range of light levels for a production line (300−750 lux) (*9*). For dark conditions, the glass jar was completely covered by aluminum foil. Temperature was 25 ± 2 °C for all storage conditions. The pH, ORP, and concentration of active chlorine of EO water were periodically measured during storage. Two independent replicated experiments were conducted for each storage condition.

pH Effect. The chlorine loss of EO water was examined at pH 4.0, 6.0, and 9.0, and compared with that of the EO water at its original pH. Chlorinated water was also tested for comparison. The pH of each solution was adjusted with 1.0 M NaOH solution and three 1.0 M buffering solutions. Acetic acid, monosodium phosphate, and sodium bicarbonate buffering solutions were used for adjusting the pH to 4.0, 6.0, and 9.0, respectively. A volume of 100 mL of each pH-adjusted solution was poured into five 150-mL beakers (surface area of 22.1 cm^2). The five beakers were stored under open and agitated conditions at 25 ± 2 °C as described previously. A magnetic stirring bar (0.8 cm diam × 1.3 cm long) was used to agitate the solution at 250 rpm. The pH and active chlorine concentration of the solution in each beaker were measured after 30, 60, 120, 180, and 240 min.

Statistical Analysis. Data were analyzed using general linear model procedures (*10*). Comparisons of means were performed using Duncan's multiple range test.

RESULTS AND DISCUSSION

Effect of Storage Conditions on Chlorine Loss. *Open Conditions.* Under open conditions, the chlorine in EO water was completely lost after 30 h when agitated and 100 h when not agitated. Storage lighting had no significant effect on chlorine loss (Figure 1).

Table 1. Rate Constants (min^{-1}) for Chlorine Loss in EO Water at 25 ± 2 °C under Open Storage Conditions[a]

	diffused light	dark
agitated	3.5×10^{-3} A	3.4×10^{-3} A
nonagitated	7.0×10^{-4} B	7.0×10^{-4} B

[a] Values in the table sharing a common letter are not significantly different ($p > 0.05$), and EO water used for the study had original pH of 2.5 to 2.6 and total active chlorine of 55 to 57 ppm.

For a better understanding of the chlorine loss mechanism with open conditions, the kinetics of chlorine loss was examined using the following assumptions: [1] the primary cause of chlorine loss is the evaporation of dissolved chlorine gas; [2] EO water is a dilute chlorine solution (55−57 ppm chlorine as Cl$_2$), and therefore, the dissolved chlorine gas concentration follows Henry's law; [3] in EO water, the ratio (r) of the concentration of dissolved chlorine gas (C_{ct}) to the concentration of total active chlorine (C_t) at time t is constant, implying that eq 1 proceeds rapidly (*11*) and does not limit the evaporation; [4] the surface mass transfer coefficient (k_m) of chlorine gas is a constant; [5] the ambient concentration of chlorine gas (or partial pressure of chlorine gas, P_a) in the air was assumed to be close to zero. Mass transfer at the gas/liquid interface under the above assumptions can be written as

$$-V\frac{dC_t}{dt} = -rV\frac{dC_{ct}}{dt} = rk_mA(P_t - P_a) = rk_mAP_t \tag{2}$$

where P_t is the vapor pressure of chlorine gas at the interface at time t, A is interface mass transfer area, and r is C_{ct}/C_t. Henry's law is given by the following relation.

$$P_t = x_tK \tag{3}$$

where x_t is the mole fraction of dissolved chlorine gas in EO water at time t and K is the Henry's law constant. Substituting eq 3 into eq 2, and assuming that $P_a \rightarrow 0$, the first-order kinetic equation was obtained.

$$-\frac{dC_t}{dt} = \frac{r^2k_mAaK}{V}C_t = kC_t \tag{4}$$

where a is a conversion factor between x_t and C_{ct} and k is the first-order rate constant for chlorine loss.

The chlorine loss under open conditions (Figure 1) was well described by eq 4, and the rate constants (k) were calculated by linear regression on a semilog plot of C_t/C_o versus t (Table 1) where C_o is the initial chlorine concentration in EO water. The calculated rate constants increased by about 5 times when agitation was applied, probably due to the acceleration of interface mass transfer of chlorine gas. The rate constants remained almost the same regardless of lighting, indicating that the effect of diffused light on the chlorine loss was small under open conditions. Previously, El Din et al. (*12*) demonstrated that the chlorine decomposition rate for chlorinated water exposed to light was 5 to 8 times higher than the rate for chlorinated water stored in dark; however, the light conditions in that study were much more intense (direct sunlight at 42−45 °C) than the diffused light (373 lux) conditions used in the present study.

The oxidation−reduction potential (ORP) of EO water also decreased during storage, consistent with the loss of oxidative chlorine (Figure 2). The effect of agitation was also clearly shown in the ORP profiles. The pH of EO water remained almost unchanged during storage (data not shown).

Closed Conditions. The first-order kinetics based on chlorine evaporation was not applicable for closed conditions. The primary mechanism of chlorine loss under closed conditions could be the self-decomposition of chlorine species in solution (*6*, *13*), because chlorine evaporation was limited.

Contrary to open conditions, lighting was a more important factor than agitation for chlorine loss under closed conditions (Figure 3). Agitation can accelerate mass transfer; however, it would not be expected to affect the decomposition of chlorine species via homogeneous reactions. Under given experimental conditions, approximately 60% of chlorine was lost after 1400

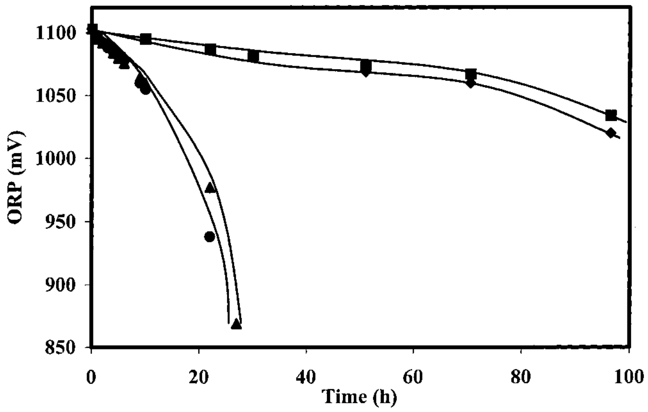

Figure 2. ORP profile of EO water stored under open conditions at 25 ± 2 °C: (◆) open/nonagitated/dark, (■) open/nonagitated/diffused light, (▲) open/agitated/dark, and (●) open/agitated/diffused light.

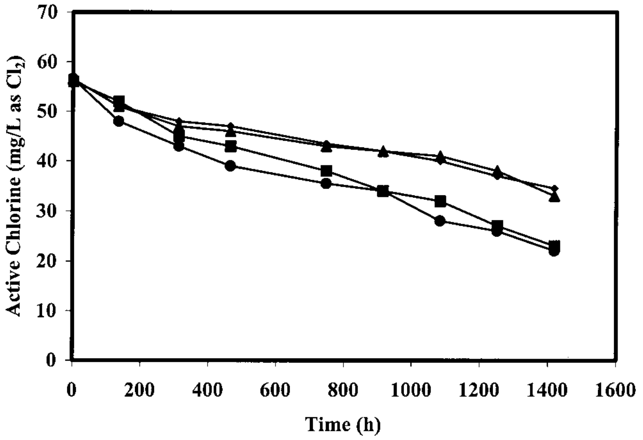

Figure 3. Active chlorine profile of EO water stored under closed conditions at 25 ± 2 °C: (◆) closed/nonagitated/dark, (■) closed/nonagitated/diffused light, (▲) closed/agitated/dark, (●) closed/agitated/diffused light.

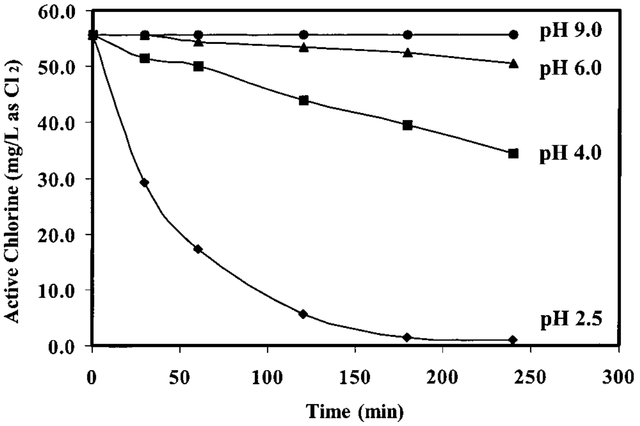

Figure 4. Active chlorine profiles of EO water under different pH conditions at 25 ± 2 °C.

Table 2. Rate Constants (min^{-1}) for Chlorine Loss in EO Water and Chlorinated Water at Two Different pH Values with Open Storage at 25 ± 2 °C

pH	EO water	chlorinated water
2.5–2.6	1.8×10^{-2}	5.2×10^{-3}
4.0	1.9×10^{-3}	5.0×10^{-4}

h when diffused light was applied, whereas about 40% of chlorine was lost under dark conditions (Figure 3), suggesting that the diffused light induced the decomposition of chlorine during storage.

The effect of lighting shown in chlorine loss was not clearly observed from the ORP profiles (data not shown). The ORP profiles obtained from closed conditions were similar to each other regardless of agitation and lighting, and only decreased slightly from about 1100 to 1085 mV. The pH of EO water also remained nearly unchanged for all storage conditions (data not shown).

Effect of pH on Chlorine Loss. The chlorine loss of EO water was greatly reduced by increasing the pH (Figure 4). The chlorine loss of chlorinated water was also reduced by increasing the pH (data not shown). As the pH increased from 2.5 to 4.0, significant decreases of *k* values (about 10-fold) were observed for both solutions (Table 2). Decrease of H$^+$ concentration with the increase of pH could shift the chemical equilibrium of eq 1 toward the formation of HOCl, which is not volatile (*14*). Therefore, the fraction of volatile dissolved chlorine gas could decrease, resulting in the reduction of chlorine evaporation. EO water yielded larger *k* values than chlorinated water at the same pH, probably due to the different chemical environments of the two solutions.

At pH values of 6.0 and 9.0, theoretically, the predominant chlorine species in a solution is not dissolved chlorine gas, but HOCl and OCl$^-$ (*6*). Therefore, chlorine loss due to the evaporation of dissolved chlorine gas is significantly reduced at these pH values, and the *k* values were not obtained. Figure 4 shows that the chlorine losses of EO water at these pH values were not significantly different from each other, but were much less than those observed at acidic pH. There was almost no chlorine loss at pH 9.0. Similar results were observed for the chlorinated water (data not shown). The observed small chlorine loss at pH 6.0 and 9.0 could be due to the self-decomposition of chlorine species, as mentioned for the chlorine loss in closed conditions.

CONCLUSIONS

EO water stored under open and agitated conditions had the highest chlorine loss rate. For open conditions, the chlorine loss was primarily through the evaporation of dissolved chlorine gas and followed first-order kinetics. Agitation enhanced the chlorine loss through evaporation by accelerating interface mass transfer of chlorine gas. For the closed conditions, EO water was much more stable than EO water stored in open conditions. The chlorine self-decomposition could be the mechanism of chlorine loss under closed conditions. The effect of diffused light on the chlorine loss of EO water was significant for the closed conditions compared to the open conditions. Agitation had no effect on the chlorine loss under closed conditions, presumably because the evaporation of chlorine gas was limited under closed conditions. Increasing the pH of EO water and chlorinated water was shown to reduce chlorine loss from these solutions. The pH adjustment of EO water may therefore be useful in situations where stable bactericidal activity is required.

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