Original Article

Effects of process conditions on chlorine generation and storage stability of electrolyzed deep ocean water

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Abstract

Electrolyzed water is a sustainable disinfectant, which can comply with food safety regulations and is environmentally friendly. We investigated the effects of platinum plating of electrode, electrode size, cell potential, and additional stirring on electrolysis properties of deep ocean water (DOW) and DOW concentration products. We also studied the relationships between quality properties of electrolyzed DOW and their storage stability. Results indicated that concentrating DOW to 1.7 times increased chlorine level in the electrolyzed DOW without affecting electric and current efficiencies of the electrolysis process. Increasing magnesium and potassium levels in DOW decreased chlorine level in the electrolyzed DOW as well as electric and current efficiencies of the electrolysis process. Additional stirring could not increase electrolysis efficiency of small electrolyzer. Large electrode, high electric potential and/or small electrolyzing cell increased chlorine production rate but decreased electric and current efficiencies. High electrolysis intensity decreased storage stability of the electrolyzed seawater and the effects of electrolysis on DOW gradually subsided in storage. DOW has similar electrolysis properties to surface seawater, but its purity and stability are better. Therefore, electrolyzed DOW should have better potential for applications on postharvest cleaning and disinfection of ready-to-eat fresh produce.

1. Introduction

Electrolyzed water is environmental friendly, has significant disinfection effects, and can comply with food safety regulations [1]. Because most surface area of the Earth is covered by seawater, it would be very useful to make sustainable applications of this resource. Electrolyzed seawater, because of its significant disinfection effects, has been used in many antifouling systems [2,3], aquaculture, and seafood processing. For example, Kasai et al [4,5] studied disinfectant effects of electrolyzed seawater on viable bacteria in hatchery seawater.
using a batch and a continuous electrolytic systems. They reported a 2–4 log reduction of viable bacteria after treated with electrolyzed seawater containing 0.5–1.0 mg/L chlorine for 1 minute. Watanabe et al [6] disinfected various utensils and equipment for aquaculture and reported a >3 log reduction of viable bacteria after treatment with electrolyzed seawater containing 0.5–1.5 mg/L chlorine for 30–120 minutes. Kasai and Yoshimizu [7] studied disinfection of seawater from fishing port using an electrolytic apparatus and found useful applications for sanitation of the fish holding tank, port deck, and fishing equipment. Kimura et al [8] reared sea urchins for 2 days using electrolyzed seawater containing 0.76 mg/L chlorine and found that 90% of bacteria in the sea urchins’ viscera were eliminated. Kasai et al [9] used electrolyzed seawater that contained 0.2 mg/L chlorine to deurate contaminated oysters and found that Escherichia coli in the oysters was reduced to below detection limits [9].

Although many applications of electrolyzed seawater had been reported in aquaculture and seafood processing, few applications have been reported in the agriculture or food processing industries, probably because of sanitary concerns. Plankton and bacteria are abundant in seawater and certain coastal seawaters have been polluted [10,11]. However, deep ocean water (DOW) is the cold, salty seawater found deep below the surface of Earth’s oceans, which makes up about 90% of the ocean volume. DOW has low temperature, typically from 0°C to 3°C, and a salinity of about 35 psu [12]. Although surface seawater could be contaminated by pollution or civilization, DOW has no such concern, because it has remained unpolluted because of high pressures and low temperatures for the past 1,000 years.

To develop electrolyzed seawater for food and agriculture applications, especially for postharvest cleaning and disinfection of ready-to-eat fresh produce, DOW and DOW concentration products are electrolyzed and their properties as well as storage stability are investigated in this study.

## 2. Materials and methods

### 2.1. Seawater samples

All seawater samples used in this study were provided by the Taiwan Yes Deep Ocean Water Co., Ltd. (Hualien County, Taiwan). DOW was drawn at 662 m below the Pacific Ocean at approximately 5.0 km off the coastline of the Hualien County in eastern Taiwan. Surface seawater was drawn at 50 m below the sea surface at approximately 1.5 km off the coastline of Hualien County. A DOW concentrate, which is a concentrated solution of DOW, a DOW salt, which is a dried product made from DOW, and a product labeled as LC-40K, which is a purified DOW solution high in magnesium and potassium minerals, were processed products of DOW produced via unit operations such as ultratillation, reverse osmosis, and vacuum evaporation (Taiwan Yes Deep Ocean Water Co., Ltd., Hualien County, Taiwan). Table 1 shows the compositions of major elements in these seawater samples. Table 2 shows a comparison on composition and property of DOW and surface seawater samples.

### 2.2. Electrolysis and storage conditions

Table 2 – A comparison on compositions and properties of surface seawater and deep ocean water samples.

| Property | Surface seawater | Deep ocean water |
|----------|------------------|------------------|
| Temperature (°C) | 22.5 – 23.8 | 9.4 – 10.4 |
| pH | 8.10 – 8.20 | 7.70 – 7.75 |
| Salinity (psu) | 34.2 – 34.5 | 34.3 – 35.0 |

Data provided by the Taiwan Yes Deep Ocean Water Co., Ltd. (Hualien County, Taiwan).

This study was divided into three parts. Part 1: 1600 mL of DOW samples and a surface seawater for comparison purpose were electrolyzed for 2 hours in a 2.0 L glass beaker electrolyzing cell equipped with a pair of 50-mm-long anodes and cathodes. The anode and cathode (Model SUR-303, Surchem C&S Internation Corp., Taipei City, Taiwan), which were titanium mesh electrode and/or titanium mesh electrode plated with 3.75 μm of platinum, were powered by a rectifier (Model MC48-4D, Surchem C&S Internation Corp., Taipei City, Taiwan), which controlled the cell potential and/or electric current of the electrolysis system. A constant-potential mode of operation was adopted. The electrodes were immersed in

| Table 1 – Compositions of major elements in seawater, deep ocean water and its products. |
|-----------------|----------------|-----------------|-------------------|------------------|-----------------|
| Element (mg/L or kg) | Surface seawater | DOW | DOW concentrate | LC-40K | DOW salt |
|--------------------|-----------------|------|-----------------|--------|--------|
| Chloride           | 19,060 – 19,860 | 18,840 – 19,510 | 28,000 – 38,000 | 100,000 – 150,000 | 550,000 |
| Sodium             | 11,320 – 11,500 | 11,380 – 11,430 | 15,000 – 20,000 | 20,000 – 30,000 | 377,000 |
| Magnesium          | 1,327 – 1,330   | 1,283 – 1,320   | 2,000 – 3,000   | 40,000 – 50,000 | 4,900  |
| Calcium            | 400 – 441       | 400 – 432       | 800 – 1,000     | 200 – 500       | 3,800  |
| Potassium          | 400 – 414       | 390 – 421       | 500 – 1,000     | 7,000 – 10,000  | 1,900  |

LC-40K is a commercialized high magnesium and potassium mineral solution made of DOW; DOW Concentrate is a concentrated solution of DOW; DOW Salt is a dried product made of DOW; LC-40K is a purified DOW solution high in magnesium and potassium minerals. All were provided by the Taiwan Yes Deep Ocean Water Co., Ltd. (Hualien County, Taiwan).

DOW = deep ocean water.

* Data provided by the Stone and Resource Industry R&D Center (Hualien County, Taiwan).

* Data provided by the Taiwan Yes Deep Ocean Water Co., Ltd. (Hualien County, Taiwan).
seawater at 60 mm beneath the surface and the electrode gap was maintained at 6.7 mm. The other operation conditions are detailed in Table 3. Effects of different seawaters, platinum plating of electrode, electrode size, electrode potential, and additional stirring were investigated. Stirring was maintained using a 16 × 30 mm (diameter × length) Teflon spindle-shape magnetic stir bar powered by a Stirrer (Model PC-101, Corning Inc., Acton, MA, USA) at speed setting of 1.2. Electrolysis parameters and electrolyte properties were monitored during the electrolysis process.

Part 2: 1 L each of the aforementioned electrolyzed seawaters produced was stored in a sealed brown glass bottle at room temperature (28–35 °C) for up to 3 weeks to study its storage stability. Seawater properties were measured near the end of each week.

Part 3: DOW and its concentration products were electrolyzed. A diluted DOW concentrate, a diluted LC-40K solution, and a DOW salt solution were prepared by diluting or reconstituting the respective original product with deionized water to the same electrical conductivity as the DOW, which was 49.9 mS/cm, for comparison purposes. All the other electrolysis conditions were the same as the D1T5 treatment in Part 1 (Table 3), except that cell potential was set at 8.0 V in this part. Electrolysis parameters and electrolyte properties were monitored during the electrolysis process.

2.3. Analytical measurements

Oxidation–reduction potential (ORP) and pH value of the electrolyzing seawaters were measured with pH/mV/ISE meters (Model Sension 4, Hach Co., Loveland, CO, USA) equipped with an ORP and a pH electrode (part # 5779601-003B and 5773597-003B, respectively, Van London Co., Houston, TX, USA). Electrical conductivity was measured with a Conductivity Meter (Model Sension 5, Hach Co.). A total chlorine test kit (Model 16900; Hach Co., Method 8209, which is based on iodometric method.) was used to measure total residual chlorine in the electrolyzed seawaters. The assay was verified periodically using a 100 ± 0.05 ppm chlorine standard solution (Orion Research Inc., Beverly, MA, USA). All measurements were done at 29 ± 1°C.

2.4. Electrolysis efficiency

Current density was calculated by dividing the electric current by the effective surface area of anode. Electric efficiency was calculated by dividing the total chlorine produced by the energy consumed. Current efficiency was calculated from the percentage ratio of the total chlorine produced to the theoretical chlorine production based on the Faraday laws of electrolysis [13].

2.5. Statistical design and analysis

This study adopted a randomized complete block design [14] in investigating the effects of different treatments on electrolyzing seawaters. Triplicate experiments were independently conducted in each part of the study. Data from the independent replicate trials were pooled and analyzed by analysis of variance test of the Statistical Analysis Systems (SAS 9.4, SAS Institute, Cary, NC, USA). Duncan multiple range test was used to determine if significant differences existed between different treatment groups. Values of \( p < 0.05 \) were considered significantly different.

Correlations between initial states of the electrolyzed seawater and their storage stability were analyzed using the Pearson correlation coefficient test of the Statistical Analysis Systems (SAS 9.4, SAS Institute) using initial level of their quality variables and final decrement ratio of the respective variable at the end of the storage period. DOW data collected in this study (labeled as D1) were pooled with surface seawater data collected in a previous study (labeled as D2) [15] for this analysis, to have better statistical inference. Some of the other storage data obtained from the two studies were also pooled and illustrated in the following sections for better inference of storage properties of electrolyzed seawaters.

3. Results and discussion

3.1. Electrolysis of DOW

Effects of different seawaters, platinum plating of electrode, electrode size, and electrolyzing cell potential, as well as additional stirring, were investigated. Results indicated that electrolysis properties of DOW were similar to electrolysis properties of surface seawater (D1T1 vs. D1T4 in Tables 3 and 4). DOW composition and salinity, which determined its electrolysis properties, were very similar to those of surface seawater, although DOW is cleaner than surface seawater because of its existence in unpolluted and stable deep ocean environments (Tables 1 and 2). Therefore, it is reasonable to
obtain these results and it is reasonable to pool electrolysis data observed in the two studies together for further statistical analyses as described previously.

### 3.2. Effects of electrodes

As shown in Tables 3 and 4, a pair of titanium anodes and cathodes produced a minimum amount of chlorine in electrolysis (D1T6), probably because titanium is not a good electrical conductor. However, when the anode was replaced with platinum-plated titanium, chlorine concentration increased significantly (D1T1 vs. D1T6). When the cathode was also replaced with platinum-plated titanium, chlorine concentration increased further but not to a statistically significant difference in this set of experiment (D1T5 vs. D1T1).

Unlike the results observed in our previous study on surface seawater [15], additional stirring did not increase electric current and current density in this study (D1T1 vs. D1T2 in Tables 3 and 4). A 2.0 L glass beaker (13 cm diameter × 18 cm high) was used for the electrolyzing cell in this study whereas a 12.9 L (16 cm diameter × 64 cm high) cylindrical polypropylene tank was used in the previous study. Electrolytes in a small electrolyzing cell could have been well mixed by turbulence generated by chloride, hydrogen, and oxygen gas bubbles during electrolysis, which made the mixing effect of additional stirring insignificant as in the case of this study. However, the effect of additional stirring could become significant when the electrolyzing cell is large and/or deep as in the case of our previous study. Therefore, additional stirring should be applied in useful situations only.

Raising cell potential from 6.0 V to 10.0 V significantly increased chlorine concentration, electric current and current density, but significantly decreased electric efficiency and current efficiency in electrolysis of deep ocean water. As shown in Table 4, doubling the electric current without significantly affecting its current density, which resulted in significant decreases in electric efficiency and current efficiency (D1T7 vs. D1T1 and D1T8 vs. D1T5 in Tables 3 and 4). The overall electric and current efficiencies of the 25 mm platinum-plated electrode group (D1T1, D1T2, D1T4, and D1T5 in Table 4) were in the ranges of 41–43 mg Cl₂/kJ and 67–70%, respectively, whereas those of the 50-mm electrode group (D1T7 and D1T8 in Table 4) were at significantly lower levels of <38 mg Cl₂/kJ and <63%, respectively. Electric efficiency and current efficiency in the range of 37–39 mg Cl₂/kJ and 80–86%, respectively, were observed in our previous study on surface seawater [15]. The current efficiency observed in the previous study are higher than those observed in this study (80–86% vs. 63–70%). A 2.0 L glass beaker (13 cm diameter × 18 cm high) was used for electrolyzing cell in this study while a 12.9 L (16 cm diameter × 64 cm high) cylindrical polypropylene tank was used in the previous study. The deep electrolyzing cell reduced the relative ratio of open surface area to cell volume and the amount of evaporation loss of chlorine gas through the open space. The large (as compared with electrode size) electrolyzing cell could reduce the speed of temperature rise and the amount of chlorine gas evaporation in electrolysis. Therefore, the low current efficiency observed in this study was probably a result of the comparatively small and shallow electrolyzing cell adopted in this study. In summary, raising cell potential, increasing electrode size, and using a small electrolyzing cell could facilitate production of high-chlorine electrolyzed seawater at the expense of losing current efficiency and electric efficiency because more electrical energy is consumed and more chlorine is lost.

### 3.3. Storage stability

Similar to our previous study on surface seawater [15], 1 L each of the electrolyzed seawaters was produced and stored in a sealed brown glass bottle at room temperature for up to 3 weeks. Results indicated that chlorine levels of the...
electrolyzed DOWs continuously decreased and the decrement ratio (i.e., decrement ratio = initial concentration/final concentration/initial concentration) continuously increased in the storage period (Figs. 1 and 2). Except for D1T6 treatment, in which chlorine level was too low to be representative, up to 67% of chlorine were lost in the 3-week storage period. This storage quality was not as good as those observed in our previous study on surface seawater, in which less than 35% of chlorine were lost and the trend of decrement leveled off in the 1st week of storage [15]. The relatively unstable keeping quality of the electrolyzed seawater in this study was partially due to their high initial temperatures (D1T1-D1T8 vs. D2T1-D2T8 in Fig. 3) and partially due to their high initial chlorine levels, which were in the range of 2582–9027 mg Cl₂/L (Table 4) as compared with the range of 1327–1830 mg Cl₂/L in our previous study [15]. The high initial temperature of D1T3 (Fig. 3) was due to high electric potential applied in that treatment (10 V vs. 6.0 V in Table 3). High temperature and high chlorine concentration could cause more chlorine loss in electrolysis and in storage because chlorine is highly volatile and unstable at high temperatures.

As explained previously, except for treatments D1T6 and D2T6, of which chlorine levels were too low to be representative, data collected in this study and our previous study [15] were pooled for statistical analysis. Figs. 3–7 illustrate the time-course variations of product temperature, electrical conductivity, ORP, pH value, and chlorine level of electrolyzed seawaters in the 3-week storage period. Temperature cooled down at the beginning of the storage and leveled off to room temperature thereafter (Fig. 3). Electrical conductivity increased at the beginning of the storage and decreased thereafter (Fig. 4). ORP increased, while pH and chlorine levels decreased in storage (Figs. 5–7, respectively).

Results of a correlation analysis between quality variables of the electrolyzed seawaters showed that chlorine level (FAC) positively correlated with ORP and temperature (Temp), whereas ORP negatively correlated with electric conductivity (EC) and pH (Table 5). Results (Table 5) also showed that decrement in chlorine level (dFAC) significantly correlated with high initial temperature (Temp), high ORP, and low initial electrical conductivity (EC). Results also showed that high initial level of quality variables significantly correlated with...
large decrement ratio of that respective variable in storage (ORP, EC, and Temp vs. dORP, dEC, and dTemp, respectively, in Table 5). Table 5 also showed that significant negative correlations between dEC and ORP, EC and dORP, dEC and FAC, EC and dFAC, and significant positive correlations between dFAC and Temp and dFAC as well as FAC and dTemp. All of these results indicated that when more vigorous conditions were adopted in electrolysis, chlorine, temperature, and ORP of the electrolyzed product increased while EC and pH decreased due to conversions of high-EC inorganic ions such as chloride to low-EC, low-pH and high-ORP compounds such as chlorine, hypochlorite, etc. In the meantime, temperature rose as electrolysis continued. As a result, more chlorine lost appeared in electrolysis and also in storage. It also indicated that, in general, the more vigorous electrolysis conditions to which the seawater sample was subjected, the more changes the electrolyzed seawater will have in storage. The effects of electrolysis on seawaters gradually subsided in storage and the electrolyzed seawaters tended to return to their original states as time passed in storage.

3.4. Electrolysis of DOW products

DOW and DOW products, including a DOW concentrate, a LC-40K solution, and a DOW salt were electrolyzed. For comparison purposes, the DOW products were diluted or reconstituted with deionized water to the same electrical conductivity as DOW before electrolysis. Results indicated that chlorine concentration, electric current, current density, electric efficiency and current efficiency of DOW, DOW salt solution, and diluted DOW concentrate were similar (Table 6), probably due to their similar compositions (Table 1) and same concentration (electrical conductivity). However, electrolysis of DOW concentrate, which was about 1.7 times as concentrated as DOW, resulted in significantly higher chlorine concentration and electric current without significantly affecting its electric and current efficiencies (Table 6). Diluted LC-40K resulted in significantly lower chlorine concentration, electric current, current density, electric efficiency and current efficiency (Table 6) due to its different compositions (Table 1). Diluted LC-40K composed of high magnesium and potassium (5.7 and 3.3 times, respectively, as in DOW) and low sodium and calcium (0.35 and 0.13 times, respectively, as in DOW).

Kirk and Ledas [16] reported that magnesium hydroxide precipitation was the main cause of fouling of cathode during seawater electrolysis and the amount of precipitates was proportional to the ion concentration in seawater. Fouling of cathode hinders electrolysis process and reduces its efficiency.

4. Conclusion

Electrolysis properties of DOW are similar to surface seawater, but its purity and stability are better. Therefore, electrolyzed DOW is more suitable for applications in postharvest cleaning and disinfection of ready-to-eat fresh produce. Increasing DOW concentration increased chlorine level without affecting electric and current efficiencies. Increasing magnesium and potassium levels in DOW decreased the chlorine level, electric concentration, electric current, current density, electric efficiency and current efficiency.

Table 5 - Pearson correlation coefficient of initial quality variables and final decrement ratio of the variables in stored electrolyzed deep ocean water and surface seawater.

| Variable | ORP  | EC   | pH   | Temp  | FAC  |
|----------|------|------|------|-------|------|
| dORP     | 0.9195** | -0.8051** | -0.7347" | 0.3248 | 0.6277 |
| dEC      | -0.9353** | 0.9486" | 0.6708" | -0.6066 | -0.8095** |
| dpH      | 0.6706" | -0.6212 | -0.4136 | 0.5961 | 0.5780 |
| dTemp    | 0.3425 | -0.3766 | -0.0700 | 0.9469" | 0.7667* |
| dFAC     | 0.7783** | -0.7066" | -0.5737 | 0.6853" | 0.7146* |
| ORP      | -0.895" | -0.793" | 0.4477 | 0.6995* |
| EC       | 0.6352 | -0.492 | -0.772" | 0.389 |
| pH       | -0.18 | 0.389 | 0.9003** |
| Temp     |      |      |      |       |      |

The variable preceded by letter d stands for decrement ratio of that variable at the end of the 3-week storage period (n = 14).

*Significant at 0.01 level.
**Significant at 0.001 level.

EC = electrical conductivity; FAC = chlorine concentration; ORP = oxidation-reduction potential; Temp = temperature.
efficiency and current efficiency. Adopting a large electrode, high cell potential and/or small electrolyzing cell increased the chlorine production rate and chlorine concentration at the expense of electric and current efficiencies. Low electrolyte stability of electrolyzed DOW in storage correlated with the intensity of previous electrolysis and the effects of electrolysis on DOW gradually subsided in storage.

Conflicts of interest

All authors declare no conflicts of interest.

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