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Original Article

Effects of electrode settings on chlorine generation efficiency of electrolyzing seawater

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ABSTRACT

Electrolyzed water has significant disinfection effects, can comply with food safety regulations, and is environmental friendly. We investigated the effects of immersion depth of electrodes, stirring, electrode size, and electrode gap on the properties and chlorine generation efficiency of electrolyzing seawater and its storage stability. Results indicated that temperature and oxidation-reduction potential (ORP) of the seawater increased gradually, whereas electrical conductivity decreased steadily in electrolysis. During the electrolysis process, pH values and electric currents also decreased slightly within small ranges. Additional stirring or immersing the electrodes deep under the seawater significantly increased current density without affecting its electric efficiency and current efficiency. Decreasing electrode size or increasing electrode gap decreased chlorine production and electric current of the process without affecting its electric efficiency and current efficiency. Less than 35% of chlorine in the electrolyzed seawater was lost in a 3-week storage period. The decrement trend leveled off after the 1st week of storage. The electrolyzing system is a convenient and economical method for producing high-chlorine seawater, which will have high potential applications in agriculture, aquaculture, or food processing.

1. Introduction

Electrolyzed oxidizing (EO) water is an antimicrobial agent which possesses strong antimicrobial activity against most pathogenic bacteria that are important to food safety and has applications in many food industries, such as fresh vegetables, fruits, eggs, poultry, and seafood. EO water is commonly produced by passing a diluted salt solution through an electrolytic cell, within which the anode and cathode are separated by a membrane. By subjecting the electrodes to direct current voltages, negatively charged ions such as chloride and hydroxide in the diluted salt solution move to the anode to give up electrons and become oxygen gas, chlorine gas, hypochlorite ion, hypochlorous acid, and hydrochloric acid, whereas positively charged ions such as hydrogen and sodium move to the cathode to take up electrons and become hydrogen gas and sodium hydroxide [1]. Two types of water

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are produced simultaneously. EO water, with low pH (2.3–2.7), high oxidation-reduction potential (ORP, > 1000 mV), high dissolved oxygen, and contains free chlorine, is produced from the anode side. By contrast, electrolyzed reducing (ER) water, with high pH (10.0–11.5), high dissolved hydrogen, and low ORP (−800 mV to −900 mV), is produced from the cathode side. ER water with strong reducing potential can be used to remove dirt and grease from items such as cutting boards and other kitchen utensils [1]. Electrolyzed water is environmentally friendly, has significant disinfection effects, and can comply with food safety regulations [2].

Electrolyzed seawater, similar to EO water, has strong disinfection effects against most pathogenic organisms and is also an effective antimicrobial agent. However, it is not as acidic as EO water and not as alkalic as ER water because it is commonly produced using nondiaphragm electrolyzing systems. EO water and ER water are generated at the anode and cathode, respectively, but are mixed in the electrolyzer, which yields a product solution of mild pH and is more user- and facility-friendly. It has been used in many antifouling systems [3,4], aquaculture, and seafood processing. For example, Kasai et al [5,6] studied disinfectant effects of electrolyzed seawater on viable bacteria in hatchery seawater using batch and continuous electrolysis systems. They reported a 2–4-log reduction of viable bacteria after treatment with electrolyzed seawater containing 0.5–1.0 mg/L chlorine for 1 minute. Watanabe and Yoshimizu [7] 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 [8] studied disinfection of seawater from a fishing port using an electrolysis apparatus and found many useful applications in sanitation of fish holding tanks, port deck, and fishing equipment. Kimura et al [9] reared sea urchins for 2 days using electrolyzed seawater containing 0.76 mg/L chlorine and found that 90% of bacteria in sea-urchin's viscera were eliminated. Kasai et al [10] used electrolyzed seawater which contained 0.2 mg/L chlorine to depurate contaminated oysters and found that *Escherichia coli* in the oysters was reduced to below detection limits. Although many applications have been reported in antifouling systems, aquaculture, and seafood processing, few papers have reported on chlorine producing efficiency, quality, and storage stability of electrolyzed seawater.

Because most of the surface area of the Earth is covered by seawater, it will be very useful to make sustainable applications of this resource. Therefore, it is interesting to study electrolyzed seawater because of its high potential in applications in agriculture, aquaculture, and food processing. As a preliminary study in developing optimal electrolyzed seawater and its manufacturing system, seawater is electrolyzed and its chlorine generation efficiency, product quality, and storage stability are investigated in this study.

2. Materials and methods

2.1. Seawater samples

Seawater samples (provided by the Taiwan Yes Deep Ocean Water Co., Ltd., Hualien County, Taiwan) were drawn at 50 m below sea surface at approximately 1.5 km off the coastline of the Hualien County in Eastern Taiwan. The seawater was kept in 30-L blue/gray high density polyethylene tanks and shipped to the laboratory by car immediately after sampling. Fundamental properties and major compositions of the seawater samples are shown in Table 1.

2.2. Electrolysis process and storage conditions

Ten liters of each seawater sample was electrolyzed for 2 hours in a 12.9-L (16 cm diameter × 64 cm high) cylindrical polypropylene electrolyzing cell equipped with a pair of 50-mm long platinum-plated titanium mesh anodes and cathodes to simulate a popular batch practice of electrolyzing seawater in plastic buckets, which is adopted by some aquaculturists and seafood processors. The anode and cathode (Model SUR-303; Surchem C&S Internation Corp., Taipei City, Taiwan), which were titanium mesh electrodes plated with 3.75 μm of platinum, were powered by a rectifier (Model MC48-4D; Surchem C&S Internation Corp.), which controlled the cell potential and/or electric current of the electrolysis system. A constant-potential mode of operation was adopted in this study. The cell potential was set at 8.0 V. The other operation conditions are detailed in Table 2. Effects of electrode size, electrode gap, electrode immersion depth beneath the seawater surface, and additional stirring were investigated. Stirring was done using a 16-mm × 40-mm (diameter × length) Teflon spindle-shape magnetic stir bar powered by a stirrer (Model PC-101; Corning Inc., Acton, MA, USA) at speed setting 2.0, which was approximately 400 rpm. Electrolysis parameters and seawater properties were monitored during the process.

One liter each of the electrolyzed seawaters produced as mentioned above was kept in a sealed brown glass bottle at room temperature (26–32°C) for up to 3 weeks to investigate its storage stability. Seawater properties were measured at the end of each week.

2.3. Analytical measurements

The ORP and pH values of the electrolyzing seawaters were measured using pH/mV/ISE meters (model Sension 4; Hach Co., Loveland, Colorado, USA) equipped with an ORP and a pH electrode (part 5779601-003B and 5773597-003B, respectively, Van London Co., Houston, TX, USA). Electrical conductivity (EC) was measured using a conductivity meter (model Sension

Table 1 – Basic properties and major compositions of seawater samples.

Property		
	Temperature (°C)	22.5 ~ 23.8
	pH	8.10 ~ 8.20
	Salinity (psu)	34.2 ~ 34.5
Element (mg/L)	Chloride	19,060 ~ 19,860
	Sodium	11,320 ~ 11,500
	Magnesium	1327 ~ 1330
	Calcium	400 ~ 441
	Potassium	400 ~ 414

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

Table 2 – Operation conditions in electrolyzing seawater.

Treatment	Electrode width (mm)	Electrode gap (mm)	Immersion depth (cm)	Stirring
T1	50	6.7	30	Yes
T2	50	6.7	30	No
T3	50	6.7	45	No
T4	50	6.7	15	Yes
T5	50	6.7	45	Yes
T6	50	120	30	Yes
T7	25	6.7	30	Yes
T8	50	6.7	15	No

5, Hach Co., Loveland, Colorado, USA). A total chlorine test kit (model 16900; Hach Co.; Method 8209, which is based on the iodometric method) was used to measure 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 carried out at 29 ± 1°C.

2.4. *Electrolysis efficiency*

Current density was calculated by dividing the electric current by the effective surface area of the 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 Faraday's laws of electrolysis [11].

2.5. *Statistical design and analysis*

This study adopted a randomized complete block design [12] 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 tests of the Statistical Analysis Systems (SAS 9.4; SAS Institute, Cary, NC, USA). Duncan's multiple range tests were used to determine if significant differences existed between different treatment groups. Values of $p < 0.05$ were considered as significantly different.

3. Results and discussion

3.1. *Electrolysis of seawater*

Seawater samples were electrolyzed according to the designated operation conditions (Table 2) in a randomized sequence. Changes of seawater properties during electrolysis are illustrated in Figs. 1–5. As shown in Fig. 1, electrolyte temperatures increased steadily during the electrolysis process due to continuous conversion of electrical energy to heat and heat dissipation at the electrodes. Fig. 2 shows that electric currents passing through the system decreased slowly in small ranges, which indicated a steady control of energy supply, and electrolysis intensity decreased slightly during the electrolysis process because more electrolytes were electrolyzed as time went by. EC of the electrolyte solutions

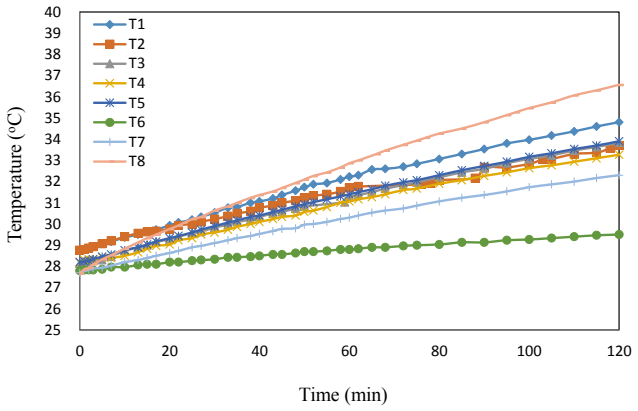

Fig. 1 – Temperature of electrolyzing seawaters (details of T1–T8 in Table 2, $n = 3$).

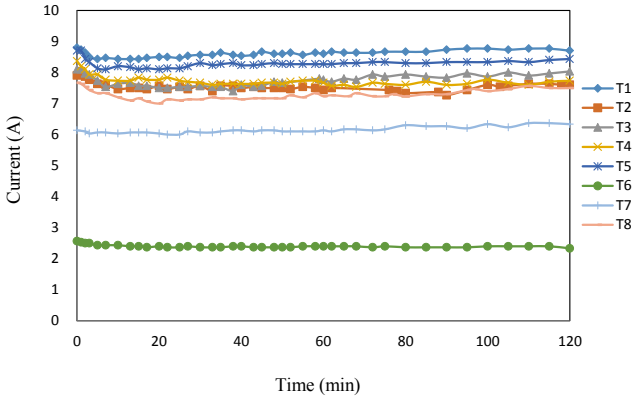

Fig. 2 – Electric current in electrolyzing seawaters (details of T1–T8 in Table 2, $n = 3$).

decreased steadily, whereas ORP increased gradually in the electrolysis process (Figs. 3 and 4, respectively). Charged ions in seawater, such as chloride, were gradually converted to uncharged and high ORP compounds such as chlorine in

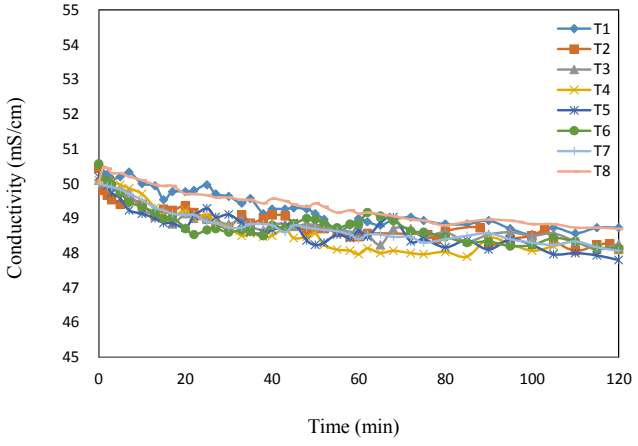

Fig. 3 – Electrical conductivity in electrolyzing seawaters (details of T1–T8 in Table 2, $n = 3$).

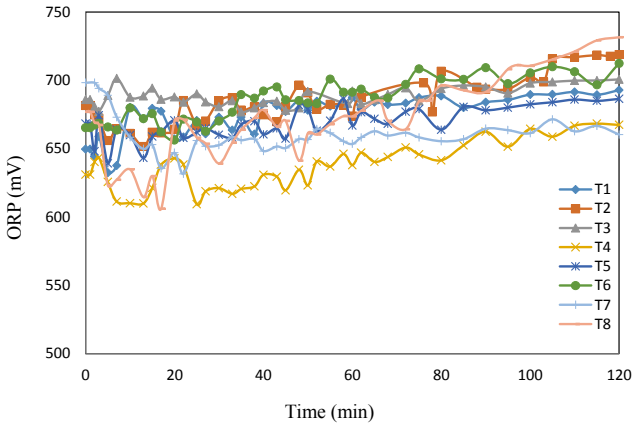

Fig. 4 – Oxidation-reduction potential (ORP) of electrolyzing seawaters (details of T1–T8 in Table 2, $n = 3$).

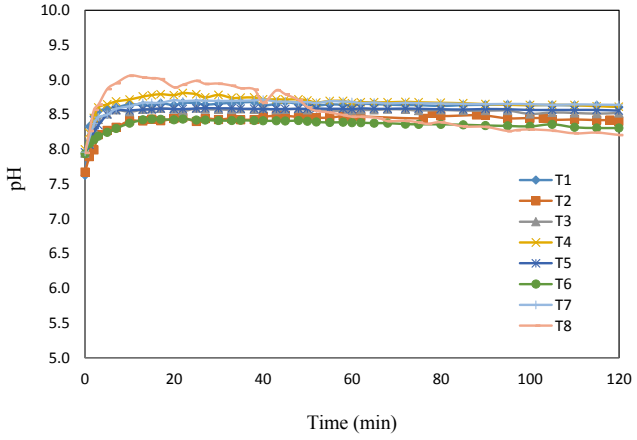

Fig. 5 – pH value of electrolyzing seawaters (details of T1–T8 in Table 2, $n = 3$).

electrolysis [13], which resulted in EC decrease and ORP increase. Fig. 5 shows variations of electrolyte pH in electrolysis. It took a few minutes for the pH probe to restore the electrolysis environment after each calibration. Therefore, it is common to record pH values in the range of 7.0 to 8.0 at the beginning of electrolysis, and the pH values caught up to their normal levels within a few minutes. As shown in Fig. 5, pH values decreased slowly in a small range of 9.0–8.2 after 10 minutes of electrolysis because chlorine, which has a low pH value, was continuously generated in electrolysis. However, the overall pH values of the seawater decreased in the alkaline range (pH > 7.0) because of the nondiaphragm system used in this study. EO seawater generated at the anode and ER seawater generated at the cathode mixed in the electrolyzer and resulted in alkali seawater.

A small amount of white/gray precipitates were also observed to form on the electrodes and in the solution. Because chloride is the predominant element in seawater (Table 1), a large amount of chlorides were converted to chlorine and its derivatives, such as hypochlorite, in electrolysis [13]. In addition, large amounts of sodium hypochlorite and calcium hypochlorite were produced. Small amounts of more unusual hypochlorites may also be formed by a salt metathesis reaction between calcium hypochlorite and various metal sulfates. This reaction leads to the formation of insoluble calcium sulfate, which will precipitate out of solution [14].

3.2. *Effects of electrode settings*

During electrolysis, cations, such as hydrogen, sodium, magnesium, calcium, and potassium ions, gain electrons at the cathode whereas anions, such as chloride, hydroxyl, and oxygen ions, donate electrons at the anode. Therefore, chlorine and/or oxygen gases are formed at the anode whereas hydrogen gas is formed at the cathode. The gas bubbles create turbulence and mix the electrolyte solution significantly. However, because large plastic containers were commonly adopted as electrolyzing cells in industry, it is of interest to simulate the situation and study the effects of different immersion depths and additional stirring on the electrolysis process. Therefore, a 12.9-L (16 cm diameter × 64 cm high) cylindrical polypropylene electrolyzing cell was adopted in this study as described in section 2.2. Results (Tables 2 and 3) indicated that additional stirring or immersing the electrodes deep under the seawater, which should create better mixing and more efficient transport of the electrolytes in solutions, slightly increased chlorine production but significantly increased electric current, current density, and, therefore, the energy consumption of the system. Overall electric efficiency and current efficiency were not improved. Electric efficiencies were in the range 37–38 mg Cl_2/kJ and current efficiencies were in the range 80–83% in this electrolyzing system.

Effects of electrode size and electrode gap on electrolysis of seawater were studied. As shown in Tables 2 and 4, using

Table 3 – Effects of depth of immersion and stirring on chlorine concentration, average electric current, current density, electric efficiency, and current efficiency in electrolysis of seawater.

Treatment	Level	Chlorine (mg Cl_2/L)		Current (A)		Current density (A/dm^2)		Electric efficiency (mg Cl_2/kJ)		Current efficiency (%)	
Depth(cm)	15	1663	a	7.7	c	12.8	c	37	a	81	a
	30	1750	a	8.0	b	13.3	b	38	a	83	a
	45	1796	a	8.4	a	14.0	a	37	a	81	a
Stir	Yes	1790	a	8.4	a	14.0	a	37	a	80	a
	No	1683	a	7.6	b	12.7	b	38	a	83	a

Mean values in the same column of the same treatment followed by different letters are significantly different.
$p < 0.05$, Duncan's test, $n = 3$.

Table 4 – Effects of different treatments on chlorine concentration, average electric current, current density, electric efficiency, and current efficiency in electrolysis of seawater.

Treatment	Chlorine (mg Cl_2/L)		Current (A)		Current density (A/dm^2)		Electric efficiency (mg Cl_2/kJ)		Current efficiency (%)	
T1	1804	a	8.4	a,b	14.0	b,c	37	a	81	a
T2	1697	a	7.5	b,c	12.5	b,c	39	a	86	a
T3	1762	a	8.0	a,b,c	13.3	b,c	38	a	83	a
T4	1736	a	8.0	a,b,c	13.4	b,c	38	a	82	a
T5	1830	a	8.7	a	14.5	b	37	a	80	a
T6	561	c	2.6	e	4.4	d	37	a	81	a
T7	1327	b	6.1	d	20.2	a	38	a	83	a
T8	1590	a	7.2	c	12.0	c	38	a	83	a

Mean values in the same column followed by different letters are significantly different.
$p < 0.05$, Duncan's test, $n = 3$.

a half-sized electrode (T7) significantly decreased chlorine production, electric current, and thus energy consumption of the system, however, its electric efficiency and current efficiency were not significantly affected. Results also indicated that increasing the electrode gap to 12 cm (T6 in Table 4) significantly decreased chlorine production and electric current of the system without affecting its electric efficiency and current efficiency. Therefore, the practice of using a small electrode and/or setting a wider electrode gap can be adopted without increasing energy consumption when slow generation and/or low-level chlorine seawater is to be produced.

3.3. *Storage stability*

One liter each of the electrolyzed seawaters was produced as mentioned above and was stored in sealed brown bottles at room temperature for up to 3 weeks. Fig. 6 shows chlorine levels of the electrolyzed seawaters and Fig. 7 displays their decrement ratios (i.e., decrement ratio = initial concentration – final concentration/initial concentration) in the storage period. In general, the chlorine level decreased at the beginning of storage and leveled off thereafter, probably due to chlorine and its derivatives being highly reactive compounds, which reacted quickly at the beginning stage (Fig. 6). Except for T6 treatment, in which the chlorine level was too low to be representative, <35% of chlorine was lost during the 3-week storage period (Fig. 7). The relatively stable keeping quality

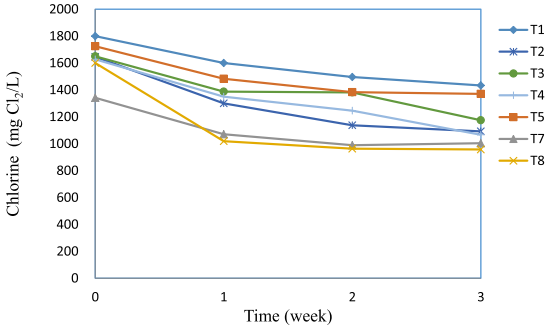

Fig. 6 – Chlorine concentration of electrolyzed seawaters during storage (details of T1–T8 in Table 2, $n = 3$). Note: T6 treatment is not included due to its chlorine level being too low to be representative.

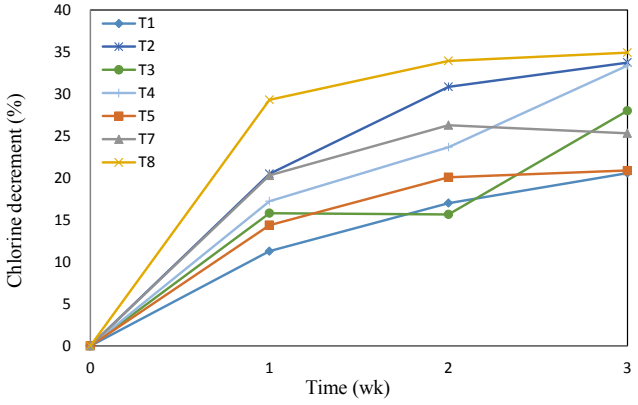

Fig. 7 – Decrement ratio of chlorine in electrolyzed seawaters during storage (details of T1–T8 in Table 2, $n = 3$). Note: T6 treatment is not included due to its chlorine level being too low to be representative.

of the electrolyzed seawaters was also partially due to their low chlorine levels, which were in the range of 1327–1830 mg Cl_2/L (Table 4). Further statistical analysis on pooled data of this study and a companion study has been done and the result has been submitted to this Journal for publication in a companion article [15].

4. Conclusion

Electrolyzed seawater can be produced using a self-assembled electrolyzer equipped with platinum-plated titanium mesh electrodes and a plastic container. The product had good keeping quality. A small electrode and/or wide electrode gap can be adopted without increasing its energy consumption when slow generation and/or low chlorine level seawater is to be produced. The electrolyzed seawater is easy and economical to produce and will have high potential applications in antifouling systems, aquaculture, or seafood processing.

Conflicts of interest

All authors declare no conflicts of interest.

Acknowledgments

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