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Original Article

Effects of electrolysis time and electric potential on chlorine generation 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. A two-factor central composite design was adopted for studying the effects of electrolysis time and electric potential on the chlorine generation efficiency of electrolyzed deep ocean water (DOW). DOW was electrolyzed in a glass electrolyzing cell equipped with platinum-plated titanium anode and cathode. The results showed that chlorine concentration reached maximal level in the batch process. Prolonged electrolysis reduced chlorine concentration in the electrolyte and was detrimental to electrolysis efficiency, especially under high electric potential conditions. Therefore, the optimal choice of electrolysis time depends on the electrolyzable chloride in DOW and cell potential adopted for electrolysis. The higher the electric potential, the faster the chlorine level reaches its maximum, but the lower the electric efficiency will be.

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1. Introduction

Electrolyzed water is an antimicrobial agent that possesses strong bactericidal effects on most pathogenic bacteria that are important to food safety. Electrolyzed water is usually produced by passing a diluted salt solution through an electrolytic cell, within which the anode and cathode are either separated by a membrane or are without a membrane separation. 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. Electrolyzed water is environmentally friendly, has significant disinfection effects, and can comply with food safety regulations [1]. As most of the planet's surface area is covered by seawater, it is reasonable to make sustainable applications of this resource. Electrolyzed seawater, because of its significant disinfection effects, has

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been used in many antifouling systems [2,3], aquaculture, and seafood processing. For example, Kasai et al [4] studied the disinfectant effects of electrolyzed seawater on viable bacteria in hatchery seawater using a batch and a continuous electrolytic system. 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 [4,5]. Watanabe and Yoshimizu [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 a fishing port using an electrolytic apparatus and found its useful applications in sanitization of fish-holding tank, port deck, and fishing equipment. Kimura et al [8] reared sea urchin 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 [9] 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 of electrolyzed seawater had been reported in aquaculture and seafood processing, only a few applications were reported in agriculture or food processing industry probably because of sanitary concerns. Plankton and bacteria are abundant in seawater, and certain coastal seawaters had been highly polluted [10,11]. By contrast, deep ocean water (DOW) is the cold, salty seawater found deep below the surface of Earth's oceans. DOW 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]. Whereas surface seawater could be contaminated by pollution or civilization, DOW presents no such concern, because it remains unpolluted in the high-pressure and low-temperature deep ocean for the past thousand years.

In order to develop electrolyzed seawater for food and agriculture applications, especially for postharvest cleaning and disinfection of ready-to-eat fresh produce, surface seawater, DOW, and DOW concentration products were electrolyzed, and their properties as well as storage stability were investigated in our previous studies [13,14]. Results in another previous study showed that the small electrode gap reduced the required cell potential and resulted in high energy efficiency. The optimal choice for electrode gap and cell

potential depends on the chlorine level of the electrolyzed DOW to be produced, and a small electrode gap is preferred [15]. As part of a continuing investigation, a two-factor central composite design is adopted for the investigation of optimal electrolysis time and electric potential for electrolyzing DOW in this study.

2. Materials and methods

2.1. Seawater samples

DOW samples used in this study were provided by Taiwan Yes Deep Ocean Water Co., Ltd. (Taipei City, Taiwan, R.O.C.). DOW was drawn at 662 m below the Pacific Ocean at approximately 5 km off the coastline of the Hualien County in eastern Taiwan. Table 1 shows a comparison of major elements, some pollution indicators, and the physical/chemical properties of DOW with those of surface seawater samples collected at a nearby area [16]. Although containing similar major elements, DOW appeared to be colder and purer than the surface seawater, which contained more nitrite as well as chlorophyll and were more alkaline in its pH values.

2.2. Electrolysis

DOW samples, 1600 mL each, were electrolyzed for designated times (Table 2) in a 2-L glass beaker electrolyzing cell equipped with a pair of 50-mm-long by 25-mm-wide anode and cathode. The anode and cathode (Model SUR-303; Surchem C&S International Corp., Taipei City, Taiwan, R.O.C.), which were titanium mesh electrode plated with 3.75 μm of platinum, were powered by a rectifier (Model MC48-4D; Surchem C&S International Corp.). A constant potential mode of operation was adopted in this study. The electrodes were immersed in seawater at 60 mm beneath the surface. Electrode gap and cell potential were maintained at 6.7 mm in electrolysis. Additional stirring was done with a 16 $\times$ 30 mm (diameter $\times$ length) Teflon spindle-shape magnetic stir bar powered by a Stirrer (Model PC-101; Corning Inc., Acton, MA, USA) at speed setting 1.2, which was approximately 200 rpm. Electrolysis parameters and electrolyte properties were monitored during the electrolysis process.

Table 1 – A comparison of major elements, and some pollution indicative compositions and properties of surface seawater and deep ocean water samples.

Category	Item	Surface seawater	Deep ocean water
Major element (mg/L or kg)	Chloride	19,060–19,860	18,840–19,510
	Sodium	11,320–11,500	11,380–11,430
	Magnesium	1327–1330	1283–1320
	Calcium	400–441	400–432
	Potassium	400–414	390–421
Composition	Nitrite (μM)	0.08–0.11	<0.02
	Chlorophyll a ($\mu\text{g/L}$)	0.12–0.19	<0.03
Property	Temperature ($^{\circ}\text{C}$)	22.5–23.8	9.4–10.2
	pH	8.10–8.20	7.56–7.70
	Salinity (psu)	34.2–34.5	33.6–34.0
Data provided by the Stone and Resource Industry R&D Center (Hualien County, Taiwan).			

Table 2 – Levels of a two-factor central composite design for studying electrolyzing deep ocean water.

Level	Electrolysis time (min)	Cell potential (V)
1	180	6.00
2	215	6.59
3	300	8.00
4	385	9.41
5	420	10.0

2.3. Analytical measurements

A total chlorine test kit (Model 16900; Hach Co., Loveland, CO, USA; Method 8209, which is based on the 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 carried out at $29 \pm 1^\circ\text{C}$.

2.4. Electrolysis efficiency

Current density was calculated by dividing the electric current by the effective surface area of anode. 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 [17]. Electric efficiency, which represents energy efficiency of the system, was calculated by dividing the total chlorine produced by the electric energy consumed.

2.5. Statistical design and analysis

A two-factor central composite design [18] was adopted for studying the effects of electrolysis time and electric potential on chlorine generation efficiency of electrolyzed DOW. The test ranges of electrolysis time and electric potential were 180–420 minutes and 6.00–10.0 V, respectively (Table 2). Four center points were replicated for the estimation of random errors. Experimental data were analyzed using the response surface regression test of the Statistical Analysis Systems (SAS 9.4; SAS Institute, Cary, NC, USA).

3. Results and discussion

As reviewed in the Introduction section of this paper, electrolyzed seawater, because of its significant disinfection effects and availability, has been used in many antifouling, aquaculture, and seafood processing systems. However, reports on design of electrolysis systems were mostly patented, and detailed information about its mechanism as well as effects on electrolysis efficiencies was very limited. Therefore, the objectives of this study were to collect information on the effects of electrolysis time and electric potential on chlorine generation efficiency of electrolyzed DOW, which is important in designing electrolysis systems and choosing operation conditions.

Because electric potential is the main driving force of the system, the higher the cell potential, the greater the amount of electric current that passes through the system and the higher the current density will be. As shown in Figure 1, current density of the electrolysis system is significantly ($p < 0.001$)

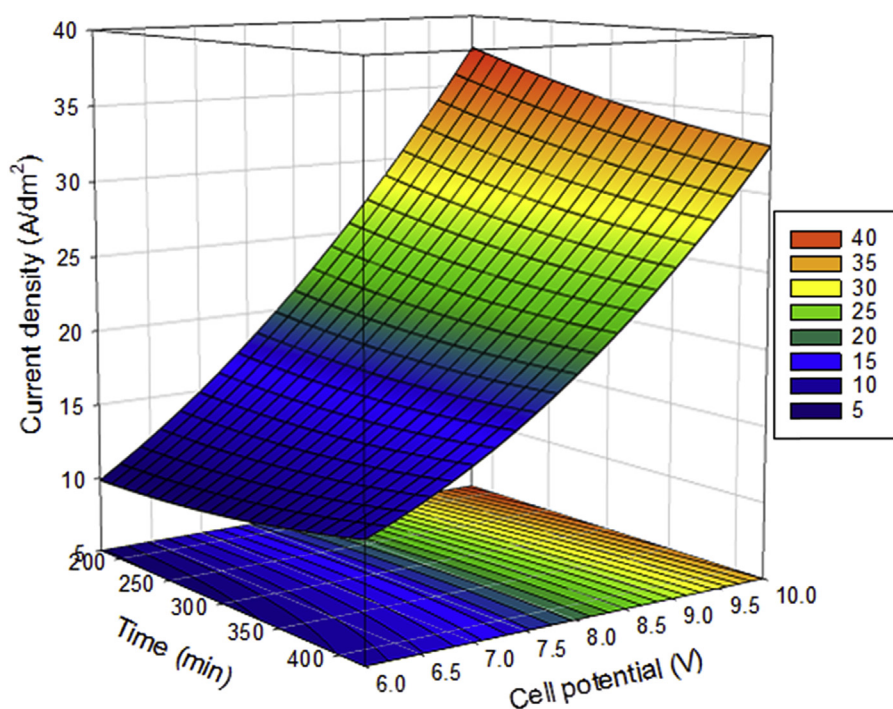


Figure 1 – Response surface and contour plots of current density with respect to electrolysis time and electric potential in electrolysis of deep ocean water.

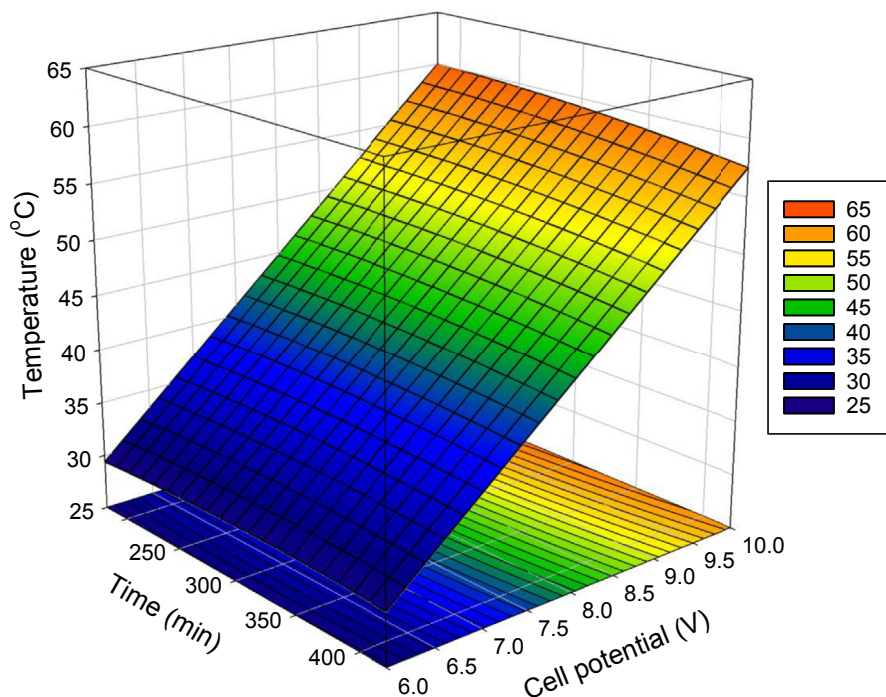


Figure 2 – Response surface and contour plots of electrolyte temperature with respect to electrolysis time and electric potential in electrolysis of deep ocean water.

affected by electric potential, whereas the effects of electrolysis time was not significant. Current density slightly increased with time at low electric potential and slightly decreased with time at high electric potential.

Electrolyte temperature increased correspondingly to electric potential but was not affected by electrolysis time in electrolysis of DOW (Figure 2). As shown in our previous

reports, electrolyte temperature increased steadily in the electrolysis process because of the continuous conversion of electrical energy to heat and heat dissipation to electrolyte through electrodes [13]. The electrolyte temperature at each cell potential remained the same throughout the electrolysis time, indicating that heat continuously dissipated to the environment during the electrolysis process.

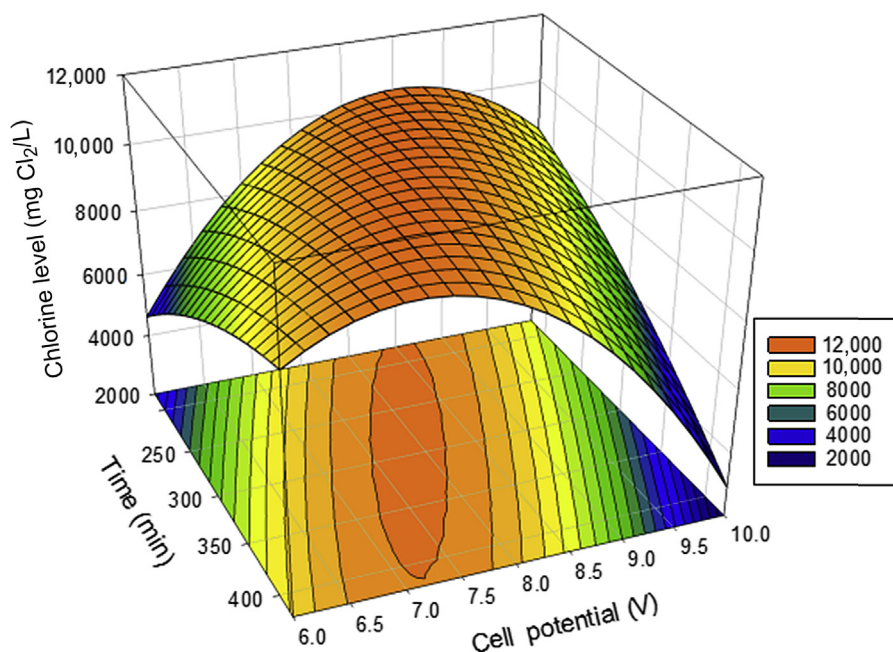


Figure 3 – Response surface and contour plots of chlorine concentration with respect to electrolysis time and electric potential in electrolysis of deep ocean water.

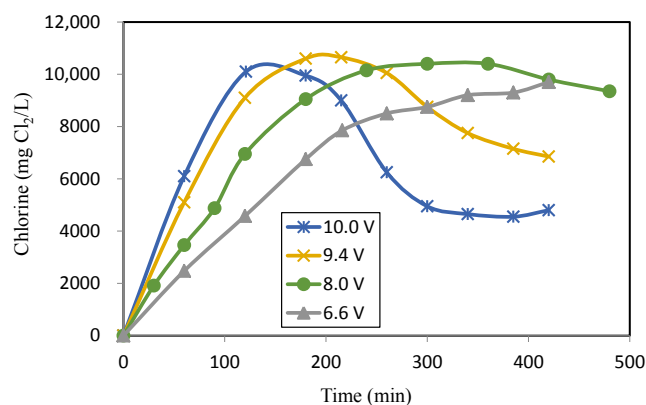


Figure 4 – Chlorine concentration of deep ocean water in electrolysis at different electric potential.

As shown in Figure 3, a response surface plot of chlorine level in electrolyzed DOW with respect to electrolysis time and electric potential appeared to be a saddle-shaped surface. Overall, chlorine concentration reached the maximal level of 10,498 mg Cl₂/L when the DOW was electrolyzed at 7.5 V for 342 minutes. There was a significant ($p < 0.05$) interaction between electrolysis time and cell potential. Chlorine concentration significantly increased with electrolysis time at low electric potential, whereas it significantly decreased with electrolysis time at high electric potential. A maximal chlorine level appeared at each electrolysis time in the electric potential ranges. The maximum levels shifted to low cell potential conditions as electrolysis time increased—which indicated

that at each electric potential, chlorine concentration reached its maximum level after being electrolyzed for a certain time interval. Then the chlorine level began to drop when electrolysis continued.

Increasing cell potential and increased current density passing through the electrodes increased the chlorine generation rate and electrolyte temperature at the same time (Figures 1 and 2). The increase in chlorine level along with electrolysis time at low electric potential (Figure 3) was ascribed to chlorine being generated and its level being built up in electrolyte from electrolysis of chloride in DOW. The decrease in chlorine level with electrolysis time at high electric potential (Figure 3) was probably due to chlorine loss at high temperature. Chlorine gas, which is generated at the anode, is very volatile especially under high temperature conditions [19,20]. It is possible that most convertible chloride had been converted to chlorine after DOW was electrolyzed for a certain time interval, and the level of residue chlorine decreased because of there is less chlorine being generated than chlorine gas being evaporated in the electrolyte. As illustrated in Figure 4, the effects appeared at the early stage of high electric potential processes because of their faster and more vigorous electrolysis conditions.

As shown in Figure 5, current efficiency is significantly affected by electrolysis time and electric potential ($p < 0.001$). The longer the electrolysis time and the higher the electric potential, the lower the current efficiency. Electric efficiency or energy efficiency of the system was significantly ($p < 0.001$) affected by electrolysis time and electric potential in a similar manner (Figure 6). In conclusion, electrolyzed DOW is suitable for postharvest cleaning and disinfection of ready-to-eat fresh produce because of its better purity and stability.

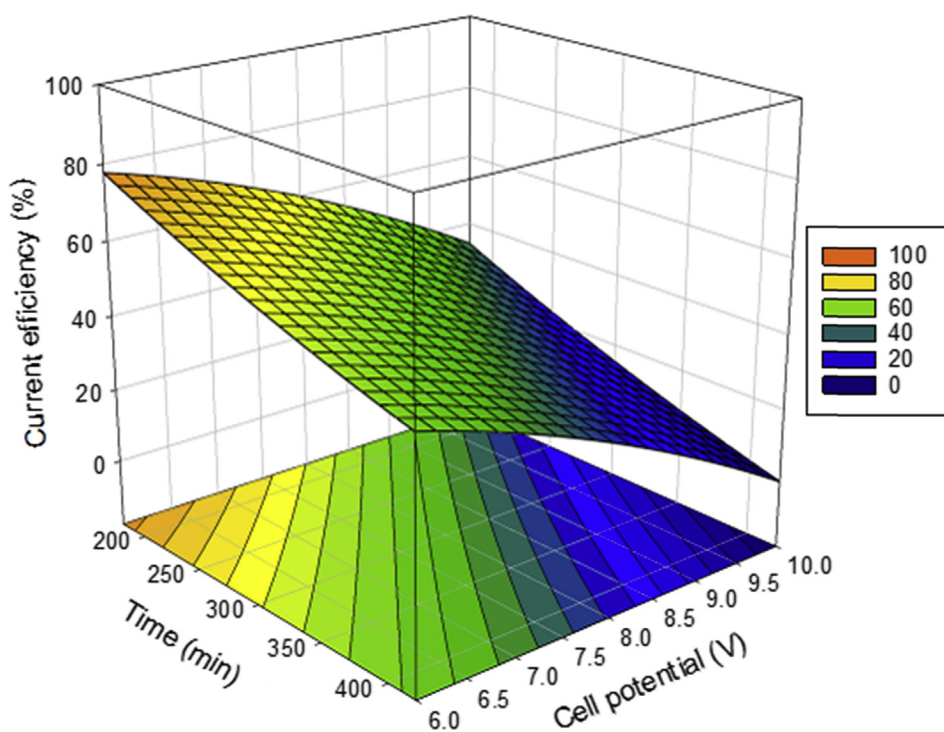


Figure 5 – Response surface and contour plots of current efficiency with respect to electrolysis time and electric potential in electrolysis of deep ocean water.

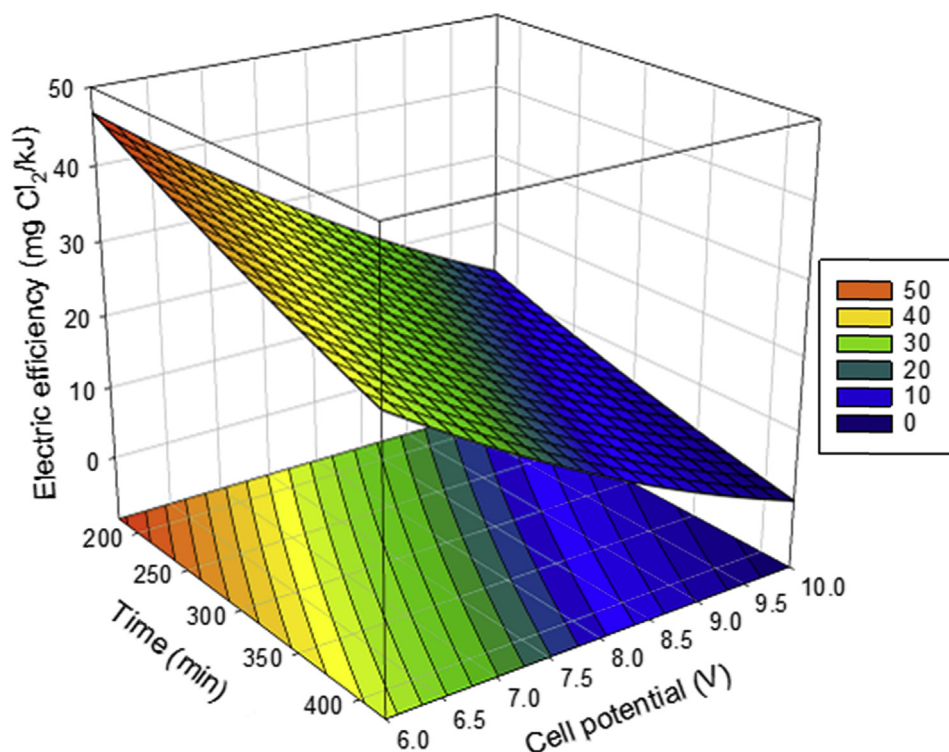


Figure 6 – Response surface and contour plots of electric efficiency with respect to electrolysis time and electric potential in electrolysis of deep ocean water.

Chlorine concentration in electrolyzed DOW reached maximal level in a batch process. However, prolonged electrolysis reduced chlorine concentration in the electrolyte and reduced current efficiency as well as electric efficiency of the operation, especially under high electric potential conditions. A properly designed continuous electrolysis mode can prevent this situation. Additional cooling of electrolyte can also reduce chlorine loss in the electrolysis process. Therefore, the optimal choice of electrolysis time depends on electrolyzable chloride in DOW and the cell potential used for electrolysis. The higher the electric potential, the faster the chlorine level will reach its maximum but the lower the electric efficiency will be.

4. Conflicts of interest

All authors have no conflicts of interest to declare.

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