Desalination and Water Treatment
www.deswater.com

1944-3994 / 1944-3986 © 2010 Desalination Publications. All rights reserved.
doi: 10.5004/dwt.2010.1780

18 (2010) 245–250
June

Evaluation of a seawater electrolysis process considering formation of free chlorine and perchlorate

Byung Soo Oh[a], Sang-Guen Oh[a], Yeon Jung Jung[b], Yun-Young Hwang[b], Joon-Wun Kang[b], In S. Kim[a,*]

[a]*Center for Seawater Desalination Plant, GIST, Oryong-dong, Buk-gu, Gwangju, Korea*
Tel.: +82-62-970-3381; Fax: +82-62-970-2584; email:iskim@gist.ac.kr
[b]*Department of Environmental Engineering, YIEST, Yonsei University, Wonju, Gangwon, Korea*

Received 3 June 2009; Accepted 15 December 2009

ABSTRACT

This study evaluated the possibility of an electrochemical process as a pre-treatment of a seawater reverse osmosis (SWRO) desalination plant. Initially, during electrolysis of seawater the formation trend of free chlorine was observed and then inactivation rate of *Bacillus sp.* isolate obtained from natural seawater was measured to evaluate the potential for reducing biofouling of SWRO membrane. As a result, the *Bacillus sp.* spores present in seawater were completely inactivated at approx. 210 s of electrolysis time, showing 2.4-time higher inactivation rate compared to chlorination alone. This study also investigated the formation trend of perchlorate (ClO_4^-) during electrolysis of seawater and its rejection by microfiltration and the SWRO membrane. After 5 min of electrolysis, 27 μg/L of ClO_4^- was produced. It was also found that 20% and 98% rejection efficiencies of ClO_4^- were observed through microfiltration and SWRO filtration. The optimum condition of the electrochemical process as a pre-treatment in the seawater desalination plant was determined to be ~4 min of electrolysis time and 110 mA/cm^2 of current density under the tested natural seawater condition.

Keywords: Electrolysis; Chlorination; Biofouling; Perchlorate; Seawater; Desalination

1. Introduction

Many countries depend on seawater desalination technology to overcome shortages of natural fresh water [1,2]. Seawater reverse osmosis (SWRO) is gradually becoming a primary choice for desalination facilities [3]. However, the fouling of the SWRO membranes, caused by suspended substances, colloids, microorganisms and soluble (in)organic matters present in seawater, still remains a severe problem requiring a prompt solution [4]. In an effort to reduce membrane fouling, pre-treatment (i.e., chlorination, filtration, flotation, etc.) of the SWRO process is applied to desalination plants [5]. In this study, an electrochemical process was introduced as a pre-treatment process, with the aim of prevention of biofouling.

Electrochemical processes for the disinfection of drinking water, with the advantage of on-site generation of chlorine (HOCl and OCl-), have largely been developed over the last few decades. Since seawater contains a huge amount of sodium chloride, which acts as an electrolyte and is a main source of free chlorine [6], the electrolysis of seawater could be proposed as an inexpensive and convenient method for the inactivation of the microorganisms that can cause biofouling. This study initially investigated the inactivation efficiency of

---

*Corresponding author.

Bacillus sp. isolates during the electrolysis of seawater. Even though the electrochemical process is expected to be an effective tool for the control of biofouling, it does have some drawbacks: mainly the formation of magnesium and calcium scale at the cathode and the formation of harmful by-products, such as haloacetic acid, trihalomethane, chlorate (ClO_3^-) and perchlorate (ClO_4^-) etc. This study focuses on the trend for the formation of ClO_4^- during the electrolysis of seawater.

ClO_4^- interferes with iodide uptake into the thyroid gland, resulting in thyroid malfunctioning that extremely hinders human mental growth [7]. Since ClO_4^- has a tetrahedral structure and a distribution of charge within a polyatomic anion, it is generally considered to be very stable in aqueous solutions [8]. Since its discovery in a number of water supplies in the western United States during 1997, ClO_4^- has recently become an important environmental issue. Ammonium perchlorate, manufactured mostly in the USA, is widely used as the primary ingredient of solid rocket propellant [9]. It has been shown to accumulate in plants, which could be a potential source of ClO_4^- exposure for humans and animals. In addition, the ClO_4^- produced is not removed by conventional water treatment processes, so human exposure could result from drinking water [10]. In this study, the removal efficiency of the ClO_4^- formed during the SWRO process was investigated to verify the safety of RO permeates for use as drinking water.

The main purpose of this study was to evaluate the electrolysis of seawater to provide a possible pretreatment to the SWRO process by investigating the formation of free chlorine, inactivation of *Bacillus sp.* isolate and the formation of ClO_4^-.

2. Methods

2.1. Preparation of Bacillus sp. isolate and sterile seawater

Natural seawater samples were collected from the East-sea, Jumunjin, Gangneung city. The characteristics of the seawater are shown in Table 1.

Table 1
Characteristics of natural seawater sample.

Parameters	Value	Parameters	Value
pH	8	Ca^{2+} (mg/L)	421
TDS (mg/L)	34,475	Mg^{2+} (mg/L)	1,395
Cl^-(mg/L)	19860	Ba^{2+} (μg/L)	8
SO_4^{2-} (mg/L)	2,665	Sr^{2+} (μg/L)	765
HCO_3^- (mg/L)	251	Boron (mg/L)	4.7
Na^+ (mg/L)	14039	DOC (mg/L)	1.45

A membrane filtration technique was used for isolation and culture of the bacteria in the seawater sample. After filtering through the 0.45 μm pore size cellulose acetate membrane, the membrane filter retaining the cells was transferred to a marine agar plate (Difco 2216) and incubated at 37°C until individual colonies grew. Based on the colony morphology, an individual colony was selected and transferred to a new medium dish, with the DNA of each subcultured colony then extracted for PCR. A universal bacterial primer set, forward primer 9F (5′-GAG TTT GAT CCT GGC TCA G-3′) and reverse primer 1512R (5′-ACG GHT ACC TTG TTA CGA CTT-3′), was used to amplify the 16S rRNA gene from each genomic DNA extract. Each single colony was identified genetically by sequencing of the 16S rRNA gene [11].

For experiments, *Bacillus sp.* isolates were inoculated into Difco™ Marine Broth 2216 (BD Co., USA), using a sterile inoculating loop dipped in a re-hydrated solution of *Bacillus sp.* isolate. Subsequently, the inoculated broth was incubated for 13 h in a shaking incubator at 37°C and 200 rpm. *Bacillus sp.* isolates were harvested by centrifugation of 1 mL volumes at 3000 rpm for 15 min., with the resultant pellets washed in 1 mL of sterile seawater and centrifuged twice further. Stock *Bacillus sp.* isolate was prepared by resuspending the final pellets in 1 mL of sterile seawater.

For spore preparation, the *Bacillus sp.* isolates were allowed to grow and sporulate on a 1/10 nutrient agar (3.74 g L^{-1} Difco™ Marine broth + 15 g L^{-1} Bacto Agar, BD Co., USA) plate for 7 days in an incubator at 37°C. The spores were harvested from the top of each plate by scraping with a sterile loop and suspended in 5 mL of sterilized seawater. The procedure for washing the spores followed that described in the EPA UV disinfection guidance manual [12]. Briefly, the suspension of collected spores was sonicated for 10 min at 50 kHz and 10°C to separate the spores from vegetative cells. Each spore suspension was washed three times by resuspending in 10 mL of sterilized deionized water, centrifuged at $3600 \times g$ and 10°C for 20 min, and subsequently preserved in 50 mL of sterile seawater (pH 8). In order to inactivate any remaining vegetative cells, the spore suspension was heated to 80°C, and held at that temperature for 10 min using a thermostatically controlled water bath (Fisher Scientific). The final spore suspension (~10^8 CFU mL^{-1}) was stored in a dark room at 4°C until used. For the preparation of synthetic seawater samples, sodium chloride ($Cl^- = 20{,}000$ mg/L) was injected into pure water, and the pH controlled at 8 using the phosphate buffer solution.

2.2. Electrochemical process and membrane filtration

Titanium (Ti) substrates were pretreated by mechanical polishing and chemical acid washing, and then coated by painting with a $Pt(NH_3)_2(NO_2)_2$ solution under the following conditions; mass fraction of Pt = 63%, Temp. = 70°C, contact time = 5 min. Thereafter, the platinum (Pt)-coated Ti cell was dried in an air oven at 70°C for 10 min, and then heated in a preheated furnace at 500°C for 5 min. An electrochemical device (Dolki Korea Ltd.), with a grid shaped Pt/Ti electrode (3 cm × 3 cm) was developed [13]. The anode and cathode were made of the same material, and placed horizontally and parallel (0.1 mm gap) in a 300 mL batch reactor. To prevent any fouling of the electrode surface, the electrode polarity was reversed every 5 s [14]. The electrical power was supplied by a DC power supply (Digital electronics Co, Korea), with the cell potential kept at a constant voltage of 30 V. Before operation, the cell was sonicated to completely desorb any materials remaining on the electrode surface from previous runs. To investigate the fate of ClO_4^- in a membrane-based seawater desalination plant, its rejection efficiency was explored using microfiltration (Cleanfil®-S, material = PVDF, module type = hollow fiber, ID/OD = 0.8/2.0 mm, pore size = 0.1 μm, mechanical strength >25kg$_f$/fiber) and SWRO membranes (RE8040-SHN, CMS®, module type = flat sheet, salt rejection = 99.75%, permeate flow rate = 5000 GPD). For the microfiltration process, small modules (effective membrane area of one module = 0.013 m^2) were manufactured and installed in a MF system. The MF system was operated at various operating pressures (3.7, 6.5 and 10 psi) to investigate the effect of trans-membrane pressure (TMP) on the removal of ClO_4^-. For the SWRO process, a standard kit (GE Osmonics) was used with an effective membrane area of 0.0125 m^2. To compare the synthetic and natural seawater, the SWRO system was operated under a fixed permeate flux of 0.5 L/min by controlling the operating pressure. Before sampling the permeate, both the MF and the SWRO systems were stabilized for 60 min under the fixed temperature condition (25°C).

2.3. Analysis of free chorine and perchlorate

Free chlorine was measured using a DPD method employing a UV/VIS spectrophotometer (HACH2010). The ClO_4^- was analyzed via ion-chromatography/mass spectrometry (IC/MS, DIONEX). The operating conditions (reagent-free IC system) of the IC/MS are summarized in Table 2.

2.4. Determination of viability of Bacillus sp. *and* Bacillus sp. *spores*

Ten-fold serial dilutions were prepared from 1 mL samples up to 1/10,000 to optimize the number of colonies (30–300 colonies/plate) grown on each agar plate. Subsequently, 0.1 mL of each of the diluted solutions was inoculated onto Difco™ Marine Agar 2216 (BD Co., USA) plates. The numbers of viable spores were measured using the spread plate method, from agar plates grown at 37°C for 24 h, with the colony-forming units (CFU mL^{-1}) then counted. The concentration of viable spores in each sample was calculated by averaging two replicate values.

Table 2
IC/MS operating conditions.

Ion chromatograph	Dionex Corporation, ICS-3000
Mobile phase	65 mM KOH
Guard and separator columns	Dionex AG20 + AS20, 250 mm × 2 mm
Flow rate	0.3 mL/min
Conductivity suppressor and current	ASRS300-2 mm, 49 mA
Column temperature	30°C
Injection volume	300 μL
Mass spectrometer	**6120 MS Quad SL, Agilent Technologies**
Capillary voltage	4 kV
Nitrogen pressure	35 psi
Fragmentor voltage	50 V
Drying gas temperature	300°C
Drying gas flow rate	10 L/min
Selected ion monitoring	m/z 99, 101, 107
Mass scan range	0.1 amu
Dwell time per mass	195 ms

3. Results

3.1. Formation of free chlorine and Inactivation of Bacillus sp. *isolate*

During electrolysis, the free chlorine (HOCl and OCl–) is produced through the following reactions [15]:

$$2Cl^- \rightarrow Cl_2 + 2e^- (E^o = 1.36 \text{ V vs. NHE}) \quad (1)$$

$$Cl_2 + H_2O \rightarrow HCl + HOCl \quad (2)$$

$$HOCl \leftrightarrow OCl^- + H^+ \text{ (pKa = 7.54 at 25°C)} \quad (3)$$

Figure 1 shows the concentrations of free chlorine produced during the electrolysis of synthetic and natural seawater samples; for both, the formation of chlorine increased with the increase of current density and electrolysis time. Also, no significant difference was observed in the chlorine concentrations between synthetic and natural seawater, with over 200 mg/L of chlorine produced after 5 min (current density = 110 mA/cm^2) of electrolysis of each seawater sample. Figure 2 illustrates

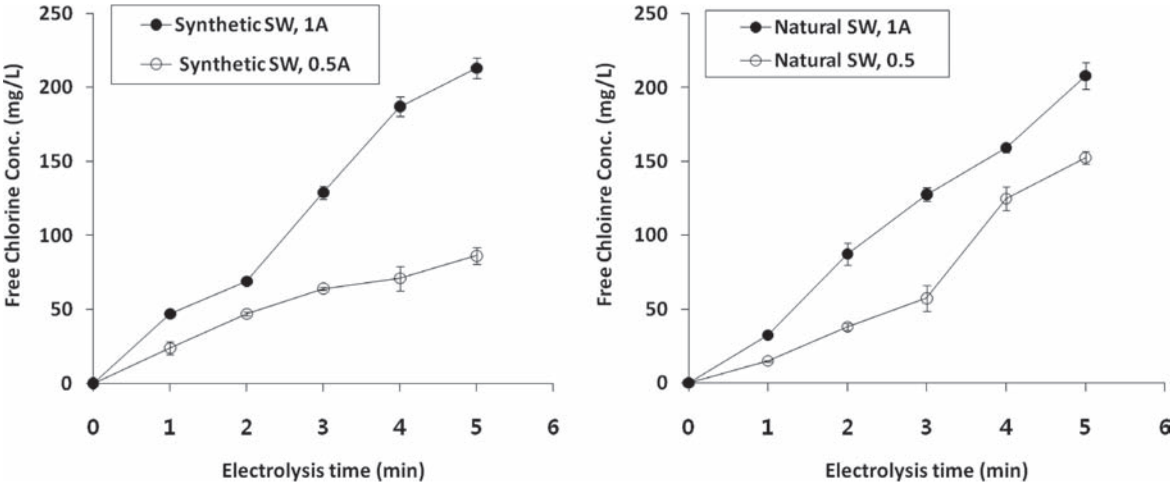

Fig. 1. Formation trend of free chlorine during electrolysis of seawater, pH 8, Temp. = 20°C, Cl⁻ = 20,000 mg/L in synthetic seawater (SW).

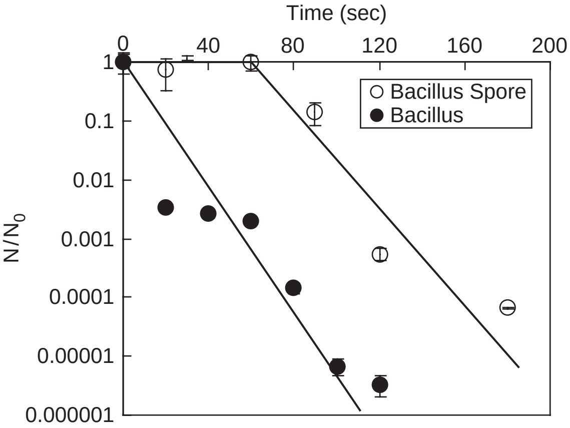

Fig. 2. Inactivation of the *Bacillus sp.* isolate during electrolysis of seawater, pH 8, Temp. = 20°C.

the inactivation rates of the vegetative cells and spores of *Bacillus sp.* isolates. In the case of *Bacillus sp.* spores, a lag phase was observed up to 60 s after the start of the electrolysis, with over 3-log removals achieved after 180 s of electrolysis. Meanwhile, *Bacillus sp.* cells were rapidly inactivated by 5-log after about 120 s, without a lag phase. In addition, the complete inactivation of vegetative cells and spores of *Bacillus sp.* isolates was observed after 120 and 180 s of electrolysis, respectively. Based on the chlorine-CT value, the disinfection efficiency of the electrochemical process (195 mg-min/L for 3-log removal) was proved to be 2.6-time higher than that by chlorination (500 mg-min/L for 3-log removal at pH = 8.2, Temp. = 20°C) of *Bacillus sp.* spores [16]. This was because the electrochemical process can produce other oxidants, such as ozone, hydroxyl radicals and chlorine dioxide, which can inactivate microorganisms via direct electrolysis of seawater. From this result, it was proved that the electrochemical process had high performance of *Bacillus sp.* spore inactivation, indicating its high potential for the reduction of the biofouling of the SWRO membrane. In addition, the end-points where microbes were completely inactivated could be determined as 140 and 210 s for *Bacillus sp.* and *Bacillus sp.* spores, respectively.

3.2. Formation trend of perchlorate and rejection by membrane filtration

Since the standard reduction potential of chlorine formation, Eq. (1), is higher than that of oxygen formation, Eq. (8), oxygen and ozone could be additionally formed in the process for producing chlorine [15]. This implies that the formation of ClO_4^- is inevitable when the electrochemical process is utilized in a seawater desalination plant. The mechanism of ClO_4^- formation in the electrochemical reactions starts with the formation of chlorate (ClO_3^-), with the ClO_3^- then transformed to ClO_4^- via anode and bulk reactions, as follows [17–20]:

Anode

$$2Cl^- \rightarrow Cl_2 + 2e^- \; (E^o = 1.359 \text{ V}) \tag{1}$$

$$6OCl^- + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + 3/2O_2 + 6e^- \quad E^o = 1.405 \text{ V} \tag{4}$$

$$6HOCl + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 12H^+ + 3/2O_2 + 6e^- \quad E^o = 0.97\text{V} \tag{5}$$

$$Cl^- + 3H_2O \rightarrow ClO_3^- + 6H^+ + 6e^- \; \text{(direct oxidation at the anode)} \tag{6}$$

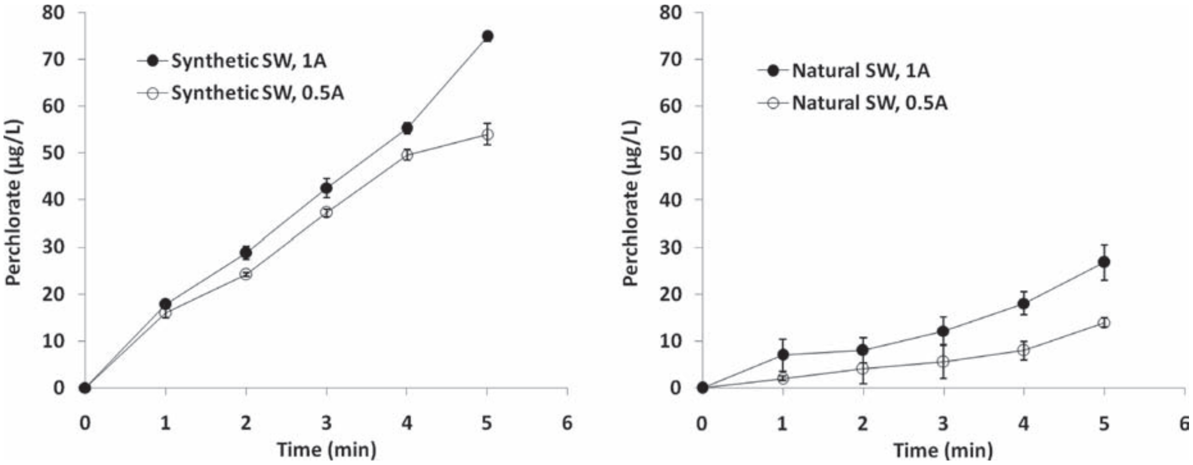

Fig. 3. Formation trend of perchlorate during electrolysis of seawater, pH 8, Temp. = 20°C, Cl^-= 20,000 mg/L in synthetic seawater (SW).

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^- \qquad E^o = 0.95 \text{ V} \qquad (7)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^o = 1.229 \text{ V} \qquad (8)$$

Bulk solution

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$
$$HOCl \leftrightarrow OCl^- + H^+ \qquad pKa = 7.5 \qquad (2),(3)$$

$$HOCl + 2ClO_2^- + H^+ \rightarrow 2ClO_2 + H_2O + Cl^- \qquad k = (1.1 \pm 0.03) \times 10^6 M^{-2}s^{-1} \qquad (9)$$

$$(H_2O \rightarrow (OH\cdot)_{ad} + H^+ + e^-)\ ClO_3^- + (OH\cdot)_{ad} \rightarrow ClO_4^- + H^+ + e^- \qquad (10)$$

Cathode

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \ (E^o = 0.68V) \qquad (11)$$

$$H_2O_2 + Cl_2 \rightarrow 2Cl^- + 2H^+ + O_2 \qquad (12)$$

$$2H^+ + 2e^- \rightarrow H_{2(g)} \qquad (13)$$

Figure 3 shows the pattern of ClO_4^- formation during the electrolysis of synthetic and natural seawater samples. Similar to the pattern of chlorine formation, the concentration of ClO_4^- in both samples during electrolysis increased with increasing current density and electrolysis time, but interestingly, a much lower concentration of ClO_4^- was observed from natural seawater than from synthetic seawater. This was because the reactions for the ClO_4^- formation by other oxidants formed during electrolysis like Eq. (10) were quenched due to background matters present in natural seawater. The detailed smechanism study is in progress and the results will be reported in the following paper. The ClO_4^- formed during the electrolysis of natural seawater was not in excess of the EPA reference dose (24.5 µg/L in drinking water) after less than 5 min of electrolysis. Considering the results on the inactivation of the *Bacillus sp.* isolate and the production of ClO_4^- during the electrolysis of natural seawater, the optimum conditions for the electrochemical process could be determined as being ~4 min of electrolysis, with a current density of 110 mA/cm^2 under the conditions tested for seawater (Table 1).

In Figs. 4 and 5, the removal efficiencies of ClO_4^- by MF and SWRO membrane processes were measured under the condition of excess ClO_4^- using both synthetic and natural seawater samples. Each process rejected about <20% and >98% ClO_4^-, respectively. From these results, it can be concluded that even though the electrochemical process produced ClO_4^- as a by-product, this

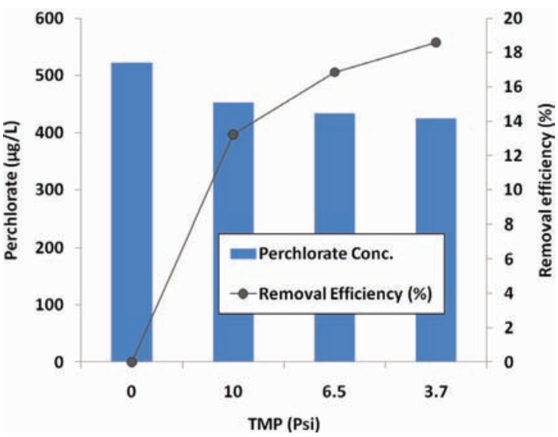

Fig. 4. Rejection of perchlorate by the MF membrane, $[ClO_4^-]_o$ = 522 µg/L, pH 8, Temp. = 20°C.

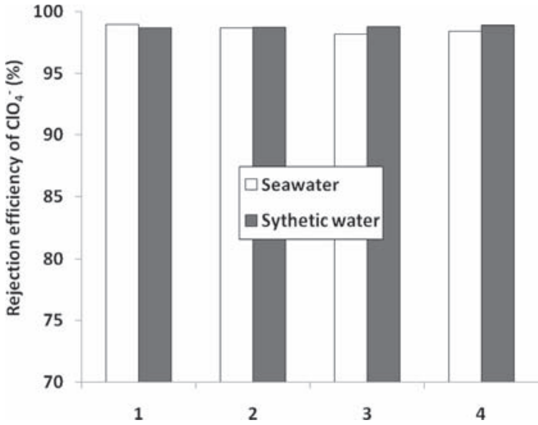

Fig. 5. Rejection of perchlorate by the SWRO membrane, $[ClO_4^-]_o$= 590 μg/L pH 8, Temp. = 20°C.

will cause no problem in a SWRO desalination plant due to the great removal efficiency of the SWRO membrane. However, it should be noted that since the rejected SWRO concentrate, which is commonly discharged into the sea, could contain about a 2-fold higher concentration of ClO_4^- than the feed water to the SWRO process, monitoring and risk assessment of the SWRO concentrate would be required if the electrochemical process is to be used.

4. Conclusions

The electrolysis of seawater produced sufficient free chlorine for use in seawater disinfection. The inactivation rate of *Bacillus sp.* spores by the electrochemical process was much faster (195 mg-min/L for 3-log removal) than that by chlorination alone (500 mg-min/L for 3-log removal). Even though the formation of perchlorate (ClO_4^-) occurred during the electrolysis of seawater, the SWRO process was able to reject the ClO_4^- with high efficiency (>98%). From these results, the optimum conditions for the electrochemical process were determined as ~4 min of electrolysis, with a current density of 110 mA/cm^2 under the conditions tested for seawater.

Acknowledgement

This research was supported by a grant (07SeaHeroA01-01) from the Plant Technology Advancement Program funded by the Ministry of Land, Transport and Maritime Affairs, Korea, and also supported by the Brain Korea 21 program of the Ministry of Education.

References

[1] P.H. Gleick, In: Schneider, S.H. (Ed.), Water Resources in Encyclopedia of Climate and Weather, Vol. 2. University Press, New York, 1996 pp. 817–823.
[2] R.F. Service, Desalination freshens up. Science, 313 (2006) 1088–1090.
[3] S. Kim, D. Cho, M.-S. Lee, B.S. Oh, J.H. Kim and I.S. Kim, SEAHERO R&D program and key strategies for the scale-up of a seawater reverse osmosis (SWRO) system, Desalination, 238 (2009) 1–9.
[4] M.G. Amiri and M. Samiei, Enhancing permeate flux in a RO plant by controlling membrane fouling, Desalination, 207 (2007) 361–369.
[5] A. Brehant, V. Bonnelye and M. Perez, Assessment of ultrafiltration as a pretreatment of reverse osmosis membranes for surface seawater desalination, Water Sci. Technol.: Water Supply, 3 (2003) 437–445.
[6] B. Cyna, D. Dourdin and D. Gatel, Drinking water production on an urban site electrochlorination, in: S. Sealey (Ed.), Mordern Chlor-Alkali Technology, Vol. 7, 1998 pp. 197.
[7] W.L. Goleman, J.A. Carr and T.A. Anderson, Environmentally relevant concentrations of ammonium perchlorate inhibit thyroid function and alter sex ratios in developing, Xenopus laevis, Toxicol. Chem, 21 (2002) 630–634.
[8] D.R. Susan and A.T. Tomas, Water analysis: Emerging contaminants and current issues, Anal. Chem., 77 (2005) 3807–3838.
[9] R.Q. Gullick, M.W. Lechvallier and T.A.S. Barhorst Occurrence of perchlorate in drinking water sources, J. AWWA, 93 (2001) 66–77.
[10] H.P. Huq, J.S. Yang and J.W. Yang, Removal of perchlorate from groundwater by the polyelectrolyte-enhanced ultrafiltration process, Desalination, 204 (2007) 335–343.
[11] J.W. Lee, S.M. Kim, J.-Y. Jung, B.S. Oh, I.S. Kim and S.K. Hong, Analysis of total bacteria, enteric members of γ-proteobacteria and microbial communities in seawater as indirect indicators for quantifying biofouling, Environ. Eng. Res., 14 (2009) 19–25.
[12] USEPA, Ultraviolet disinfection guidance manual. EPA 815-D-03-007, 2003.
[13] B.S. Oh, S.Y. Park, Y.J. Jung, K.W. Baek, T.M. Hwang, K.S. Cho and J.-W. Kang, Application of platinum and titanium materials as an electrode for hygiene purpose, Mater. Sci. Forum, 544–545 (2007) 199–202.
[14] S.W. Lee, K.M. Kang, J.K. Lee, K.H. Lee and H.J. Park, Removal of fouling from seawater by changing poles for electrolysis reaction, Appl. Chem., 12 (2008) 81–84.
[15] K. Rajeshwar and J. Ibanez, Environmental Electrochemistry, Academic Press, New York, 1997.
[16] H.J. Son, M. Cho, J.E. Kim, B.T. Oh, H.M. Chung and J.Y. Yoon, Enhanced disinfection efficiency of mechanically mixed oxidants with free chlorine, Water Res., 39 (2005) 721–727.
[17] N. Munichandraiah and S. Sathyanarayana, Kinetics and mechamism of anodic oxidation of chlorate ion to perchlorate ion on lead dioxide electrodes, J. Appl. Electrochem., 17 (1987) 33.
[18] L.R. Czarnetzki and L.J.J. Janssen, Formation of hypochlorite, chlorate and oxygen during NaCl electrolysis from alkaline solution at an RuO_2/TiO_2 anode, J. Appl. Electrochem., 22 (1992) 315.
[19] L.J.J. Janssen and V.D. Heyden, P.D.L. Mechanism of anodic oxidation of chlorate to perchlorate on platinum electrodes, J. Appl. Electrochem., 25 (1995) 126.
[20] J.H. Bradley, Electrolytic destruction of urea in dilute chloride solution using DSA electrodes in a recycled batch cell, Water Res., 39 (2005) 2245..