Reverse electrodialysis for perchlorate abatement in salt water

Benny Marie B. Ensano, Yeonghee Ahn*

Department of Environmental Engineering, Dong-A University, Busan 49315, Republic of Korea, Tel. +82-51-200-7677; Fax: +82-51-200-7683; email: yahn@dau.ac.kr

Received 22 February 2021; Accepted 11 May 2021

ABSTRACT

Perchlorate (ClO₄⁻) is a toxic anion that inhibits iodine uptake by the thyroid gland and subsequently disrupts thyroid hormone production. In this study, the feasibility of using reverse electrodialysis (RED) was examined for the treatment of perchlorate in salt (5% NaCl; w/v) water. RED uses direct electricity, produced by salinity gradients in a membrane stack, to drive the electrochemical treatment of wastewater. Operational conditions such as salinity gradient (S.G.), number of membrane pairs, and stack solution flowrates were varied and their effects on electricity generation and perchlorate reduction were investigated. Experimental batch results showed that a higher number of membrane pairs and salinity gradient gave higher values of power density, which also resulted in higher abatement of perchlorate. In contrast, the reduction of perchlorate was lowered upon increasing the stack solution flowrate. The maximum abatement of perchlorate (38.76%) was achieved using 15 pairs of cation and anion exchange membranes and 5 M/0.005 M salinity ratio (S.G. 1,000) of high and low concentrated NaCl solutions at 1.5 mL/min stack solution flowrate. This study successfully demonstrated that RED can be a sustainable alternative method for the abatement of perchlorate in salt waters.

Keywords: Perchlorate reduction; Salinity gradient energy; Reverse electrodialysis; Saltwater

1. Introduction

Perchlorate is an emerging endocrine-disrupting compound that is ubiquitously detected in soil, groundwater, and drinking water sources at significant levels [1–3]. Ingestion of this toxic anion interferes with thyroid hormone production affecting human growth and mental development [4]. The ion-exchange process is the most common treatment method for perchlorate-laden waters but does not degrade or reduce perchlorate. This process just transfers perchlorate from the contaminated waters to the salt solution used for resin regeneration, producing spent regenerant (waste salt solution) containing high concentrations of perchlorate. The spent regenerant then requires subsequent treatment prior to disposal [5,6].

Studies have reported that perchlorate can be degraded by perchlorate-reducing bacteria (PRB) [7–9]. However, like other microorganisms, PRB is highly dependent on environmental conditions, such as salt concentration, pH, and temperature, which then affect their performance to degrade perchlorate [10–12].

Electrochemical methods studied over the recent years showed that electrical water and soil treatment was effective to remove contaminants [13–15]. The electrochemical reduction of perchlorate using different electrodes, such as nickel [15], titanium [16], and tin [17], has also been investigated and has shown promising results but the high cost of electricity required to drive the reduction remains a bottleneck for its widespread application.

Sustainable technology can generate electrical energy and simultaneously perform wastewater treatment. Reverse electrodialysis (RED) is a considered green water treatment technology because the electrochemical remediation process is carried out without the need for an external energy source. In this study, the feasibility of using reverse electrodialysis (RED) was examined for the treatment of perchlorate in salt (5% NaCl; w/v) water.
electrical energy. It converts salinity gradient into useful power using a membrane stack that consists of alternating anion and cation exchange membranes placed in between the electrode compartments [18–20]. Two solutions of different salt concentrations are introduced at the opposite sides of the stack assembly that selectively drives the cations and anions to move towards the cathode and anode, respectively. The flow of these charged ions produces an electromotive force (E) between the electrodes causing the electrons to flow from anode to cathode via an external wire. The wastewater is introduced into the electrode chamber where the pollutants are being degraded via redox processes. RED can be utilized to capture electrical energy economically using salinity gradients from seawater, freshwater, salt pond and brine solution.

RED is different from electrodialysis reversal (EDR) [21]. In EDR, two main streams flow adjacent in the membrane stack: the product stream and the concentrated RED stream. The wastewater enters the ‘product’ chamber and travels up the length of the membrane stack. Upon application of electricity, the positive and negative charge ions from the feed water migrate through the cation and anion exchange membranes, respectively, and get concentrated in the adjacent ‘concentrate’ chamber. The effluent of the product chamber is called the processed water while that of the concentrate chamber is the brine reject. The polarity of the electrode is reversed periodically in order to prevent scaling on the membranes, hence maintaining a stable flux. To simply put, wastewater is being treated in RED by electrochemical degradation at the electrode chamber while in EDR, treatment of water occurs via ion removal only. In addition, RED is more sustainable because, unlike EDR, it does not need an external power supply since it can produce its own electrical energy driven by the salinity gradient.

RED has been employed in only a handful of studies for the abatement of both organic and inorganic pollutants. Scialdone et al. [22] successfully applied the RED process to convert toxic Cr$^{6+}$ into harmless Cr$^{3+}$ in contaminated water. In another study, Scialdone et al. [23] effectively removed Acid Orange 7 from an aqueous solution using RED cell equipped with 40–60 cell pairs of membrane stack. Meanwhile, Zhou et al. [24] simultaneously generated 0.06 W/m² output power density while degrading 98% of ammonia using the active chlorine produced in RED.

RED can be also combined with other technologies for enhanced wastewater remediation. For example, the integration of RED with microbial fuel cells into a hybrid microbial reverse electrodialysis cell (MRC) resulted in an improved cathodic abatement of Cr$^{6+}$ [25]. MRC based Fenton process showed excellent performance for the complete decolorization and mineralization of an azo dye (Orange G) [26]. A photocatalytic reverse electrodialysis cell, which is composed of photoanode, RED stack and cathodic chambers, was reported to efficiently extract salinity gradient power for better degradation of rhodamine B, a refractory water pollutant [27,28].

In this study, the applicability of RED as a sustainable method was explored to reduce perchlorate from saltwater. Carbon tissue was used as the electrode material because it is inexpensive and widely available. The main objective is to assess the influence of experimental parameters (i.e., no. of membrane pairs, salinity gradient, and stack solution flowrate) on perchlorate removal efficiency as well as generation of electricity. To the best of our knowledge, this is the first study on the effective removal of perchlorate using RED. It is worth noting that the focus of the study is to utilize the energy generated in the cell to drive the perchlorate reduction. This study intends to create a perchlorate reducing technology that is energy independent. Hence, our priority is to degrade perchlorate and not on the production of a significant amount of electricity.

2. Materials and methods

2.1. Materials

All chemicals used in this study were analytical grade and were used without further purification. Sodium chloride (NaCl, purity >99.5%) was purchased from Junsei Chemical Co., Ltd., (Japan). NaOH (purity >99%) and H$_2$SO$_4$ (purity >99%), used for pH adjustment, were procured from Sigma-Aldrich Chemical Company, Inc., (St. Louis, MO, USA) and Kanto Chemical Co., Inc., (Tokyo, Japan), respectively. Perchlorate standard, used for ion chromatography (IC) and stock solution preparation, was obtained from AccuStandard Inc., (New Haven, CT, USA). Salt solutions used in the RED experiment were prepared with NaCl and ultrapure water. Ultrapure water (resistivity >18.2 MW cm at 25°C; Ultra 370 Series aquaMAX$^{TM}$, Ultra Water Purification System, Younglin) was utilized for solution preparations.

2.2. Experimental set-up

A laboratory-scale RED cell was used in this study (Fig. 1). The membrane stack, located between the anode and cathode chambers, was consisted of alternating Neosepta AMX anion and Neosepta CMX cation exchange membranes separated by silicon rubbers (0.3 mm thickness). Two Nafion membranes (proton exchange membranes) were specifically used as CEM to separate the stack compartment from the electrode chambers. Carbon tissues (24 cm$^2$ surface area) were used as anode and cathode and were connected in series with a fixed resistor through an external wire. Low concentrated (LC) salt solution was introduced into the chamber next to the anode and consequently flowed across the stack exiting at the chamber next to the cathode. On the other hand, high concentrated (HC) salt solution entered from the chamber next to the cathode and flowed across the stack exiting at the chamber next to the anode. These configurations were possible due to the design of the silicon rubber (Fig. 1) as adapted from a previous study [29]. The flow rates of the HC and LC solutions were controlled by a digital peristaltic pump (EMP 600A; EMS Tech., Korea).

2.3. Experimental procedure

Batch experimental runs were carried out in this study. Parameters varied were the number (N) of membrane pairs, salinity gradient (S.G.), initial perchlorate concentration,
and stack solution flowrates (Table 1). Salinity gradient was the salinity ratio of HC and LC solutions. In each run, 7.5 mL of cathodic solution was fed into the cathodic compartment. The cathodic solution, artificial saltwater contaminated with perchlorate, was composed of a predetermined concentration (1 mg/L) of perchlorate and 5% (W/V; 0.86 M) NaCl solution. The anodic compartment contains 0.25 M H2SO4 anodic solution. The reaction time was set to 1 h for all runs. Experiments were performed in duplicates and the average values ± standard deviation were determined and presented in this study.

2.4. Analysis

The potential drop across a fixed resistor and the current intensity were measured using a digital multimeter (Fujian OW18B, China). Power density (W/m²) was then calculated by obtaining the product of the voltage (V) and current (A) divided by the electrode surface area (m²). Meanwhile, after each batch experiment, a 5 mL sample was taken for pH measurement and perchlorate analysis. The pH of the sample was measured using a pH meter (Istek Model 915 PDC; Seoul, South Korea). All samples obtained were first filtered with 0.22 mm Chromdisc® syringe filters followed by a silver cartridge (OnGuard™ II; Dionex, USA) to remove the excess chloride which could otherwise interfere with the perchlorate analysis. They were again filtered with syringe filters. Perchlorate concentrations were then analyzed using a Dionex ICS-1100 ion chromatography (Dionex, Sunnyvale, CA, USA) equipped with an analytical column AS16 (Dionex, USA), a guard column AG16 (Dionex, USA), and a chemical suppressor AERS.
500 (Dionex, USA). The detection limit for perchlorate was 0.62 μg/L. The eluent used to separate the sample ions was 60 mM NaOH solution, prepared by diluting 3.14 mL of 50% (w/v) NaOH solution (Fisher Scientific, New Jersey, US) into 1 L with deionized water.

3. Results

To assess the effects of the number of membrane pairs on the abatement of perchlorate using RED, batch experiments were performed using 5, 10 and 15 pairs of anion and cation exchange membranes. Initial perchlorate concentration equivalent to 1 mg/L and stack solution flow rate of 1.5 mL/min were used. The HC and LC salt solutions flowing through the membrane stack had concentrations equal to 5 M and 0.005 M, respectively, giving a salinity ratio (S.G.) of 1,000. From Fig. 2 it can be observed that both perchlorate removal efficiency and power density output increased linearly with the number of membrane pairs. The maximum power (0.0054 W/m²) produced using 15 pairs of membranes was adequate to reduce 38.76% of perchlorate in the cathodic compartment. At lower N values (N = 5 and 10), the perchlorate removal efficiencies were 13.07% and 22.59% at power densities equal to 0.0029 and 0.0045 W/m², respectively. The increase in power density and pollutant removal at increasing values of N were also observed by other literature investigating RED. Scialdone et al. [22] observed that when 10 and 50 number membrane pairs were used, 3.7 and 55 W/m² were produced by the RED cell (geometric area of 100 cm²) resulting in 99% removal of toxic Cr⁶⁺ at 1 h and 9 min, respectively. In the abatement of a recalcitrant azoic dye (Acid Orange 7), Scialdone et al. [23] showed that higher power density output and faster total organic carbon removal were achieved using 60 pairs rather than 40 pairs of membranes.

Fig. 3 presents the changes in perchlorate removal efficiency and power generation when the salinity ratio of the concentrated (HC) and dilute (LC) stack solutions was varied at 50 (5 M/0.1 M), 100 (5 M/0.05 M), 500 (5 M/0.01 M) and 1,000 (5 M/0.005 M). The number of membrane pairs, stack solution flowrate and initial perchlorate concentration were maintained at 15, 1.5 mL/min, and 1 mg/L, respectively. There was no significant difference in the perchlorate removal efficiencies using 50 and 100 salinity gradients, showing 14.81% and 14.14% removal efficiencies, respectively. However, when it was increased to 500 and 1,000 the perchlorate removal increased up to 25.04% and 38.76%, respectively. Meanwhile, the power density output continuously rose at increasing salinity gradients with the highest value obtained at S.G. 1,000 (0.0054 W/m²) followed by S.G 500 (0.0038 W/m²), S.G. 100 (0.0015 W/m²) and S.G. 50 (0.0009 W/m²).

The influence of stack solution flowrate on perchlorate abatement and power density output is illustrated in Fig. 4. Stack solution flowrate was increased from 1.5 to 4.5 mL/min at initial perchlorate concentration of 1 mg/L.

Table 1
Various parameters employed in this study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of membrane pairs</td>
<td>5, 10, 15</td>
</tr>
<tr>
<td>Salinity gradient (conc. of NaCl in HC and LC salt solutions)</td>
<td>S.G. 50 (HC, 5 M; LC, 0.1 M)</td>
</tr>
<tr>
<td>Stack solution flowrate (mL/min)</td>
<td>1.5, 3.0, 4.5</td>
</tr>
</tbody>
</table>

Fig. 2. Perchlorate removal efficiency and power density output at varying number of membrane pairs. (Experimental conditions: initial perchlorate concentration = 1 mg/L; stack solution flowrate = 1.5 mL/min; S.G. = 1,000).

Fig. 3. Perchlorate removal efficiency and power density output at different salinity gradients. (Experimental conditions: initial perchlorate concentration = 1 mg/L; stack solution flowrate = 1.5 mL/min; N = 15).
salinity ratio of 1,000, and 15 number of membrane pairs. Results showed that both power generation and perchlorate removal efficiencies decreased when stack flowrate was increased. The highest removal of perchlorate (38.76%) was obtained when the flowrates of high and low concentrated stack solution were 1.5 mL/min. The performance of the reactor was lowered at 3 and 4.5 mL/min flowrates showing 22.26% and 18.09% removal efficiencies, respectively.

For the presence of possible intermediates during perchlorate reduction, the ion-exchange chromatograms of perchlorate were checked at initial ($t = 0$ h) and final reaction time ($t = 1$ h) (Fig. 5). Optimal experimental conditions were used: stack flowrate 1.5 mL/min, salinity gradient = 1,000 and number of membrane pairs = 15. From the figure, it is evident that no new peaks are observed after an hour of the RED process suggesting that perchlorate was completely reduced to Cl\textsuperscript{-}. It is difficult to compute the mass balances since the wastewater used in this study is salt water (5% NaCl) with a very high concentration of chloride. The exact amount of chloride produced via the reduction of perchlorate is negligible compared to the total amount of chlorine in the sample.

4. Discussion

In RED, the salinity gradient energy is being converted to electrical energy by the movement of anions and cations towards the anode and cathode, respectively, through the help of a stack assembly. The flow of these charged ions produces an electromotive force between the electrodes causing the electrons to flow from anode to cathode via an external wire. The electromotive force for a stack assembly can be estimated by Nernst Eq. (1):

$$E = \frac{2NaRT \ln \left( \frac{a}{d} \right)}{F}$$

where $E$ is the electromotive force (V), $N$ is the number of membrane pairs, $a$ is the average permselectivity of the membrane pair, $R$ is the universal gas constant (8.314 J/
mol K), $T$ is the temperature (K), $a_i$ and $a_j$ the solute activities in concentrated (HC) and diluted (LC) solutions, respectively, and $F$ is the Faraday constant (96,485 C/mol).

The change in power generation as a function of $N$ can therefore be explained by Eq. (1). It can be seen from the equation that the electromotive force produced by the stack assembly increases with the number of membrane pairs. At a higher $E$ value, more electrons are transferred to the cathode, which is then used for the electrochemical reduction of perchlorate. Perchlorate reduction in the cathode chamber involves several steps, but the rate-determining step is the conversion of perchlorate to chloride anion [Eq. (2)] [15]. This chloride ion is then easily reduced to chloride ions [Eq. (3)].

$$\text{ClO}_3^- + 2H^+ + 2e^- \rightarrow \text{ClO}_2^- + H_2O$$ (2)

$$\text{ClO}_2^- + 6H^+ + 6e^- \rightarrow \text{Cl}^- + 3H_2O$$ (3)

Also, according to Nernst Eq. (1), the electromotive force is positively correlated to the ratio of the solute activities of the concentrated and diluted salt solutions ($a_i/a_j$) [23]. The higher the salinity ratio, the higher the salinity gradient energy and the greater the driving force on the electrode reactions [28]. Scialdone et al. [22] explained that when the salinity gradient is low, the potential penalty caused by the oxidation and reduction of water in the anode and cathode, respectively, is high with respect to the overall potential, hence affecting the reduction of perchlorate in the cathodic chamber.

Meanwhile, stack flowrates promote the fluid mixing inside the stack which improves the ratio of ion concentrations in the bulk liquid and the membrane-solution interface. This in turn increases the power output of the RED cell. However, too low stack flowrate leads to an increase in resistance and a reduction of electromotive force due to the concentration polarization on both sides of the stacked membrane while too high stack flowrate increases pressure drops as well as consumes more pumping energy [24]. Both conditions can result in a decrease in output power density, therefore, it is best to optimize the stack solution flowrate. According to Li et al. [26], optimal flowrates for LC and HC solutions vary for each RED system. The optimal flowrate for the degradation of Orange G using MRC based Fenton process was found to be 0.5 mL/min. In another study, the highest ammonia removal efficiency was achieved when the stack flowrate was 200 mL/min [24]. Scialdone et al. [22] attained faster and complete removal of Cr(VI) via the RED process at flowrate as low as 90 mL/min.

5. Conclusions

This research successfully demonstrated that RED can be a sustainable alternative method for the abatement of perchlorate in salt waters such as spent regenerant brine produced from the ion-exchange process that is the most common treatment method for perchlorate contaminated water. The use of saltwater in the cathode chamber also served as an electrolyte which decreases the use of additional chemicals and hence, operating cost. With RED, about 38.76% of perchlorate (initial concentration, 1 mg/L) and 0.0054 W/m² of power density can be achieved in an hour using 15 pairs of anion and cation exchange membranes at salinity ratio of 1,000 and stack solution flowrate of 1.5 mL/min. Electricity production and perchlorate removal efficiencies were shown to be significantly affected by the number of membrane pairs, salinity gradient and stack solution flowrate. The electromotive force generated by the stack assembly can be enhanced when the number of membrane pairs and salinity gradient are increased. On the other hand, stack solution flowrate exhibited indirect relation both to perchlorate abatement and power density output.

This study is still in the preliminary phase and warrants further experiments, however, the feasibility of the RED cell as an energy-efficient perchlorate reducing technology was successfully demonstrated by the results obtained. The power density obtained in this study was very low but enough to remove 38% of perchlorate from saltwater. With further improvements, like optimization of the number of membrane pairs, stack flowrate and salinity gradient, electricity generation can be increased as well as the perchlorate reduction. Other electrode materials with better conductivity can also be explored for enhanced power output. It is recommended to scale up the RED cell size and carry out experiments in continuous mode to accommodate higher wastewater volumetric capacity and achieve enhanced perchlorate removal efficiency. It is also best to conduct kinetic and optimization studies for large-scale applications. Also, energy capture in the RED stack can be maximized with the use of microbial oxidation of organic matter in the anodic compartment by integrating microbial fuel cell and RED processes.

Acknowledgments

This research was supported by the National Research Foundation, Korea (project no. NRF-2017R1A2B4011805).

Ethical statement

This article does not contain any studies with human participants or animals performed by any of the authors.

References


