Electrochemical reduction of nitrate using divided electrolytic cell by proton exchange membrane

Ho Young Cha[1,2a], Youngho Park[1b], Kee-Won Seong[1c] and Ki Young Park[*1]

[1]*Department of Civil and Environmental Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, Korea*
[2]*Department of Civil and Environmental Engineering, Sejong University, 209 Neungdong-ro, Gwangjin-gu, Seoul 05006, Korea*

Abstract. The electrochemical reduction of nitrate using a divided electrolytic cell in combination with Zn cathode and (Pt)/Ti anode reduced the high concentrations of nitrate (1,000 mg NO_3-N/L). A proton exchange membrane (Nafion-117) was used to increase the nitrate reduction efficiency by preventing the re-oxidation of nitrite produced during the reduction process. The current density and anolyte concentration, considered as parameters, were tested to assess the electrochemical reduction of nitrate. The reduction of nitrate shortened the electrolysis time in proportion to the current density, and the time for 90% removal was 5 h at 5 mA/cm^2, 3 h at 10 mA/cm^2, and 1.8 h at 20 mA/cm^2. The yields of ammonia were approximately 50%-55% of the initial nitrate-nitrogen concentration regardless of the current density and was insignificantly related to the anolyte concentration.

Keywords: anolyte concentration; divided electrolytic cell; electrodialysis; limiting current density; proton exchange membrane

1. Introduction

Currently, biological, chemical, and physical treatment techniques have been studied and applied in the field of nitrate removal from water. Among the current nitrate removal technologies, reverse osmosis (RO), ion exchange (IX), and electrodialysis (ED) are used to separate rather than reduce benign nitrogen gas (Park *et al.* 2018, Werth *et al.* 2021). Therefore, the above technologies produce highly concentrated nitrate, which is a serious problem that requires frequent regeneration of the resin and cleaning of the system (Schoeman and Steyn 2003, Samatya *et al.* 2006, Min *et al.* 2021). Biological treatment for nitrate at levels of approximately 20-300 mg N/L is considered a more economical process than IX, ED, and chemical reduction. However, biological denitrification is slow and incomplete; it requires intensive maintenance and a constant supply of organic substrates for optimal C/N ratio, thereby, affecting the disposal of biomass sludge (Chiu *et al.* 2007). The chemical reduction of nitrate using hydrogen or metals, for example iron and Pd-based catalysts, is an attractive alternative (Fanning 2000, Barrabesa and Sab 2011, Constantinoua *et al.* 2010, Pintar and Batista 2007, Kim *et al.* 2013), but low efficiency, the disposal of large amounts of sludge, concerns regarding the process stability and safety, and high costs have prevented its wide application

(Hiscock *et al.* 1991).

To overcome these drawbacks, electrochemical reduction has been proposed as an alternative technology in the removal of nitrates, nitrites, and ammonia in alkaline media (Horányi and Rizmayer 1985). Since then, the electrochemical reduction of nitrate has been studied using various cathode materials, such as Zn, Pb, Ni, Fe, Cu, Ti, Sn, Cu-Zn, Cu-Ni, Au, and Ag. (Dima *et al.* 2003, Li *et al.* 2009, *Lee et al.* 2018).

Furthermore, electrochemical methods are advantageous, such as the lack of chemicals required before or after the treatment, no sludge production, limited area occupied by the plant, and relatively low investment costs (Li *et al*. 2009, Min *et al*. 2019). Therefore, for the removal of ions from industrial wastewater, such as metal plating, electronics, nuclear or fertilizers, and concentrated wastewater from drinking water, electrochemical reduction is a promising route (Garcia-Segura *et al.* 2018, Min *et al.* 2020, Oh *et al.* 2020).

Usually, nitrate is reduced during the cathodic cycle, mainly to nitrite and nitrogen gas. Recently, many studies have focused on electrochemical treatment methods (Kim *et al.* 2013, Park *et al.* 2017, Lee *et al.* 2018, Xu *et al.* 2018) Polatides *et al.* (2005) indicated that nitrate was reduced during the cathodic cycle to nitrite, ammonia, and nitrogen, which is electrochemically inactive. However, the reduced nitrite could be re-oxidized to nitrate in the anode by reverse reactions (Reyter *et al.* 2011). Consequently, an ion-exchange membrane could be used as a barrier between the cathode and the anode, and only the proton produced on the anode side would be permitted to the cathode side; although, the limited lifetime of the electrolytic cells and the consumption of electricity could result in major drawbacks (Carmo *et al.* 2013).

*Corresponding author, Ph.D., Professor
 E-mail: kypark@konkuk.ac.kr
[a] Ph.D.
[b] M.Sc. Student
[c] Ph.D., Professor

The Nafion-117 membrane with the Ti/Pd-Co-Cu cathode was successfully applied to separate the cathode from the anode compartment (Szpyrkowicz *et al.* 2006). Membrane electrolysis first produced Cl_2 via the membrane electrolysis of brine. Recently, the membrane electrolysis method was used for nitrate reduction in water to avoid the generation of undesirable byproducts such as nitrite and ammonium (Reyter *et al.* 2011, Bosko *et al.* 2014, Vazač *et al.* 2014). The operating parameters with a significant influence on the electrochemical denitrification processes include the electrode material, cathode/anode surface area ratio, current input, pH, conductivity, sodium chloride (NaCl) concentration, and initial nitrate ion concentration (Bosko *et al.* 2014).

The reduction of both nitrate and nitrite in acidic media occurs at more positive potentials than in the alkaline media (Bouzek *et al.* 2001); nitrate reduction in acidic solution occurs on Cu, Cd, and Zn, but not on Ni and Pb (Scharifker *et al.*, 2000). The reduction of nitrate in alkaline media has attracted considerable attention on fundamental and applied research in several industrial sectors (Garcia-Segura *et al.* 2018). A reduction in the nitrate concentration from 1,000 to 18 mg/L was achieved in a weakly alkaline $NaHCO_3$ solution (Paidar *et al.* 2002).

Currently, the industrial use of electrochemical nitrate removal is challenged in several ways; for example, low selectivity to nitrogen, formation of nitrite intermediates and release of ammonia, unsuitable electrodes, change in cathode properties due to deposition of metal impurities on the cathode, release of off-gases, requirement of significant quantities of make-up water, and disposal of NaOH by-products (Martínez *et al.* 2007). One of the main issues in the electrochemical reduction of nitrate is the production of ammonia, which causes environmental concern and is restricted in certain industrial sectors, such as the drinking water industry.

Ideally, electrocatalytic nitrate reduction can sidestep the limitations of the other alternatives, provided that an efficient and selective reduction of nitrate to N_2 gas is achieved. Low-temperature catalytic denitrification driven by electrical energy is particularly interesting, considering that the driving force can, in principle, be obtained from renewable sources, thus creating a veritable "green" approach to nitrate reduction (Duca and Koper 2012). divided electrolytic cell with Nafion-117 as a proton exchange membrane (PEM) with Zn cathode and (Ir+Ru)/Ti

The main objectives of this study are to (1) reduce the high nitrate concentration (1,000 mg NO_3-N/L) using a divided electrolytic cell with Nafion-117 as a proton exchange membrane (PEM) with Zn cathode and (Ir+Ru)/Ti anode, and (2) investigate the effect of operating parameters such as current density and anolyte concentration (NaCl) on nitrate reduction.

2. Materials and methods

2.1 Experimental setup

The electrolytic cell (Zignentech Co. Ltd., MEA-100, Korea), made of acrylic material, is a device with two half compartments designed to install an anode and a cathode. The assembly of an electrolytic cell is completed by placing an ion exchange membrane between the anode and cathode compartments (Fig. 1). In this study, the effective volumes of the anode and cathode compartments were 90 and 180 mL, respectively. Additionally, Nafion-117 (DuPont, Inc.), which only conducts protons (H^+), was used as an ion-exchange membrane, separating the anode and cathode compartments.

The surface area of both, the cathode and anode was 84 cm^2 (8.4 × 10 cm) and the inter-electrode distance was 30 mm. The cathode materials used were Zn and the anode used was a Pt/Ti plate (Pt 3 microns), which was washed with acid and deionized water before the next test. The DC power supply (Odecore Co. Ltd., EX 100-18, Korea) had a voltage range of 0-105 V and a current range of 0-18.9 A, and operated at constant current (CC) and constant voltage (CV) modes.

2.2 Experimental methods

Synthetic nitrate solution (1,000 mg NO_3-N/L) was prepared by dissolving sodium nitrate in deionized water, and NaCl was used as an anode electrolyte (anolyte) at concentrations of 0.01, 0.1, and 0.5 M, to investigate the chloride oxidation. The DC power supply was controlled at CC mode at current densities of 5, 10, and 20 mA/cm^2.

During the electrolysis, 1 mL of sample was collected at specific sampling time (i.e., every 0.5 h and/or every 1 h) from the anode and cathode compartments, respectively. The collected samples were analyzed for the concentrations
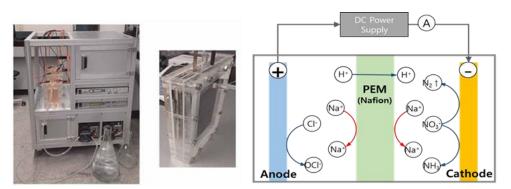

Fig. 1 Schematic diagram and photograph of the electrochemical reactor

of nitrate, nitrite, and ammonia. The pH of the solutions (initial pH, 6.5~6.8) were not adjusted, and the pH variation was monitored in this study. The samples were analyzed immediately to minimize the effect on pH. If any delay was observed in analysis, the pH was adjusted by adding an appropriate amount of 0.1 N H_2SO_4 to suppress the change in the sample. The pH was measured in each compartment and the changes were monitored during electrolysis. Furthermore, the pH was measured separately to prevent contamination of the analytical sample. After the measurement, the solution was immediately poured into the respective compartment. All the experiments were performed at room temperature (20-22°C).

2.3 Experimental analysis of nitrate and its by-products

In all the experiments, 1 mL of sample was collected at each sampling time (i.e., 0.5 h and/or every 1 h) from the anode and cathode compartments. All measurements of nitrate and its by-products were conducted using standard methods (HACH, USA). The concentration of nitrate was analyzed using the chromotropic acid method. Nitrite and ammonia were analyzed using diazotization and salicylate methods, respectively. The concentration of chlorine was also analyzed from standard methods for the examination of water and wastewater (4500-Cl).

3. Results and discussion

3.1 Effect of current density

The effect of current density on nitrate reduction was investigated using a Zn cathode and an (Ir+Ru)/Ti anode. The experiment was conducted in a batch operation mode in divided electrolytic cells with PEM. Applying a potential gradient moves anions the anode and cations to the cathode, causing the ions to move. As the current density changes, the nitrate removal efficiency has a logarithmic dependence. The performance of electrolysis is compared with a polarization curve obtained by plotting the cell voltage against the current density. Overvoltage and ohmic losses increase with increasing current density. Electrolysis cell performance is determined in a membrane electrode assembly consisting of a PEM, a positive electrode and a negative electrode. One of the biggest advantages of PEM electrolysis is that it can operate at high current densities (Carmo *et al.* 2013).

The experimental conditions were as follows: the current supply was in the CC mode, and the supply currents in each condition were 0.42, 0.84, and 1.68 A. Therefore, dividing this current by an electrode area of 84 cm^2 results in a current density of 5, 10, and 20 mA/cm^2. The initial concentration of the electrolyte solution in each compartment was the same; the anolyte, NaCl at 100 mM and catholyte at 1,000 mg NO_3-N/L (71.4 mM).

Fig. 2 shows the effect of current density on electrochemical reduction of nitrate using a divided electrolytic cell separated by PEM (Nafion-117). According

to Ohm's law, R = V/I; current and voltage are proportional to each other at the same resistance. Therefore, the voltage after 2 h of stabilization was 4.5 V at 5 mA/cm^2, 5.3 V at 10 mA/cm^2, and 6.69 V at 20 mA/cm^2, respectively. However, the voltage change from 2 h - 6 h was less than 0.2 V.

In this experiment, using an electrolytic cell separated by a proton exchange membrane, there is no passage of ions between the anode and cathode compartment, and due to the nature of the Nafion membrane, only proton ions migrate from the anode to the cathode compartment. As a result, nitrate is reduced to nitrogen gas at the cathode using the transferred proton ions. According to Ohm's Law, as the current increases, the voltage increases and the resistance increases. Therefore, the increase in temperature will be caused by an increase in resistance due to an increase in current and voltage.

In all the three cases, the temperature rapidly increased within 2 h and continued to increase gradually after 2 h. Initially, temperatures ranged from 20.0 to 22.0°C; after 2 h, the temperatures were 26.0°C at 5 mA/cm^2, 29.0°C at 10 mA/cm^2, 39°C at 20 mA/cm^2. Akarsu *et al.* (2017) reported that the temperature of the electrode increases over time, regardless of the material of the electrode, and that the higher the applied voltage, the higher the temperature. Temperature is an important parameter during the electrolysis of nitrates in water because it affects the water content and ion transport water in the anion exchange membrane (El Midaoui *et al.* 2002) and membrane resistance generally decreases with increasing temperature due to an increase in ion mobility through the membrane (Raka *et al.* 2021). The efficiency of an electrochemical process increases with increasing current density at high temperatures (Modisha and Bessarabov 2016) and many studies have demonstrated that the electrochemical reduction efficiency of nitrate increases with increasing temperature (El Midaoui *et al.* 2002, Xu *et al.* 2018, Guo *et al.* 2020).

In contrast, the pH variation was similar in all the three conditions. The anolyte pH (initial pH 5.9-6.1) rapidly decreased to less than 1.57-2.35, within 30 min; while the catholyte pH (initial pH 6.1-6.2) rapidly increased to 12.7-12.8, or greater within 30 min. The pH decrease in the anolyte can be explained by the effect of dissociated hydrogen ions (H^+) during the reaction between chlorine and water, produced by the oxidation reaction of chloride ion on the anode surface. The pH increase in the catholyte can be explained by the effect of hydroxide ions (OH^-) generated on the cathode surface when nitrate is converted to nitrite and ammonia, which indirectly indicates nitrate reduction. Moreover, another cause of pH change was weighted by water electrolysis. The causes of pH changes in the anode and cathode compartments can be explained with reference to Eqs. (1)-(7) as follows:

(Reaction of cathode compartment)

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \tag{1}$$

$$NO_3^- + 3H_2O + 5e^- \rightarrow 0.5N_2 + 6OH^- \tag{2}$$
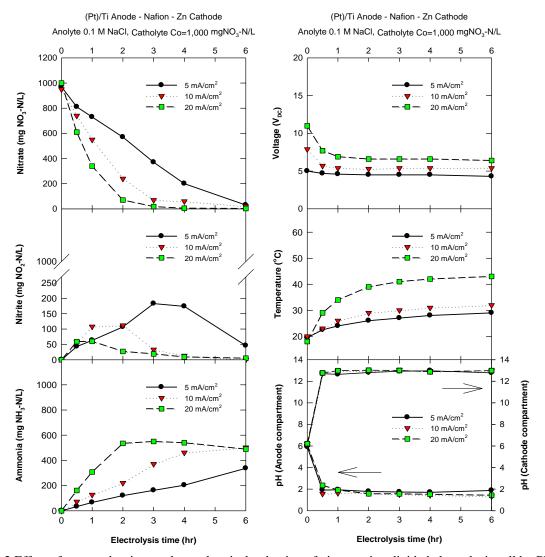
Fig. 2 Effect of current density on electrochemical reduction of nitrate using divided electrolysis cell by PEM

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^- \qquad (3)$$

$$NO_2^- + 2H_2O + 3e^- \rightarrow 0.5N_2 + 4OH^- \qquad (4)$$

$$NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 7OH^- \qquad (5)$$

(Reaction of anode compartment)

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (6)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad (7)$$

The results of nitrite generation were interesting. The higher the current density (and/or voltage), the lower the nitrite concentration, and faster the nitrite generation occurs. The highest concentrations were 183 mg NO_2-N/L at 3 h (5 mA/cm^2), 112 mg NO_2-N/L at 2 h (10 mA/cm^2), and 60 mg NO_2-N/L at 1 h (20 mA/cm^2). The behavior of nitrite between generation and disappearance was characteristic of the reaction intermediates.

The result of ammonia is noteworthy; it reacted with the chlorine produced in the anode compartment. As a result, the highest concentration of ammonia appeared faster at a higher current density (and/or voltage). The maximum yields were 337 mg NH_3-N/L in 6 h (5 mA/cm^2), 502 mg NH_3-N/L in 6 h (10 mA/cm^2), and 550 mg NH_3-N/L at 3 h (20 mA/cm^2). The ammonia yield at 5 mA/cm^2 is estimated from the results of 10 and 20 mA/cm^2, and is expected to increase to approximately 500 under sufficient reaction time. Thus, the yield of ammonia could be approximately 50%–55% of the initial nitrate-nitrogen concentration, regardless of the current density.

Fig. 3 presents the reactions in the anode compartment. With only NaCl in the anode compartment, the chloride ion is oxidized on the anode surface to form Cl_2, which immediately reacts with water and dissociates into HOCl, Cl^-, and H^+ (Eqs. (6) and (7)).

The primary and secondary end products of the breakpoint reaction were N_2 and nitrate, respectively (Eqs. (8) and (9)). The weight ratio of chlorine to ammonia that is required to reach the breakpoint, assuming N_2 is the major end product is, 1:7.6; the ratio on a molar basis is, 1:1.5 (March and Gual 2007).

$$NH_4^+ + 1.5\ HOCl \rightarrow 0.5N_2 + 1.5H_2O + 2.5\ H^+ + 1.5Cl^- \qquad (8)$$

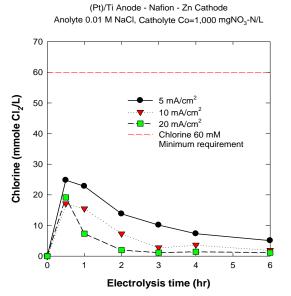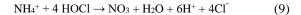Fig. 3 Chlorine generation according to current density at anolyte 100 mM NaCl

$$NH_4^+ + 4\,HOCl \rightarrow NO_3 + H_2O + 6H^+ + 4Cl^- \tag{9}$$

Under these experimental conditions, the NO_3-N molar concentration (mM) in the cathode solution was 71.4 mM; the yield of ammonia was approximately 0.55 and the concentration of ammonia was approximately 40 mM. If this value is substituted in Eq. (1), 60 mM of HOCl is required. Additionally, according to the experimental conditions, the molar concentration of anolyte (NaCl) was 100 mM, which was approximately 150% of the required amount. Particularly, producing 60 mM HOCl was necessary, which is the initial molar concentration, considering the Cl_2 yield; therefore, the initial concentration should be at least 100 mM (assuming a yield of 0.6).

However, the maximum yield of chlorine was 25 mM at 5 mA/cm² (0.5 h), 17 mM at 10 mA/cm² (0.5 h), and 19 mM at 20 mA/cm² (0.5 h). These values revealed a steady decrease after 0.5 hours of electrolysis and were less than half of the required chlorine (60 mM). Therefore, it was concluded from the result of the anodic reaction that the concentration of the anolyte should be increased.
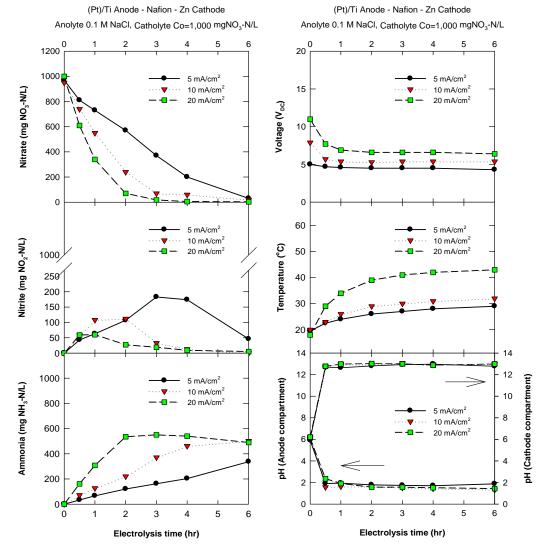

Fig. 4 Effect of anolyte concentrations on electrochemical reduction of nitrate using divided electrolysis cell by PEM
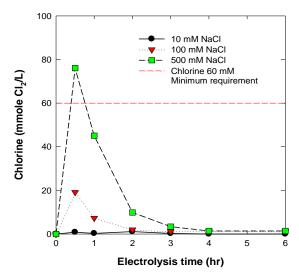
3.2 Effect of anolyte concentration

The effect of anolyte concentration on nitrate reduction was investigated using Zn cathode and (Ir+Ru)/Ti anode. The experiment was conducted by batch operation of divided electrolytic cells with PEM. For the experimental conditions, the current supply was constant current mode, and the supply current at each condition was the same at 1.68 A and 20 mA/cm^2 in terms of current density (electrode area 84 cm^2). The initial concentration of catholyte was 1,000 mg NO$_3$-N/L (71.4 mM), and the concentration of anolyte was 10, 100, and 500 mM, respectively.

Fig. 4 shows effect of anolyte concentrations on electrochemical reduction of nitrate using divided electrolysis cell with PEM (Nafion-117). According to Ohm's law, I = V/R, voltage and resistance are proportional to each other at the same current and the resistance affects voltage and temperature. In this experimental condition, the concentration of the catholyte of 10, 100 and 500 mM NaCl can be considered as the resistance of each condition.

In electrolysis, the voltage decreases with the increase in ion activity due to the increase in temperature. Additionally, as the resistance increases due to the decrease in the ion activity, the voltage increases. The voltage of the intermediate stabilization zone plateaued. Therefore, the change in voltage can be predicted by considering the change in temperature. First, when the anolyte concentration was 500 mM NaCl, the temperature gradually increased from 16.4°C to 29.10°C for 6 h. When the concentration of the anolyte was 100 and 10 mM NaCl, the temperature increased sharply until 2 h and gradually increased after 2 h. After 6 h of electrolysis, the temperature was 43 and 59.5°C at 100 and 10 mM NaCl, respectively. In nitrate reduction operating in CC mode, the temperature rise is the main reason for the decrease in ions in the solution due to nitrate reduction. Thus, the resistance increases continuously under constant current conditions, and consequently, the temperature rises.

Similar to the previous case, the pH change was from 6.1 to 6.3 in the initial phase, but the pH of the anolyte rapidly decreased to 1.7 to 2.35 or less within 30 min. Conversely, the pH of the catholyte increased rapidly from 6.1 to 6.3 in the initial period to 12.6 to 13.0 during the same period of time. The nitrite generation results showed a temporary increase in the concentration at 0.5 h and 1 h, which was negligible after 2 h. The maximum concentration at 1 h was 104 mg NO$_2$-N/L at 10 mM NaCl, 60 mg NO$_2$-N/L at 100 mM NaCl, and 129 mg NO$_2$-N/L at 500 mM NaCl. The behavior of nitrite between generation and disappearance was typical of the reaction intermediates. As a result, ammonia production was the highest at 2 h, when nitrate and nitrite were practically removed, and was insignificantly related to the anolyte concentration. The ammonia yield was 51.4%, 53.5%, and 51.6% at 2 h, respectively, and decreased after 2 h.

Fig. 5 shows the reaction for chlorine generation in the anode compartment during electrolysis. Because only NaCl is present in the anode compartment, the chloride ion is oxidized on the anode surface to form Cl$_2$, which reacts

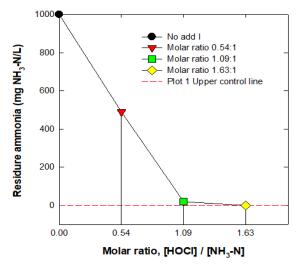Fig. 5 Chlorine generation according to anolyte concentration at 20 mA/cm^2

Fig. 6 Ammonia removal by break point chlorination

with water and dissociates into HOCl, Cl$^-$, and H$^+$ (Eqs. (6) and (7)). The primary and secondary end products of the breakpoint reaction were N$_2$ and nitrate, respectively (Eqs. (8) and (9)).

Under these experimental conditions, the molar concentration of nitrate in the catholyte was 71.4 mM; ammonia yield was approximately 0.55 and the molar concentration of ammonia was approximately 40 mM. If this value is substituted in Eq. (8), 60 mM of HOCl is required. Therefore, it was necessary to produce 60 mM HOCl, which is the initial molar concentration, considering the Cl$_2$ yield. However, only one result satisfied this value; 71 mM of chlorine was produced in 30 min under conditions of 500 mM NaCl and 20 mA/cm^2 current density. An experiment was conducted to reduce nitrate in the cathode compartment and simultaneously oxidize chloride ions in the anode compartment. However, the breakpoint chlorination experiment, in which the subsequent two products reacted and converted to nitrogen

gas, was discontinued. This is because it is very difficult to balance the two reaction rates.

4. Conclusions

In this study, the electrochemical reduction of nitrate using a Nafion-117 divided electrolytic cell with Zn cathode and (Pt)/Ti anode resulted in the reduction of high concentrations of nitrate (1,000 mg NO_3-N/L). The effects of current density and anolyte concentration on the electrochemical reduction of nitrate were investigated. From the results of the effect of the current density, the maximum nitrite concentration was lowered and the time to reach the maximum nitrite concentration was faster. The nitrite behavior between generation and disappearance was typical of the reaction intermediates. The highest concentration of ammonia was generated rapidly at higher current densities, and the yield of ammonia was approximately 50%-55% of the initial nitrate-nitrogen concentration, regardless of the current density. From the results of the effect of the anolyte concentration, the nitrite generation results showed a temporary increase in the concentration at 0.5 and 1 h, and a negligible concentration after 2 h. The yield of ammonia was the highest at 2 h, when nitrate and nitrite were almost completely removed, and was approximately 51%-54% of the initial nitrate-nitrogen concentration and its relation with the anolyte concentration was insignificant.

Acknowledgments

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