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Selective reduction of highly concentrated nitrate by electrochemical method using a combination of Zn and Ti/Ir–Ru electrodes

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ABSTRACT

Treatment of wastewater contaminated by highly concentrated nitrate was studied by electrochemical method using a combination of Zn cathode and Ti/Ir–Ru anode in an undivided cell. We observed that almost 76% of initial nitrate (1,000 NO_3^-–N mg/L) was removed in 8 h by electrodenitrification without significant production of undesirable by-products (i.e., nitrite and ammonia). Variations of pH and temperature were also monitored during the electrochemical nitrate reduction, which showed an increase in both pH (up to 12.5) and temperature (up to 41.5°C), resulting in the enhanced nitrate reduction in this study. The nitrate removal efficiency increased (30% → 76% → 84%) as the current density increased (20 → 40 → 60 mA/cm^2), but it was not a linear increase due to the increase of hydrogen evolution at high current density. The increase in paired electrode number from one to four led to the enhanced nitrate removal from 72% to 100% in 8 h reaction time. Moreover, we observed a remarkable increase in nitrate removal by using a combination of one anode and two cathodes (86% in 8 h) without productions of nitrite and ammonia due to the acceleration of nitrate reduction by increasing number of cathode.

Keywords: Nitrate; Electrochemical method; Zn cathode; Ti/Ir–Ru anode; Operation parameters

1. Introduction

Contamination of nitrate (NO_3^-) in water resources has gradually increased in the world due to excessive consumption of fertilizer in agricultural activities and discharge of poorly treated wastewater from industrial facilities [1–4]. Because nitrate can cause methemoglobinemia for infants and can be potentially transformed to carcinogenic nitrosamine in human body [5,6]. World Health Organization has set a strict regulation at the maximum contaminant level (10 NO_3^-–N mg/L) of nitrate for drinking water [7]. In the efforts to effectively remove nitrate, a variety of nitrate treatment technologies have been developed using biological treatments, reverse osmosis, ion-exchange, and catalytic reaction [8–11]. However, some drawbacks have arisen during the biological treatments (e.g., need of careful operation for optimal microbial growth and production of excessive amount of microbial sludge), membrane processes (e.g., need of secondary treatment for removal of highly concentrated nitrate after the treatment), and catalytic reaction (e.g., need of efficient collection system for precious noble catalysts after its use).

To overcome the problems, a novel electrochemical method has been developed for efficient, easy, and economical denitrification process [12–16]. A variety of monometallic

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cathodes (e.g., Cu, Ag, Ni, Sn, Bi, Pb, Al, Zn, and In), the reactive sites for the nitrate reduction to nitrite (NO_2^-), ammonia (NH_4^+), and nitrogen gas (N_2), have been investigated for their electrochemical activity toward the nitrate reduction by using cation exchange membrane in divided electrochemical cell [17,18]. Although Pd showed a remarkable selectivity toward a desirable by-product (i.e., N_2) (90%) [19], most of monometallic cathodes revealed the low N_2 selectivity (<67%) [17,18]. This indicates that use of expensive noble metals can guarantee the high N_2 selectivity during the electrochemical nitrate reduction in divided electrochemical cell.

On the other hand, the possibility of oxidation of ammonia to N_2 has also been reported by the electrochemical method using Ti/IrO_2–Pt and IrO_2 anodes [20,21]. In the presence of chloride ion in the solution, chlorine gas can be generated at the anode surface ($2Cl^- \rightarrow Cl_2 + 2e^-$), then the chlorine generated can immediately react with water to form hypochlorous acid (HOCl) ($Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$), which can also be changed to hypochlorite ion (OCl^-) in the range of pH from 6 to 12 [21]. Therefore, the oxidation of ammonia to N_2 gas could be expected by both hypochlorous acid and hypochlorite ion ($2NH_3 + 3HOCl \rightarrow N_2 + 3HCl + 3H_2O$ and $2NH_3 + 2OCl^- \rightarrow N_2 + 2HCl + 2H_2O$) in undivided electrochemical cell. Indeed, Li et al. [22–24] reported the simultaneous reduction of nitrate and oxidation of ammonia by a combination of cathodes (Fe, Cu, Ti, and Cu–Zn) and an anode (Ti/IrO_2–Pt) in the undivided electrochemical cell, resulting in no detection of ammonia and nitrite as by-products.

For the electrochemical cell, the type of cathode and anode can significantly influence the efficiency of nitrate removal and N_2 selectivity. In the cathode part, Cu and Fe have shown the effective nitrate reduction during the operation of undivided electrochemical cell [23], but monometallic Zn has seldom been investigated in the system. For the anode part, both IrO_2 and RuO_2 have shown the higher performance for ammonia oxidation than Pt anode [21] and Ti/TiO_2–RuO_2, Ti/RuO_2, and Ti/IrO_2–Pt were well examined as effective anodes [25,26]. This implies that the use of Ir and Ru (Ti/IrO_2–RuO_2, Ti/Ir–Ru) may lead to the enhanced N_2 selectivity by ammonia oxidation in undivided electrochemical cell. However, a limited knowledge has been provided for the combination of nitrate reduction by Zn cathode and ammonia oxidation by Ti/Ir–Ru anode to date. In addition, most of the previous studies were used a relatively low concentration of nitrate (up to several hundred of NO_3^-–N mg/L) even though the nitrate wastewater usually contains higher than 1,000 NO_3^-–N mg/L after the productions of fertilizers, explosives, and foods [27]. Therefore, the main objectives of this study were to (1) perform the reduction of highly concentrated nitrate (i.e., 1,000 NO_3^-–N mg/L) using a combination of Zn cathode and Ti/Ir–Ru anode in undivided electrochemical cell, (2) investigate the effect of operating parameters such as current density, number of paired cathode and anode, NaCl concentration, and (3) improve the N_2 selectivity by adjusting the number of cathode and anode.

2. Experimental

2.1. Electrochemical apparatus

A 2 L of rectangular parallelepiped electrochemical cell was manufactured with acrylic material (Fig. 1). For each cell, a Zn plate and a Ti/Ir–Ru plate (IrO_2 50 wt%; RuO_2 50 wt%) were used as the cathode and anode, respectively, with the same surface area of 150 cm^2 (10 × 15 cm). The spacing of each electrode was 5 mm. We applied DC power supply in a voltage range of 3.6–5.0 V and a current range of 3–18 A in this study.

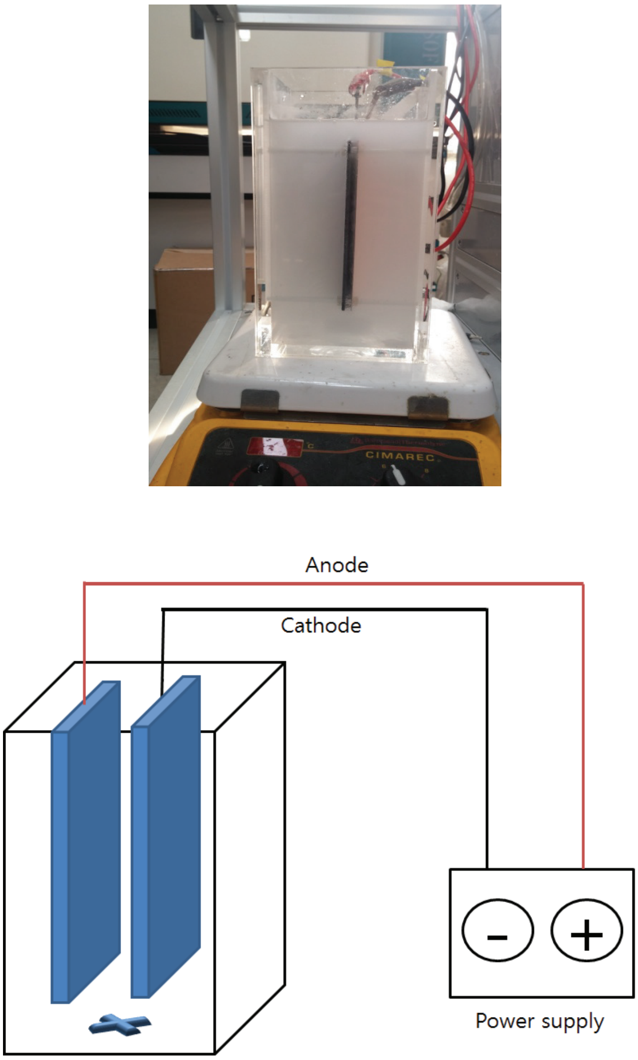

Fig. 1. Schematic experimental apparatus.

2.2. Experimental methods

In general, 1,000 NO_3^-–N mg/L of synthetic nitrate solution was prepared by sodium nitrate in deionized water. Different concentration of NaCl was added into the prepared nitrate solution as a background electrolyte. Approximately, 2 L of synthetic nitrate solution containing NaCl was poured into the electrochemical cell and the reaction initiated by application of specific current density. A 2 mL of sample was collected at each sampling time (i.e., every 1 h) during the electrochemical nitrate removal and used for analysis of nitrate, nitrite, and ammonia concentrations. The solution pH (initial pH: 6.5–6.8) was not maintained in this study. The striping of ammonia was tested by capturing stripped ammonia using H_2SO_4 solution at pH 12 and temperature around

40°C during the experiments. To investigate the effect of current density, different currents were applied at 20, 40, and 60 mA/cm^2 using one anode and one cathode (1A-1C) electrochemical cell. Effect of surface area (i.e., number of paired electrodes) was investigated using 1A-1C, 2A-2C, and 4A-4C of electrodes. We also investigated the effect of NaCl concentration (0.1 and 0.25 M) using 2A-2C electrochemical cell. Finally, the effect of number of electrode was investigated by using 2A-1C and 1A-2C in this study.

2.3. Analytical methods

All measurements for nitrate and its by-products were conducted by following standard methods (Hach: nitrate (method 8039), nitrite (method 8507), ammonia (method 10031)). The concentration of nitrate was analyzed by standard method (chromotropic acid method). Nitrite and ammonia were analyzed by diazotization and salicylate methods, respectively. The concentration of chlorine was also analyzed by standard methods for the examination of water and wastewater (4500-Cl). The removal of nitrate ($R_{NO_3^-}$, Eq. (1)) and product selectivity ($S_{product}$, Eqs. (2)–(4)) was calculated as follows:

$$R_{NO_3^-}(\%) = 100 \times \frac{\left[NO_3^- - N\right]_i - \left[NO_3^- - N\right]_f}{\left[NO_3^- - N\right]_i} \tag{1}$$

$$S_{NO_2^-}(\%) = 100 \times \frac{[NO_2^- - N]_f}{\left[NO_3^- - N\right]_i - \left[NO_3^- - N\right]_f} \tag{2}$$

$$S_{NH_4^+}(\%) = 100 \times \frac{[NH_4^+ - N]_f}{\left[NO_3^- - N\right]_i - \left[NO_3^- - N\right]_f} \tag{3}$$

$$S_{N_2^-}(\%) = 100 \times \frac{\left[NO_3^- - N\right]_i - \left[NO_3^- - N\right]_f - \left[NO_2^- - N\right]_f - \left[NH_4^+ - N\right]_f}{\left[NO_3^- - N\right]_i - \left[NO_3^- - N\right]_f} \tag{4}$$

The subscripts *i* and *f* denote the initial and final concentrations of each N species.

3. Results and discussion

3.1. Electrochemical removal of nitrate by Zn cathode and Ti/Ir–Ru anode

Fig. 2(a) shows the variations of nitrate and by-products (i.e., nitrite–N and ammonia–N) during the electrolysis by 1A-1C electrode in the presence of 0.5 M NaCl at a constant current density (i.e., 40 mA/cm^2). The concentration of nitrate continuously decreased to 236 mg/L in 8 h with production of insignificant amounts of by-products. The variation of pH during the reaction showed a rapid increase (pH 11.7) within 1 h then slow increase up to 12.5 in 8 h (Fig. 2(b)), indicating that the electrochemical reduction of nitrate in this study proceeded mostly at high alkaline condition. We did not observe the significant ammonia stripping in this experiment. The increase in pH was mainly due to the electrochemical reduction of nitrate and hydrolysis, which can produce large amounts of hydroxyl ion during the reaction [22]. It has been reported that (1) decrease of pH can promote the hydrogen formation showing a negative effect on the nitrate reduction and (2) alkaline media can suppress the hydrogen evolution during the nitrate reduction, resulting in the enhanced nitrate reduction [24]. The productions of ammonia and nitrite were almost negligible during the electrochemical reduction of nitrate in this study. It has been well known that the production of ammonia increased at the first stage then continuously decreased to zero value at the last stage in undivided electrochemical cell [22]. This shows that the ammonia generated from Zn cathode can be effectively oxidized to N_2 by both hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) produced from Ti/Ir–Ru anode as described above. We also observed an increase of solution temperature from 28°C to 41.5°C in 5 h and then decreased to 36°C in 8 h (Fig. 2(b)). It has been reported that the increase of temperature can enhance the diffusion rate and the adsorption strength [24]. Therefore, we could conclude that both uncontrolled pH and temperature positively influenced the effective nitrate reduction to N_2 in this study.

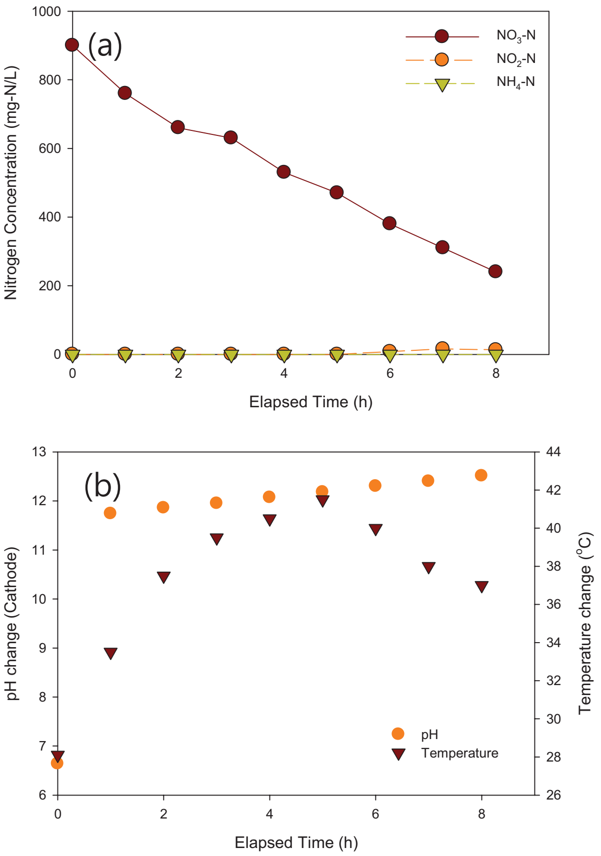

Fig. 2. (a) Removal of nitrate and its by-products production during the electrochemical nitrate reduction in an undivided cell. (b) Variations of pH and temperature during the electrochemical nitrate reduction in this study. Experimental condition: 1A-1C electrode in the presence of 0.5 M NaCl at current density of 40 mA/cm^2.

3.2. Effect of current density

Fig. 3 shows the effect of applied current density on the electrochemical nitrate reduction by 1A-1C electrode in the presence of 0.5 M NaCl. We observed almost 33%, 76%, and 84% of removal efficiency in 8 h reaction time at current density of 20, 40, and 60 mA/cm^2, respectively. The result obtained from this study showed that the increase of current density in undivided electrochemical cell, especially working with Zn and Ti/Ir–Ru electrodes can positively influence the nitrate reduction efficiency. However, the reduction efficiency of nitrate did not linearly increase with respect to increase of current density. This may be due to the increase of hydrogen evolution at high current density, which can increase the power consumption. It has been reported that lower current density can produce small amount of hypochlorite acid because of linear relationship between ammonia oxidation rate and current density, which can result in high production of ammonia with low N_2 selectivity [28]. However, we did not observe the significant productions of nitrite and ammonia at different current densities (data not shown), indicating that the current density of 20 mA/cm^2 was already high enough to produce a certain amount of hypochlorite acid in this study. By considering both the nitrate reduction efficiency and energy consumption, we selected 40 mA/cm^2 as an optimal current density for further investigations.

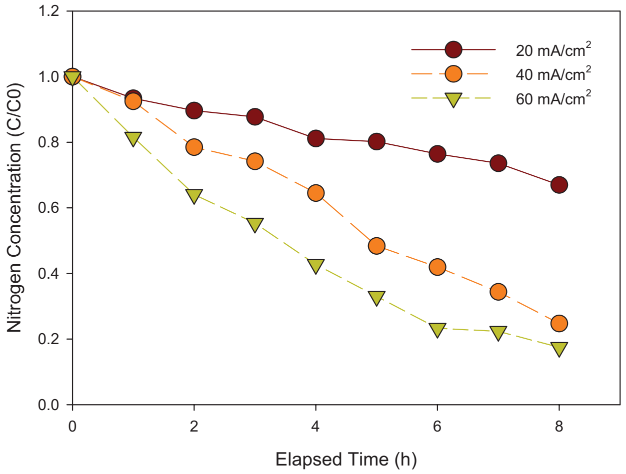

Fig. 3. Effect of current density on the electrochemical nitrate reduction. Experimental condition: 1A-1C electrode in the presence of 0.5 M NaCl at current density of 20, 40, and 60 mA/cm^2.

3.3. Effect of number of cathode and anode

Fig. 4(a) shows the effect of number of paired electrode on the electrochemical nitrate reduction with NaCl (0.5 and

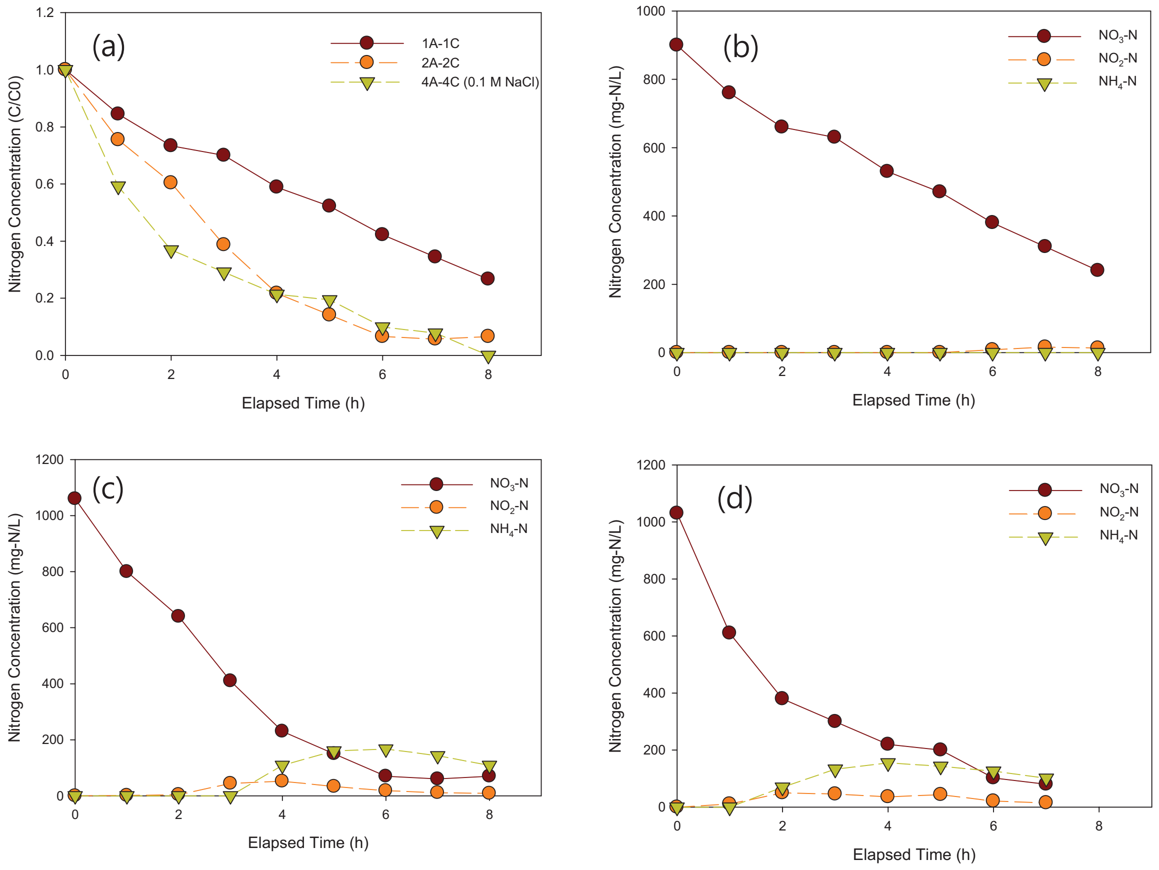

Fig. 4. (a) Effect of paired electrode number on the electrochemical nitrate reduction and production of by-product in cases of (b) 1A-1C, (c) 2A-2C, and (d) 4A-4C. Experimental condition: 1A-1C and 2A-2C with 0.5 M NaCl at current density of 40 mA/cm^2, 4A-4C electrodes with 0.1 M NaCl at current density of 40 mA/cm^2.

0.1 M NaCl). The nitrate removal efficiency increased from 72% to 94% in 8 h as the paired electrode increased from one to two. The increase in reactive surface area for electrochemical reduction of nitrate may increase the removal efficiency of nitrate. However, the concentrations of ammonia (up to $S_{NH_4^-} = 17\%$) and nitrite (up to $S_{NO_2^-} = 5\%$) significantly increased during the nitrate removal using 2A-2C (Fig. 4(c)) as compared with that of 1A-1C (Fig. 4(b)), indicating that the increase in number of paired electrode can inhibit the N_2 selectivity. The removal efficiencies in the range of 4–8 h reactions by using 4A-4C with 0.1 M NaCl (Fig. 4(d)) were very similar with those obtained from 2A-2C, which resulted in the production of significant amounts of either nitrite or ammonia. The N_2 selectivity during the electrochemical nitrate reduction can be dependent on the several factors (e.g., pH, current density, and background electrolyte). When we increased the number of paired electrode, the reduction kinetics of nitrate also increased resulting in the enhanced production nitrite compared with that of 1A-1C (2A-2C showed almost three times higher nitrate removal than that of 1A-1C at 3 h). Thus, the limited amount of nitrite could react with cathode in the 2A-2C experiment leading to the decrease in N_2 selectivity with the increase in the ammonia production despite of twice higher surface area for cathode in 2A-2C. The concentration of NaCl did not significantly influence the nitrate removal efficiency in this study (Fig. 5), indicating that the increase of paired number of electrode by more than two seems to be inappropriate due to the cost of electrodes. In the early stage (in 4 h), no significant production of both nitrite and ammonia was observed in both cases for 0.1 and 0.25 M NaCl. After 5 h, the production of nitrite increased up to 38 ppm (0.1 M NaCl) and 55 ppm (0.25 M NaCl) and decreased them to less than 10 ppm in 8 h, while we observed the continuous increase in ammonia concentration up to 125 and 155 ppm in 8 h. However, this small difference (compared with total N concentration: 1,000 ppm) seems to be not significant in this study. Therefore, we can conclude that the enhancement in nitrate removal by increasing number of paired electrode may not guarantee proportional increase of removal efficiency and production of desirable by-products (i.e., N_2).

To enhance the N_2 selectivity, we varied the number of anode and cathode using combinations of 2A-1C and 1A-2C (Fig. 6). We observed almost 47% of removal efficiency after 8 h reaction by using 2A-1C, which was much lower than that of 1A-1C. The increase of anode electrode can produce more HOCl at the anode surface, resulting in the enhancement of both the ammonia oxidation to N_2 [20] and nitrite oxidation to nitrate [29]. Therefore, the increase of only anode number seems to enhance the nitrite oxidation to nitrate when the same amount of nitrate was reduced by one cathode leading to the increase of nitrate concentration in the cell. Indeed, the production of nitrite in case of 2A-1C was insignificant during the reaction, indicating that most of nitrite produced from cathode surface could be reoxidized to nitrate again in this study. Compared with the case of 2A-1C, we observed a remarkable increase in nitrate removal by using 1A-2C (86% in 8 h) mainly due to the acceleration of nitrate reduction by increasing number of cathode. In addition, we did not observe any significant productions of ammonia and nitrite by using 1A-2C (data not shown), which is comparable with that of 2A-2C. Although the removal efficiency with

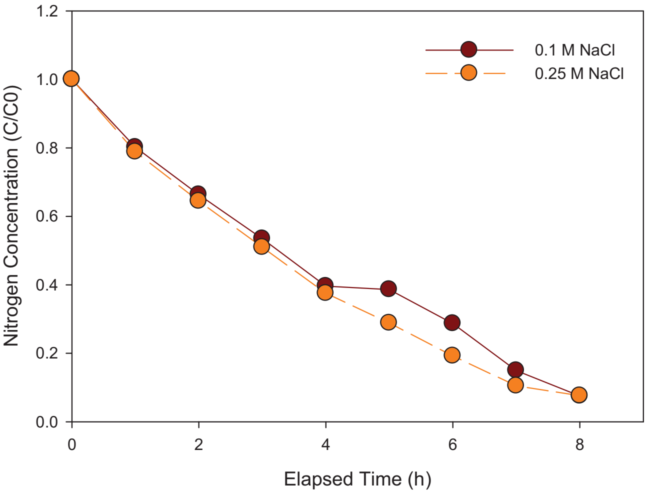

Fig. 5. Effect of NaCl concentration on the electrochemical nitrate reduction in this study. Experimental condition: 2A-2C with 0.1 and 0.25 M NaCl at current density of 40 mA/cm^2.

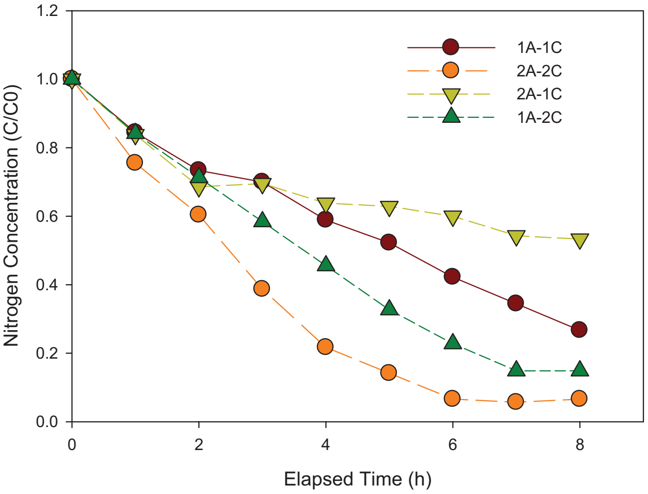

Fig. 6. Effect of number of electrode (1A-1C, 2A-2C, 2A-1C, and 1A-2C) on the electrochemical nitrate reduction. Experimental condition: 0.5 M NaCl at current density of 40 mA/cm^2.

1A-2C (86%) was slightly lower than that of 2A-2C (94%), no production of by-products in case of 1A-2C can provide a promising alternative for enhancement of electrochemical reduction of nitrate to N_2 without increasing the number of both anode and cathode, but with only increasing the number of cathode in undivided electrochemical cell. The results obtained from this study show that the variation of number of electrode can significantly differentiate the removal efficiency of electrochemical nitrate reduction and its by-product selectivity together.

4. Conclusions

We treated the highly concentrated nitrate by the electrochemical method using Zn cathode and Ti/Ir–Ru anode in undivided cell. A pair of Zn cathode and Ti/Ir-Ru anode showed the effective nitrate reduction to N_2 with production of low amounts of ammonia and nitrite when 1,000 NO_3^-–N mg/L was applied in study. Although other cathode materials such as Cu and Fe have shown the effective nitrate reduction to date, we first introduced a novel pair combination (i.e., Zn cathode and Ti/Ir–Ru anode) to selectively reduce highly concentrated nitrate to N_2 in this study. The results can be applied to selective ex situ treatment system for highly concentrated nitrate in industrial wastewater after productions of cellophane, explosives, fertilizers, and other metals. In addition, we showed that the removal efficiency of nitrate and its by-product production were significantly affected by the various operation parameters (i.e., current density, pH, and number of electrode). The results obtained from the parametric studies can help to design the effective and cost-effective denitrification process using the electrochemical method and to maximize the removal efficiency and N_2 selectivity by considering operation conditions.

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