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Electrochemical nitrate reduction using a cell divided by ion-exchange membrane

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Abstract. Electrochemical reduction of nitrate was studied using Zn, Cu and (Ir+Ru)-Ti cathodes and Pt/Ti anode in a cell divided by an ion exchange membrane. During electrolysis, effects of the different cathode types on operating parameters (i.e., voltage, temperature and pH), nitrate removal efficiency and by-products (i.e., nitrite and ammonia) formation were investigated. Ammonia oxidation rate in the presence of NaCl was also determined using the different ratios of hypochlorous acid to ammonia. The operating parameter values were similar for all types of cathode materials and were maintained relatively constant. Nitrate was well reduced and converted mostly to ammonia using Zn and Cu cathodes. Ammonia, produced as a by-product of nitrate reduction, was oxidized in the presence of NaCl in the electrochemical process and the oxidation performance was enhanced upon increasing the hypochlorous acid-to-ammonia ratio to 1.09:1. Zn and Cu cathodes promoted the nitrate reduction to ammonia and the produced ammonia was finally removed from solution by reacting with hypochlorite ions. Using Zn or Cu cathodes, instead of noble metal cathodes, in the electrochemical process can be an alternative technology for nitrate-containing wastewater treatment.

Keywords: electrochemical reduction; nitrate; divided cell; ion exchange membrane

1. Introduction

Nitrate contents in surface water and especially in ground water have gradually increased due to increased fertilizer consumption and discharge of poorly treated industrial wastewater (Squillace *et al.* 2002, Showers *et al.* 2008). Nitrate can have harmful effects on human beings, such as ‘blue baby syndrome’ (methemoglobinemia) for infants, liver damage and cancer (carcinogenic nitrosamine) (Gupta *et al.* 2000, Li *et al.* 2009, Park *et al.* 2017). The maximum permissible nitrate concentration has been determined by different regulations (10 mg NO_3-N/L for drinking water in Republic of Korea, 50 and 15 mg NO_3-N/L for adults and children, respectively, in European country). To meet these criteria, various nitrate treatment technologies have been developed based on biological and physicochemical methods.

Biological treatment is implemented that convert nitrate to nitrogen gas by bacterial activities. The by-products are seldom produced and not required further treatments for by-product during biological treatment (Mook *et al.* 2012). Thus, the operating cost is lower than physicochemical methods. Although biological treatments have these advantages, it may be an improper approach due to the high risk of clogging by microorganisms, the need for the external carbon source to maintain appropriate carbon-to-nitrogen (C/N) balance and time consumption. Besides, biological treatment methods are difficult to apply for high nitrate concentrations in wastewater because highly concentrated wastewater hinders bacterial activities. Ion exchange, reverse osmosis, electrodialysis and adsorption (by activated carbon) are typical physicochemical methods for nitrate treatment (Lee *et al.* 2017). The physicochemical treatment methods have the definite advantages of high nitrate reduction efficiency and less time consumption (Kim *et al.* 2017). However, the operation cost for physicochemical methods are relatively high due to energy expense, complicated system configuration, material regenerating and large investment (Lin *et al.* 2002, Qin *et al.* 2005).

To overcome the problems of conventional nitrate removal processes and remove nitrate efficiently, electrochemical methods have received considerable attention and have been successfully applied to treat highly concentrated nitrate in waste water (Grimm *et al.* 1998, Li *et al.* 2009, Chakrabarti *et al.* 2011). The advantages of electrochemical nitrate treatment include high efficiency,

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ambient operating conditions, compact equipment size, low sludge production and short time consumption (Dash and Chaudhari 2005, Li *et al*. 2009). During the electrochemical process, nitrate is mainly reduced to electrochemically inactive nitrite, ammonia and nitrogen gas. The nitrite and ammonia by-products of nitrate reduction are subsequently oxidized to nitrate and nitrogen, respectively. Re-oxidization of nitrite to nitrate occurs during the anodic cycle and reduce nitrate reduction efficiency. The re-oxidization can be prevented using an ion exchange membrane installed as a barrier between the electrodes. Only protons that produced on the anode side can penetrate the membrane and reach the cathode side (Carmo *et al*. 2013). Previous studies have successfully demonstrated separation of cathode from anode compartment and have reported improved nitrate reduction efficiency (Szpyrkowicz *et al*. 2006, Kim *et al*. 2015). The challenge is to find sustainable operating conditions to achieve desirable electrochemical nitrate reduction performance.

The aim of this study was to investigate the electrochemical reduction of nitrate using Zn, Cu and (Ir+Ru)-Ti cathodes and Pt/Ti anode in a divided cell. A laboratory-scale electrochemical reactor was operated with a cell divided by cation exchange membrane. The effects of the different cathode materials on operating parameters, nitrate reduction efficiency and production of ammonia and nitrite by-products were also demonstrated.

2. Materials and method

2.1 Experimental setup

The electrolytic cell device (MEA-100, Zignentech, Korea) was designed to install anode and cathode in two half cells composed of acrylic material (Fig. 1). The effective volume of electrolytic cell was 270 mL (90 and 180 mL for the anode and cathode compartments, respectively).

The cell was divided by assembling an ion exchange membrane between the anode and cathode compartments. In this study, a cation exchange membrane (CEM) (CMX, Astom Corp., Japan) was used for partitioning the electrolytic cell and its properties are shown in (Table 1). The CMX is a commercialized membrane that includes sulfonic acid groups as fixed charges. The membrane is widely applied to electro-membrane systems.

The anode and cathode surface areas were both 84 cm^2 (8.4 cm width and 10 cm length) and the inter-electrode distance was 30 mm. Zn, Cu and (Ir+Ru)/Ti plates (corrosion-resistive cathode) were used as cathodes in this study. Each of the three types of cathode was paired with an anode (Pt/Ti plate) and the nitrate reduction efficiencies obtained with the different cathode materials were compared. The DC power supply (EX 100-18, ODA Technology, Korea) provided voltage and current of 0-105 V and 0-18.9 A, respectively. The voltage and current ranges were controlled in the constant voltage (CV) and constant current (CC) mode.

Fig. 1 Electrochemical reactor used in this study

Table 1 Properties of cation exchange membrane (CEM)

	Title	CMX (standard grade)
Characteristics	Type	Strongly acidic
	Electric resistance	3.0 Ω·cm^2
	Mechanical strength	High mechanical strength
	Burst strength	≥ 0.40 MPa
	Thickness	0.17 mm
Recommended field of application	Temperature	≤ 40℃
	pH	0-10

Synthetic nitrate solution was prepared as the catholyte (i.e., cathode electrolyte) and the concentration was adjusted at 300 mg NO_3-N/L (~21.5 mM) using sodium nitrate ($NaNO_3$) with deionized water. A sodium chloride (NaCl) solution (500 mM) was used as anolyte (i.e., anode electrolyte). DC power supply was controlled in the CC mode at a current density of 5 mA/cm^2.

The ammonia removal in the electrochemical process was evaluated under the conditions of ammonia solution with added chloride (Cl^-). The synthetic ammonia solution was prepared and the concentration was adjusted as 1,000 mg NH_3-N/L. Experiments were conducted with chloride ion addition at different chloride-to-ammonia ratios of 0.54, 1.09 and 1.63. After 1 h of experimental time, residual ammonia concentrations were measured after reaction with chloride ion in solution.

2.2 Analytical methods

During the test period, 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, respectively. The changes in nitrate, nitrite and ammonia concentrations over time were analyzed. The analyses were performed using water quality test kit product (Water Test Kit, Hach, Germany) and spectrophotometer (DR2500, Hach, Germany). The test kit is based on the AWWA standard test method. The nitrate, nitrite and ammonia were analyzed using chromotropic acid, diazotization and salicylate methods, respectively.

The pH (initial 6.5-6.8) was not controlled and monitored during electrolysis treatment. The pH levels of the samples were measured using a pH meter (Orion Star

A216, Thermo, U.S.A.) equipped with a combined glass-reference electrode. Most samples were analyzed shortly after sampling to minimize the effects on pH change and 0.1 N H_2SO_4 was added to the rest of the samples to prevent pH change during storage. The pH value was measured for each electrode compartment and was monitored during electrolysis. The minimum amount of sample (~30 mL) was collected and the measuring was carefully conducted to avoid any change of properties. After measuring, the collected samples were injected back into the cell to maintain constant effective volume of the electrolytic cell. All measurements were performed at room temperature.

3. Results and discussion

3.1 Changes of operation parameters

In this study, changes in operating parameters (i.e., voltage, temperature and pH) were investigated during nitrate reduction through electrolysis (Fig. 2).

No effects of cathode materials on the operating parameters were observed. During electrolysis, the voltages of tests were dropped from 5.5 to 3.5 V and were kept relatively constant after 0.5 h. The temperature of catholyte was not significantly increased either and was maintained at 22°C for 2 h of electrolysis (initial temperature, 20°C). In contrast, the pH values were drastically changed with progress of the electrochemical process. The anolyte pH (initial, 6.5-6.7) and catholyte pH (initial, 7.2-7.3) were rapidly decreased and increased to below 2 and over 12 within 0.5 h, respectively. Decrease in pH of the anode compartment can be explained by the effect of dissociated protons from the reaction of chlorine, produced by oxidation of chloride ions oxidation reaction on the anode surface and water. The increasing pH of the catholyte is likely due to generation of hydroxide ions on the cathode surface. This increase in pH upon hydroxide ion generation can be an indirect evidence of nitrate reduction to nitrite and ammonia. Other evidences for pH change could be found by water electrolysis.

The four aforementioned reactions in the anode and cathode compartments can be written as follows (Case 1-4);

Case-1 (Anode compartment); reactions of chloride ions

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

Case-2 (Anode compartment); oxygen evolution by water electrolysis

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

Case-3 (Cathode compartment); nitrate reduction

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$

$$NO_3^- + 3H_2O + 5e^- \rightarrow 0.5N_2 + 6OH^-$$

$$NO3^- + 6H2O + 8e^- \rightarrow NH3 + 9OH^-$$

$$NO2^- + 2H2O + 3e^- \rightarrow 0.5N2 + 4OH^-$$

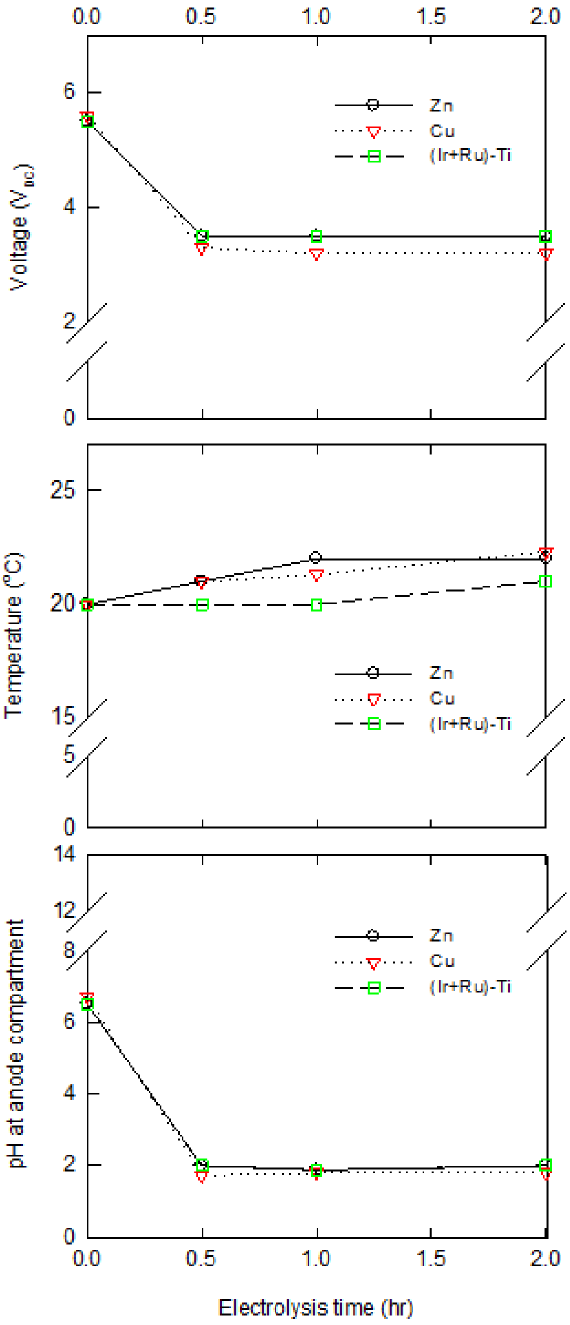

Fig. 2 Changes in operating parameters during nitrate reduction (current: 5 mA/cm^2, anolyte: 0.5 M NaCl)

$$NO2^- + 5H2O + 6e^- \rightarrow NH3 + 7OH^-$$

Case-4 (Cathode compartment); hydrogen evolution by water electrolysis

$$H2O + 2e^- \rightarrow H2 + 2OH^-$$

3.2 Performance of nitrate reduction with different types of cathodes

The effect of cathode material on electrochemical nitrate reduction was investigated. Total three kinds of cathodes (i.e., Zn, Cu and Ir+Ru/Ti plate) were used and Pt/Ti plate was used as anode. A current density of 5 mA/cm^2 was used in all electrolysis experiments. Fig. 3 shows that electrolysis with Zn and Cu cathodes exhibited similar trends regarding nitrate reduction efficiency and by-product (i.e., nitrite and ammonia) production.

The nitrate concentration decreased with progression of electrolysis for all cathodes and only differed in the decreasing rate. Among the three types of cathodes, Zn and Cu well reduced nitrate and the order of nitrate reducing rate was Zn > Cu > (Ir+Ru)/Ti. The reduction ratios after 1 h of electrolysis for Zn and Cu were 95 and 89%, respectively. In contrast, (Ir+Ru)/Ti cathode showed less than 36% nitrate reduction over the same electrolysis time (1 h). Previous researchers have also reported high nitrogen removal efficiency of the Zn cathode. Li *et al.* (1988) revealed that the Zn electrode among Ni, Fe, Pb and Zn cathodes showed the highest nitrogen removal rate in the electrolysis in CC mode. Dortsiou *et al.* (2012) also achieved 90% nitrate reduction using Zn cathode over 1.5 h of electrolysis.

A similar amount of ammonia production was observed during electrolysis with Zn and Cu cathodes, whereas the least amount of ammonia was produced using the (Ir+Ru)/Ti cathode. The ammonia produced using Zn and Cu cathodes increased over the initial 1 h and then decreased. Since the same anode material was used in all the experiments, the different amounts of ammonia produced during electrochemical nitrate reduction could be attributed to differences in the cathode materials.

During electrochemical nitrate reduction, no nitrite accumulation was detected for Zn and Cu cathodes. However, nitrite tends to accumulate in the first 1 h and was then relatively constant for the (Ir+Ru)/Ti cathode. Previous researchers reported that nitrite can be produced as an intermediate product during nitrate reduction and may be reduced to nitrogen gas or ammonia (Mácová and Bouzek 2005).

After 1 h of electrolysis, distribution of nitrogen species in the aqueous phase were normalized (Fig. 4). Although the nitrate was well reduced using Zn and Cu cathodes, most of the nitrate was converted to ammonia. Ammonia is the one of main products generated and is considered a major hindrance to effective electrochemical denitrification (Mook *et al.* 2012). To overcome this issue, chloride salt is widely used. In this process, chlorine ion is oxidized in the reactor and reacts with water to form hypochlorous acid (HOCl). The hypochlorite ion, reacts with nitrite and ammonia to produce nitrate and nitrogen (Li *et al.* 2009, Chakrabarti *et al.* 2011). Sodium chloride is usually selected as the chloride salt for chlorine ion oxidation (Lin and Wu 1996, Abuzaid *et al.* 1999, Li *et al.* 2009).

3.3 Ammonia removal under presence of chloride ions

Since ammonia concentration decreases in the presence of NaCl, efficient total nitrate reduction rate can be achieved during electrolysis. In the presence of Cl$^-$ ions, hypochlorite ions may be formed during electrolysis, which would convert the ammonia to nitrogen gas and nitrite to nitrate. The ammonia removal efficiencies with different HOCl/NH$_3$ ratios are shown in Fig. 5.

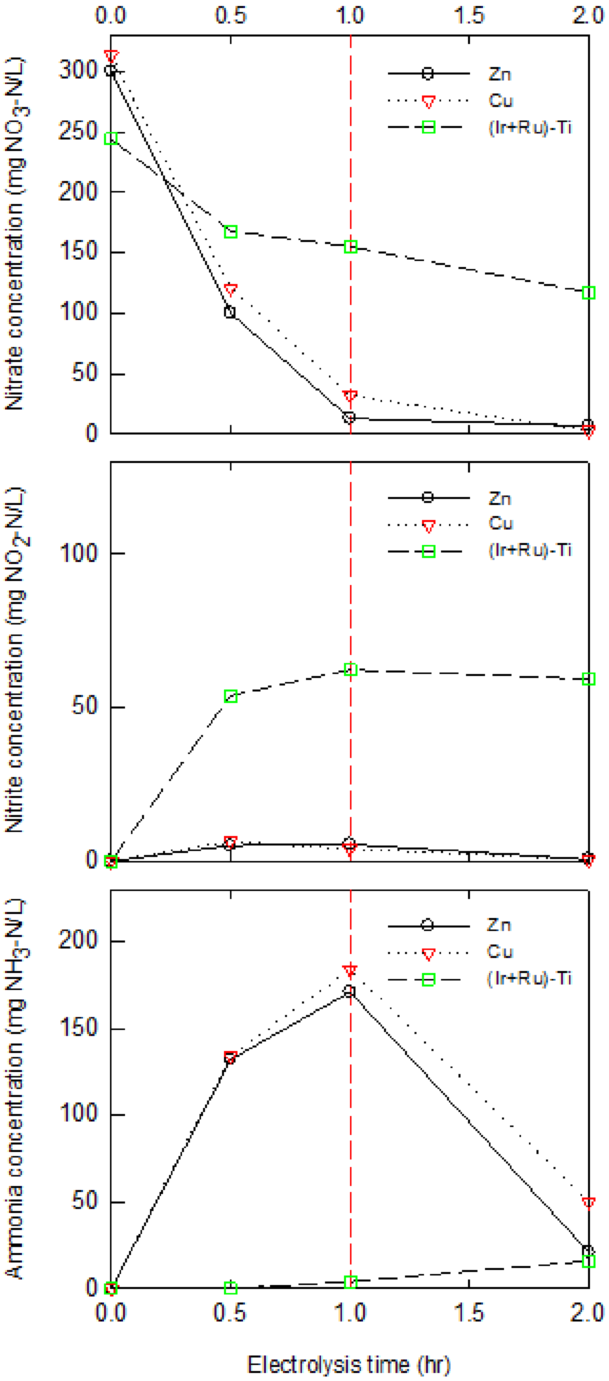

Fig. 3 Nitrogen concentrations for different cathode material types in aqueous phase (current: 5 mA/cm^2, anolyte: 0.5 M NaCl)

The residual ammonia concentration in solution was significantly reduced with increasing ratio of hypochlorous acid to ammonia. When the ratio of hypochlorous acid to ammonia is higher than 1.09, no relative effect on ammonia removal was observed. This suggests that ammonia can be efficiently removed when appropriate concentration of chloride ions exist in the electrochemical nitrate reduction. Therefore, using Zn or Cu cathode with chloride ion, instead of noble metal cathode, can be an appropriate technology to treat nitrate-containing wastewater.

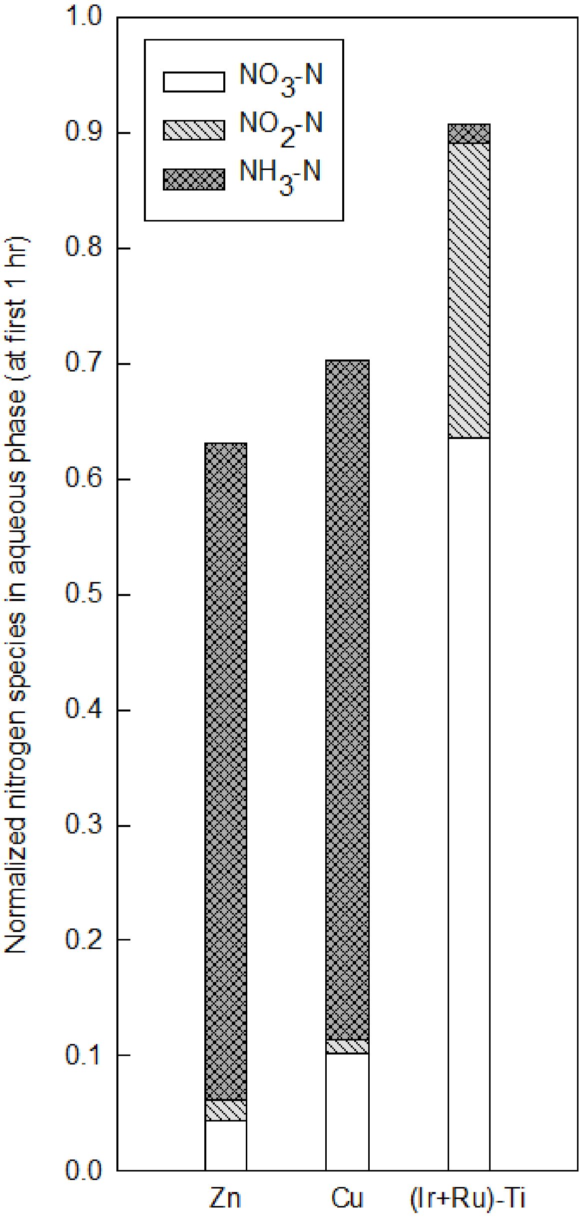

Fig. 4 Normalization of existing forms of nitrogen in the aqueous phase (current: 5 mA/cm^2, anolyte: 0.5 M NaCl)

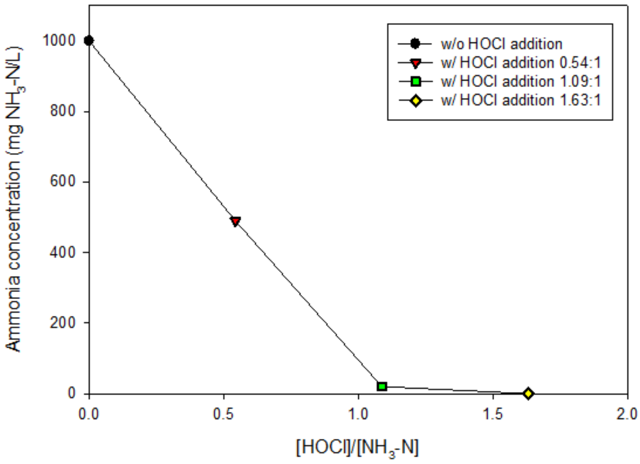

Fig. 5 Ammonia-nitrogen removal by reaction with hypochlorite ions

4. Conclusions

The electrochemical removal of nitrate was studied using Zn, Cu and (Ir+Ru)-Ti cathodes and Pt/Ti anode in a cell divided by ion exchange membrane.

- No significant difference in operating parameters (i.e., voltage, temperature and pH) was observed depending on the type of cathode material and the values were maintained relatively constant during electrochemical nitrate reduction.
- Zn and Cu cathodes showed better performance for nitrate reduction than the (Ir+Ru)-Ti cathode. In terms of by-product (i.e., nitrite and ammonia) formation, most of the nitrate was converted to ammonia using Zn and Cu cathodes and significant nitrite production was observed with (Ir+Ru)-Ti cathode.
- The presence of NaCl was necessary for oxidizing the ammonia by-product in the process. Ammonia concentration in solution was drastically decreased with increasing of the ratio of hypochlorous acid to ammonia to 1.09:1.
- This strategy, using Zn or Cu cathode instead of a noble metal cathode in the presence of chloride ion, can be an appropriate technology for nitrate-contaminated wastewater treatment.

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