



## Simultaneous reduction of nitrate and oxidation of by-products using electrochemical method

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### ABSTRACT

Electrochemical denitrification was studied with an objective to enhance the selectivity of nitrate to nitrogen gas and to remove the by-products in an undivided electrochemical cell, in which Cu–Zn cathode and Ti/IrO<sub>2</sub>–Pt anode were assembled. In the presence of 0.50 g/L NaCl as supporting electrolyte, the NO<sub>3</sub><sup>−</sup>–N decreased from 100.0 to 9.7 mg/L after 300 min electrolysis; no ammonia and nitrite were detected in the treated solution. The surface of the cathode was appeared to be rougher than unused after electrolysis at initial pH 6.5 and 12.0. After electrolysis of 5 h at the initial pH 3.0, passivation of the Cu–Zn cathode was observed. The reduction rate slightly increased with increasing current density in the range of 10–60 mA/cm<sup>2</sup> and temperatures had little effect on nitrate reduction. Nitrate could be completely removed by the simultaneous reduction and oxidation developed in this study, which is suitable for deep treatment of nitrate polluted water.

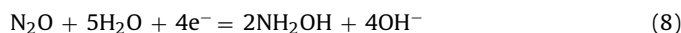
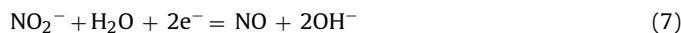
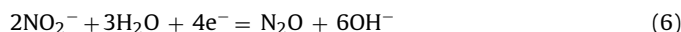
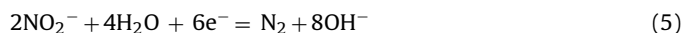
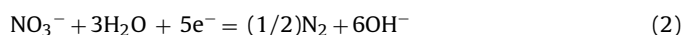
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### 1. Introduction

Numerous worldwide regions have been the victims of nitrate contamination of water resources [1]. Sources of nitrate include overfertilization, animal feces, industrial effluents and human wastes. Nitrate-contaminated water above the permissible drinking water limit is toxic to human health, specifically to children [2–4]. A maximum limit of 50 mg/L NO<sub>3</sub><sup>−</sup> (15 mg/L NO<sub>3</sub><sup>−</sup> for infants), 0.5 mg/L NO<sub>2</sub><sup>−</sup> and 0.5 mg/L NH<sub>3</sub> in drinking water were permitted [5–8]. Numerous efforts have been reported so far on the removal of nitrate such as biological method [9,10]. Biological denitrification needs a continuous monitoring, such as addition of a carbon source, pH control, temperature maintenance, and also requires the removal of by-products such as nitrite. Extractive methods like reverse osmosis and ion exchange resins [11–13] are also largely used to remove nitrates. However, these techniques produce a large amount of effluents, which must be treated later and therefore increase the overall cost of the process.

In recent, the electrochemical reduction of nitrate is receiving more and more attention due to its convenience, environmental respectability, and low cost in-use [14–28]. The major electrochem-

ical reactions involved in the electrochemical nitrate reduction are [14]:

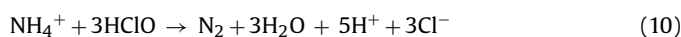


The reduction of nitrate to the nontoxic nitrogen gas is proved to be difficult since it is one of the eight possible products [18,22]. When the supporting electrolyte is acid nitrite, ammonia, hydroxylamine and hydrazine will be the by-products; furthermore, in basic or neutral electrolyte, it was found [15,29,30] that the main by-products during electrochemical reduction of nitrate were nitrite and ammonia. In the past few years, various electrodes [16–43] have been used in electrochemical denitrification such as Cu, Ni, Zn, Pb, Cu/Zn, Pt. It has been reported [34,41–43] that the passivation of Cu cathode during electrolysis, while Cu–Zn alloy is known

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as an efficient promoter for nitrate electro-reduction. In general, applications of the electrochemical process for denitrification are limited due to generation of ammonia and nitrite. The difficulty is to find the proper condition to perform both cathodic reduction of nitrate and anodic oxidation of the produced ammonia.

On the other hand, electrochemical oxidation of ammonia has been widely studied [44–51]. If chloride ion was present in the treated water, during electrolysis chlorine is generated at the anode and immediately reacts with water to form hypochlorite, which would react with ammonia. The overall reaction occurring in the anodic solution between hypochlorite and ammonia can be expressed as follows:



According to the results obtained by Pressley et al. [52], by using sodium hypochlorite or chlorine to oxidize the ammonia, nitrogen is the main stable product. Kim et al. [47] reported that the performances of the electrode on the electrolytic decomposition of ammonia were totally in the order of  $\text{RuO}_2 \approx \text{IrO}_2 > \text{Pt}$  in both the acid and alkali conditions. It also has been reported [53,54] that  $\text{Ti/TiO}_2\text{-RuO}_2$  and  $\text{Ti/RuO}_2$  for removal of ammonia. Therefore, to find the proper condition to perform both cathodic reduction of nitrate and anodic oxidation of the produced ammonia and nitrite in the presence of chloride ion is possible.

The aim of this work is to completely remove nitrate in polluted water using the electrochemical reduction in an undivided cell, and to find a proper condition to perform both cathodic reduction of nitrate and anodic oxidation of the produced ammonia and nitrite. The influence of several parameters, such as chloride concentration, current density, initial pHs, constant pHs, temperatures and addition time of chloride ion were studied. The corrosion and passivation of cathodes were also investigated so as to better improve the efficiency of electrochemical denitrification.

## 2. Materials and methods

### 2.1. Electrochemical apparatus

A cylindrical electrochemical cell was designed with a net working volume of 400 mL. The electrolysis cell was manufactured by acrylic plates with four outer spots for the electrodes assembled. For each cell, Cu–Zn (Cu: 62.2 wt.%; Zn: 37.8 wt.%) plate of 75 cm<sup>2</sup> (15 cm × 5 cm) was used as the cathode and  $\text{Ti/IrO}_2\text{-Pt}$  electrode ( $n(\text{IrO}_2)$ : 78 wt.%; Pt: 22 wt.%) (TohoTech company, Japan) with the same area as the anode, a distance of 8 mm between the two electrodes was set. A DC power supply with a voltage range of 0–50 V and a current range of 0–5 A was employed.

### 2.2. Methods

In the present study, synthetic nitrate solutions with initial nitrate nitrogen concentrations of 100 mg/L were prepared for the electrolysis experiments. 0.5 g/L  $\text{Na}_2\text{SO}_4$  was added into all the experiments in order to enhance the conductivity. 400 mL of synthetic nitrate solution was poured into the electrochemical cell, the reaction started with the application of specified current density. At different intervals, 1.5 mL of sample was drawn from the electrochemical cell for analysis. The electrolysis was ceased when either 90% of initial nitrate was converted or 5 h elapsed. The desired pH was maintained using dilute NaOH (0.1 and 0.01 N)/ $\text{H}_2\text{SO}_4$  (0.1 and 0.01 N) solutions. The initial pHs were set at 3.0, 6.5 and 12.0. Constant pHs were set to be 4.0–4.8, 6.9–7.9, and 9.2–10.1 by buffering solution (Wako).

To investigate the effect of sodium chloride (NaCl) dosage, the NaCl of 0, 0.50, 1.00 g/L (w/v) were added into the synthetic nitrate solutions, respectively.

Effect of current densities were investigated under galvanostatic control at different current densities of 5, 10, 20, 40, 60 mA/cm<sup>2</sup>. To compare the effect of temperatures, the experiments were performed at 25, 40 and 60 °C kept on water bath and at the temperature uncontrolled.

### 2.3. Detection of free radicals species and oxidizing substance

To measure the production of free radicals and oxidizing substance formed during the electrochemical treatment, NaCl solution at concentration of 0.50 g/L containing 0.2 μmol/L RNO (*p*-nitrosodimethylaniline) was used because RNO reacts rapidly with free radicals or oxidizing substance such as hypochlorous acid selectively. 0.50 g/L  $\text{NaSO}_4$  was added in the solution as supporting electrolyte. The bleaching of RNO solution was measured by absorbance changes at 440 nm. Samples were taken at intervals of 1, 2, or 5 min and absorbance of RNO solution was measured by spectrophotometer (DR/4000U, USA).

### 2.4. Analysis

All analyses were done according to standard methods [55]. Nitrate was determined by standard colorimetric method using spectrophotometer (DR/4000U Spectrophotometer, USA), and nitrite was analyzed by ion chromatography (Yokogawa IC7000, AS9-HC column). The determination of ammonia was performed by Ion meter (Ti 9001, Toyo chemical laboratories Co., Ltd.). Dissolved copper and zinc content of the filtered samples were detected using plasma emission spectrophotometer equipment (JARERUASSHU, ICAP-575). Surface morphology of cathode was characterized *ex situ* by atomic force microscopy (Digital Instruments, Dimension™3000, USA). The possible formation of hydrazine and hydroxylamine was not investigated because the treated solutions were changed into basic after electrolysis, in which hydrazine and hydroxylamine will not be produced [15].

## 3. Results and discussion

### 3.1. Performance of nitrate reduction with different NaCl dosages

Fig. 1 shows the variation of total nitrogen, nitrate-N, nitrite-N, and ammonia-N during electrolysis with different dosages of NaCl. A current density of 40 mA/cm<sup>2</sup> was used in most nitrate reduction electrolysis as it exhibited a relatively high reduction rate in our experiments. It can be seen from Fig. 1 that the electrochemical nitrate reduction had different behavior with different dosages of NaCl; moreover, the effect on by-product production was also different. Under the condition of no NaCl addition (Fig. 1(A)), the concentration of nitrate decreased with respect to treatment time, it decreased from 100.0 to 2.8 mg/L in 300 min. The ammonia-N increased from 0 to 60.9 mg/L; and the nitrite-N increased at the first 60 min, then decreased to 0 at the 240 min. The total nitrogen decreased from 100 to 63.8 mg/L. In the presence of 0.50 g/L NaCl and 1.00 g/L NaCl addition (Fig. 1 (B)), the nitrate-N decreased from 100.0 to 9.7 mg/L and 11.3 g/L, respectively; no ammonia and nitrite were detected in both the treated solution after 300 min, while the ammonia-N increased at the first 120 min, after that time it decreased to 0 in the presence of 0.50 g/L NaCl. As only nitrate was present in the treated solution, the total nitrogen decreased from 100.0 to 9.7 mg/L and 11.3 g/L, respectively. It was very clear that the total nitrogen sharply decreased comparing to that without the addition of NaCl. The nitrate was assumed probably to be reduced into nitrogen gas, however, in the future, it still to be confirmed whether other gaseous nitrogen compounds were formed during reduction. The nitrate reduction rate without NaCl addition was higher than that in the presence of NaCl. It was due to

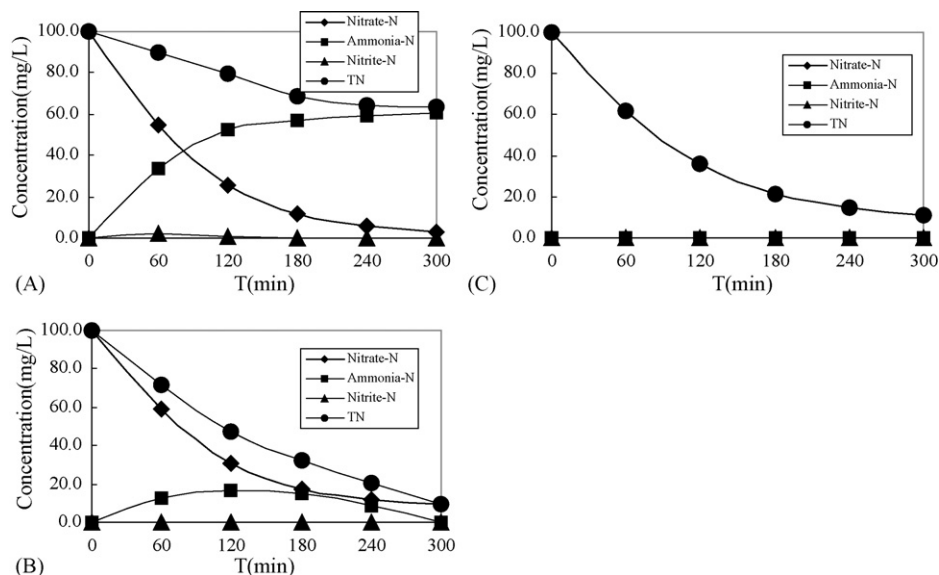


Fig. 1. Nitrate converted to nitrite, ammonia and nitrogen with different NaCl additions.  $I = 40 \text{ mA/cm}^2$  (A) no NaCl; (B) 0.50 g/L NaCl; (C) 1.00 g/L NaCl.

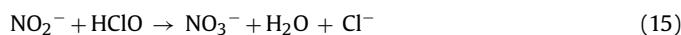
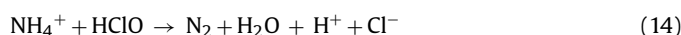
that nitrate reduction was retarded in the presence of chloride ion. Dash et al. [48] used titanium as cathode to electrochemically reduce the nitrate, found that the nitrate reduction in the presence of 250 mg/L sodium chloride was retarded, whereas sulfate had little effect on the nitrate reduction. In the presence of chloride ion, the efficiency for nitrate reduction was reduced to 43%, whereas in simulated ground water the nitrate removal was above 71%, and the TN removal were lower. However, in the present study, the efficiencies for total nitrogen removal were 90.3% with 0.50 g/L and 88.7% with 1.00 g/L NaCl addition. The reason why the nitrate reduction efficiency is higher than Barada's results was assuming to be Cu–Zn alloy cathodes used during the electrolysis. Mácová and Bouzek [56] found that brass containing Zn higher than 35 wt.%, lower than 41 wt.% will significantly influence the kinetic of current density, and higher electrocatalytic activity of Cu–Zn alloy containing Zn of 35–41 wt.% than both Cu and Zn was observed.

According to Rajeswar et al. [57], oxidizing hypochlorite ion will be formed during electrolysis in the presence of chloride ion.



The hypochlorite acid formed during the electrolysis would oxidize the by-products of ammonia and nitrite, which were assumed

to be oxidized into nitrogen gas and nitrate, respectively [52].



In order to confirm the production of free radicals or oxidizing substance and the oxidation ability during electrolysis, RNO bleaching experiments were carried out. Fig. 2 shows the absorbance of RNO sharply decreased in the initial 5 min on Ti/IrO<sub>2</sub>–Pt anode, and the bleaching ratio was more than 80%. However, it shows that the absorbance had almost no change without NaCl, indicating that formation of hypochlorous acid, which was an important bleaching factor during the electrolysis [58,59].

As shown in Fig. 1, ammonia formation was decreased by addition of NaCl; and the total nitrogen sharply decreased comparing to that without NaCl, which suggested that an appropriate concentration of chloride ion in the nitrate solution exist during the electrolysis process, in which the nitrate can be efficiently removed and no by-products will be formed. It could be considered that an optimum NaCl addition in the present experiment is 0.50 g/L, and the electricity power consumption is about 1.29–1.38 g NO<sub>3</sub><sup>−</sup>-N/KWH. In the future, it is still need to be studied for further reducing the power consumption.

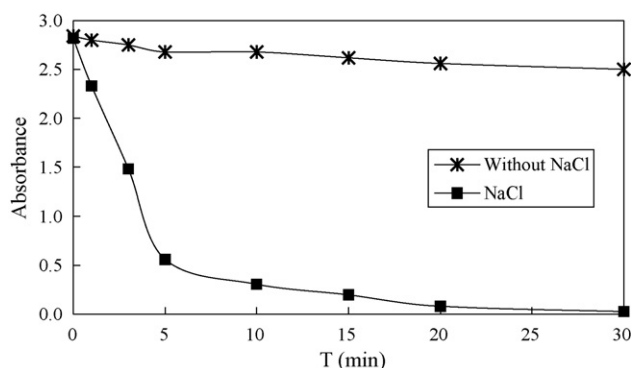


Fig. 2. Electrochemical bleaching of 200 μmol/L in 0.50 g/L NaCl solution as a function of treatment time at Ti/IrO<sub>2</sub>–Pt anode;  $I = 40 \text{ mA/cm}^2$ .

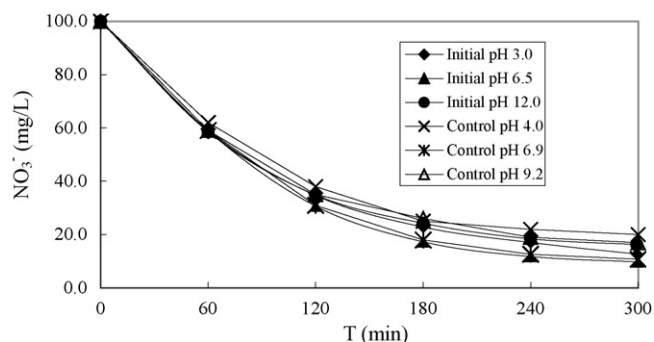


Fig. 3. Nitrate reduction with respect of time at different initial pHs and constant pHs,  $I = 40 \text{ mA/cm}^2$ , 0.50 g/L NaCl.

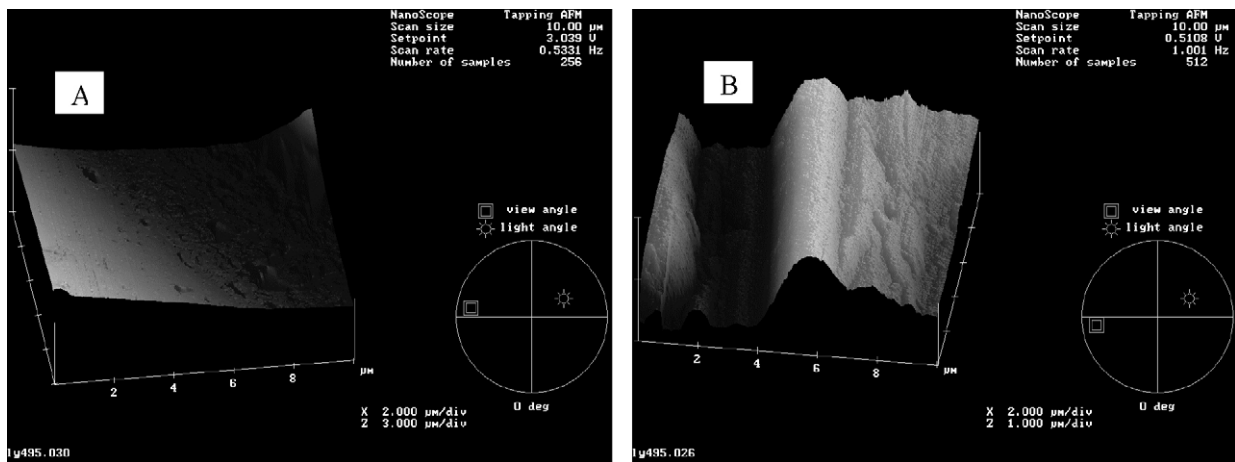


Fig. 4. AFM photograph of (A) an unused and (B) a 5 h used for electrolysis Cu/Zn cathode at initial pH 6.5.

### 3.2. Influence of initial pHs and constant pHs

The effect of different initial pHs and constant pHs on the nitrate reduction was shown in Fig. 3. It can be seen that the tendencies of reduction of nitrate were similar both at different initial pHs and constant pHs; the nitrate-N decreased from 100.0 to 9.7–20.0 mg/L in 300 min; the ammonia-N increased at the first 120 min, and then the ammonia-N in all experiments decreased to 0 at the 300 min (data not shown); no nitrite was detected in the treated solution. In buffer solution, the pHs of the solutions were kept constant between 4.0–4.8, 6.9–7.9, and 9.2–10.1, respectively. It was found that in all buffer solutions, good performances for nitrate reduction were achieved, while at low pH 4.0–4.8, the nitrate reduction rate was the lowest; and at high pH 9.2–10.1, the nitrate reduction rate was the highest. At the initial pHs of 3.0, 6.5, and 12.0, the pHs of the solutions sharply increased to 11.2, 11.8, and 12.1 in the first 60 min, and then to 11.8, 12.0, and 12.2 in 120 min, respectively; after that the pHs kept almost constant. Under the uncontrolled pHs of 3.0, 6.5, and 12.0, the ammonia-N increased from 0 to 12.6, 16.8 and 18.9 mg/L at the first 120 min, respectively, and then the ammonia-N in all experiments decreased to 0 at the 300 min; no nitrite was detected in the treated solution. As the treated solutions both become alkaline in the presence and absence of NaCl, the increasing of pH was mainly due to the reactions of nitrate reduction and hydrolysis. During electrolysis, reactions of nitrate reduction and hydrolysis were taken place, as shown in Eqs. (1)–(9), in which large amount of hydroxyl ion was produced. The increments of final pH value suggested that the production of  $H^+$  did not match the production of  $OH^-$  ion [29,30]. Cattarin [60] found that the electrochemical reduction of nitrate in highly alkaline solution with Cu electrode gave mainly ammonia at very negative potential; it is in agreement with our experiment data. While Derek et al. [61] found that nitrate reduced to ammonia in high yield at a copper cathode in aqueous acidic perchlorate and sulphate media. The reason why our experiment results were different from the results obtained by Derek et al. was assumed to be the different conditions in our experiments, especially electrodes and electrolyte. Mácová and Bouzek [56] found that higher electrocatalytic activity of Cu–Zn alloy was observed, by which  $NH_3$  was found to be the main  $NO_3^-$  reduction product. In our experiments, it was demonstrated clearly by Figs. 1 and 3 that nitrate was mainly reduced to ammonia, and the ammonia was further oxidized by HClO produced by the anode of Ti/IrO<sub>2</sub>–Pt.

At the initial pH 3.0, the color of the cathode was observed to be changed to silvery white during the electrolysis. The silvery white layer probably resulted in the passivation of the Cu–Zn alloy,

leading to the decrease in the rate of nitrate reduction from 87.3 to 62.7% in the second time using. It was found [62] the gradual deactivation of surface of the copper cathode during reduction of nitrate, considered CuH or CuH<sub>2</sub> to be the most probable formation on the cathode. Another reason for the presence of amorphous copper is the destruction of the metal surface layer crystalline structure by the evolved hydrogen [34,40,41]. This does not correspond to our observation of the formation of a silvery white layer consisting of fine particles covering the cathode surface. The change of the cathode surface color in the present experiment indicates selective copper dissolution. The silvery white layer was carefully scraped off the electrode, and dissolved by HCl + HNO<sub>3</sub> solution (3:1). After analysis of the solution by plasma emission spectrophotometer equipment, it was found that the ratio of Cu:Zn (w/w) was 70.8:29.2, comparing to 62.2:37.8 of the unused electrode, which confirmed that copper was selectively dissolved during electrolysis at initial pH 3.0. That was assumed to be the reason of the passivation of the electrode, as Zn was less active than Cu for nitrate reduction [56].

At the initial pH 6.5 and 12.0, no passivation of cathodes was observed. The surface of the cathode appeared to be rougher than unused after electrolysis (Fig. 4). The great harshness of the surface of the used electrode compared with the smooth surface of the unused, leads to an increase of its specific area. The analysis of the electrolyte after electrolysis for 5 h at current density of 40 mA/cm<sup>2</sup> indicated that the concentrations of copper and zinc in the electrolyte were less than 0.10 and 0.06 mg/L, respectively. Polatides et al. [43] found that after electrolysis for 12 h the concentration of copper and zinc in the electrolyte was 2.5 and 14.1 mg/L, respectively. The low rate of the corrosion in our experiments was due to the fact that the corrosion of the electrodes is limited by applying a direct current.

### 3.3. Influence of temperature and current density

The effect of applied current density on nitrate reduction during the electrochemical reduction of nitrate was shown in Fig. 5. As seen, the nitrate reduction rate almost did not increase with increasing current density in the range of 10–60 mA/cm<sup>2</sup>, especially from 40 to 60 mA/cm<sup>2</sup>. The little increase in reduction rate was probably due to higher hydrogen gas generation in the structure of the electrode. While at current density 5 mA/cm<sup>2</sup>, the nitrate reduction rate was obviously slower than that of 10 mA/cm<sup>2</sup>–60 mA/cm<sup>2</sup>; moreover, ammonia (4.8 mg/L) was detected in the treated solution after 300 min electrolysis. As it has been reported [51] that the ammonia oxidation rate was linearly in accordance with cur-

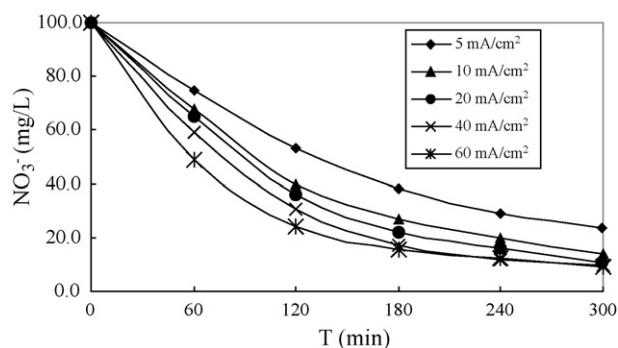


Fig. 5. Nitrate reduction with respect of time at different current density, 0.50 g/L NaCl.

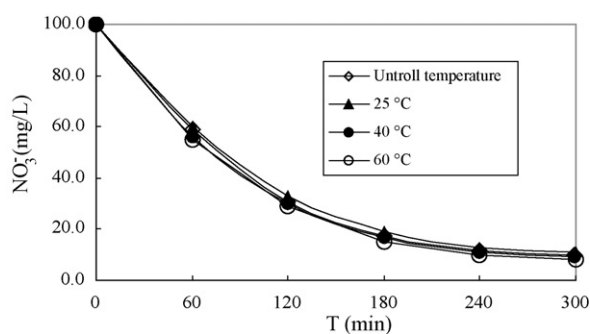


Fig. 6. Nitrate reduction with respect of time at different temperatures,  $I = 40 \text{ mA/cm}^2$ , 0.50 g/L NaCl.

rent density, at lower current density of  $5 \text{ mA/cm}^2$ , less amount of hypochlorite acid was produced, which was not enough to oxidize all of the ammonia. Therefore, in the present experiments, in order to remove all of the by-products, the current density should higher than  $5 \text{ mA/cm}^2$ . At current density of 5, 10, 20, 40, and  $60 \text{ mA/cm}^2$ , the potentials were kept constant at about 3.8–4.1, 5.6–6.0, 7.8–8.1, 9.8–10.1 and 11.9–12.2 V, respectively. Considering the economy factor, low current density is favorable; however, in practical use, it depends on the treatment condition for selection of more suitable current density.

Fig. 6 shows the influence of the reaction temperatures on nitrate reduction. Under the condition of uncontrolled temperature, the temperature of the treated solution increased from 25.0 to 48.5 °C after 300 min electrolysis. During electrolysis, the amount of electrical energy that must be added at least equals the change in Gibbs free energy of the reactions (nitrate reduction, etc.) plus the losses in the system. The losses can (in theory) be arbitrarily close to zero, so the maximum thermodynamic efficiency equals the enthalpy change divided by the free energy change of the reaction. But in actual electrolysis, the electric input is larger than the enthalpy change of the reaction, so some energy is released in the form of heat, and then the temperature of the solution will increase. In general, increasing temperature could affect the reduction rate of nitrate in several ways, for example, by increasing the rate of diffusion and the strength of the adsorption. The rates of nitrate removal at uncontrolled temperature, 40, 60 °C were slightly higher than that at 25 °C, e.g. from 100 to 11.2 mg/L at 25 °C and 9.7 mg/L at uncontrolled temperature, respectively. Increasing temperature favored ammonia formation and reduced nitrogen formation as previously reported [63]. It was due to different pH change of the catholyte at different temperature during the electrolysis, e.g. at 300 min, the treated solution pH changed from 6.5 to 11.8 at 25 °C and to 12.1 at uncontrolled temperature, respectively. The pH change was a natural result of the various reactions of nitrate reduction (Eqs. (1)–(3)). In basic solutions, increasing pH could suppress hydrogen evolution and increase ammonia formation [64]. Consequently, the nitrate reduction rate increased slightly when the temperature was increased from 25.0 to 48.5 °C. The ammonia-N in all treated solution increased at the first 120 min and then decreased to 0 at 300 min.

### 3.4. Influences of addition time of NaCl

The effect of different addition time of NaCl on nitrate reduction was shown in Fig. 7. At the current density of  $40 \text{ mA/cm}^2$ , the nitrate-N decreased from 100.0 to 9.7, 10.8, and 9.6 mg/L in 300 min at the addition time of 0, 120, 180 min, respectively. Although no obvious difference of total nitrogen was observed after 300 min treatment at the different NaCl addition times, changes in the nitrate-N and ammonia-N during electrolysis were rather different with different NaCl addition times; nitrate-N was rapidly reduced

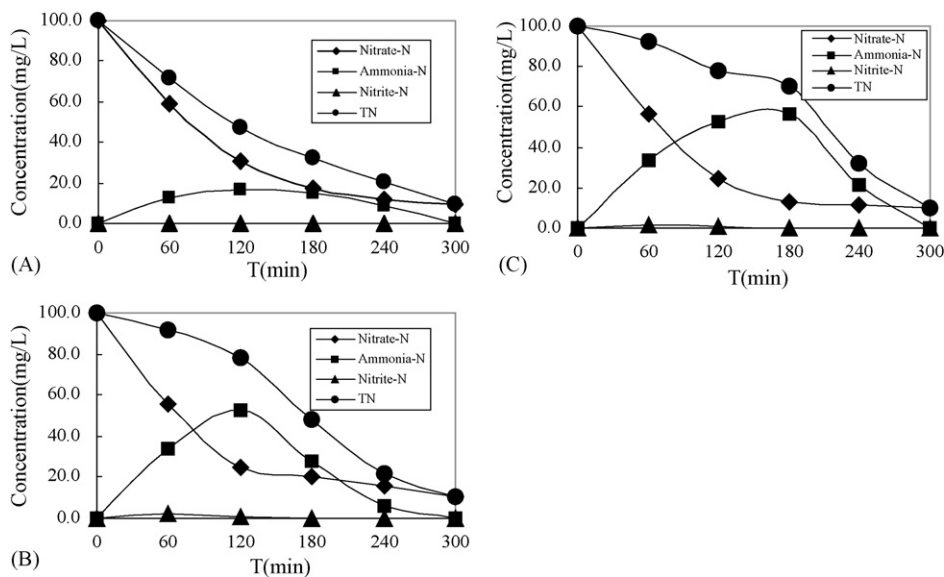


Fig. 7. Nitrate converted to nitrite, ammonia and nitrogen at different NaCl addition time. 0.50 g/L NaCl, initial pH 6.5,  $I = 40 \text{ mA/cm}^2$ . (A) Addition of NaCl at initial electrolysis; (B) addition of NaCl at 120 min; (C) addition of NaCl at 180 min.

and a large amount of ammonia was produced before addition of NaCl, and nitrite was also produced during electrolysis. After the addition of NaCl, both ammonia and nitrite were removed. As stated above, it was due to the oxidation of ammonia and nitrite by hypochlorite produced during electrolysis. Ammonia and nitrite were assumed to be oxidized into nitrogen gas or nitrate, respectively, it can be also demonstrated by comparison of Fig. 7(A–C). Therefore, it needs addition of chloride ion to completely remove the nitrate using electrochemical reduction approach.

#### 4. Conclusions

In order to develop the complete reduction method of nitrate, cathodic reduction of nitrate and anodic oxidation of the by-products were investigated with an undivided cell using a Cu–Zn plate as cathode and Ti/IrO<sub>2</sub>–Pt plate as anode for treatment of the synthetic nitrate solution. It can be concluded: (1) the nitrate-N decrease from 100.0 to 9.7 mg/L in the presence of 0.50 mg/L NaCl after 300 min electrolysis at the current density of 40 mA/cm<sup>2</sup>, and no ammonia and nitrite were detected in the treated solution; (2) neutral initial pH contributed to the nitrate reduction and basic pH favored the ammonia production; (3) less than 0.10 mg/L of copper and 0.06 mg/L of zinc were detected in the 300 min treated solution, the surface of the cathode was appeared to be rougher than unused after electrolysis; (4) temperatures in the range of 25–60 °C had little effect for nitrate reduction, and the obvious effect of current density on the nitrate was not observed in the range of 10–60 mA/cm<sup>2</sup>, while at 5 mA/cm<sup>2</sup> the nitrate reduction rate was relatively slow and ammonia was detected in the treated solution.

In the present study, the nitrate was removed completely by electrochemical approach using Cu–Zn cathode and Ti/IrO<sub>2</sub>–Pt anode with the addition of NaCl, it is a worthy method for treatment of nitrate polluted water.

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