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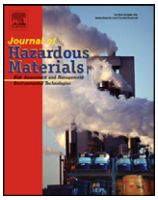

# Simultaneous reduction of nitrate and oxidation of by-products using electrochemical method

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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/$IrO_2$–Pt anode were assembled. In the presence of 0.50 g/L NaCl as supporting electrolyte, the $NO_3^-$–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/$cm^2$ 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.

## 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 $NO_3^-$ (15 mg/L $NO_3^-$ for infants), 0.5 mg/L $NO_2^-$ and 0.5 mg/L $NH_3$ 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 electrochemical reactions involved in the electrochemical nitrate reduction are [14]:

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

$$NO_3^- + 3H_2O + 5e^- = (1/2)N_2 + 6OH^- \tag{2}$$

$$NO_2^- + 5H_2O + 6e^- = NH_3 + 7OH^- \tag{3}$$

$$NO_2^- + 4H_2O + 4e^- = NH_2OH + 5OH^- \tag{4}$$

$$2NO_2^- + 4H_2O + 6e^- = N_2 + 8OH^- \tag{5}$$

$$2NO_2^- + 3H_2O + 4e^- = N_2O + 6OH^- \tag{6}$$

$$NO_2^- + H_2O + 2e^- = NO + 2OH^- \tag{7}$$

$$N_2O + 5H_2O + 4e^- = 2NH_2OH + 4OH^- \tag{8}$$

$$2H_2O + 2e^- = H_2 + 2OH^-(\text{sidereaction}) \tag{9}$$

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:

$$NH_4{}^+ + 3HClO \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \qquad (10)$$

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 $RuO_2 \approx IrO_2 > Pt$ in both the acid and alkali conditions. It also has been reported [53,54] that $Ti/TiO_2–RuO_2$ and $Ti/RuO_2$ 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 acryl 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 $cm^2$ (15 cm × 5 cm) was used as the cathode and $Ti/IrO_2–Pt$ electrode $n(IrO_2$: 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 $Na_2SO_4$ 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)/$H_2SO_4$ (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/$cm^2$. 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 $NaSO_4$ 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 cooper 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$^{TM}$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/$cm^2$ 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