Efficient electrochemical reduction of nitrate to nitrogen using Ti/IrO₂–Pt anode and different cathodes

Miao Li, Chuanping Feng, Zhenya Zhang, Norio Sugiyura

School of Water Resources and Environment, China University of Geosciences (Beijing), No. 29 Xueyuan Road, Haidian District, Beijing 100083, China

Doctoral Program in Life and Environmental Sciences, University of Tsukuba, Tsukuba 3058572, Japan

ARTICLE INFO

Article history:
Received 29 January 2009
Received in revised form 19 March 2009
Accepted 24 March 2009
Available online 1 April 2009

Keywords:
Nitrate
Electrochemical reduction
Cathodic reduction
Anodic oxidation
Sodium chloride

ABSTRACT

Electrochemical reduction of nitrate using Fe, Cu, and Ti as cathodes and Ti/IrO₂–Pt as anode in an undivided and unbuffered cell was studied. In the presence of appropriate amount of NaCl, both cathodic reduction of nitrate and anodic oxidation of the by-products of ammonia and nitrite were achieved by all cathodes under a proper condition. Both in the absence and presence of NaCl, the order of nitrate removal rate was Fe > Cu > Ti. The nitrate removal was 87% and selectivity to nitrogen was 100% in 3 h with Fe cathode in the presence of NaCl. Ti/IrO₂–Pt anode played an important role during nitrate reduction, especially in the presence of NaCl, at which by-products could efficiently be oxidized. Moreover, atomic force microscopy (AFM) investigation shown Ti/IrO₂–Pt anode was suitable for nitration reduction and the surface roughness of all cathodes increased. The concentrations of Fe, Cu, and Ti in the electrolyte were less than 0.15, 0.12 and 0.09 mg/L after 3 h electrolysis, respectively.

1. Introduction

Intolerable level of nitrate ion, with nitrogen in the +5 oxidation state, was contained in many sources of water, especially in areas of intensive agriculture [1,2]. In some industrial sectors, nitrate is the problem of nuclear waste treatment, where it significantly increases the volume of waste and has a negative impact on its cohesion after solidification [3]. Nitrate can cause serious health problems in humans such as the “blue baby syndrome” in infants, liver damage and cancer [4–6]. A maximum limit of 50 mg/L NO₃⁻ for infants, 0.5 mg/L NO₂⁻ and 0.5 mg/L NH₃ in drinking water were permitted [1,7–9]. For the reduction of nitrate, biological denitrification needs a continuous monitoring, such as pH control, addition of a carbon source, temperature maintenance [10–12]. Extractive methods like reverse osmosis and ion exchange resins [13,14] result in the second pollution, so it must be treated later and therefore increase the overall cost of the process. Heterogeneous catalysis also could result in the second pollution and the cost is relatively high. As electrochemical reduction of nitrate [15–17] has high treatment efficiency, no sludge production, small area occupied and relatively low investment costs, it has been focused on by a large number of researchers recently.

In the last decades, lots of cathodes [18–22] such as Cu, Fe, Zn, Pt/Ir, Pd, and Au have been used in electrochemical denitrification. Some electrodes [23–26] like Cu and Fe were known as relatively efficient promoters for nitrate electro-reduction. However, as the reduction of the NO₃⁻ ion is one of the few means of removing it from polluted waters, electrochemical reduction of nitrate lead to a relatively broad spectrum of products, such as N₂ gas, NH₂OH, N₂O, NH₃ [26–28,23,29]. During electrochemical reduction of nitrate, the simultaneous electrochemical oxidation of ammonia to nitrogen has been proved to be difficult, when the potential of electrolysis is constant [30–32]. A high electrocatalytic activity has been obtained using a Cu/Zn cathode and a Pt anode [33]. PdRh₁.₅/Ti mini-mesh electrode has been used to remove nitrate ions from wastewater [34]. It has been reported [35] that a high rate of nitrate reduction and a high selectivity of nitrogen (92%) were obtained by Sn cathode and Pt anode. During the cathodic cycle, the nitrates are mainly reduced to nitrites, ammonia and nitrogen, which is further electrochemically inactive. Consequently, the produced nitrite and ammonia, before their diffusion to the bulk, are oxidized to the initial nitrate and nitrogen during the anodic cycle, respectively. The difficulty is to find the proper condition to perform both cathodic reduction of nitrate and anodic oxidation of the produced ammonia. In general, applications of the electrochemical process for denitrification are limited due to generation of ammonia and nitrite.

On the other hand, if chloride ion was present in the solution, chlorine is generated at the anode and immediately reacts with water to form hypochlorite, which would react with ammonia during electrolysis. The overall reaction occurring in the anodic solution between hypochlorite and ammonia can be expressed as:
follows:

\[
2\text{NH}_4^+ + 3\text{HClO} \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 5\text{H}^+ + 3\text{Cl}^- \tag{1}
\]

It was reported [36] that nitrogen is the main stable product by using sodium hypochlorite or chlorine to oxidize the ammonia. A good performance for the removal of ammonia has been found with Ti/\text{IrO}_2–\text{RuO}_2 [37,38]. It was also reported [39] that ammonia can be efficiently removed with appropriate amount of chloride concentration. Therefore, it is possible 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.

In previous studies, Ti/IrO\(_2\)–Pt anode has seldom been investigated for nitrate reduction. Moreover, as Fe, Cu and Ti cathodes have been proved to be relatively efficient promoters for nitrate electro-reduction [24,25,41], and the combinations of Ti/IrO\(_2\)–Pt anode and Fe, Cu and Ti cathodes have never been studied, those combinations were employed in the present experiments. The aim of this work is to completely remove nitrate and removal of by-products 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 cathode materials, chloride ion, the corrosion and passivation of cathodes were investigated so as to better improve the efficiency of electrochemical denitrification.

2. Experimental

2.1. Electrochemical measurements

Cyclic voltammetric (CV) measurements were obtained in a conventional three-electrode Pyrex glass cell using a ministat potentiostat, a PCI-100 computer interface and an ALS Software (ALS Limited, Model 660), at room temperature. The working electrodes were Fe, Cu and Ti electrodes. Ti/IrO\(_2\)–Pt flag electrode was used as counter electrodes. An Ag/AgCl (sat.) was served as the reference electrodes. All potentials are quoted against the Ag/AgCl electrode. All glassware was cleaned in boiling \(\text{H}_2\text{SO}_4–\text{HNO}_3\) to remove organic contaminants. Solutions were prepared with reagent grade chemicals (Wako, Japan) and ultra-pure water (resistivity ~ 18.2 M\(\Omega\) cm). All of the solutions studied were deaerated by bubbling \(\text{N}_2\) gas for 10 min prior to the electrochemical measurements (ALS Limited, Model 660). The working electrode was cycled between 0.4 and −2.0 V at a scan rate of 200 mV/s three times before collecting stable polarisation data.

2.2. Batch electrolysis

A 200-mL electrolysis cell (Fig. 1) was manufactured by acryl material. For the cell, Fe, Cu and Ti plates of 75 cm\(^2\) (15 cm \(\times\) 5 cm) were used as the cathode and Ti/IrO\(_2\)–Pt (TohoTech Company, Japan) with the same area as the anode, a distance of 8 mm between the two electrodes was set. The immersed areas of the anode and cathode in the treated solution were the same at 40 cm\(^2\). ADC power supply with a voltage range of 0–50 V and a current range of 0–5 A was employed.

2.3. Methods

In the present study, a synthetic nitrate solution with initial nitrate nitrogen concentration of 100.0 mg/L was 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. To investigate the effect of sodium chloride dosage on the complete nitrate reduction, the NaCl of 0 to 0.5 g/L (w/v) were added into the synthetic nitrate solutions, respectively. 200 mL of synthetic nitrate solution prepared as above 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 3 h elapsed.

2.4. Analysis

All analyses were done according to standard methods [40]. Nitrate was determined by standard colorimetric method using spectrophotometer (DR/4000U Spectrophotometer, USA), and nitrite was analyzed by ion chromatography (Yokogawa IC7000, A59-FC column). The determination of ammonia was performed by Ion meter (Ti 9001, Toyo chemical laboratories Co., Ltd.). Dissolved cooper and zinc content of the samples were detected using plasma emission spectrophotometer equipment (ICAP-575, Jareruashhu). Surface morphology of cathode was characterized ex situ by atomic force microscopy (AFM) (Digital Instruments, DimensionTM3000, 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 [27].

3. Results and discussion

3.1. Voltammetric investigations

Fig. 2 shows the cyclic voltammograms obtained for the reduction of nitrate with Fe, Cu and Ti used as the working electrodes and Ti/IrO\(_2\)–Pt electrode as the counter electrode. In Fig. 2(A) and (C), in the base electrolyte, the main observed processes are the onset of water electrolysis to produce hydrogen at about −1.0 to −1.2 V. In Fig. 2(B), an obvious peak was observed at around \(E = +0.65\) V. The peak was attributed to the oxidation/reduction of \(\text{C}_{6}\text{H}_{5}\text{O}^+\) to Cu species [41]. A more negative potential value (−1.2 V) for the hydrogen evolution process was observed, which agrees with the larger over potential of copper towards the latter electrode process [42,43]. In all cases the addition of nitrate gives rise to rather broad waves that extend from about −1.0 up to −1.6 V, the maximum being reached at the more negative potentials. In all cases during the bath electrolysis, the current yield at −0.80 V and −1.00 V is very low and \(\text{NO}_3^-\) ions are converted mainly to \(\text{NO}_2^-\) in the absence of \(\text{NaCl}\). While the current yield at −1.00 V and −1.20 V is relatively high and \(\text{NO}_3^-\) ions are converted mainly to \(\text{NH}_3\) in the absence of \(\text{NaCl}\). The results obtained for the copper electrode agree with previous findings reported in the literature for the same electrode in alkaline solutions [24,26].
3.2. Performance of nitrate reduction in the absence of NaCl

Fig. 3 shows the variation of total nitrogen, nitrate–N, nitrite–N, and ammonia–N during electrolysis by different cathodes in the absence of NaCl. A current density of 20 mA/cm² was used in most nitrate reduction electrolysis as it exhibited a relatively high reduction rate in the present experiments. It can be seen from Fig. 3 that the highest nitrate reduction rate was obtained with the Fe cathode, while that with the Ti cathode was the lowest. The concentration of nitrate decreased with respect to treatment time in all cases, it decreased from 100.0 to 7.2, 41.0 and 69.2 mg/L in 180 min by Fe, Cu, and Ti cathodes, respectively. On the other hand, the ammonia–N increased from 0 to 51.1, 21.2 and 18.9 mg/L, respectively. Although the highest nitrate reduction rate was obtained with the Fe cathode, the highest selectivity of nitrate reduction to nitrogen gas was achieved with the Cu cathode. It was probably because the material of Cu could some extent inhibit the hydrogen evolution reaction [20, 44]. As previous mentioned, Cu has a more negative potential value (−1.2 V) for the hydrogen evolution than Fe and Ti, less amount of hydrogen was produced, led to the low selectivity of ammonia formation and high TN removal rate with Cu cathode. The results agreed with previous study, in which it was reported that Fe cathode has the high selectivity of nitrate reduction to ammonia, and very less concentration of nitrite has been detected in the treated solution [24]. As the anodes used in the experiments were same material, cathode should be attributed to contribute the selectivity was different.

The nitrite–N with Fe, Cu, and Ti cathodes increased at the first stage, and then decreased almost to zero. That was in agreement with previous research [29, 33], which proved nitrite was an intermediate product during nitrate reduction, and it was probably further reduced into nitrogen gas or ammonia, or oxidized into nitrate again at anode. The total nitrogen with Fe, Cu, and Ti cathodes decreased from 100.0 to 58.2, 63.8, 88.9 mg/L, respectively. It is also reported that by Fe cathode no decrease in total nitrogen concentration was detected [24]. The reason why the selectivity of nitrate reduction to nitrogen was relatively high in the present experiment was due to the utilization of Ti/IrO₂–Pt anode. As Ti/IrO₂–Pt anode had relatively high oxidation ability [45], certain amount of nitrite and ammonia, before their diffusion to the bulk, are oxidized to the initial nitrate and nitrogen during the anodic cycle, respectively.

In all, it can be concluded that Fe cathode is more suitable for nitrate reduction than Cu and Ti cathodes in the absence of NaCl as supporting electrolyte because of its high nitrate reduction rate.

3.3. Performance of nitrate reduction with different NaCl dosages

3.3.1. Fe cathode

Fig. 4 shows the variation of total nitrogen, nitrate–N, nitrite–N, and ammonia–N during electrolysis with Fe cathode. The nitrate–N in the presence of 0.3 and 0.5 g/L NaCl decreased from 100.0 to 9.0 and 12.9 mg/L in 180 min, respectively (Fig. 4(A)). The concentration of total nitrogen at 0.5 g/L NaCl addition was same with that in the nitrate–N as only nitrate was present in the treated solution (Fig. 4(B)). The nitrate reduction rate at higher NaCl dosage was lower than that at lower NaCl addition. The reason was assumed that nitrate reduction was retarded in the presence of chloride ion. It was reported [46, 47] that the effectiveness of the halide in poisoning nitrate reduction, due to the potential of these anions to be specifically adsorbed on the electrode surface. The specifically adsorbed anions inhibit the reduction of nitrate because they decrease the active surface area of the electrode. It has been found [24] that the nitrate reduction in the presence of 250 mg/L sodium chloride was retarded with Ti cathode, whereas sulfate had little effect on the nitrate reduction. In the present study, the efficiency for nitrate removal were 91.0% with 0.3 g/L and 86.7% with 0.5 g/L NaCl addition, respectively. However, according to Dash et al. [24], in the presence of chloride, the efficiency for nitrate reduction was reduced to 43%, whereas in simulated ground water the nitrate removal was above 71%. The reason why the nitrate reduction efficiency is higher than Dash’s results was assumed to be the
Nitrate converted to nitrite, ammonia and nitrogen by Fe (A), Cu (B), and Ti (C) cathodes, 20 mA/cm², no NaCl addition.

In the presence of 0.3 g/L NaCl The ammonia–N increased from 0 to 11.8 mg/L at the first 60 min, after that time the ammonia–N decreased to 2.0 mg/L at the 180 min; no nitrite was detected in the treated solution. While in the presence of 0.5 g/L NaCl (Fig. 3 (B)), no ammonia and nitrite were detected in the treated solution. As hypochlorite ion will be formed in the presence of chloride ion during electrolysis [48,49], the by-products of ammonia and nitrite would be oxidized to form nitrogen gas and nitrate [36].

\[
\begin{align*}
2\text{Cl}^- &\rightarrow \text{Cl}_2 + 2e^- \\
\text{Cl}_2 + \text{H}_2\text{O} &\rightarrow \text{HClO} + \text{H}^+ + \text{Cl}^- \\
\text{HClO} &\rightarrow \text{ClO}^- + \text{H}^+ \\
\text{NH}_4^+ + \text{HClO} &\rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{H}^+ + \text{Cl}^- \\
\text{NO}_2^- + \text{HClO} &\rightarrow \text{NO}_3^- + \text{H}_2\text{O} + \text{Cl}^-
\end{align*}
\]

In the presence of 0.3 and 0.5 g/L NaCl, the total nitrogen decreased from 100.0 to 11.0 and 13.2 mg/L, respectively. It was very clear that the total nitrogen sharply decreased comparing to that without the addition of NaCl (Fig. 3(A)), which suggested that if an appropriate concentration of chloride ion exists during the electrolysis process using Ti/IrO₂–Pt as anode and Fe as cathode, both cathodic reduction of nitrate and anodic oxidation of the by-products of ammonia and nitrite would be achieved, finally nitrate could be completely removed.

3.3.2. Cu cathode

Fig. 5 shows the nitrate reduction with different NaCl additions by Cu cathode. In the presence of 0.3 and 0.5 g/L NaCl, the nitrate–N decreased from 100.0 to 43.0 and 44.6 mg/L in 180 min, respectively. No ammonia and nitrite were detected in the treated solution after 180 min electrolysis. That did not agree with the previous study, which concluded that the presence of chloride ion in the solution did not change the essential nature of the nitrate reduction [46,47]. It is probably due to the relatively high oxidation ability of the Ti/IrO₂–Pt anode used in the present experiment, with which more hypochlorite ion was formed during electrolysis [45]. The large amount of hypochlorite acid formed would efficiently oxidize the by-products of ammonia and nitrite. Comparing to the results obtained by Fe cathode, the nitrate reduction rate by Cu cathode was low whether in the presence or absence of NaCl (Figs. 3 and 4). Furthermore, the nitrate reduction rate was not influenced by different NaCl addition. Also, the total nitrogen sharply decreased comparing to that without NaCl as only nitrate was present in the treated solution (data not shown).
3.3.3. Ti cathode

Fig. 6 shows the variation of nitrate–N during electrolysis by Ti cathode. In the presence of 0.3 and 0.5 g/L NaCl, the nitrate–N decreased from 100.0 to 75.6 and 85.4 mg/L in 180 min. No ammonia and nitrite were detected in the treated solution. Comparing to Fe and Cu cathodes, the nitrate reduction rate with Ti cathode was very low. That is in contradict with previous study, which [24] reported that although Fe electrodes exhibited the maximum reducing condition and Ti showed the minimum, Ti electrode had better performance for nitrate reduction in the absence NaCl. Also, the reason was assumed to be the Ti/IrO2–Pt anode used in the present study. It can be seen that high oxidation of anode could inhibit the reduction ability of cathode, though it could enhance the oxidization of ammonia and nitrite during the anodic cycle.

Fig. 7. AFM photograph of an unused (A) and a 9 h (B) used for electrolysis Fe, Cu, and Ti cathodes.
3.4. Analysis of electrode surfaces and the electrochemical solution

Polatides et al. [50] found that after electrolysis for 12 h by a pulsing potential with Cu/Zn cathode, the concentrations of copper and zinc in the electrolyte were 2.5 and 14.1 mg/L, respectively, which are the allowed limit for drinking water. In the present experiment, analysis of the electrolyte after electrolysis for 3 h at a current density of 20 mA/cm² revealed that the concentrations of Fe, Cu, and Ti in the electrolyte were less than 0.15, 0.12 and 0.09 mg/mL, respectively. The low rate of corrosion observed in the experiments was attributed to the fact that corrosion of the electrodes was limited by application of a constant potential. The surface roughness of all cathodes increased after electrolysis (Fig. 7), and the electro- catalysis may be accelerated because the specific area of cathode increased. The Fe cathode appeared to become the most rough, while that of the Ti cathode the least. Comparing to an unused cathode, 3–5% increases in nitrate reduction rate was found at a 9 h used Fe, Cu, Ti cathodes. The surface of the anode appeared to remain unchanged after electrolysis, implying that Ti/IrO₂–Pt anode were suitable for nitrate reduction.

4. Conclusions

Electrochemical reduction of nitrate using Fe, Cu, and Ti cathodes and Ti/IrO₂–Pt anode in an undivided and unbuffered cell was studied. This study demonstrated the applicability of electrochemical process for removal of nitrate.

The conclusions are drawn as follows.

(1) In the absence and presence of NaCl, the highest nitrate reduction rate was obtained with Fe cathode (93%), and the lowest with Ti cathode (31%).

(2) In the presence of 0.5 g/L NaCl, a proper condition of performing both cathodic reduction of nitrate and anodic oxidation of the by-products of ammonia and nitrite was achieved by all cathodes, especially by Fe cathode, with which the nitrate removal rate was 87% and selectivity to nitrogen was 100% in 3 h.

(3) Ti/IrO₂–Pt anode played an important role on nitrate reduction products, especially in the presence of NaCl.

(4) As the nitrate reduction rate was high and the selectivity of nitrate to nitrogen gas was 100% in the presence of chloride ion with Fe as cathode and Ti/IrO₂–Pt as anode, the combination of Fe cathode and Ti/IrO₂–Pt anode is a worthy method for treatment of nitrate-polluted water.


