Electrolytic denitrification with an ion-exchange membrane in groundwater
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ABSTRACT
Nitrate contamination of groundwater is an important issue in rural areas. In this study, an electrolytic method for the denitrification of groundwater was investigated in a laboratory reactor. We used an ion-exchange membrane, employing a titanium oxide anode and five kinds of cathode for the investigation. The nitrate removal efficiencies with Cu, Pb, Ti/Ir/Ru, Ti/Ir/Ta, and Zn cathodes were 30.0%, 59.9%, 73.8%, 23.3%, and 80.6%, respectively. A cation-selective membrane was employed to separate the electrode compartments, and only the proton produced in the anode side was permitted to the cathode side in order to avoid reversible reactions. In terms of the nitrate removal, good experimental results were obtained by using the membrane reactor equipped with the Zn cathode. The nitrate concentration level dropped from 30 to 6 mg/L, which is below the limit for drinking water. The pH was not affected significantly by the current density and it increased up to 9.0 at 100 mA/cm². The nitrate removal efficiency showed the highest value with 1 mM of NaCl as an electrolyte. The impression was that membrane electrolysis made it possible to avoid the re-oxidation problem. It appears clear that electrolytic denitrification with an ion-exchange membrane is a very effective process with a mean energy consumption of only between 26.9 and 112.9 kWh/kg-NO₃.

Key words | denitrification, electrolysis, ion-exchange membrane, nitrate

INTRODUCTION
The contamination of groundwater by nitrate has become a serious water-pollution problem. Nitrate contamination in groundwater and surface water is getting worse because of the increasing use of synthetic nitrogen fertilizers and livestock manure in intensive agriculture (Shrimali & Singh 2001; Lacasa et al. 2011). Nitrate can cause severe health problems in humans, such as ‘blue baby syndrome’ in infants, liver damage, and cancer (Gupta et al. 2000; Majumdar & Gupta 2000; Li et al. 2009). The maximum permissible contamination level for nitrate concentration in drinking water is 10 mg/L in South Korea, while it is 50 mg/L for adults and 15 mg/L for children in the member states of the European Union (WHO 1995; Dash & Chaudhari 2005; Lacasa et al. 2011).

There are many processes to remove nitrate from groundwater, among which biological denitrification has the advantage of reducing nitrate to nitrogen. However, this technique has limited applicability because of the potential for adverse effects on the quality of the drinking water, which would require extensive post-treatment to eliminate bacteria and metabolic substances. The alternative physico-chemical treatment methods for removing nitrate from potable water are ion exchange, electrodialysis, and reverse osmosis. However, the need for treatment of the ensuing concentrated brine waste could pose a significant obstacle, as the disposal of this waste would be an additional problem (Dortsiou et al. 2008).

In contrast, much attention is being paid to electrochemical treatment for nitrate reduction in polluted
groundwater because of the convenience of the method. The electrochemical treatment of groundwater is inexpensive and is an environmentally sound technology, as the resulting product is harmless nitrogen (Cheng et al. 2005). In addition, the electrochemical reduction of nitrate is a highly efficient treatment, does not produce sludge, occupies a limited area, and the investment cost is relatively low. Usually, the nitrate is reduced during the cathodic cycle mainly to nitrite and nitrogen gas. Recently, many research studies have focused on the electrochemical reduction method. The research of Polatides et al. (2005) has indicated that the nitrate is reduced during the cathodic cycle to nitrite, ammonia, and nitrogen, which is further electrochemically inactive.

However, the reduced nitrite could be re-oxidized to nitrate in the anode by the reverse reactions (Reyter et al. 2008). Consequently, an ion-exchange membrane could be used as a barrier between the cathode and the anode, and only the proton produced in the anode side would be permitted to the cathode side, although the limited lifetime of the electrolysis cells as well as consumption of electricity could be major drawbacks of this type of method (Carmo et al. 2013). In our research, a Naﬁon 117 membrane with a Ti/Pd–Co–Cu cathode was successfully used to separate the cathodic from the anodic compartments (Szpyrkowicz et al. 2006). Membrane electrolysis first started to produce Cl2 by the membrane electrolysis of brine. Recently, the membrane electrolysis method in the reduction of nitrate in water has been used to avoid the generation of undesired byproducts such as nitrite and ammonium (Mayrhofer et al. 2009; Reyter et al. 2011; Bosko et al. 2014; Vazač et al. 2014). The operating parameters that have a signiﬁcant inﬂuence on the electrochemical denitriﬁcation processes include the electrode material, cathode/anode surface area ratio, current input, pH, conductivity, sodium chloride (NaCl) concentration, and the initial concentration of nitrate ions (Lide & Frederikse 1997; Bosko et al. 2014).

In this study, the electrolytic denitrification of groundwater was investigated for converting nitrate to nitrogen gas. We focused our work on the membrane electrolysis technique under various current densities and electrolyte conditions.

MATERIALS AND METHODS

Simulated groundwater (SGW) was prepared as a 30 mg/L NO3-N concentration, with KNO3, using distilled water. NaCl was used as an electrolyte at 100 mM to investigate the cathode material and the current density. The sodium chloride was varied from 0 to 200 mM to optimize the electrolyte concentration. All the experiments were performed at room temperature.

The reactor was made from an acrylic material and, for the electrochemical reactor, TiO2 was used as the anode, while Zn, Cu, and Pb were compared as the cathodes. Two alloyed materials were tested as corrosion-resistant cathodes: Ti/Ir/Ru and Ti/Ir/Ta. A cation-selective membrane (Asahi Glass Cation Exchange Membrane, Japan) was used as a separation device between the anode and the cathode. This membrane carried the proton that was produced in the cathode side to the anode side. The surface area of the Zn, Ti plate was 150 cm² (10 cm × 15 cm).

The reactor was designed for the improvement of denitrification at the cathodic electrode, as is shown in Figure 1. The ion-exchange membrane was located between the cathode electrode and the anode electrode. The protons produced in the cathode were decreased by the permeability of the ion-exchange membrane to the proton. Therefore, nitrate could be easily reduced during the reaction in the cathodic electrode. The electrochemical reactor setup included two power-supply units, of which the applied voltage range was 0–105 V and the current range was 0–18.9 A (Power supply, Ex 100-18, Odacore Co., Korea).

In all the experiments, more than 5 mL of the sample was collected for analysis from the electrochemical cell at intervals of every 0.5, 1, 2, 3, and 6 h. Ion chromatography (IC 2000 series, Dionex, USA) was used to determine the nitrate. Ammonia nitrogen was analyzed according to Standard Methods (APHA, AWWA, WPCF 1998).

RESULTS AND DISCUSSION

Screening of cathode materials

A batch experiment was performed to remove the nitrate, with different materials supplied for the cathodic electrode.
The current density was 10 mA/cm² in the experiment, and Ti was used for the anode. Cu, Ti, Pb, and Zn were tested to choose the anode material. The electrolyte concentration was 100 mmol/L of NaCl, and the duration of the experiment was 6 hours.

Figure 2 shows the effect of the nitrate removal with different cathode materials. The removal rates for nitrate were 4%, 22.5%, 4.5%, and 80% with Cu, TiO₂, Pb, and Zn, respectively. The Zn electrode was the most efficient cathode for removing the nitrate and was therefore selected as the cathode material for this research. Cu, TiO₂, Pb, and Zn are transition metals and the standard reduction potentials for TiO₂, Zn, Pb, and Cu are −1.628 E₀, −0.763 E₀, −0.126 E₀, and −0.153 E₀, respectively. When Ti was located in the cathode side, the standard reduction potential of Zn, Pb, and Cu was higher than it was for TiO₂. The standard reduction potential with Zn is the highest among the metals for this work. Among the materials used (Cu, TiO₂, Pb, and Zn), Zn has the greatest ability for nitrate removal.

The corrosion resistance of based electrodes is one of the major parameters for practical application. Ti/Ir/Ru and Ti/Ir/Ta were also studied as corrosion-resistant cathodes. In an electrolytic denitrification process with ion-exchange membrane, significant nitrogen removal was obtained with a corrosion-resistant Ti/Ir/Ru cathode displaying a comparable efficiency of nitrate reduction to the Zn cathode.

**pH profile with various current densities**

Figure 3 shows the pH at different constant current densities, using Zn and TiO₂ as the cathode and the anode, respectively. The current density was adjusted to 25, 50, and 100 mA/cm² with a simulated solution of 30 mg/L. The pH was measured after collecting 5 mL of a sample. The pH was found to increase continuously until the electrode reaction stopped, especially at 100 mA/cm². The research of Cheng et al. (2005) indicated that nitrate is removed by chemical reaction (refer to Equations (1)–(8), below). OH⁻ was produced from nitrate and nitrite as they were being removed; therefore, the pH rose when the electrochemical reaction progressed (Meyer et al. 2014).

At the end of the reaction, the pH values achieved were 8.65, 8.97, and 9.01 at 25 mA/cm², 50 mA/cm², and
100 mA/cm² current densities, respectively.

\[ 2H^+ + 2e^- \rightarrow H_2 \]  
(1)

\[ 4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \]  
(2)

\[ NO_3^- + H_2O + 2e^- \leftrightarrow NO_2^- + 2OH^- \]  
(3)

\[ NO_3^- + 3H_2O + 5e^- \leftrightarrow 1/2N_2 + 6OH^- \]  
(4)

\[ NO_3^- + 6H_2O + 8e^- \leftrightarrow NH_3 + 9OH^- \]  
(5)

\[ O_2 + 2H_2O + 4e^- \leftrightarrow 1/2N_2 + 4OH^- \]  
(6)

\[ NO_2^- + 2H_2O + 3e^- \leftrightarrow NH_3 + 7OH^- \]  
(7)

\[ NO_2^- + 4H_2O + 4e^- \leftrightarrow NH_2OH + 5OH^- \]  
(8)

Effect of current density

Figure 4(a) shows the removal of nitrate under various current conditions in the reactor. Zn was used as cathode and the anode applied was TiO₂. The current density was adjusted to 25, 50, and 100 mA/cm² to simulate groundwater. It was found that the higher the current density that was applied, the better was the efficiency of nitrate removal, with the nitrate removal efficiency at a current density of 100 mA/cm² being the highest. It follows from Equations (3) to (5) (see above) that nitrate is removed by a chemical mechanism (Lacasa et al. 2011). At the end of the reaction, the concentrations of nitrate had decreased from 30 to 21 mg/L, 17 mg/L, and 15 mg/L at 25 mA/cm², 50 mA/cm², and 100 mA/cm² current densities, respectively.

Figure 4(b) shows the ammonium variation under various current conditions in the reactor. The current densities in this reaction were 25, 50, and 100 mA/cm². Again, it was found that the higher the current density that was applied, the better the nitrate removal efficiency that was achieved. In the early phase, ammonium increased within 30 minutes, but, after 1 hour, the ammonium decreased. During the initial stage of the reaction, the concentration of ammonium was elevated (refer to Equations (5) and (7)) for 1 hour, after
which the concentration declined continuously (refer to Equations (9)–(11)), as was indicated by Cheng et al. (2005).

\[
\begin{align*}
\text{NH}_3 + 3\text{OH}^- & \leftrightarrow \frac{1}{2}\text{N}_2 + 3\text{H}_2\text{O} + 3e^- \quad (9) \\
\text{NH}_3 + 9\text{OH}^- & \leftrightarrow \text{NO}_3^- + 6\text{H}_2\text{O} + 8e^- \quad (10) \\
\text{NH}_3 + 7\text{OH}^- & \leftrightarrow \text{NO}_3^- + 5\text{H}_2\text{O} + 6e^- \quad (11)
\end{align*}
\]

The mean energy consumption of electrolytic denitrification with an ion exchange membrane ranged between 26.9 and 112.9 kWh/kg-NO₃ with the Zn cathode. Cheng et al. (2005) reported an energy consumption of 40–220 kWh/kg-NO₃ with Ti/Pd-Rh as cathode and Reyter et al. (2011) reported an energy consumption of 20 kWh/kg-NO₃ with copper as cathode in paired electrolysis processes.

**Influence of different concentrations of supporting electrolyte**

It is important to mention that the concentration of electrolytes affects denitrification efficiency during electrolysis. Electrolysis coupled with a cation-selective membrane enables the separation between the cathode and the anode chambers. Using NaCl, the electrolyte concentration in the anode chamber was changed from 0 to 200 mM to find the optimum concentration, while the groundwater was being treated in the cathode chamber. Figure 5 shows the removal of nitrate at different electrolyte concentrations. A higher concentration of NaCl as an electrolyte improved the nitrogen removal rate, which was maximized at 1 mM of NaCl. The denitrification was significantly hindered when the concentration of NaCl was higher than 50 mM. This is because the Cl⁻ effectively reacted owing to the higher reducibility of Cl⁻ as compared to nitrate.

The removal of nitrate by electrolysis could follow the first-order kinetic model, where the rate is proportional to the dissolved contaminant concentration [C] (Dash & Chaudhari 2005), as follows:

\[
d\text{C}/dt = k_1[C] \quad (12)
\]

where \( k_1 \) (min⁻¹) is the observed first-order rate coefficient.

The values of the first-order kinetic parameters are given in Table 1. Dash & Chaudhari (2005) obtained a maximum first-order rate coefficient of 0.006947 min⁻¹, using metallic iron without a membrane at pH 7. In this study, the maximum coefficient was 0.0151 at 1 mM of electrolyte concentration in the anode chamber, which was twice as high compared with the previous study without using a cation membrane in the compartment.

**CONCLUSION**

The electrochemical reduction of nitrate has received a lot of attention because of its convenience and the treatability of nitrate as well as environmental sustainability without harmful byproducts. In this study, electrodes such as TiO₂, Cu, Pb, Ti/Ir/Ru, Ti/Ir/Ta, and Zn as the cathode were estimated to remove nitrate in the groundwater. In addition, the effect of

| Table 1 | First-order kinetic parameters |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | 0 mM            | 0.1 mM          | 0.5 mM          | 1 mM            | 10 mM           | 50 mM           | 100 mM          | 200 mM          |
| \( k_1 \) (min⁻¹) | 0.0030          | 0.0134          | 0.0104          | 0.0151          | 0.0112          | 0.0088          | 0.0092          | 0.0092          |
| \( R^2 \)       | 0.9737          | 0.9748          | 0.9722          | 0.9752          | 0.9699          | 0.9285          | 0.9377          | 0.9952          |
the current density was evaluated with an ion-exchange membrane in electrochemical denitrification. The results of the batch experiment to determine the cathode material showed that the conversion of nitrate to nitrogen was heavily dependent on the electrode material used. During the batch test, Zn was found to have the best nitrate removal rate as a cathodic electrode. Ti/Ir/Ru also presented future possibilities for practical application as a corrosion-resistant cathode. The current density was adjusted to 25, 50, and 100 mA/cm² to estimate the effect of nitrate removal with different current densities. The nitrate concentrations were decreased to 20 mg/L, 17 mg/L, and 15 mg/L at 25 mA/cm², 50 mA/cm², and 100 mA/cm² current densities, respectively. Ammonium production with various current densities indicated that the ammonium concentration increased for 30 minutes; however, after 1 hour, the ammonium concentration dropped to below 1.5 mg/L. The optimum electrolyte concentration in the anode side was 1 mmol of NaCl. The use of cation-selective membranes enables higher operating temperatures without fears about the stability of the membrane. This process converted nitrate to nitrogen with a mean energy consumption between 26.9 and 112.9 kWh/kg-NO₃.

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REFERENCES


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