AN *IN-SITU* DENITRIFICATION AND OXIDATION PROCESS WITH INJECTION OF ELECTROLYTIC HYDROGEN AND OXYGEN

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Continuous treatments of synthetic groundwater were conducted by using an *in-situ* denitrification and oxidation process, and measurements of water quality parameters such as nitrate, nitrite, DO, *etc.* were made over one year. In the *in-situ* process, hydrogen gas and oxygen gas were produced by using an electrolytic cell and were injected separately into a laboratory scale aquifer filled with glass beads. Experimental results demonstrated that stable denitrification and oxygenation of groundwater were achieved. During the initial phase of experiment, nitrite was accumulated in a hydrogen-injected zone; however, it was oxidized to nitrate in subsequent oxygen-injected zone. In addition, water quality parameters such as TOC, SS, turbidity and chromaticity were smaller in the effluent than influent, and no clogging problem was observed. From these results, we concluded that the present process has several superior performances in terms of stability, effluent water quality and simplicity in long-term operation.

Key Words: *in-situ, denitrification and oxygenation, groundwater, hydrogen, oxygen, SPE electrolysis*

1. INTRODUCTION

Nitrate contamination in groundwater due to over use of nitrogen fertilizer and/or inappropriate managements of livestock waste has become one of worldwide environmental issues. Especially in shallow aquifers, contamination is serious, where relatively higher DO exists¹⁾. Several researches have been carried out to study the remediation of contaminated groundwater as a drinking water source²⁻⁴⁾. *In-situ* biological denitrification is one of the most promising processes, owing to relatively low cost, decomposition to a harmless product and nitrogen gas^{5, 6)}.

Denitrification is a respiratory process in which bacteria use nitrate or nitrite as a terminal electron acceptors⁷⁾. Different types of organic hydrogen donors such as methanol⁸⁾, ethanol⁹⁾ and sucrose¹⁰⁾ have been used. These studies demonstrated that denitrification rates are sufficiently high, but at the same time, the occurrence of secondary pollution problem caused by injected substance as well as clogging problems caused by excessive growth of heterotrophic bacteria and/or produced nitrogen gas⁹⁻¹²⁾. On the other hand, autotrophic *in-situ* denitrification has been proposed in former studies,

demonstrating no or lesser secondary pollution and clogging problems¹³⁻¹⁶⁾.

However, to our knowledge, former studies on autotrophic *in-situ* denitrification process indicated that effluent from the process contains no or very low dissolved oxygen (DO) and small but certain amounts of organic carbon. Groundwater flows out to stream or lake when water table is higher than water level of stream or lake^{17, 18)}. In this case, we think that low DO in effluent may affect and change original subsurface environments. In addition, supplement of oxygen will be needed when a part of purified groundwater flows out to surface water or treated water is used for cultivation of aquatic life forms besides drinking water supply. In this regard, effluent containing DO may be more preferable.

In our former studies^{19, 20)}, a combined biological and electrochemical denitrification process equipped with solid polymer electrolyte (SPE) membrane electrode was studied, and the simplicity in operation and superior performance with small amount of energy consumption were demonstrated. By an application of electric current to SPE membrane electrode, hydrogen gas and oxygen gas are available concurrently. Therefore, in

this study, focusing on nitrate contaminated shallow aquifers, an *in-situ* denitrification process using electrolytic hydrogen and oxygen was designed; and continuous experiments were conducted to evaluate the denitrification and oxygenation performances.

2. MATERIALS AND METHODS

(1) Experimental apparatus

Fig. 1 shows the experimental apparatus used in this study. The dimensions of a laboratory scale aquifer were 1950 mm in length, 25 mm in width and 780 mm in height, respectively. The aquifer was filled with glass beads ($\phi=2$ mm). Total volume and effective liquid volume of aquifer were about 40 l and 16 l, respectively. HRT was calculated based on the effective liquid volume. 18 sampling ports were allocated in horizontal and vertical directions with 300 mm interval, as shown in Fig. 1.

To realize a uniform flow, a synthetic groundwater was fed and withdrawn continuously by using peristaltic pumps. Flow rate of every peristaltic pump was checked almost every day. However, as shown in Fig. 1, peristaltic pumps were not set for two withdrawn lines to keep the groundwater flow rate of the influent and effluent at a constant value. In addition, the effluent from aquifer was discharged through an overflow weir to keep the water level.

In experiment, hydrogen and oxygen gases were produced by using a SPE membrane electrode, and were injected using peristaltic pumps at the bottom of port 6 and port 15, respectively.

To avoid algal growth, the aquifer and every tube were covered with a light-shielding curtain or aluminum foil. The apparatus was placed in a chamber where temperature was controlled at 20 degree Celsius.

Fig. 1 Scheme of *in-situ* denitrification.

(2) Continuous experiment

Table 1 shows a composition of synthetic groundwater used in this study, which was prepared by dissolving each constituent in deionized water. Conditions of continuous experiments were shown in Table 2. Before the experiments, an enriched denitrifying culture¹⁹⁾ and a supernatant of soil/water mixture were inoculated into the aquifer, and batch treatments of synthetic groundwater were conducted for 18 days in the same manner for gas injections in continuous experiments.

As shown in Tables 1 and 2, three different runs (Runs 1 to 3) were conducted with constant flow rate, temperature, influent nitrate concentration, oxygen injection rate were kept constant, while concentration of NaHCO₃ and hydrogen injection rate were changed. The concentration of NaHCO₃ (i.e. 102 mg-C/l) was set referring to a concentration range of 2.81 to 484.8 mg-C/l in groundwater reported in former studies²¹⁻²³⁾.

In continuous experiments, mass balances on hydrogen and oxygen were evaluated in zones “ANAERO” and “AERO” near injection ports of hydrogen and oxygen, respectively. These zones were shown in left and right sides of Fig. 1, respectively.

Table 1 Composition of synthetic groundwater.

Chemical	Concentration (mg/l)
K ₂ HPO ₄	1.76
KH ₂ PO ₄	2.08
MgSO ₄ ·7H ₂ O	4.00
FeCl ₃ ·6H ₂ O	1.92
NaCl	0.96
CaCl ₂	1.12
NaNO ₃ (as N)	15
NaHCO ₃ (as C)	10.2~102
TOC (Deionized water)	2.6

Table 2 Experimental conditions.

	Run 1	Run 2	Run 3
Flow rate (Q)	5.8±0.1 l/d		
HRT	2.65~2.74 d		
Temperature	20±2 °C		
NaHCO ₃ (as C)	10.2 mg/l	102 mg/l	
H ₂ gas	8.6±1.0 mmol/d		15.8±1.9 mmol/d
O ₂ gas	6.2±1.2 mmol/d		

(3) Sampling and analytical methods

Liquid samples were taken from influent, ports 1-18 and effluent by using syringe, while gas sample from gas effluent and three way cocks equipped near the gas injection points by Tedlar bags. Liquid samples for the measurement by ion chromatography were filtered using a $0.45\ \mu\text{m}$ syringe-driven membrane filter (25CS045AN, Advantec), while no filtration was made for other samples.

Ionic constituents such as nitrate (NO_3^-), nitrite (NO_2^-), chloride ion (Cl^-) and sulfate (SO_4^{2-}) were measured with ion chromatography (HIC-10A, Shimadzu). Total organic carbon (TOC), DO and pH were measured with TOC analyzer (TOC5000A, Shimadzu), DO meter (Ultra DO meter, Central Kagaku Corp), and pH meter (pH510, Eutech instruments), respectively. Turbidity and chromaticity were measured by using digital turbidity/chromaticity meter (WA-PT-4DG, Kyoritsu Chemical Check Lab. Corp). Temperature in thermostatic chamber was monitored by using temperature recorder (TR-71D, T&D Corp).

(4) Mass balances of hydrogen and oxygen

In this study, the mass balances of hydrogen gas and oxygen gas were evaluated according to zone “ANAERO” and zone “AERO”, respectively.

The equation for hydrogen gas is as follows:

$$Q_{\text{H}_2} = Q_{\text{De}} + Q_{\text{O}_2} + Q_{\text{Ex}} + Q_{\text{Ex,gas}} \quad (1)$$

Where Q_{H_2} is the amount of hydrogen gas injected per day, Q_{De} and Q_{O_2} are equivalent amounts of hydrogen used for denitrification and oxygen utilization, and Q_{Ex} and $Q_{\text{Ex,gas}}$ are those discharged with bulk liquid and gas effluent, respectively. Q_{Ex} and $Q_{\text{Ex,gas}}$ were measured directly and the amount of Q_{De} and Q_{O_2} were calculated by the following equations:

$$Q_{\text{De}} = 2.5 \times Q \times (C_{\text{Nin}} - C_{\text{Nout}}) / 14 \quad (2)$$

$$Q_{\text{O}_2} = 2 \times (Q \times (DO_{\text{in}} - DO_{\text{out}}) / 32) \quad (3)$$

Where Q is the flow rate, C means concentration and subscripts Nin and Nout of C mean nitrate of influent and effluent for the zone “ANAERO” in Fig. 1, respectively.

The equation for oxygen gas is as follows:

$$Q_{\text{O}_2} = Q_{\text{O}_{2\text{ox}}} + Q_{\text{Ex,gasO}_2} + Q_{\text{H}_2\text{dis}} + Q_{\text{TOCde}} + Q_{\text{Ni}} \quad (4)$$

Where Q_{O_2} is the amount of oxygen gas injected per day, $Q_{\text{O}_{2\text{ox}}}$ and $Q_{\text{Ex,gasO}_2}$ are the amount of DO increased in zone “ANAERO” and discharged to gas effluent, respectively. $Q_{\text{H}_2\text{dis}}$, Q_{TOCde} and Q_{Ni} are the equivalent amounts of utilized hydrogen discharged from the zone “ANAERO”, TOC degradation and nitrification from nitrite to nitrate, respectively. $Q_{\text{O}_{2\text{ox}}}$ and $Q_{\text{Ex,gasO}_2}$ are measured directly and the amount of $Q_{\text{H}_2\text{dis}}$, Q_{TOCde} and Q_{Ni} were calculated by the

following equations:

$$Q_{\text{H}_2\text{dis}} = 0.5 \times Q_{\text{Ex}} \quad (5)$$

$$Q_{\text{TOCde}} = Q \times (\text{TOC}_{\text{in}} - \text{TOC}_{\text{out}}) / 12 \quad (6)$$

$$Q_{\text{Ni}} = Q \times (C_{\text{Nin}} - C_{\text{Nout}}) / 28 \quad (7)$$

Where TOC_{in} and TOC_{out} are influent and effluent concentrations of TOC in the zone “AERO”, C means concentration and subscript Nin and Nout of C mean nitrite of influent and effluent for the zone “AERO” in Fig. 1, respectively.

3. RESULTS AND DISCUSSION

(1) Nitrogen removal

Fig. 2 shows time course changes in nitrate and nitrite concentrations at positions of 0 m (influent), 0.75 m, 1.05 m, and 2 m (effluent) in Runs 1 to 3, respectively. In addition, pH values at the same positions were shown in Fig. 3. Concentrations and pH values shown in both figures were average values of liquids obtained along three vertical sampling ports.

In Run 1, nitrate concentrations decreased from the influent concentration and nitrite concentrations increased at the position of 0.75 m from the inlet. This position corresponded to the place where hydrogen was injected (i.e. at the bottom of port 6). At the position of 1.05 m, nitrite concentrations decreased and nitrate concentrations increased slightly, while at the position of 2 m (effluent), nitrite concentrations gradually decreased and became nearly zero. Values of pH increased up to around 10 at the position of 1.05 m and then decreased. These results indicated that denitrification started immediately after the continuous experiment started. Moreover, nitrite produced by the injection of hydrogen was oxidized

Fig. 2 Time courses of nitrate and nitrite.

Fig. 3 Time courses of pH.

to nitrate by the injection of oxygen. As nitrite is much more toxic than nitrate²⁴⁾, oxidation of nitrite to nitrate may be advantageous in reducing toxicity of effluent.

In Run 2, the concentration of inorganic carbonate ions was increased from 10.2 to 102 $mg\text{-}C/l$, thus pH variations along aquifer were buffered and maintained around 8.5 to 9 (Fig. 3). Accumulation of nitrite shrunk and more stable denitrification was achieved. Nitrite was produced sometimes at the position of 1.05 m , but it was completely removed in the effluent. If growth of denitrifying bacteria is neglected, the complete denitrification of nitrate with hydrogen can be represented by the following reaction⁵⁾:

Total removal efficiency of nitrate by aquifer in Runs 1 and 2 were in the range of 20 to 40%. From reaction 8, it can be considered that these poor removal efficiencies were attributed to smaller amount of hydrogen gas injected (8.6 $mmol/d$ in Run 1 and Run 2) in comparison with a stoichiometrically required amount (15.8 $mmol/d$) for nitrate loading in this study.

In Run 3, the hydrogen injection rate was increased to 15.8 $mmol/d$ corresponding to a stoichiometrical amount for the complete removal of influent nitrate. Nitrate removal efficiencies increased up to around 70% and very stable denitrification was achieved with no significant accumulation of nitrite (The detection limit of nitrite was less than 0.1 mg/l according to experimental test). Total nitrogen concentration of effluent was less than 10 $mg\text{-}N/l$ (Drinking water quality standards, Ministry of Health, Labour and Welfare of Japan, 2003). Fig. 4 shows mass balance on hydrogen gases in Runs 2 and 3, based on the Eqs. 1~3. In Fig. 4, percentages to Q_{H_2} for each term in the right side of Eq. 1 were shown.

Fig. 4 Comparison of mass balance on hydrogen gases, where 100% indicates the amount of hydrogen injected.

As shown, hydrogen gas injected was almost completely consumed by or discharged to terms in Eq. 1. From Fig. 4, it can be said that a satisfactory mass balance was obtained and most data indicated more than 90% of the injected hydrogen gas was consumed by denitrification (Q_{De}) and DO consumption (Q_{O_2}). The amount of hydrogen gas discharged to gas phase was negligibly small, indicating no or very rare occurrence of problems such as hydrogen explosion. In Run 3, a stoichiometrical amount of hydrogen was injected, but a part of hydrogen was used for DO utilization, so that it can be considered that the corresponding value of removal efficiency (i.e. about 30 %) was reduced.

(2) Oxygenation

Fig. 5 shows time course changes in DO in aquifer as well as influent and effluent. Influent synthetic groundwater contained about 7 to 9 mg/l . DO decreased below 2 or 3 mg/l at the position of 0.75 m , and then slightly increased at the position of 1.05 m , while DO in effluent contained more than 15 mg/l . This is attributed to the oxygen injection into aquifer. From these results, it was considered that a part of

Fig. 5 Time courses of DO.

Fig. 6 Comparison of mass balance on oxygen gases, where 100% indicates the amount of oxygen injected.

oxygen injected was transported upstream by diffusion in aquifer.

Fig. 6 shows mass balance results on the following fractions of oxygen in the zone “AERO” in Fig.1 according to Eqs. 4~6.

From Fig. 6, it was found a half of injected oxygen was used for oxygenation. In addition, the rests were discharged to gas phase or utilized for oxidations of incoming hydrogen and TOC. Moreover, total fractions considered in Eq. 4 were roughly about 90% (i.e. 10% smaller than the amount of oxygen injected) and the amount of oxygen utilized for nitrification of nitrite in Fig. 6 was negligibly small in comparison of that of oxygen injected. The reason was not known, but it was supposed that a part of DO in effluent was escaped to atmosphere.

(3) Turbidity, chromaticity, TOC and others

Fig. 7 shows time course changes of turbidity and chromaticity in a part of Run 2 and Run 3. These water qualities tended to decrease with distance of aquifer and became to around 0.2 NTU and 2.0 PCU in influent, respectively. These values meet the current drinking water standard²⁵⁾. As glass beads have a poor adsorption capacity of these parameters, it was thought suspended solids as well as soluble and colloidal constituents exerting chromaticity were absorbed or attached to biofilms formed on glass beads²⁶⁾.

Fig. 8 shows time course changes of TOC and difference of TOC between influent and effluent. Deionized water used in this study contained about 2.6 mg/l TOC on average. Although data variations were observed, the TOC difference between influent and effluent was about -0.83 mg/l, indicating TOC produced in aquifer was removed. As Schnobrich *et al.* (2007) reported a slight accumulation of TOC (i.e. 0.387 ± 0.25 mg/l as C) in an *in-situ* hydrodenitrification

Fig. 7 Time courses of turbidity and chromaticity.

process, it is considered that TOC produced in denitrification zone was removed aerobically in the oxygen injection zone²⁷⁾.

During the continuous experiment over one year, no clogging problem was observed. In addition, a visible thin film was observed on the surface of glass beads. It was thought these were attributed to small net growth rates of autotrophic microorganisms in aquifer. Concentrations of chloride ion and sulfate ion in Runs 1 to 3 were almost kept constant through the aquifer, which were around 2.00 mg/l and 1.60 mg/l, respectively. Based on experimental results in Figs. 2, 5, 7, and 8, it can be concluded that the present *in situ* process has superior performances in terms of stability, effluent water quality, and simplicity in operation. A further kinetic study will be needed to analyze and evaluate the performance more precisely under different operation and design conditions.

Fig. 8 Time courses of TOC.

4. CONCLUSIONS

Based on experimental and analyzed results in this study, the following conclusions can be drawn:

- 1) Except initial startup period, continuous and stable treatments of a synthetic groundwater were achieved over one year.
- 2) Nitrate removal efficiencies increased up to around 70% and very stable denitrification was achieved with no significant accumulation of nitrite.
- 3) Water quality parameters such as TOC, turbidity and chromaticity tended to be smaller in effluent concentrations.
- 4) More than 90% of hydrogen gas injected was utilized for denitrification and DO consumption and a very small amount of hydrogen gas leaked out from the aquifer; thus it can be expected that occurrence of explosion is extremely low.

These results mentioned above indicate the effectiveness of the present *in-situ* process; however, a further long-term study under different hydrogen/oxygen injection conditions as well as kinetic analysis would be needed to evaluate the optimum design and operation conditions.

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