



SIMULTANEOUS OXIDATION AND REDUCTION TREATMENTS OF POLLUTED WATER BY A BIO-ELECTRO REACTOR

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ABSTRACT

Application of a bio-electro reactor for treatment of various kinds of polluted water was investigated experimentally. Aqueous solution of nitrate, ammonium and/or organic matter were used as synthetic polluted water. Denitrification of the nitrate polluted water without organic matter proceeded effectively by utilizing hydrogen gas produced by electrolysis of water in the reactor. The bio-electro reactor was also available for the treatment of nitrate polluted water containing organic matter when the C/N concentration ratio was up to 1.0 under the condition of 100 mA of applied electric current. The nitrate removal efficiency from nitrate polluted water containing acetate at C/N=1.0 was more than 90% at 5 hours of HRT and 80% even at 2.8 h HRT. For the treatment of ammonium polluted water, nitrification and denitrification proceeded simultaneously in a bio-electro reactor where nitrifying and denitrifying microorganisms were immobilized on the electrodes. The results obtained in this study suggested that the bio-electro reactor system was capable of application for oxidation and reduction treatments of the nitrate and ammonium polluted water.

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KEYWORDS

Bio-electro reactor; biofilm; carbon electrode; denitrification; electric current; electrolysis; hydrogen donor; immobilized bacteria electrode; nitrification.

INTRODUCTION

From the standpoint of the conservation of environment and water resource, nitrogen removal from wastewater and nitrate-polluted ground water has been one of the most important problems. Biological denitrification has been an available process for nitrate removal from various kinds of polluted water. For biological nitrate reduction to nitrogen gas, hydrogen donor is necessary as electron source. The hydrogen donor requirements can be provided to the treatment system by internal source such as organic matter contained in the polluted water and cell tissue and/or by external sources. However, it has been needed to develop efficient treatment processes in function of the constituents present in the polluted water.

In some biological denitrification processes for wastewater, sufficiently contained organic matter may be used as hydrogen donor to support denitrification efficiently (Tchobanoglous and Burton, 1991). Whereas an external source of hydrogen donor must be added to the system in the treatment of nitrate polluted water that have no or little hydrogen donor (Klapwijk *et al.*, 1981). The removal process using the external hydrogen donor source such as methanol reaches high rate denitrification, however, a post-treatment process is necessary to remove excess methanol from the system, since its excessive addition is essentially needed to promote denitrification (Claus *et al.*, 1985; Hoek *et al.*, 1987). Utilization of hydrogen gas as external source

of hydrogen donor is an alternative and may be favorable for denitrification treatment of nitrate polluted groundwater (Kurt *et al.*, 1987). However, poor solubility of hydrogen gas in water caused low efficiency in the utilization of hydrogen provided to the system and also incomplete denitrification that appears as accumulation of nitrite.

In our previous study (Sakakibara and Kuroda, 1993; Sakakibara *et al.* 1994 a), a novel denitrification process was investigated by a bio-electro reactor. The bio-electro reactor consisted of immobilized denitrifying bacteria electrode as cathode and carbon electrode as anode. In the bio-electro reactor, denitrifying bacteria immobilized on the cathode utilize immediately hydrogen gas produced by electrolysis of water on the surface of cathode and reduce nitrate to nitrogen gas as following overall reaction formula; electrolysis of water on cathode;



denitrification using hydrogen gas in the denitrifying biofilm on cathode;



On the other hand, overall electrochemical reactions on anodic carbon electrode might occur as follows (Kinoshita, 1988; Sakakibara *et al.*, 1994 b);



or



In that bio-electro reactor system, feasibility of denitrification by utilizing hydrogen gas efficiently and simple denitrification control by applying electric current was demonstrated by low strength nitrate solution (Sakakibara and Kuroda, 1993).

A bio-electro reactor system may be applicable to some oxidation treatments as well as reduction treatment by hydrogen gas produced, if the anodic reactions such as oxygen formation and other electrochemical oxidation can be utilized to. In this study, the extent of application of the reduction (denitrification) and oxidation treatment by the bio-electro reactor for constitution of polluted water was investigated experimentally. At the first step of this investigation, removal treatment of polluted water containing nitrate and organic matter at various concentration ratio was carried out in batch and continuous experiments. In addition feasibility of the application of a bio-electro reactor system to removal of ammonium, i.e. nitrification and denitrification treatments, was investigated using the synthetic polluted water.

MATERIALS AND METHODS

Batch Experiment

A schematic of the batch experimental apparatus was shown in Figure 1(a). The apparatus consisted of a cylindrical vessel made of poly vinyl chloride resin, circulation pump and gas collector. Immobilized denitrifying bacteria electrodes and carbon electrodes were installed in the vessel as cathode and anode, respectively, and connected to DC power supply. Bulk liquid in the reactor was mixed by a circulation pump. The liquid volume of the reactor was 7.9 l and the total cathodic surface area immersed in the liquid was 1270 cm². The temperature of the reactor was controlled at 38 °C with water bath.

The immobilized denitrifying bacteria electrode as cathode was prepared through the following procedure; a mixed culture suspension of denitrifying bacteria obtained from a denitrification plant of exudate from sanitary landfill was inoculated into the reactor. Aqueous solution of nitrate, acetate, n-butyrate and other trace nutrients was added periodically to the reactor in order to enrich and adhere the bacteria on the surface of the electrodes for two months. After the suspension of the enriched culture have been discharged completely from the reactor, the denitrifying bacteria adhered on the electrodes were acclimatized with periodical addition of aqueous solution of nitrate and other trace inorganic nutrients, and 100 mA of electric current applied continuously for two months.

After the reproducible nitrate reduction to nitrogen gas has been confirmed, batch experiments were carried out using synthetic wastewater prepared by dissolving sodium nitrate (35 mg-N•l⁻¹) in tap water. Acetate, one of the typical organic matter contained in wastewater, was used at various concentrations. The conditions of batch experiments were listed in Table 1. The initial C/N concentration ratios shown in Table 1 express the concentration ratio between total carbon in acetate and total nitrogen in nitrate in the prepared synthetic wastewater. Measurements were made for time course changes of gas production and concentration of nitrate, nitrite, and acetate. ORP and pH of the bulk liquid in the reactor was also measured.

Continuous Experiment

A schematic of continuous experimental apparatus was shown in Figure 1(b). The apparatus consisted of a carbon cylinder, a carbon rod, circulation pump and gas collector. The carbon cylinder and the carbon rod were installed concentrically and used as cathode and anode, respectively. The denitrifying bacteria were adhered on the inner surface of the carbon cylinder used as cathode and acclimatized as described above. The liquid volume of the reactor was 2.8 l and effective surface area of the cathode was 1100 cm².

After confirming steady nitrate reduction to nitrogen gas with continuous feeding of nitrate solution prepared by dissolving sodium nitrate in tap water, the continuous experiments were carried out by changing HRT and C/N feeding ratio. The experimental conditions for continuous operation were listed in Table 2.

TABLE 1 EXPERIMENTAL CONDITION OF BATCH OPERATION,

run No.	initial nitrate conc. [mg-N•l ⁻¹]	initial C/N conc. ratio [-]	current [mA]	temperature [°C]
B-1	34.7	0	100	38
B-2	29.2	0.7	100	38
B-3	36.7	1.0	100	38
B-4	35.4	1.5	100	38
B-5	37.4	4.5	100	38
B-6	37.6	4.7	0	38

TABLE 2 EXPERIMENTAL CONDITION OF CONTINUOUS OPERATION

run No.	HRT* [h]	nitrate conc. [mg-N•l ⁻¹]	influent C/N ratio [-]	current [mA]	anodic electrode**
C-1	67.2	42.5	0	100	AC
C-2	24.0	42.5	0	100	AC
C-3	12.0	42.5	0	100	AC
C-4	12.0	42.5	0	100	G
C-5	9.0	42.5	0	100	G
C-6	5.0	42.5	0	100	G
C-7	5.0	42.5	1	100	G
C-8	3.5	42.5	1	100	G
C-9	2.8	42.5	1	100	G

*HRT; hydraulic retention time, **AC; Amorphous carbon, G; Graphite

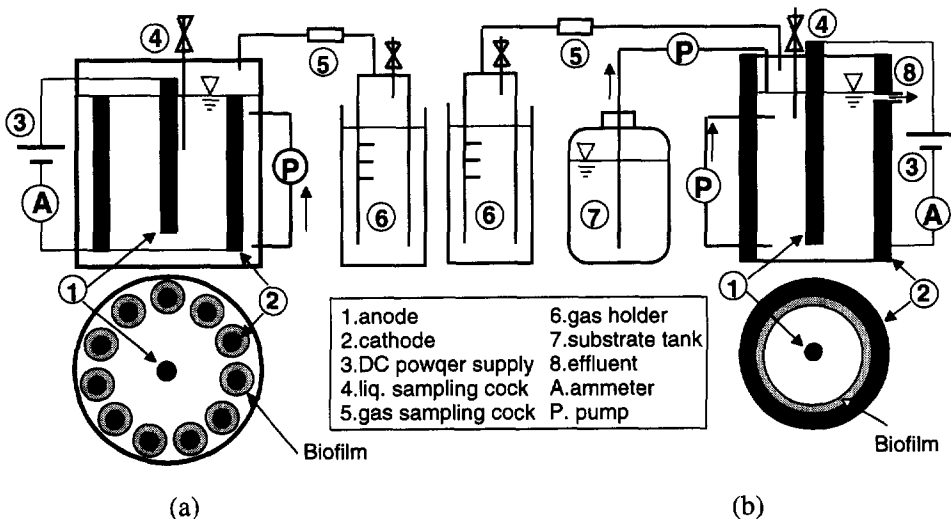


Fig. 1 schematic diagrams; (a) batch experimental apparatus, (b) continuous experimental apparatus

Experiment of Treatment of Ammonium polluted Water

The experiments of nitrogen removal from ammonium polluted water were carried out by using a bio-electro reactor equipped with immobilized nitrifying and denitrifying bacteria electrodes. The immobilized bacteria electrodes were prepared as follows; an activated sludge obtained from a municipal wastewater treatment facility was inoculated into a reactor where carbon and/or stainless steel electrodes were immersed. An aqueous solution of ammonium acetate and other trace nutrients was added periodically to enrich and immobilize the bacteria on the electrodes. An oxic condition was maintained in the reactor by aeration. Batch experiments were performed by using $50 \text{ mg-N}\cdot\text{l}^{-1}$ of ammonium acetate solution and 80 mA of applied electric current in the reactor with aeration.

Analytical Methods

Prior analysis, all the liquid samples were filtered by cellulose nitrate membrane filter ($0.2 \mu\text{m}$ of nominal pore size). Nitrate and nitrite were analyzed by a high performance liquid chromatography (Shimadzu LC-6A). Acetate concentration was measured by injection of $0.2 \mu\text{l}$ liquid sample into a gas chromatography equipped with a flame ionization detector (Ohkura 103 FP SSC-1). Total nitrogen and ammonium concentrations were measured by standard methods. The gas composition was analyzed by a TCD gas chromatography (Shimadzu GC-3BT) and the amount of gas evolved to gas phase was measured by a gas collector connected to the headspace of the reactor. ORP was measured by $\text{Ag}/\text{AgCl}/(3.3 \text{ M}) \text{ KCl}$ electrode.

RESULTS AND DISCUSSION

Denitrification Treatment of Nitrate Solution Contained no Organic Matter

Figure 2 showed the time course of nitrate removal from nitrate solution in the absence of organic matter. ORP and pH in the reactor are also shown. Neither hydrogen gas produced by electrolysis of water nor nitrite were detected in the reactor while nitrate remained (data omitted). This result indicated that biological denitrification was supported efficiently by hydrogen gas in the continuous operation system.

ORP showed anoxic condition and pH was maintained around neutral value during reaction period. It may have been caused by electrochemical oxidation of anodic electrode as show eq. (3). A favorable condition for nitrate reduction by denitrifying bacteria may have maintained in the system since carbon dioxide derived from anodic carbon acted as buffer.

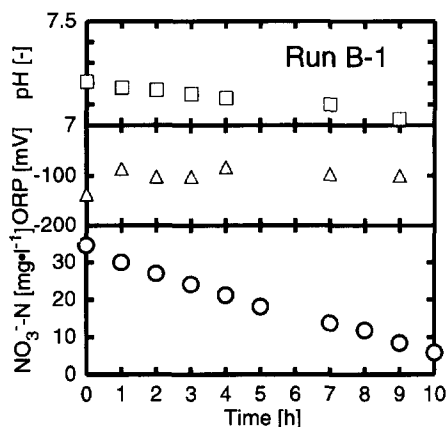


Fig. 2 Change of nitrate concentration and values of pH and ORP at run B-1

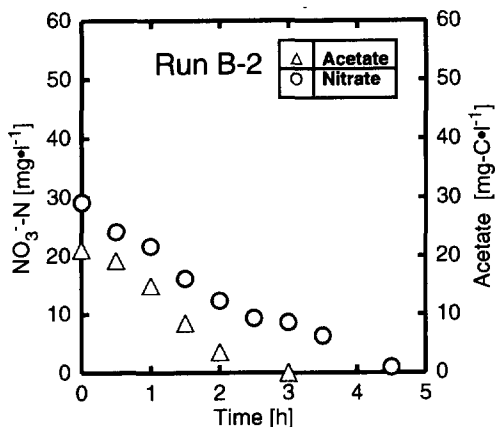


Fig.3 Change of nitrate and acetate concentrations at run B-2 (0.7 of C/N and 100 mA of electric current)

Removal of Nitrate and Organic Matter from Polluted Water

Figure 3 showed the time course change of nitrate and acetate concentrations under the condition of C/N ratio of 0.7 and 100 mA of applied electric current. Hydrogen gas was not detected while nitrate remained in

the reactor. Nitrate and acetate concentrations decreased linearly with the elapse of time. After whole amount of acetate has been degraded, removal of remained nitrate proceeded continuously; however its rate decreased and was nearly equal than the observed at Run B-1. These results indicate that nitrate and organic matter could be removed simultaneously since the organic matter as well as hydrogen gas produced by electrolysis of water, supported denitrification. In addition, denitrification rate was increased by simultaneous utilization of hydrogen gas and organic matter.

Figures 4 and 5 showed the time course change of nitrate and acetate concentration under the condition of C/N ratio of 1.0 and 100 mA (Run B-3) and C/N ratio of 1.5 and 100 mA (Run B-4), respectively. In the experimental run of C/N=1.0 (Figure 4), both nitrate and acetate concentrations decreased linearly during the run. However, in the experimental run of C/N = 1.5 (Fig. 5), nitrate and acetate were simultaneously removed until nitrate was completely transformed. After this point, acetate concentration was held almost constant. This results suggested that acetate may have been removed because the denitrifying bacteria immobilized on cathode surface utilized it as hydrogen donor for nitrate reduction to nitrogen gas. However, organic matter such as acetate is favorable for heterotrophic denitrifying bacteria to propagate, so, existence of adequate amount of organic matter may promote denitrification effectively.

Table 3 listed the results of the batch experiments with respect to the overall denitrification rates and the acetate remained after complete removal of nitrate in the reactors. The denitrification rate was accelerated by the existence of organic matter with nitrate and increased with a higher initial concentration ratio between organic matter and nitrate, i.e. initial C/N. This was caused by simultaneous utilization of acetate and hydrogen gas produced by electrolysis of water to reduce nitrate to nitrogen gas at the cathodic biofilm. However, acetate remained at high concentration of against that of nitrate while nitrate was removed efficiently at high rate. In the experiments that were carried out by applying 100 mA of electric current, residual acetate was observed at initial C/N ratio over 1.0. These results suggested that the bio-electro reactor operated at 100 mA of applied electric current was applicable to simultaneous removal of nitrate and organic matter from the polluted water at C/N concentration ratio up to 1.0, because complete removal of these pollutants could be performed at high rate without any post-treatment system.

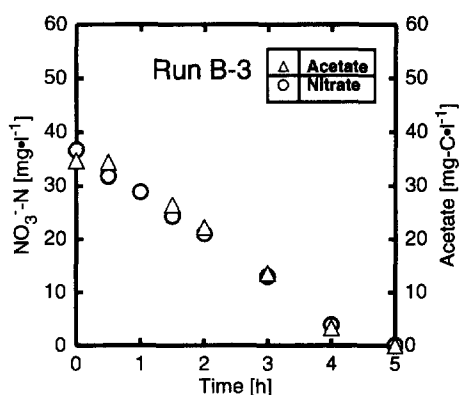


Fig. 4 Change of nitrate and acetate concentrations at run B-3 (1.0 of C/N and 100 mA of electric current)

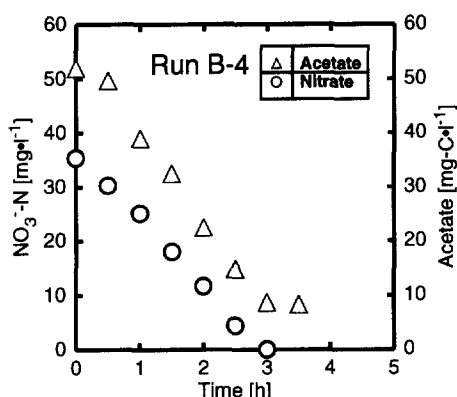


Fig. 5 Change of nitrate and acetate concentrations at run B-4 (1.5 of C/N and 100 mA of electric current)

TABLE 3 NITRATE REMOVAL RATE AND RESIDUAL ACETATE CONCENTRATION OBTAINED FROM BATCH EXPERIMENTS

run No.	initial C/N conc. ratio [-]	nitrate removal rate [mg-N·l ⁻¹ ·h ⁻¹]	residual acetate [mg-C·l ⁻¹]
B-1	0	2.9	-
B-2	0.7	9.4	0
B-3	1.0	8.6	0
B-4	1.5	13.7	8.0
B-5	4.5	12.1	97.4

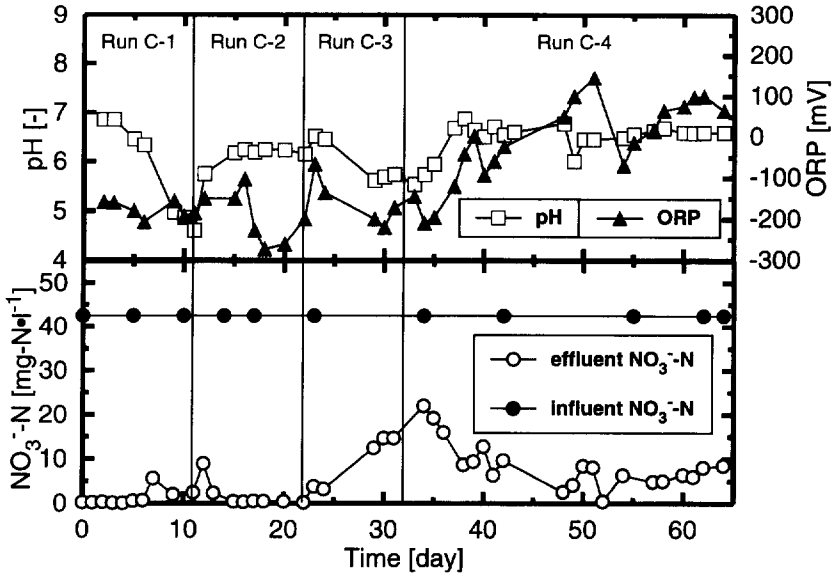


Fig. 6 Nitrate concentration in the reactor effluent and pH and ORP values under different continuous operations (from run C-1 to run C-4)

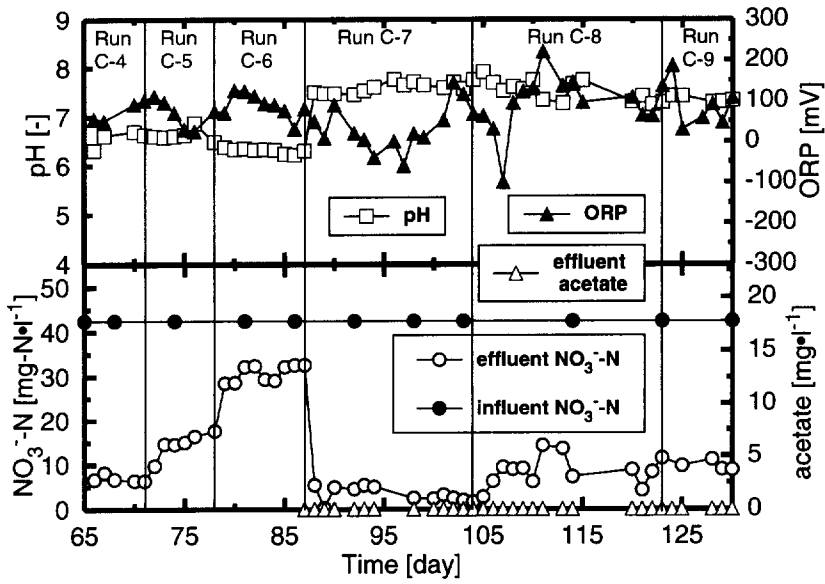


Fig. 7 Nitrate and acetate concentrations in the reactor effluent and pH and ORP values under different continuous operations (from run-C-4 to run C-9) (continued from Figure 6)

Effect of HRT on Removal of Nitrate and/or Organic Matter

Denitrification of nitrate polluted water in the absence of organic matter. Figures 6 and 7 showed nitrate and acetate concentrations of reactor influent and effluent under different continuous operating conditions.

ORP and pH values in the reactor are also shown in these figures. In all the continuous experimental runs, nitrite were not detected in the reactor effluent (data omitted). As can be observed, in the experimental runs from C-1 to C-6, nitrate removal was carried out efficiently by utilizing hydrogen gas produced by electrolysis of water at HRT between 12 and 24 hours. Assuming a theoretical production of hydrogen gas based on Faraday's law and stoichiometric nitrate reduction followed by eq. (2), complete reduction of nitrate to nitrogen gas can be performed at 12 h HRT. Actual removal efficiency was about 83 % against the theoretical value at 12 h HRT (Run C-3 and C-4). Since pH was maintained in a favorable range for denitrifying bacteria (around neutral value), it seems that pH was controlled by the electrochemical production of CO₂ on the anodic electrode. ORP value increased at lower HRT and showed slight oxidic condition. However, denitrifying activity of the denitrifying bacteria immobilized on cathode were not affected apparently.

Treatment performance of the water contained nitrate and acetate. In Figure 7, the results of experimental runs from C-7 to C-9 were shown. The C/N ratio in the influent was selected at 1.0 by referring to the results of the batch experiments. Hydrogen gas was not detected in the reactor during the experimental period from run C-7 to C-9 (data omitted). As can be seen in Figure 7, removals of nitrate and acetate were steadily proceeded during the period of each experimental run. At 5h HRT, nitrate concentration of 2.5 mg-N. l⁻¹ remained in the reactor effluent, whereas acetate was removed completely. Acetate was not detected in the reactor effluent even when the reactor was operated at 2.8 h HRT. Nitrate in reactor effluent increased at lower HRT. However, the effluent nitrate concentration was about 10 mg-N•l⁻¹ even when the HRT was controlled at 2.8 h., therefore, it was confirmed that nitrate removal could be performed efficiently. Judging from that acetate was removed completely and that hydrogen gas produced on the cathode surface was not detected in the reactor, we concluded that denitrification in cathodic biofilm promoted by simultaneous utilization of acetate and hydrogen gas.

ORP in the bulk liquid of the reactor varied between anaerobic and slight oxidic conditions and pH was maintained at about neutral value during the period of experimental runs from C-7 to C-9. As described previously, these conditions may have controlled by the electrolytic system.

Table 4 listed the average nitrate and acetate concentrations in the effluent reactor as well as denitrification efficiency and denitrification rate in each experimental run from C-7 to C-9. The removal efficiency of nitrate decreased at lower HRT. More than 90% and about 80% of nitrate were removed at 5h HRT and 2.8 h HRT, respectively. In addition, the nitrate removal rate increased slightly when 5.0 h HRT was decreased to 2.8 h.

TABLE 4 EXPERIMENTAL RESULTS FROM RUN C-7 TO RUN C-9

run No.	influent C/N[-]	HRT [h]	effluent		nitrate removal efficiency[%]	nitrate removal rate [mg-N•h ⁻¹]
			ave. nitrate [mg-N•l ⁻¹]	acetate [mg-C•l ⁻¹]		
C-7	1	5.0	2.5	0	93	22.5
C-8	1	3.5	9.2	0	78	26.0
C-9	1	2.8	10.0	0	76	32.5

Feasibility of Nitrogen Removal from the Water Containing Ammonia-nitrogen

Figure 8 and 9 showed the time course change of total-nitrogen (T-N), ammonium and nitrate concentrations. The dissolved oxygen (DO) concentration of bulk liquid is also shown. As can be observed in these figures, the ammonium concentration and T-N decreased with the elapse of time. After nitrate concentration has increased sharply up to 10 mg-N•l⁻¹ at the beginning of experiment (4 hours), it decreased with the elapse of time. These results suggested that nitrification reaction proceeded steadily by utilization of oxygen gas in the bio-electro reactor tested. In addition, denitrification occurred by simultaneous utilization of hydrogen gas produced by electrolysis of water and acetate though DO concentration of bulk liquid was more than 4 mg•l⁻¹ and ORP showed aerobic condition. The denitrification may have occurred at the deeper position of the biofilm immobilized on the surface of the electrodes since it seems that this region is maintained at anoxic conditions.

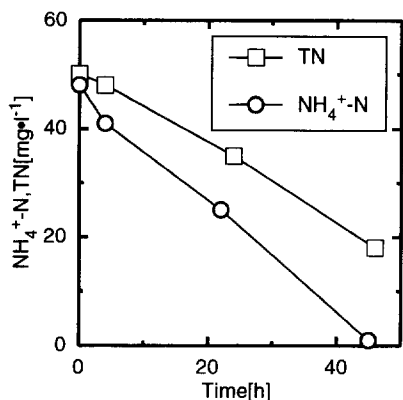


Fig. 8 Change of ammonium and total nitrogen (T-N) concentrations in the reactor

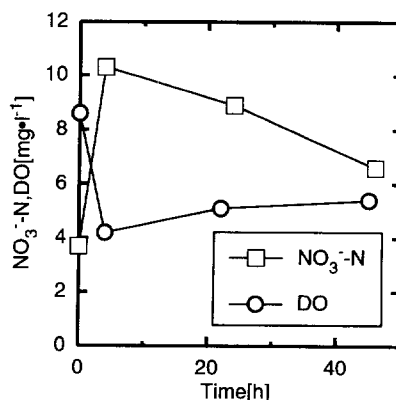


Fig. 9 Change of nitrate and dissolved oxygen (DO) concentrations in the reactor

CONCLUSIONS

The feasibility of application of a bio-electro reactor to reduction and oxidation treatments of various kinds of polluted water was investigated. Following results were obtained.

1) A bio-electro reactor was applicable to denitrification treatment of nitrate polluted water which did not contain any organic hydrogen donor by using immobilized denitrifying bacteria electrodes as cathode. Moreover, it suggested that a bio-electro reactor is an alternative system for the treatment of nitrate polluted water containing organic matter since denitrification reaction proceeds efficiently at high rate and organic matter is also removed by utilizing for denitrification as hydrogen donor.

2) The removal of nitrate and acetate was performed without any residuals under the condition of 100 mA of applied electric current at C/N ratio expressed as the concentration ratio between total carbon and total nitrogen in nitrate up to 1.0.

3) Nitrification and denitrification proceeded simultaneously in the bio-electro reactor which consisted the electrodes immobilized nitrifying and denitrifying microorganisms. The both reactions may occurred by utilizing hydrogen and oxygen gases produced by electrolysis of water.

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