



# THE DENITRIFICATION AND NEUTRALIZATION PERFORMANCE OF AN ELECTROCHEMICALLY ACTIVATED BIOFILM REACTOR USED TO TREAT NITRATE-CONTAMINATED GROUNDWATER

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## ABSTRACT

Continuous denitrification of nitrate-contaminated groundwater containing dissolved oxygen (DO),  $\text{SO}_4^{2-}$ , and no buffer was carried out with three identical electrochemically activated biofilm reactors. The reactors consisted primarily of denitrifying biofilm attached to the surface of the cathode, an amorphous carbon employed as the anode, and a DC power supply. In the reactors, denitrification and neutralization caused by  $\text{H}_2$  and  $\text{CO}_2$  produced from the cathode and the anode, respectively, occurred simultaneously when an electric current was applied. A complete-mix reactor model coupled with a biofilm-electrode model was developed in conjunction with a limiting-current theory. When the biofilms were sufficiently acclimated and adapted to the electric current, the denitrification performance calculated using the model was in fairly good agreement with experimental results. © 1997 IAWQ. Published by Elsevier Science Ltd

## KEYWORDS

Biofilm-electrode system; reactor model; biofilm model; denitrification; electric current; drinking water; ground water; hydrogen; neutralization; nitrate.

## INTRODUCTION

Nitrate contamination of groundwater is a cause of great concern because nitrate concentrations higher than 10mg-N/L (the drinking water standard set by the World Health Organization) have been observed in many sources of drinking water supplies. A number of investigations show that such contamination is particularly serious in shallow aquifer, which contains relatively high levels of DO; investigations further indicate that nitrogen fertilizers such as  $(\text{NH}_4)_2\text{SO}_4$  and human and animal sewage are a major source of this contamination (Follett, 1989; Kasuya et al., 1994).

The process of biological denitrification is considered an effective technology in the treatment of nitrate-contaminated water, because nitrate is converted to a non-toxic compound,  $N_2$ ; therefore, several types of bioreactors have been studied using proper electron donors such as alcohol and hydrogen gas (Kurt *et al.*, 1987; Chalupa, 1988). Sakakibara and Kuroda (1993) proposed an electrochemically activated biofilm reactor in which denitrifying microorganisms were immobilized on the surface of the cathode and an electric current was applied using an amorphous carbon as the anode. It was concluded that the application of an electric current promoted simultaneous denitrification and neutralization through the uses of  $H_2$  and  $CO_2$  produced by the electrolysis of water (Kinoshita, 1988; Sakakibara *et al.*, 1994b).

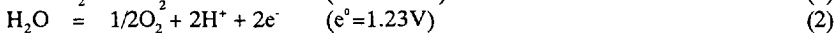
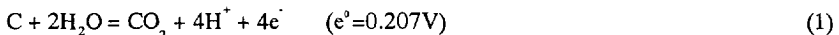
A one-dimensional biofilm-electrode model (Sakakibara *et al.*, 1994a) showed that the fundamental response of biofilm-electrode systems to an applied electric current can be divided into three regions; linear, plateau, and decline regions. In the linear region, denitrification is  $H_2$ -limited, in that the denitrification rate increases linearly with the electric current until nitrate transport begins to control the denitrification rate. In the plateau and decline regions, part of the  $H_2$  is leaked out to the bulk liquid, which can lead to a decrease in the reactor's performance.

Flora *et al.* (1994) analyzed and modeled a biofilm-electrode reactor (BER) that treats a nitrate solution in the presence of a phosphate buffer. A steady-state biofilm model was coupled with a completely-stirred reactor (CSTR) model and the performance was compared with experimental results. An excellent agreement was demonstrated when the biofilm-electrode system was in the linear region; it was also shown that in the plateau and/or decline regions  $H_2$ -inhibition kinetics might be used to explain the reduction in the denitrification rate at large electric currents.

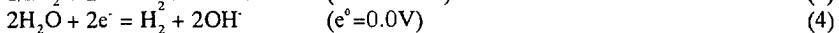
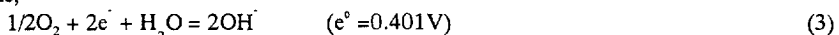
This paper describes the performance of an electrochemically activated biofilm reactor, or simply biofilm-electrode reactor (BER), which is operated in the linear region and treats nitrate-contaminated groundwater containing DO,  $SO_4^{2-}$ , and no buffer. Three identical BERs were used in the experiment and their performances were compared with a complete-mix reactor model developed according to a well-established mass and charge balance theory in conjunction with a limiting-current theory.

## DEVELOPMENT OF A COMPLETE-MIX REACTOR MODEL

*Electrochemical and biological reactions.* When electrodes are inserted into a solution containing nitrate and DO, and a sufficient potential of the order of several volts is applied, the following electrochemical reactions will be observed at the anode;



and at the cathode;



where  $e^0$  is the standard electrode potential. Eq. (1) shows a carbon dissolution reaction that occurs predominantly in cases where amorphous carbons are used as the anode (Kinoshita, 1988). A slightly larger value for  $e^0$  (about 0.4 to 0.5 V) in Eq. (1) was measured (Kinoshita, 1988), but even this potential is appreciably smaller than that in Eq. (2). The  $CO_2$  produced is dissolved and then dissociates into bicarbonate and carbonate ions. For the cathodic reactions, on the other hand, the standard electrode potential is larger in Eq. (3) than in Eq. (4).

Electrochemical reactions having smaller anodic and/or larger cathodic potentials can be predominant in electrochemical systems; therefore, it is thought that the reactions (1) and (3) proceed until DO is consumed by reaction (3). When DO is consumed and its concentration is zero at the surface of the cathode (or the applied electric current is larger than a limiting current for oxygen reduction,  $i_L$ ), hydrogen can be produced

and then utilized for denitrification (Kurt et al., 1987);



**A Simplified Biofilm-Electrode Model.** A one-dimensional biofilm-electrode model in a former study (Sakakibara et al., 1994a) showed that in the linear region the net denitrification rate under anoxic conditions increases linearly with the electric current; this is represented by

$$J_{\text{NO}_3^-} = \frac{i_c}{5F} \quad (6)$$

where  $i_c$  is electric current density at the cathode, all subjected to  $\text{H}_2$  evolution, and  $F$  is Faraday's constant.

When DO exists in influent, the net reaction rates of  $\text{O}_2$  reduction,  $\text{H}_2$  evolution, and denitrification are represented as a function of  $i_c$  and/or  $i_L$  as follows;

when  $i_c \leq i_L$ ,

$$\begin{aligned} J_{\text{O}_2} &= \frac{i_c}{4F} \\ J_{\text{H}_2} &= 0 \\ J_{\text{NO}_3^-} &= 0 \end{aligned} \quad (7)$$

when  $i_c > i_L$ ,

$$\begin{aligned} J_{\text{O}_2} &= \frac{i_L}{4F} \\ J_{\text{H}_2} &= \frac{i_c - i_L}{2F} \\ J_{\text{NO}_3^-} &= \frac{i_c - i_L}{5F} \end{aligned} \quad (8)$$

where  $J_{\text{O}_2}$  and  $J_{\text{H}_2}$  are the net reaction rates at the surface of the cathode for  $\text{O}_2$  reduction and hydrogen evolution, respectively. The production rate of inorganic carbon (IC) is assumed to be represented by

$$J_{\text{IC}} = \eta_{\text{IC}} \frac{i_a}{4F} \quad (9)$$

where  $\eta_{\text{IC}}$  is a yield coefficient for the formation of IC from the carbon electrode and  $i_a$  is the electric current density at the anode.

In Eqs. (7) and (8), an excess electric current over the limiting-current ( $i_L$ ) for  $\text{O}_2$  reduction is required in order to produce  $\text{H}_2$  and thereby to initiate denitrification. Fig. 1 shows the effects of DO and nitrate on the excess electric current required for complete denitrification. Influent DO concentration is assumed at 10 mg/L for different nitrate concentrations, and the limiting current  $i_L$  is approximated by

$$i_L = \frac{4FC_{\text{O}_2}}{a_c \theta} \quad (10)$$

The calculation results show that roughly 30 % of the electric current should be applied in excess to reduce 10mg-N/L of nitrate, and this number gradually decreases with increasing  $\text{NO}_3^-$  concentration in the influent.

**A Complete-Mix Reactor Model.** Assuming that gaseous compounds such as  $\text{H}_2$ ,  $\text{CO}_2$ , and  $\text{N}_2$  are in equilibrium between gas and liquid phases and are represented by Henry's law, a set of mass balance

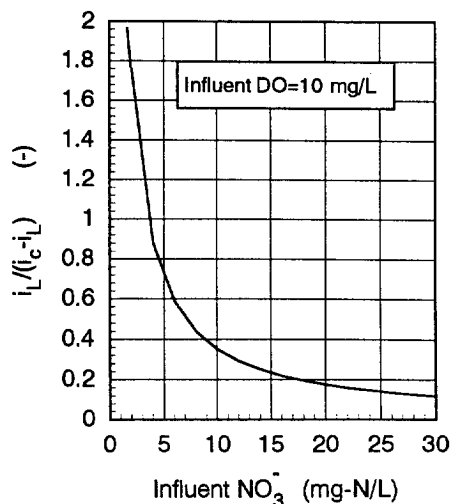


Figure 1. Effects of DO and nitrate on excess electric current required for complete denitrification.

equations at steady-state conditions are obtained in a complete-mix reactor. The governing equations are shown in Table 1. In Eq. (12), the sum of the partial pressures of H<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub> was assumed to be 1.0

Table 1. A complete-mix reactor model.

Mass balance equations;	Gas phase;
IC: $\frac{C_{ICf} - C_{IC}}{\theta} + a_c J_{IC} - \frac{P_{CO_2}}{RT} G' = 0$ (11-1),	$P_{H_2} + P_{CO_2} + P_{N_2} = 1$ (12)
O <sub>2</sub> : $\frac{C_{O_2f} - C_{O_2}}{\theta} - a_c J_{O_2} = 0$ (11-2),	Electroneutrality;
H <sub>2</sub> : $-\frac{C_{H_2}}{\theta} + a_c (J_{H_2} - 2.5J_{NO_3}) - \frac{P_{H_2}}{RT} G' = 0$ (11-3),	$C_{CA} - C_{AN} - C_{IC}(\alpha_1 + \alpha_2) + C_{H^+} - \frac{K_w}{C_{H^+}} = 0$ (13)
NO <sub>3</sub> : $\frac{C_{NO_3f} - C_{NO_3}}{\theta} - a_c J_{NO_3} = 0$ (11-4),	$\alpha_1 = (1.0 + \frac{C_{H^+}}{K_1} + \frac{K_2}{C_{H^+}})^{-1}$ (13-1)
N <sub>2</sub> : $\frac{C_{N_2f} - C_{N_2}}{\theta} + a_c \frac{J_{NO_3}}{2} - \frac{P_{N_2}}{RT} G' = 0$ (11-5),	$\alpha_2 = (1.0 + \frac{C_{H^+}}{K_2} + \frac{C_{H^+}^2}{K_1 K_2})^{-1}$ (13-2)

where  $C_i$  is a molar concentration of substance  $i$ ,  $a_c$  and  $a_a$  are specific surface areas of the cathode and the anode,  $\theta$  is hydraulic retention time,  $J_{H_2}$  and  $J_{O_2}$  are fluxes for hydrogen evolution and O<sub>2</sub> reduction at the surface of the cathode,  $G'$  is gas production rate,  $K_w$  is dissociation constant of water,  $R$  is gas constant,  $p_j$  is partial pressure of gas constituent  $j$ , and  $T$  is absolute temperature, respectively.  $\alpha_1$  and  $\alpha_2$  are distribution coefficients of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. The subscripts of  $f$ , CA, and AN mean feed solution, cation, and anion, respectively.

atm. Electroneutrality is expressed by Eq. (13) for ionic constituents of nitrate, carbonate, and bicarbonate ions, H<sup>+</sup>, OH<sup>-</sup>, and other supporting electrolytes.

## MATERIALS AND METHODS

Fig. 2 shows a schematic of the experimental apparatus used. Three identical biofilm reactors were used in the experiment. The reactors consisted of an amorphous carbon anode, a stainless cathode on which denitrifying microorganisms were immobilized, a mixing device to realize a complete-mix condition, and a DC power supply. Porous matrix (polyurethane foam) was attached to the surface of the cathode as a support medium to keep the biofilm stable. The effective liquid volume and surface area of the cathode were 0.205 L and 251 cm<sup>2</sup>, respectively. The details of the apparatus have been reported elsewhere (Sakakibara *et al.*, 1994b).

Table 2. Composition of synthetic groundwater.

Inorganic constituent	
K <sub>2</sub> HPO <sub>4</sub> : 9.4 (mg/L),	Cl <sup>-</sup> : 7-9 (mg/L)*
KH <sub>2</sub> PO <sub>4</sub> : 11.1 (mg/L),	NO <sub>3</sub> <sup>-</sup> : 3-5 (mg-N/L)*
NaCl: 5.1 (mg/L),	SO <sub>4</sub> <sup>2-</sup> : 4-5 (mg-S/L)*
CaCl <sub>2</sub> : 6.0 (mg/L),	pH: 6.9-7.6*
FeCl <sub>2</sub> · 6H <sub>2</sub> O: 10.2 (mg/L)	
MgSO <sub>4</sub> · 7H <sub>2</sub> O: 21.3 (mg/L)	

\* Original well water

Fig. 3 shows the relationship between carbon dissolution rates and electric current density ( $i_a$ ) for the amorphous carbon used in this study. The IC production rates increased with increasing  $i_a$  and were in fairly close agreement with Eq. (1) at an electric current density of about 0.1 mA/cm<sup>2</sup> or less. At larger electric current densities, however, some organic carbon was produced from the carbon electrode used in this study.

Tables 2 and 3 show the composition of synthetic groundwater and the experimental conditions in this study, respectively. Groundwater was prepared by dissolving 1.4 mM (i.e. 20mg-N/L) of NaNO<sub>3</sub> and a slight amount of inorganic nutrients such as phosphorus into well water, which originally contained about 0.14 mM (i.e. 4 mg-S/L) of SO<sub>4</sub><sup>2-</sup>, 1 mM of inorganic carbon, and a saturated amount of DO. Biofilms were built with organic substrates (glucose, formate, and acetate) for a period of three months, and then the

groundwater was fed continuously and a range of electric currents was applied (Table 3). Initially the applied electric current was kept constant at 5 mA in Run A and thereafter changed in a stepwise manner in Run B. In these experiments, measurements were made for effluent concentrations of nitrate, nitrite, sulfate, and pH; and these data were compared among the reactors. Ionic constituents such as nitrate were measured using an ion-chromatograph (Yokogawa Analytical Systems, IC7000).

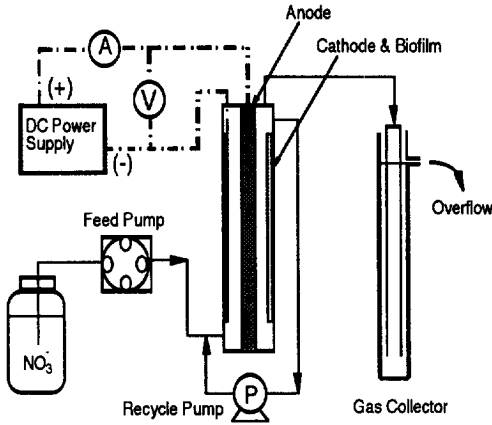


Figure 2. Schematic of experimental apparatus.

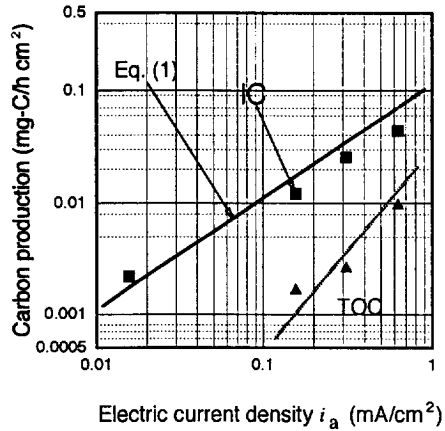


Figure 3. IC production rates of amorphous carbon used in this study.

Table 3. Experimental conditions.

Run No.	Electric current I (mA)	Influent $\text{NO}_3^-$ (mg-N/L)	HRT (h)		
			Reactor No.1	Reactor No.2	Reactor No.3
A	5.0	20.0	10.0	10.0	10.0
B-1	1.0	21.7	9.8	9.8	9.8
B-2	1.0	21.7	49.8	49.8	50.0
B-3	10.0	23.5	11.6	12.9	12.3
B-4	7.5	24.0	11.2	10.0	11.4
B-5	2.5	24.0	11.9	12.5	11.4
B-6	0.0	22.9	5 - 10	5 - 10	5 - 10
B-7	2.5	24.3	10.0	10.0	10.0

## RESULTS AND DISCUSSION

### Stability and Denitrification Performance

**Start-up period.** Fig. 4 shows a comparison of denitrification performances among the three reactors in Run A (Table 3). The applied electric current was 5 mA, which corresponds to the stoichiometric current needed to reduce all the DO and nitrate in the influent. The effluent nitrate concentrations and gas production rates were significantly larger in Reactor No. 1 in comparison with Reactors No. 2 and No. 3. The main component of the produced gas was  $\text{H}_2$  in Reactor No. 1, whereas it was  $\text{N}_2$  in No. 2 and No. 3. That is,

for the start-up period effective denitrification was not achieved in Reactor No. 1.

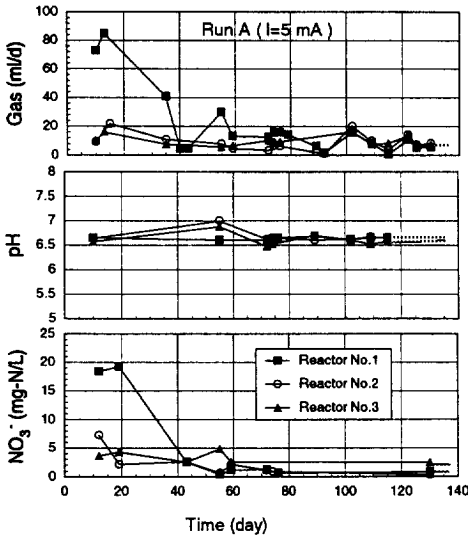


Figure 4. Comparison of denitrification performances in Run A (start-up period).

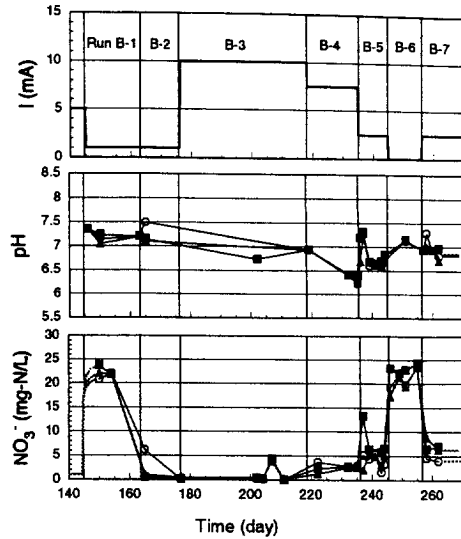


Figure 5. Denitrification performance in Run B (after adaptation to electric current).

After about one month of operation, however, the effluent nitrate concentrations in Reactor No. 1 decreased to about 1 or 2 mg-N/L, and the gas production rates tended to settle down to a certain steady-state value. At that point, effluent quality and gas production rates were almost the same among the reactors. These results demonstrate that some period of adaptation to the electric current may be required in order to ensure stable denitrification. The pH level of the effluent was in the range from 6.5 to 7.0, which is not significantly affected by the nitrate concentrations.

**Denitrification and neutralization performance.** Fig. 5 shows the responses in Run B, where electric currents were applied in a stepwise manner. The effluent nitrate concentrations varied with the applied electric current but were almost the same among all the reactors for any given level of electric current. Nitrate removal efficiencies were in the range from 0 to about 100%. In contrast to the nitrate concentration, most pH values at the various electric currents were around neutral; regardless of that, large differences in removal efficiency were observed and buffers such as phosphate were not added. It is thought that observed neutralization is due to the formation of  $\text{CO}_2$  from carbon electrode (Fig. 3) and subsequent dissociations into bicarbonate and carbonate ions.

In Run B-3, an electric current of 10 mA was applied, which was about two times the stoichiometric current required for complete denitrification. In subsequent runs, electric currents were decreased and then stopped altogether in Run B-6. We expected that this would result in the effluent nitrate concentration become instantaneously equal to the influent concentration. However, effluent concentrations remained about 2 to 3 mg-N/L less than the influent. This seems to be attributable to endogenous respirations of microorganisms and/or the presence of  $\text{H}_2$  gas in the polyurethane matrix, which was produced in the foregoing runs (e.g. Run B-3).

In Fig. 6, experimental results of nitrate removal efficiency and pH level were plotted against the applied electric current at the cathode, where the removal efficiency in Run B-5 was verified using a denitrification rate in Run B-6 ( $I=0\text{mA}$ ). Data obtained after one year of operation were also plotted. Except at relatively small electric currents, the removal efficiency increased with increasing electric current until nitrate was completely removed. When the electric current was relatively small and not sufficient to reduce nitrate

completely, the removal efficiency (or denitrification rate) declined to zero. In the case of Fig. 6, the effluent sulfate concentrations were almost the same as those for the influent, and the effluent nitrite concentrations were negligibly smaller than the influent nitrate concentrations (most were less than 0.1 mg-N/L). It is interesting to note, therefore, that the biofilm reactors achieved complete denitrification without nitrite accumulation or sulfate reduction.

### Comparison of Model Predicts

By using the reactor model shown in Eqs. (7) to (9) and (11-1) to (13-2), the effluent quality and removal efficiency of nitrate can be calculated for a given set of operation parameters such as HRT and electric current. In Fig. 6, the calculation results are shown and compared with the experimental results. The parameters used for the calculation are listed in Table 4, in which the limiting-current density  $i_L$  was obtained from Eq. (10).

As shown in Fig. 6, the calculation results were very similar to the experimental results. When the electric current was smaller than about 1 mA (or  $i_e < 0.004 \text{ mA/cm}^2$ ), the denitrification rates dropped to zero because of the suppression of  $\text{H}_2$  due to  $\text{O}_2$  reduction. The pH level of the effluent was kept around neutral in spite of different electric currents. This is attributable to a well-balanced relation with regard to the alkalinity formation in Eq. (5) and the neutralization in Eq. (1), which can produce an optimum pH range for denitrifying microorganisms without any pre-addition of buffers such as phosphate. On the other hand, as shown in Fig. 3, some organic carbon was produced at electric current densities larger than about  $0.1 \text{ mA/cm}^2$ . Islam et al. (1993) reported a sharp increase in the effluent COD at currents larger than 30 mA (i.e. corresponding to  $i_a = 0.2 \text{ mA/cm}^2$ ). Therefore, when such a large electric current is applied, an additional treatment should be considered in order that organic compounds not accumulate.

### CONCLUSIONS

The performance of electrochemically activated biofilm reactors that treat nitrate-contaminated groundwater containing  $\text{DO}$ ,  $\text{SO}_4^{2-}$ , and no buffer was demonstrated. By applying an electric current using an amorphous carbon as the anode, well-balanced reactions of denitrification and neutralization occur simultaneously at different electric currents. Sulfate reduction and nitrite accumulation were not observed. A reactor model coupled with a biofilm-electrode model in conjunction with the limiting-current theory is useful in evaluating the fundamental performance of the present biofilm reactor, when the biofilms are sufficiently acclimated and adapted to electric current.

Table 4. Parameter values used for calculation.

$a_s = 1.22$	( $\text{cm}^2/\text{cm}^3$ ),	influent pH = 7.5	(-)
$\bar{\theta} = 10$	(h),	$i_L = 2.7 \cdot 10^{-3}$	( $\text{mA}/\text{cm}^2$ )
$C_{\text{NO}_3^-} = 1.0$	(mM),	$\eta_{ic} = 1.0$	(-)
$C_{\text{NO}_2^-} = 1.7$	(mM),	$K_1 = 10^{6.3}$	(-)*
$C_{\text{O}_2} = 0.31$	(mM),	$K_2 = 10^{10.3}$	(-)*
$C_{\text{Ni}_2} = 0.55$	(mM),	$K_w = 10^{-14}$	(-)*

\*Adopted from Perry and Chilton (1973).

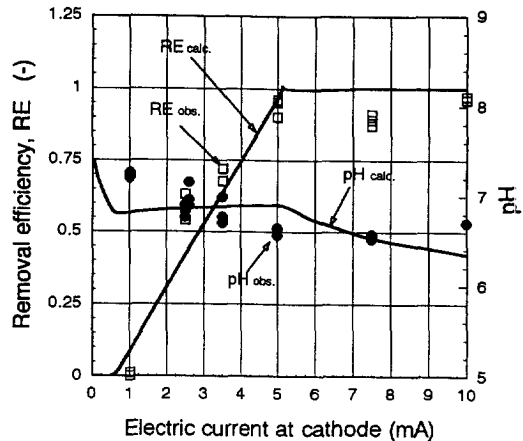


Figure 6. Relation between removal efficiency of nitrate, effluent pH, and applied electric current.

## ACKNOWLEDGMENT

This investigation was supported in part by Grant-in-Aid for Developmental Scientific Research from the Ministry of Education, Science and Culture of Japan.

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