

## (36) TREATMENT OF NITRATE AND PESTICIDE CONTAMINATED WATER BY A COMBINED BIOFILM-ELECTRODE REACTOR/ADSORPTION PROCESS

生物膜電極槽と吸着槽組み合わせプロセスによる硝酸塩、農薬汚染水の処理

Z. Feleke\*, Y. Sakakibara\* and M. Kuroda\*

Z.ファラカ\*, 榊原豊\*, 黒田正和\*

**Abstract;** Performance of a combined biofilm-electrode reactor/adsorption process for the removal of nitrate and trace pesticide from contaminated drinking water has been investigated. In long-term (more than 200 days) continuous experiments, influent and effluent concentrations of nitrate, nitrite, isoprothiolane and gas composition were measured at different electric current and pesticide loading conditions. Experimental results showed that complete and stable denitrification was achieved in BER without accumulation of nitrite and nitrous oxide. Nitrate removal ranges from 0 to 100% depending on electric current and inhibition by isoprothiolane was not observed. Isoprothiolane is removed by adsorption onto either granular activated carbon or silicone resin in the adsorption column. Removal efficiency of isoprothiolane exceeding 97 % was achieved and effluent concentration was below the guideline value (40 µg/l). The adsorption of isoprothiolane onto GAC and silicone conformed to Langmuir isotherm model. From these results, it is concluded that the combined process is applicable to treat nitrate and pesticide contaminated drinking water. More over, from comparison with former studies, possible methods to further enhance the decomposition of pesticide were suggested.

**Keywords;** nitrate, pesticides, biofilm-electrode reactor, adsorption, drinking water

### 1. INTRODUCTION

Water pollution by pesticides and nitrate from routine agricultural practices is a common, and growing problem in the major agricultural areas of the world (Hallberg, 1987). Concern for possible health consequences has led to the adoption of a guideline values (10 mg NO<sub>3</sub>-N/l) in water for human consumption (WHO, 1984). Guideline values of pesticides in drinking water varies according to the type of the compound and its toxicity (WHO, 1984). In regions where pesticide contamination is a problem, nitrate concentrations are often high (Hallberg, 1987). Efforts are being made to control the use of synthetic chemicals in agriculture (Cook et al., 1996) but in the mean time, nitrate and pesticide must be treated when their concentration exceed the maximum contaminant level in water resources.

Pesticides may be removed by adsorption on granular activated carbon (GAC) or powdered activated carbon (PAC), oxidation with ozone or ozone plus hydrogen peroxide, and air stripping (AS) (Klark et al., 1988). Among these methods, adsorption on to GAC seems to be the most feasible process for the removal of trace pesticides from drinking water and the adsorption characteristics of several pesticides onto activated carbon have been reported (Haist-gulde et al., 1993).

Nitrate can be removed by physicochemical processes such as ion exchange (IE), reverse osmosis (RO) and electrodialysis (ED) or by biological processes. The physicochemical treatment processes, however, have poor selectivity for nitrate, relatively expensive to operate and are limited because of the production of concentrated wastes (Dhab, 1987). Biological denitrification is considered as an effective technology mainly because nitrate is reduced to an innocuous nitrogen gas. Various types of

---

\*Department of Civil Engineering, Gunma University

\*群馬大学建設工学科

bioreactors have been studied and applied in full-scale using heterotrophic denitrifying microorganisms (Mateju et al., 1992). These processes involve the addition of external organic substrates and production of biological sludge. A relatively clean autotrophic denitrification process using hydrogen as electron donor has been reported (Kurt et al., 1987).

Recently, a biofilm-electrode reactor (BER) where autotrophic denitrification was stimulated by electrochemical generation of hydrogen gas within the reactor was investigated (Sakakibara & Kuroda, 1993). The BER process is an attractive alternative to the traditional biological and physicochemical treatment methods (Feleke et al., 1998), and the extent of denitrification can be controlled by adjusting electric current (Sakakibara and Kuroda, 1993). In addition, biomass production in BER is very low (Islam and Suidan, 1998).

To remove both nitrate and pesticides, a combination of two processes (GAC/IE) and a single process (RO) were proposed (Goodrich et al., 1991). Combined membrane bioreactor/PAC adsorption process was also developed for simultaneous denitrification and pesticide removal (Urbain et al., 1996). This process requires continuous addition of ethanol and PAC. A combination of BER and adsorption processes can also be possibly applied to treat drinking water contaminated with nitrate and pesticides. However, the presence of toxic pesticides, particularly fungicides and bactericides in water, may inhibit biological activities of denitrifying microorganisms (Bollag and Henninger, 1976).

The primary purposes of this study are to investigate long-term performance of the BER in the presence of pesticide and to evaluate the feasibility of a combined BER/adsorption process for the treatment of nitrate and pesticides. The dithiolidenemalonate fungicide, isoprothiolane (IPT), was used as a test pesticide. Isoprothiolane and its transformation products are detected at high frequency in water bodies in Japan (Fukushima et al., 1995) and it is categorized under item for monitoring with a guideline value of 40 µg/l or less (Environmental water quality standard of Japan, 1993). The possibilities of biological and electrochemical degradation of isoprothiolane in BER were also evaluated. Batch and continuous single solute adsorption tests were conducted to determine the adsorption capacity of GAC and silicone for isoprothiolane.

## 2. MATERIALS AND METHODS

### 2.1 Continuous BER experiments

The experimental apparatus used in this study is shown schematically in Figure 1. Three identical reactors denoted as No. 1, 2 and 3 were used in parallel. The BERs consist of an amorphous carbon anode, a cylindrical stainless cathode, on which denitrifying microorganisms were immobilized by using a porous matrix (polyurethane foam), and a DC power supply. Effective liquid volume of the reactor and cathode surface area were 0.205 l and 251 cm<sup>2</sup>, respectively. To achieve complete mixing, the water inside the reactor was recirculated at a rate of 0.3 l/min. These BERs had been operated for over 2 years, receiving continuous input of ground water containing NO<sub>3</sub><sup>-</sup> and trace inorganic nutrient, prior to the commencement of the present experiment. Similar performance of the BERs for denitrification in the absence of pesticides has been confirmed during this period of operation (Feleke et al., 1998). In this study, to investigate the long-term effect of pesticide (isoprothiolane) on

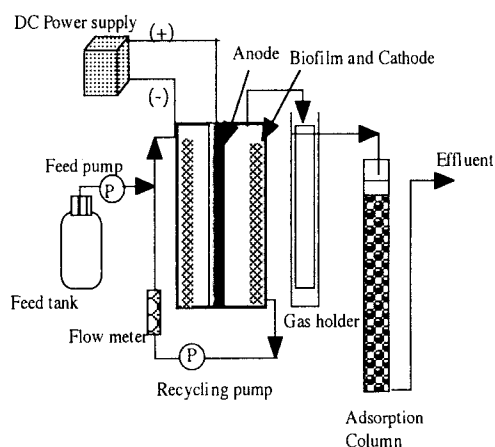


Fig. 1. Schematic of experimental apparatus.

denitrification, reactors 1 and 2 were operated at the same electric current (2.0 ~ 2.5 mA) and different pesticide loading conditions. The influent isoprothiolane concentration to reactor 1 varied from 100 to 300 µg/l, whereas that of reactor 2 was from 10 to 160 µg/l. Reactor 3 was operated at electric current from 0 to 10 mA.

The composition of groundwater used in this study is shown in Table 1. The groundwater was fed continuously into the BER at a recycling line with peristaltic pump. Throughout the experiment, HRT was maintained at about 10 hr. Teflon tubings (NITTA MOORE) with different diameter were used at feed, recycling and effluent lines of the Process.

A control electrochemical reactor without denitrifying biofilm was also operated at different electric current to determine if direct electrochemical reactions of nitrate and isoprothiolane can occur in this system under experimental conditions used for continuous experiment. The electric current was varied from 0 to 10 mA. The fed solution is sterile distilled water containing only about 20 mg/l NO<sub>3</sub><sup>-</sup> and 350 µg/l of isoprothiolane. Disinfection of the reactor and recycling line was made frequently to eliminate any residual microbial activity. The result obtained from this abiotic experiment was compared with that of biological experiment.

### 2.3 Adsorption experiments

Two types of adsorbents were tested: GAC (Wako Pure Chemical Industries Ltd.) and silicone resin (Tigers Polymer Co. Ltd.). To determine the equilibrium adsorption capacity of the adsorbents for isoprothiolane, batch sorption tests were conducted at a constant temperature (20 °C) and constant pH (6.5). In an isotherm experiments, different amounts of adsorbent were added to a 300-ml Erlenmeyer flasks. Subsequently, a known volume of a solution containing the target compound was transferred into each flask. Upon equilibration, the remaining liquid-phase concentration was measured, and the solid-phase concentration was calculated via a mass balance. Screening batch adsorption testes conducted over 3-week period at different initial concentrations (data not indicated) showed that equilibrium was reached with in 1-week agitation. Blank was included with the isotherm experiments to evaluate adsorbate losses by mechanisms other than adsorption. No losses were detected in the blank over the 1-week equilibration time. Continuous adsorption tests were conducted to determine the single-solute breakthrough capacity of columns packed with GAC and silicone. The column diameter and bed height is 0.3 cm and 50 cm, respectively. Distilled water spiked with isoprothiolane was introduced into the columns configured as an up flow reactors. The empty bed contact time (EBCT) was maintained at about 5 minutes.

### 2.2 Continuous BER/Adsorption experiments

After evaluating the performance of BERs in the presence of isoprothiolane, the effluent streams were fed to an adsorption column connected to BER as shown in Fig. 1. In the cases of reactor 1 and 2, the adsorption column was packed with activated carbon. The effluent of reactor 3 was fed into a column packed with silicone material. Between the BER and adsorption column, a gas separation device was installed. The columns are made up from acrylic pipe with internal diameter of 3.5 cm. The effective height of the adsorption column bed was 60 cm. The flow rate was the same as that of the BER. The BERs were operated at constant electric current of 2.5 mA and the adsorption columns were operated at constant pesticide loading. Nitrate and isoprothiolane concentrations were monitored at the inlet and outlet of the BERs and the adsorption columns.

Table 1. The composition of influent groundwater used.

Parameters	concentration (mg/l)
NO <sub>3</sub> <sup>-</sup> -N	22.5
NO <sub>2</sub> <sup>-</sup> -N	ND*
SO <sub>4</sub> <sup>2-</sup> -S	8.1
PO <sub>4</sub> <sup>3-</sup> -P	1.9
Cl <sup>-</sup>	17.6
IPT	0.150
Na <sup>+</sup>	49.3
K <sup>+</sup>	8.0
Ca <sup>2+</sup>	23.5
Mg <sup>2+</sup>	8.5
pH	6.9
NH <sub>4</sub> <sup>+</sup> -N	ND*

\*Not Detected

## 2.4 Analytical procedures

All samples were filtered through a 0.2- $\mu\text{m}$  cellulose nitrate membrane filters (ADVANTEC, Toyo Roshi Ltd.) prior to analysis. Procedures of the preparation of sample for analysis were performed as described in the standard methods (APHA et al., 1995). Stock isoprothiolane solution was prepared by dissolving pesticide grade isoprothiolane (Wako Pure Chemical Industries Ltd.) in ethanol (99.5 %). A set of five calibration standards was prepared from the stock solution. Samples were extracted using solid phase extraction (SPE) column (EnvirElut Pesticide, Varian). The samples extracted with SPE were eluted with dichloromethane. To check the extraction efficiency, standard solutions were also prepared by dissolving isoprothiolane (solubility is 48 mg/l) in deionized water and extracted with dichloromethane in the same manner as the samples. The extraction method had an efficiency of 98% in the concentration range 2 to 2000  $\mu\text{g/l}$ .

Isoprothiolane was analyzed by gas chromatograph (Shimadzu GC-17A), equipped with electron capture detector and fused silica capillary column (Shimadzu) with DB-5 stationary phase. The GC oven was heated from 50 to 190  $^{\circ}\text{C}$  at 20  $^{\circ}\text{C}/\text{min}$ , from 190 to 210  $^{\circ}\text{C}$  at 30  $^{\circ}\text{C}/\text{min}$  and finally to 280  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C}/\text{min}$ . GC/MS analysis of isoprothiolane was also made with a quadrupole mass spectrometer (Shimadzu GCMS-QP5050A) with GC inlet and electron impact ionization (EI). The GC column oven was heated from 50 to 120  $^{\circ}\text{C}$  at 30  $^{\circ}\text{C}/\text{min}$ , 120 to 270  $^{\circ}\text{C}$  at 15  $^{\circ}\text{C}/\text{min}$  and finally held at 270  $^{\circ}\text{C}$  for 2 minutes. The type and dimension of the column is similar to that used in GC-ECD.

Nitrate and other ions listed in Table 1 were measured with an ion chromatograph (IC 7000 Series II, Yokogawa Analytical Systems). Gas composition was measured using TCD gas chromatograph (Shimadzu GC-8A).

## 3. RESULTS AND DISCUSSION

### 3.1 BER Performance

**Abiotic electrochemical reactor.** Fig. 2 shows the influent and effluent concentrations of  $\text{NO}_3^-$  and isoprothiolane of the control electrochemical reactor. Segall and Bruell (1992) showed nitrate was electrochemically reduced. In this figure, for the applied electric current up to 10 mA, the influent in the cathode in electroosmotic systems. As shown in the influent and effluent concentrations of nitrate are nearly the same. Thus, it is considered that electrochemical nitrate reduction did not occur under the experimental conditions used in this study. This is possibly due to a larger surface overpotential of the electrochemical reduction of nitrate in comparison to hydrogen

evolution (Newman, 1991). On the other hand, the effluent concentration of isoprothiolane was always lower than that of the influent, but the removal was not related to the applied electric current. The catalytic property of the electrode material, the current density and the type and concentration of the compound may influence the destruction of organic pollutants in electrochemical systems (Feng et al., 1995). The decreasing trend of isoprothiolane removal as a function of time in Fig. 2 suggests that for the initial

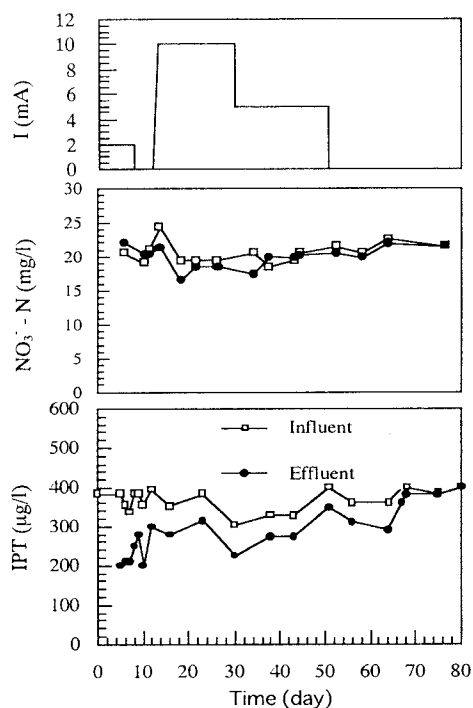


Fig. 2. Performance of the abiotic electrochemical reactor.

operating period of about 60 days, the removal mechanism is adsorption onto different reactor components.

**Effect of pesticide loading.** Fig. 3 shows the influent and effluent concentration of nitrate, nitrite and isoprothiolane for Reactors 1 and 2 as a function of time. The applied electric current was 2.0 mA, which is much lower than the stoichiometric current needed for complete reduction of nitrate in the influent. The influent concentration of isoprothiolane to reactor 2 was in the range from 100 to 350  $\mu\text{g/l}$ , corresponding to loading rate from 244 to 853  $\mu\text{g/l.d}$  for a period of 200 days. This concentration range

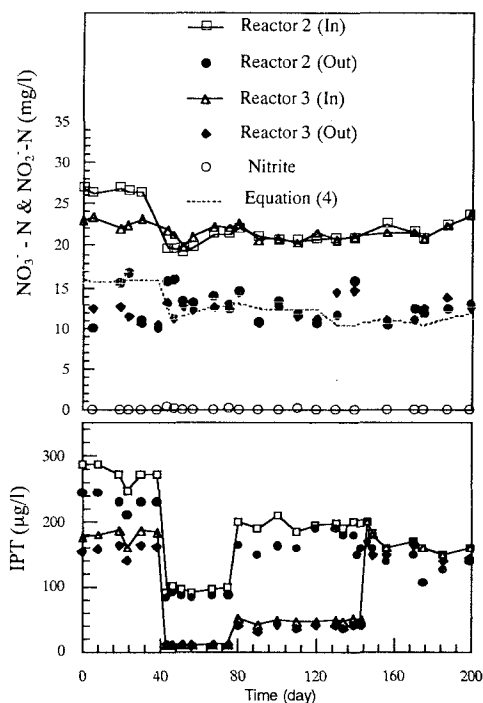


Fig. 3. Performance of the two BERs (reactor 1 and 2) at constant electric current (2.0 mA) and different isoprothiolane loading conditions.

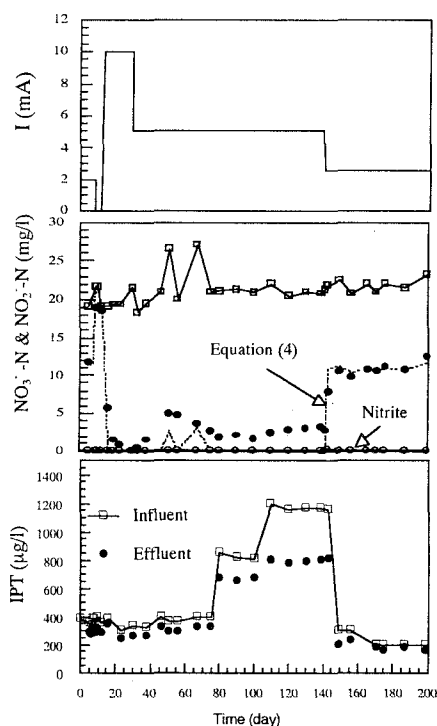
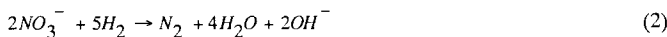


Fig. 4. Performance of the BER (reactor 3) at different electric current.

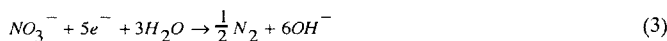
is higher than that can be encountered in water body at present state of pollution (Fukushima et al., 1995). However, it is considered that, this may provide information regarding the response of the process at higher loading condition. The influent to reactor 2 was from 10 to 160  $\mu\text{g/l}$  (loading rate from 24.4  $\mu\text{g/l.d}$  to 390  $\mu\text{g/l.d}$ ) for the same period of time as for reactor 1. Regardless of the significant difference in pesticide loading, performance of nitrate removal of both reactors was nearly the same and stable. Further, in few cases nitrite was detected at concentration less than or equal to 0.05 mg/l and  $\text{N}_2\text{O}$  in the gas phase was below the detection limit of gas chromatograph (about 0.01 %). These results indicate that in the concentration range tested, isoprothiolane did not affect denitrification. Therefore, the inhibition of an intermediate step of nitrate reduction by pesticide, especially, bactericides or fungicides, which may result in the accumulation of  $\text{NO}_2^-$  or the gaseous oxides (Bollag and Henninger, 1976) is not be a problem at low pesticide concentration.

**Effect of electric current.** In the BER, electrolysis of water results in the evolution of hydrogen gas at

the cathode according to equation (1) and consequently, autotrophic denitrification using hydrogen gas as electron donor proceeds according to equation (2) (Kurt et al., 1987):



Net reaction is:



i.e., five electron equivalents are required to reduce one mole of nitrate.

When carbon electrode is used as anode, the production of carbon dioxide may be predominant according to the following reaction (Kinoshita, 1988):



To estimate the effluent nitrate concentration based on Faraday's law and stoichiometry of denitrification reaction of equation (3), a complete-mix reactor model (Sakakibara et al., 1997) was used by assuming 100% efficiency in the utilization of the applied current:

$$\frac{C_{NO_3-f} - C_{NO_3}}{\theta} - a_c \left( \frac{i_c}{5F} \right) = 0 \quad (5)$$

where  $C_{NO_3-f}$  and  $C_{NO_3}$  are the influent and effluent nitrate concentration (mole/l) respectively,  $a_c$  is specific surface area of the cathode ( $cm^2/l$ ),  $i_c$  is the cathode current density ( $C/h.cm^2$ ),  $F$  is Faraday's constant (96,487 C/mole) and  $\theta$  is hydraulic retention time (h).

Fig. 4 shows the influent and effluent concentration of nitrate, nitrite and isoprothiolane at different applied electric current for reactor 3 as a function of time. As seen in the figure, the effluent nitrate concentration varied depending on the electric current applied. The dotted line shows the effluent nitrate estimated using equation (5). The same calculation results were also shown in Figure 3. The calculated results for effluent nitrate concentration are in close agreement with the experimental results. Nitrite appeared in few cases at concentrations less than or equal to 0.05 mg/l, regardless of the variable electric current.

On the other hand, the effluent isoprothiolane concentration depends on loading and no relation with electric current was observed in the applied current range up to 10 mA. The removal efficiency of isoprothiolane in BER was very small, particularly at lower influent concentrations. This may indicate that the carbon anode may not be effective in catalyzing the oxidation of isoprothiolane.

The production of  $CO_2$  from carbon anode (reaction (4)) is beneficial to neutralize the increase in pH due to denitrification. The production of inorganic carbon as a function of anodic current density has been reported in former study (Sakakibara et al., 1997). The maximum inorganic carbon production rate for the applied current density range used in this study is about 0.002 mg-c/h  $cm^2$ . This result shows that the life-time of the anode is sufficiently long. However, to enhance anodic oxidation of organic micropollutants, catalytic metal anodes may be utilized (Feng et al., 1995).

### 3.2 BER/Adsorption Process Performance

**Adsorption isotherms.** Since the capacity of an adsorbent for micropollutant elimination depends on the adsorbability of trace compound, batch single-solute adsorption tests were conducted, prior to the continuous treatment study. Figure 5 (a) and 6 (a) depicts the single-solute isoprothiolane isotherm for GAC and silicone, respectively at initial concentration of 700  $\mu g/l$ . The experimental data are fitted to

the linearized form of Langmuir isotherm model:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m \beta} \left( \frac{1}{C_e} \right) \quad (6)$$

where  $q_e$  is the amount adsorbed (mg/g),  $C_e$  is the concentration remaining in solution,  $q_m$  is maximum adsorption capacity (mg/g) and  $\beta$  is a constant.

Fig. 5 (b) and 6 (b) show the Langmuir isotherm for the adsorption of isoprothiolane onto GAC and silicone, respectively. The Langmuir parameters  $q_m$  and  $\beta$  are also shown for each adsorbent. Comparison of the results in Fig. 5 and 6 show that, the isoprothiolane adsorption capacity of GAC is much larger than that of silicone. The surface area available on silicone for adsorption and the effect of polymer properties are not investigated systematically in this study. However, the conformity of experimental results to the Langmuir isotherm model may suggest that the capacity can be improved if silicone material with high porosity is used.

**Continuous treatment.** Fig. 7 shows the influent and effluent concentrations of nitrate, nitrite and isoprothiolane of the combined process. In order to simulate pesticide concentration in contaminated groundwater or surface water, the influent concentration was reduced to about 150  $\mu\text{g/l}$ . As shown in the figure, nitrate removal in the three BERs is according to theoretical relation of equation (4). The applied electric current was set at 2.5 mA which corresponds to the reduction of about 10 mg N/l

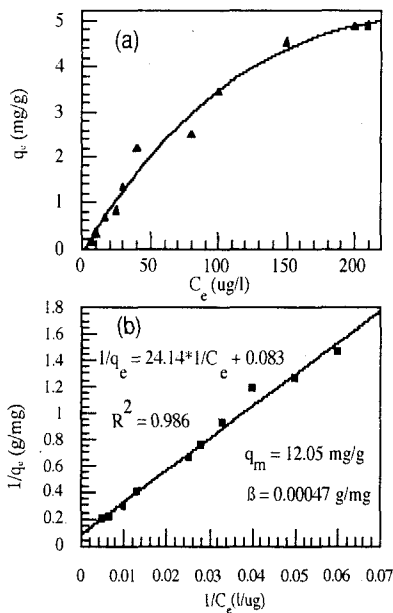


Fig. 5. Adsorption isotherm of isoprothiolane onto GAC (a) and the Langmuir plot (b) ( $C_0 = 0.7$  mg/l).

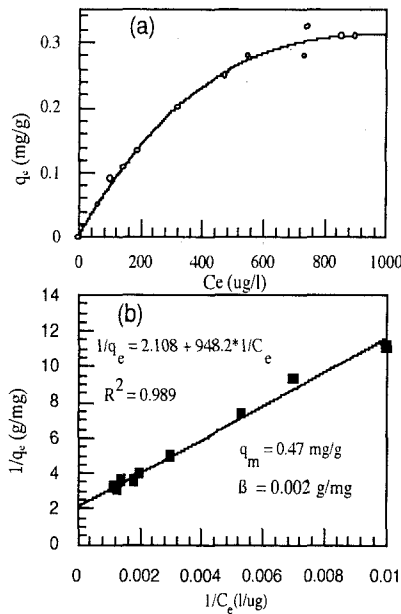


Fig. 6. Adsorption isotherm of isoprothiolane onto silicone (a) and the Langmuir plot (b) ( $C_0 = 0.7$  mg/l).

achieved in many full scale and pilot scale processes (Mateju et al., 1992).

The effluent isoprothiolane concentration was decreased below the detection limit of gas chromatograph (about 2  $\mu\text{g/l}$ ) for the columns packed with activated carbon and less than or equal to 6  $\mu\text{g/l}$  for the column packed with silicone material. Removal efficiency of isoprothiolane was larger than 97 % and effluent concentration was much lower than the guideline value (40  $\mu\text{g/l}$ ) for a period

of 100 days. Topp and Smith (1993) also reported effective adsorption (greater than or equal to 90 %) of the pesticides atrazine and alachlor onto different plastics and silicone rubber. These results show that nitrate and trace concentration of pesticides can be removed effectively by combining the BER and an adsorption column in series. Breakthrough did not occur in the operation time of 100 days. Except  $\text{NO}_3^-$  and isoprothiolane, the concentrations of other ions listed in Table 1 were not affected in this combined process (data not indicated). As compared to physicochemical processes such as RO and GAC/IE, the BER/adsorption process does not remove or introduce other ions.

A separate continuous single-solute breakthrough experiments using small columns packed with GAC and silicone (data not indicated) showed that complete breakthrough capacity of GAC and silicone columns to maintain the effluent isoprothiolane concentration below 40  $\mu\text{g/l}$  guideline value are 1.4 mg/g and 0.17 mg/g, respectively. The result for GAC is in close agreement with that obtained from the Langmuir isotherm model (1.6 mg/g). For silicone, the value is larger than that estimated from Langmuir model (0.06 mg/g), possibly due to the dynamic nature of the continuous column. Further study will be needed to elucidate the adsorption phenomena of pesticides on silicone.

### 3.3 Comparison to former studies

Kishimoto et al. (1999) reported biodegradation of isoprothiolane in paddy field soils under aerobic and anaerobic conditions. Their result showed that biological degradation rate of this pesticide is very slow under anaerobic condition compared to that observed under aerobic condition. In an attempt to identify the possibility of biological degradation of isoprothiolane under denitrifying condition in the present study, the influent concentration was increased up to 1200  $\mu\text{g/l}$ , and maintained for about 40 days as shown in Fig. 3. During this period, the removal efficiency of isoprothiolane was increased to about 33 %. Further more, some peaks were detected with GC/MS that were consistently present, but could not be identified. Since the removal is low under anaerobic condition, combination of aerobic biological process may enhance the decomposition of isoprothiolane as well as biological regeneration of GAC or silicone packed columns. Feakin et al. (1995) reported the biological regeneration of GAC column by using atrazine as a test pesticide.

Recently, electrochemical degradability of various organic pollutants have been investigated by different researchers (Feng et al., 1995; Cheng et al., 1997; Zor et al., 1998). Their results showed that the type and catalytic properties of the electrode materials are important factors, which control the degradation of organic compounds. Therefore, adaptation of proper electrode may also enhance electrochemical degradation of pesticides.

The above comparisons to former studies suggest that different options are still possible to enhance biological and electrochemical degradation of isoprothiolane in the present BER/adsorption process.

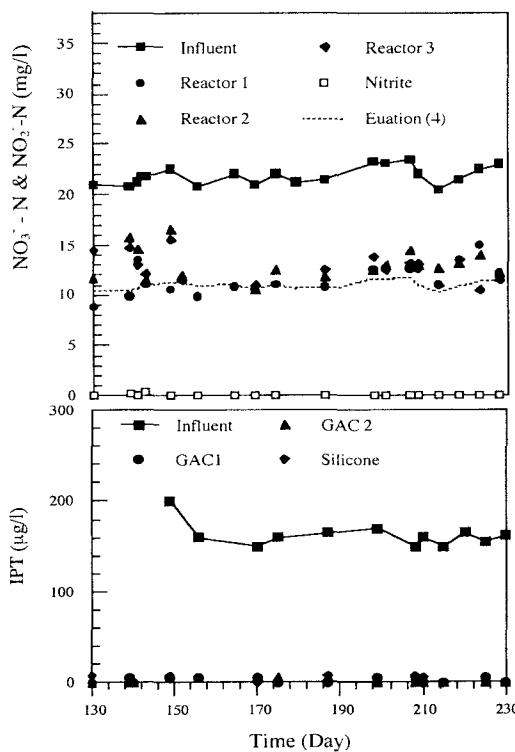


Fig. 7. Performance of the combined BER/adsorption process.



#### 4. CONCLUSIONS

Performance of a combined biofilm-electrode reactor/adsorption process for denitrification and pesticide removal was investigated. Denitrification performance of the BER was stable at variable electric current and in the presence of a fungicide isoprothiolane. No intermediate accumulation of nitrite and nitrous oxide occurred in BER. Isoprothiolane removal exceeding 97 % was achieved in the column packed either with activated carbon or silicone material, and the effluent concentration was below the guideline value (40 µg/l) over 100 days of operation. Isoprothiolane adsorption onto GAC and silicone conformed to the Langmuir isotherm model.

From these results we conclude that the combined BER/Adsorption process can be applied to treatment of nitrate and trace pesticide contaminated water. In the light of recent researches where fixed bed GAC adsorber is regenerated biologically (Feakin et al., 1995) and electric current is used to detoxify micropollutants (Feng et al., 1995), improvement of the performance of this process may still be possible. Further research will be needed to address such possibilities and to evaluate the removal of other pesticides amenable to biodegradation in BER/adsorption process.

#### REFERENCES

- APHA, AWWA, WPCF (1995) Standard Methods for the Examination of Water and Wastewater, 19th edn., American Public Health Association, Washington D.C.
- Bollag J. and Kurek J. (1980) Nitrite and Nitrous oxide Accumulation During Denitrification in the Presence of Pesticide Derivatives. *Appl. And Env. Microbiol.*, **39**(4), 845-849.
- Cheng F., Fernando Q. and Korte N. (1997) Electrochemical Dechlorination of 4-chlorophenol to Phenol. *Environ. Sci. Technol.*, **31**, 1074-1078.
- Cook G., Hunt G., Stone C. and Canterbury H. (1996) Reducing Diffuse Pollution Through Implimentation of Agricultural Best Management Practices: A Case Study. *Wat. Sci. Tech.*, **33**, 191- 196.
- Dhab F. M. (1987) Treatment Alternatives for Nitrate Contaminated Ground Water Supplies. *Environmental Systems*, **17**, 65 - 75.
- Environment Agency, Government of Japan (1994) Quality of The Environment in Japan. Tokyo.
- Feakin S., Blackburn E. and Burns G. (1995) Inoculation of granular activated carbon in a fixed bed with S-triazine degrading bacteria as a water treatment process. *Wat. Res.*, **29**(3), 819-825.
- Feleke Z., Araki K., Sakakibara Y., Watanabe T. and Kuroda M. (1998) Selective Reduction of Nitrate to Nitrogen Gas In A Biofilm-electrode Reactor. *Wat. Res.*, **32**(9), 2728-2734.
- Feng J, Houk L., Johnson C., Lowery N. and Cary J. (1995) Electrocatalysis of Anodic Oxygen-Transfer Reactions: The Electrochemical Incineration of Benzoquinone. *J. Electrcchem. Soc.*, **142**(11) 3626-3631.
- Fukushima M., Yamaguchi Y. and Yamada A. (1995) Temporal Trends of Pesticide Pollution in River Water Used as a Source of Potable Water. *Water Supply*, **13**(3/4), 107-112.
- Goodrich A., Lykins W. and Klark M. (1991) Drinking Water From Agriculturally Contaminated Groundwater. *J. Environ. Qual.*, **20**, 707-717.
- Hallberg R. (1987) Agricultural Chemicals in Groundwater: Extent and Implications. *American Journal of Alternative Agriculture*, **2**(1), 3-15.
- Haist-Gulde B., Baldauf G. and Brauch J. (1995) Removal of Organic Micropollutants by Activated Carbon: In Hand Book of Environmental Chemistry, **Vol. 5**, Springer-Verlag, Berlin.
- Islam S. and Suidan T. (1998) Electrolytic Denitrification: Long Term Performance and Effect of Current Intensity. *Wat. Res.*, **32**(2), 528-536.
- Kinoshita K. (1988) Carbon, Electrochemical and Physicochemical Properties. John Willey and Sons, New York.
- Kishimoto S., Momonoi K., Komatsu T. and Kameya T. (1999) Behavior of Isoprothiolane in a Paddy

- Field. *Proceedings of 33<sup>rd</sup> Annual Conference of Japan Society on Water Environment*, 503.
- Klark M., Fronk A. and Lykins W. (1988) Removing Organic Contaminants from Groundwater: A cost and performance evaluation. *Environ. Sci. Technol.*, **22**(10), 1126-1129.
- Kurt M., Dunn I. J. and Bourne J.R. (1987) Biological Denitrification of Groundwater Using Autotrophic Organisms with  $H_2$  in a Fluidized-Bed Biofilm Reactor. *Biotechnology and Bioengineering*, **29**, 493 - 501.
- Mateju V., Cizinska S., Krejci J. and Janoch T. (1992) Biological Water Denitrification. *Enzyme Microb. Technol.*, **14**, 170 - 183.
- Newman J. S. (1991) *Electrochemical Systems*. Prentice Hall, New Jersey.
- Sakakibara Y. and Kuroda M. (1993) Electric Prompting and Control of Denitrification. *Biotechnology and Bioengineering*, **42**, 535 - 537.
- Sakakibara Y., Araki K., Watanabe T. and Kuroda M. (1997): The Denitrification and Neutralization Performance of an Electrochemically-activated Biofilm Reactors Used To Treat Nitrate-contaminated Ground water. *Wat. Sci. Tech.*, **36**(1), 61-68.
- Segall B. A. and Bruell C. J. (1992) Electroosmotic Contaminant-removal Processes, *Jour. Environ. Engrg., ASCE*, **118**, 84 - 100.
- Topp E. and Smith W. (1992) Sorption of Herbicide Atrazine and Metolachlor to Selected plastics and Silicone Rubber. *J. Environ. Qual.*, **21**, 316-317.
- Urbain V., Benoit R. and Manem J. (1996) Membrane Bioreactor: A New Treatment Tool. *J. AWWA*, May, 75 - 86.
- WHO (1984): *Guidelines for Drinking Water Quality*, **1**, Geneva.
- Zor S., Yazic B., Erbil M. and Galip H. (1998) The Electrochemical Degradation of Linearalkylbenzene sulfonate (LAS) on Platinum Electrode. *Wat. Res.*, **32**(3), 579-586.