Nitrate and pesticide removal by a combined bioelectrochemical/adsorption process

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Abstract Biological denitrification and trace pesticide removal in a combined biofilm-electrode reactor/adsorption process has been investigated. In long-term (more than 260 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. Isoprothiolane (IPT) was removed by adsorption onto either granular activated carbon or silicone resin. Removal efficiency of IPT exceeding 97% was achieved and effluent concentration was below the guideline value (40 µg/l). Theoretically predicted effluent concentrations were in good agreement with the observed results. From these results, it is concluded that the combined process is applicable to treat nitrate and pesticide contaminated drinking water. Moreover, from comparison with former studies, different possible options to further enhance the decomposition of pesticide were suggested.

Keywords Adsorption; biofilm-electrode reactor; drinking water; nitrate; pesticide

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). In recognition of this problem and because of concern for possible health consequences a guideline value of 10 mg NO$_3^-$–N/l has been recommended 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 implement best agricultural practices in order 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 exceeds the maximum contaminant level in water resources.

To remove both pesticides and nitrate a combined granular activated carbon/ion exchange process (GAC/IE) and reverse osmosis (RO) process were proposed (Goodrich et al., 1991). Although the GAC seems to be the most feasible process to remove trace pesticides, the physicochemical treatment processes have poor selectivity for nitrate and are limited because of the production concentrated wastes (Dhab, 1987). The combined membrane bioreactor/powdered activated carbon (PAC) adsorption process was also developed for heterotrophic denitrification and pesticide removal (Urbain et al., 1996). This process requires continuous addition of ethanol and PAC and large volumes of sludge may be produced.

Kurt et al. (1987) studied a relatively clean autotrophic denitrification process using hydrogen as electron donor. Recently, a biofilm-electrode reactor (BER) in which autotrophic denitrification was stimulated by electrochemical generation of hydrogen gas within the reactor was studied (Sakakibara and Kuroda, 1993).

In this study the feasibility of nitrate and pesticide removal by a combined BER/adsorption process was investigated. 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 as an item for monitoring with a guideline value of 40 µg/l or less (Environmental water quality standard of Japan, 1993). The possibility of abiotic degradation of isoprothiolane in BER was also evaluated. Continuous single-solute adsorption tests were conducted to determine the breakthrough adsorption capacities of GAC and silicone resin for isoprothiolane.

**Materials and method**

**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 effective liquid volume of the reactor and cathode surface area were 0.205 l and 251 cm², respectively. Details of the experimental apparatus have been described elsewhere (Sakakibara et al., 1997). Prior to the commencement of the present experiment, the BERs had been operated for over 2 years, receiving continuous input of ground water containing NO₃⁻ and trace inorganic nutrient. 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 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 of 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 an 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 by a recycling line with peristaltic pump. Throughout the experiment, HRT was maintained at about 10 hr. Teflon tubing (NICHIAS Corp.) with different diameter was used in the feed, recycling and effluent lines of the process.

A control electrochemical reactor without denitrifying biofilm was also operated at different electric currents to determine if direct electrochemical reactions of nitrate and isoprothiolane can occur in this system under the experimental conditions used for continuous experiment. The electric current was varied from 0 to 10 mA. Initially, groundwater with composition similar to that shown in Table 1 was fed in to the reactor for about 20 days. Thereafter, the reactor and recycling line were disinfected frequently to eliminate any residual microbial activity and a sterile distilled water containing only about 20 mg/l NO₃⁻ and 350 µg/l of isoprothiolane was fed. The result obtained from this abiotic experiment was compared with that of a biological experiment.

**Figure 1** Schematic of experimental apparatus

Adsorption experiments

The adsorbents used were GAC (purchased from Wako Pure Chemical Industries Ltd.) and silicone resin (from Tigers Polymer Co. Ltd.). A separate continuous adsorption test was conducted to determine the single-solute breakthrough capacity of small columns packed with GAC and silicone. The column diameter and bed height is 0.6 cm and 30 cm, respectively. Distilled water spiked with isoprothiolane was introduced into the adsorption columns configured as up flow reactors. The empty bed contact time (EBCT) was maintained at about 17.5 minutes.

BER/Adsorption experiments

After evaluating the performance of BERs in the presence of isoprothiolane, the effluent streams were fed to an adsorption column connected in series to BER as shown in Figure 1. The effluents of reactor 1 and 2 were introduced into the adsorption columns packed with activated carbon, and that 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.

Analytical methods

All samples were filtered through 0.2-µm cellulose nitrate membrane filters (ADVANTEC, Toyo Roshi Ltd.) prior to analysis. Procedures for 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 a solid phase extraction (SPE) column (EnvirElut Pesticide, Varian). The samples extracted with SPE were eluted with dichloromethane. The extraction method had an efficiency of 98% in the concentration range 2 to 2000 µg/l (Feleke et al., 1999).

Table 1 Composition of influent groundwater and effluent from the combined process (I=2.5 mA)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent</th>
<th>Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃⁻-N</td>
<td>22.5</td>
<td>10.2</td>
</tr>
<tr>
<td>NO₂⁻-N</td>
<td>ND*</td>
<td>0.01</td>
</tr>
<tr>
<td>SO₄²⁻-S</td>
<td>8.1</td>
<td>7.6</td>
</tr>
<tr>
<td>PO₄³⁻-P</td>
<td>1.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>17.6</td>
<td>17.3</td>
</tr>
<tr>
<td>IPT</td>
<td>0.150</td>
<td>&lt;0.002**, &lt;0.006**</td>
</tr>
<tr>
<td>Na⁺</td>
<td>49.3</td>
<td>48.3</td>
</tr>
<tr>
<td>K⁺</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>23.5</td>
<td>19.3</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>8.5</td>
<td>6.4</td>
</tr>
<tr>
<td>pH</td>
<td>6.9</td>
<td>6.6</td>
</tr>
<tr>
<td>NH₄⁺-N</td>
<td>ND*</td>
<td>ND*</td>
</tr>
</tbody>
</table>

*Not detected; **GAC, ++Silicone
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°C at 20°C/min, from 190 to 210°C at 30°C/min and finally to 280°C at 10°C/min.

GC/MS analysis of isoprothiolane was also made with a quadrapole mass spectrometer (Shimadzu GCMS-QP5050A) with GC inlet and electron impact ionization (EI). The GC column oven was heated from 50 to 120°C at 30°C/min, 120 to 270°C at 15°C/min and finally held at 270°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 a TCD gas chromatograph (Shimadzu GC-8A).

**Results and discussion**

**BER performance**

**Electrochemical reactor.** Figure 2 shows the influent and effluent concentrations of NO₃⁻ and isoprothiolane of the control electrochemical reactor. For the first one-week, the influent and effluent concentration of nitrate were the same. Starting from day 8, however, the effluent concentration declined. To evaluate whether microbial growth in the reactor contributed to the observed removal, the reactor components were disinfected frequently starting from day 22 and sterilized distilled water containing only nitrate and isoprothiolane was fed. As shown in the figure, for the applied electric current up to 10 mA, the influent and effluent concentrations of nitrate are nearly the same from day 22 onward. Therefore, the observed disappearance of nitrate is presumably due to the growth of active microorganisms on the surface of the cathode. Segall and Bruell (1992) showed nitrate was electrochemically reduced on the cathode in electro-osmotic systems. However, 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; Zor et al., 1998). Adaptation of proper electrodes and optimization of the current density can possibly enhance electrochemical pesticide degradation. The decreasing trend of isoprothiolane removal as a function of time in Figure 2 suggests that for the initial operating period of about 60 days, the removal mechanism is adsorption onto different reactor components.

**Effect of pesticide loading.** Figure 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 µg/l, corresponding to a loading rate from 244 to 853 µg/l.d for a period of 200 days. This concentration range is higher than can be encountered in the water body at the 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 conditions. The influent to reactor 2 was from 10 to 160 µg/l (loading rate from 24.4 µg/l.d to 390 µg/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. Moreover, in a few cases nitrite
was detected at concentrations less than or equal to 0.05 mg/l and N2O 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 NO2 or the gaseous oxides (Bollag and Henninger, 1976) is not 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 Eq. (1) and consequently, autotrophic denitrification using hydrogen gas as electron donor proceeds according to Eq. (2) (Kurt *et al.*, 1987):

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- 
\]  
\[
2NO_3^- + 5H_2 \rightarrow N_2 + 4H_2O + 2OH^- 
\]

Net reaction is:

\[
NO_3^- + 5e^- + 3H_2O \rightarrow \frac{1}{2} N_2 + 6OH^- 
\]

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

To estimate the effluent nitrate concentration based on Faraday’s law and stoichiometry of denitrification reaction of Eq. (3), a complete-mix reactor model (Sakakibara *et al.*, 1997) was used by assuming 100% efficiency in the utilization of the applied current and no inhibition of denitrification by pesticide:

\[
\frac{C_{NO_3} - C_{NO_3}}{\theta} = \alpha_c \left( i_c \frac{FC}{5F} \right) = 0 
\]

where \(C_{NO_3}\) and \(C_{NO_3}\) are the influent and effluent nitrate concentration (mole/l) respectively, \(\alpha_c\) is specific surface area of the cathode (cm²/l), \(i_c\) is the cathode current density (C/h.cm²), \(F\) is Faraday’s constant (96,487 C/mole) and \(\theta\) is hydraulic retention time (h).

Figure 4 shows the influent and effluent concentration of nitrate, nitrite and isoprothiolane at different applied electric currents 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 predicted using Eq. (4). 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 a 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. In an attempt to identify the possibility of biological degradation of isoprothiolane under denitrifying conditions in the present study, the influent concentration was increased up to 1200 µg/l, and maintained for about 40 days as shown in Figure 4. During this period, the removal efficiency of isoprothiolane was increased to about 33%. Furthermore, some peaks were detected with GC/MS that were consistently present, but could not be identified. Kishimoto et al. (1999) reported biodegradation of isoprothiolane in paddy field soils under aerobic and anaerobic conditions. Their result also showed that biological degradation rate of this pesticide is very slow under anaerobic conditions compared to that observed under aerobic condition. Since the removal is slow under anaerobic conditions, combination of aerobic process may enhance the decomposition of isoprothiolane.

BER/adsorption process performance

Breakthrough capacity. Breakthrough curves of GAC and silicone resin for isoprothiolane are shown in Figure 5. A former batch adsorption study (Feleke et al., 1999) showed that the adsorption of isoprothiolane onto GAC and silicone resin conformed to the Langmuir isotherm model. The equilibrium adsorption capacities of GAC and silicone to maintain the isoprothiolane at about 40 µg/l or less were 1.6 mg/g and 0.06 mg/g, respectively. Using these results and assuming plug flow reactor, the effluent concentration of the packed column was predicted as a function of bed volumes of treated water. As shown in the figure, the experimental results are in close agreement with calculated results indicating that, the service time of the packed column can be predicted using the Langmuir model.
Continuous treatment. Figure 6 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 µg/l. As shown in the figure, nitrate removal in the three BERs is according to the theoretical relation of Eq. (4). The applied electric current was set at 2.5 mA which corresponds to the reduction of about 10 mg N/l achieved in many full scale and pilot scale processes (Matějů et al., 1992).

The effluent isoprothiolane concentration was decreased below the detection limit of the gas chromatograph (about 2 µg/l) for the columns packed with activated carbon and less than or equal to 6 µg/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 µg/l). Topp and Smith (1992) also reported effective adsorption (greater than or equal to 90%) of the pesticides atrazine and metolachlor onto different plastics and silicone rubber. As expected from the results of continuous experiments (Figure 5) breakthrough did not occur for the three packed columns in the operation time of 130 days.
which corresponds to about 113 bed volumes of treated water. Simulated effluent isoprothiolane concentration is also shown in Figure 6 (dotted line pointed by arrow).

These results show that nitrate and trace concentration of pesticides can be removed effectively by combining the BER and an adsorption column in series. The concentration of other ions was not affected in this combined process (see Table 1). As compared to physicochemical processes such as RO and GAC/IE, the BER/adsorption process does not remove or introduce other ions. Possible modes by which the service time of the adsorption column can be extended include electrochemical oxidation and enhancing microbial activity in the combined process. Further study will be needed to address such options.

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 130 days of operation. The experimental results were in good agreement with the theoretically predicted effluent concentrations for nitrate in the BER and for isoprothiolane in the adsorption column.

From these results we conclude that the combined BER/Adsorption process can be applied for the 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 organic pollutants (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 and/or electrochemical decomposition in the BER/adsorption process.

References


