Ⅶ-119　　SIMULTANEOUS REMOVAL OF NITRATE AND PESTICIDE

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1. INTRODUCTION

In recent years, concern has developed about the contamination of groundwater and surface water caused by the excessive use of nitrogen fertilizers in intensive agriculture and application of pesticides (Bouwer, 1989).

Table 1 shows several processes proposed to treat contaminated water . Most processes, however, are not selective, relatively expensive to operate, and limited by the production of concentrated waste streams; and furthermore, their performance may be affected by other major ionic constituents such as Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^- and Cl^- (Baldauf, 1993) . In addition, most of the methods can not be applied for the simultaneous removal of the two contaminants.

In this study, a denitrifying biofilm-electrode reactor (BER) which involves direct immobilization of autotrophic denitrifying microorganisms on the surface of the cathode and production of hydrogen gas as an electron donor by electrolysis of water (Sakakibara & Kuroda, 1993) was used to remove nitrate and pesticides concurrently from contaminated water supplies.

Table 1. Available and proposed technologies .

Chemical	Processes	Limitations
NO_3^-, NO_2^-	Ion Exchange (IE)	PS, WD
	Reverse Osmosis(RO)	PS, HTC, WD
	Biofilm Reactor (BR)	
	-Hterotrophic	S, SS, MC, OP
	-Aoutotrophic	S
	Electrodialysis(ED)	PS, HTC, WD
	IE-BR	PS, WD
Pesticides	Granular Activated C(GAC)	PS, WD
	Air Stripping(AS)	Only for VP, AP
	Chemical Oxidation(CO)	Some pesticides
NO_3^- &		
Pesticides	Reverse Osmosis(RO)	WD, HTC
	GAC/IE	HTC, WD

S = Selective, PS = Poor Selectivity, WD = Waste Disposal,
HTC = High Treatment Cost, VP = Volatile Pesticides,
AP = Air Pollution,　 SS = Suspended Solids,
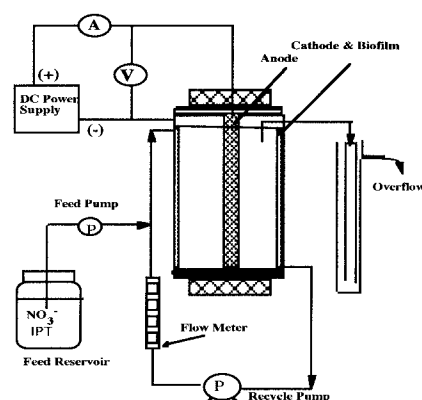MC = Microbial Contamination, OP = Organic Pollution,

Fig. 1. Schematic of Experimental Apparatus.

2. MATERIALS AND METHODS

The experimental apparatus used in this study is shown schematically in Figure 1. Three identical BERs were used in parallel. The reactors consist of an inner amorphous carbon anode and a stainless cathode on which denitrifying microorganisms were immobilized by using polyurethane foam. Effective liquid volume of the reactor was 0.205 l. The composition of feed water used in this study is shown in Table 2. Anions and cations listed in Table 2 were measured with an ion chromatograph (IC 7000 Series II, Yokogawa Analytical Systems). Procedures of the preparation of sample for analysis were performed as described in the standard methods (APHA et al., 1995). Gas composition was measured using TCD gas chromatograph (Shimadzu GC-8A). Isoprothiolane was measured by using gas chromatograph equipped with ECD detector(Shimadzu GC-17A).

### Table 2. Characteristics of influent water used in this study

Chemical	NO_3^--N	SO_4^{2-}-S	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	pH	IPT
Conc. (mg/l)	24	8.1	17.6	23.5	8.5	49.4	8.0	6.9	50 ~ 500 (μ g/l)

KEY WORDS : Biofilm-electrode reactor; denitrification; pesticides removal; Drinking water.

3. RESULTS AND DISCUSSIONS

Nitrate and Isoprothiolane Removal : When electric current is applied, the H_2 evolution at the cathode coupled with denitrification can be expressed by the following overall reaction :

$$NO_3^- + 5e^- + 3H_2O = 0.5N_2 + 6OH^- \qquad (1)$$
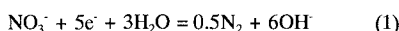
The extent of applied electric current (moles of electrons) with regard to the biological denitrification can be represented by the following dimensionless parameter η_i that is a molar ratio of the applied electron to nitrogen loading rate:

$$\eta_i = \frac{I / 5FA}{C_{NO_3^- f} / a\overline{\theta}} \qquad (2)$$

where I = electric current (C/hr or C/s), F= Faraday's constant (C/mole), A = surface area of the cathode (cm²), a = specific surface of the cathode (cm²/effective liquid volume (l), $C_{NO_3^- f}$ is the influent nitrate concentration(mole/l), and θ = hydraulic retention time (hr).

Figure 2 shows the influent and effluent concentrations of NO_3^--N and IPT at electric currents of 2.0 and 3.5 mA. The result showed that nitrate was removed according to the stoichiometric relation of the overall denitrification reaction of Equation (1) while the average effluent concentration of IPT was maintained at about 80 μg/l. The IPT removal efficiency varied from 84% to 100%, depending on the loading rate (data not shown here). The removal efficiency was nearly 100% at low loading condition and decreased to about 84% at higher loading.

Effect of electric current and Polarity change : Figure 3 shows the effect of electric current application on the effluent (C_{out}) to influent (C_f) ratio of nitrate, calcium, magnesium and other major ions. In the η_i values ranging from 0 to 1, the concentration ratio of nitrate varied according to the relation of Equation (1). At the same time, the concentration ratio of Ca^{2+} and Mg^{2+} were decreased as η_i increase. This is attributable to precipitation of Ca^{2+} and Mg^{2+} on the surface of the cathode (Feleke et al., in press). In an attempt to remove the precipitates, the electric current was reduced from 10 mA ($\eta_i = 2$) to 0.0mA ($\eta_i = 0.0$) and then to -2.0mA ($\eta_i = -0.4$, reversing the polarity of the electrodes). The result shows that by reversing the polarity a certain amount of Ca^{2+} and Mg^{2+} were redissolved immediately from the reactor. Mg^{2+} could also be redissolved by reducing the applied current to 0 mA.

During the experiments of polarity change, reduction of nitrate and formation of NH_4^+ were not observed and pH in the reactor was maintained around neutrality (7.1 - 7.2). After the experiment of polarity reversal, the polarity was reset again and denitrification was conducted at electric current of 2 mA. The effluent nitrate concentration declined quickly without accumulation of nitrite and stable denitrification was achieved.
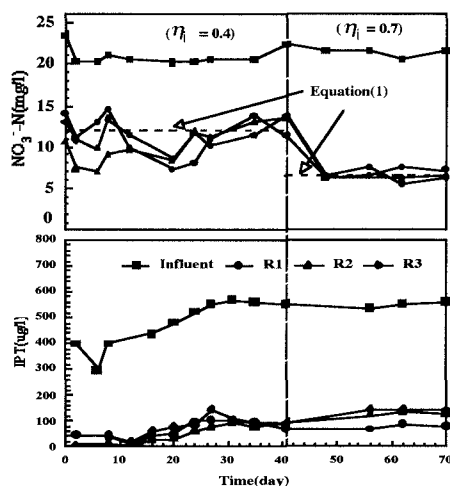

Fig. 2. Influent and effluent concentrations of isoprthiolane(IPT) and nitrate at electric current of 2.0 and 3.5 mA.
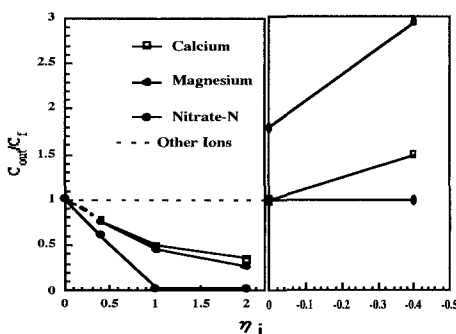

Fig. 3. The variation of effluent to influent concentration ratio of NO_3^--N, Ca^{2+}, Mg^{2+} and other ions as a function of the extent of electric current application (η_i).

4. CONCLUSIONS

Simultaneous removal of nitrate and pesticide from contaminated water was demonstrated by using a biofilm-electrode reactor (BER). Continuous experiment by applying different electric current showed that denitrification was a linear function of electric current, whereas isoprothiolane removal depended on loading rate. Maximum removal efficiency of nitrate and isoprothiolane achieved in this study was nearly 100%.

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