

Comparative study on the bio-electrochemical denitrification equipped with a multi-electrode system

M. Prosnanský, T. Watanabe and M. Kuroda

Department of Civil and Environmental Engineering, Waseda University, 3-4-1 Okuba, Shinjuku, Tokyo 169-8555 Japan (E-mail: prosnan@hotmail.com)

Abstract Three biofilm-electrode reactors (BERs) with multiple cathodes were applied to investigate the effect of electrode configuration and flow direction on denitrification under laboratory-scale conditions. The distribution of nitrate, DO and pH varied among applied BERs, as a consequence of a different electrode position in the reactors, bringing about a difference in the performance. Flow-through configuration of electrodes with a downstream anode appears to be the most suitable configuration since nitrite did not accumulate in the effluent only in this experiment and the current-denitrification efficiency at low current densities was high. Thus, it is recommended for a low-loading operation.

Keywords Biofilm-electrode reactor; denitrification; flow-by; flow-through; multi-electrode system

Introduction

Bio-electrochemical denitrification is a promising process for treatment of nitrate-contaminated waters containing no electron donor because it can be easily operated by controlling the electric current. In addition, it appears to be a cost-effective process (Prosnansky *et al.*, 2002).

Fundamental characteristics of the bio-electrochemical reactor (BER) have chiefly been investigated by using a pair of electrodes (Sakakibara and Kuroda, 1993; Sakakibara *et al.*, 1994; Kuroda *et al.*, 1997). The results revealed that within relatively low current densities, denitrification with high efficiency occurred and denitrification rate increased with increasing current density. However, at higher current density, current-denitrification efficiency decreased (Islam and Suidan, 1998) and denitrification rate was limited. Recently, a multi-cathode BER was proposed (Sakakibara and Nakayama, 2001) as a method to increase the denitrification rate. It consisted of one anode and multiple cathodes, which brought about an enlarged specific surface area of cathode in the reactor. It could attain high rate operation by applying high electric currents while maintaining low current densities and developing more uniform distribution of hydrogen gas in the reactor.

Other factors affecting the performance of BER are the advective and the diffusional permeation of oxygen into the cathodic region from anode, formation of pH profile derived from bio-electrochemical reactions and migration of ionic species. The electrode configuration and flow direction against electrodes in the reactor seem to affect these factors. Therefore, the objective of this study is to reveal the effect of electrode configuration and flow direction on the bio-electrochemical denitrification by a laboratory-scale experiment. In this investigation, two different flow directions against electrode surface, flow-through and flow-by, were tested. In the flow-through system, the anode was installed either upstream or downstream (Figure 1).

Methods

Bio-electrochemical reactors

The detailed structure of the multi-cathode BER was described elsewhere (Prosnansky *et al.*, 2002; Prosnansky and Kuroda, 2002). Three laboratory-scale reactors tested in this

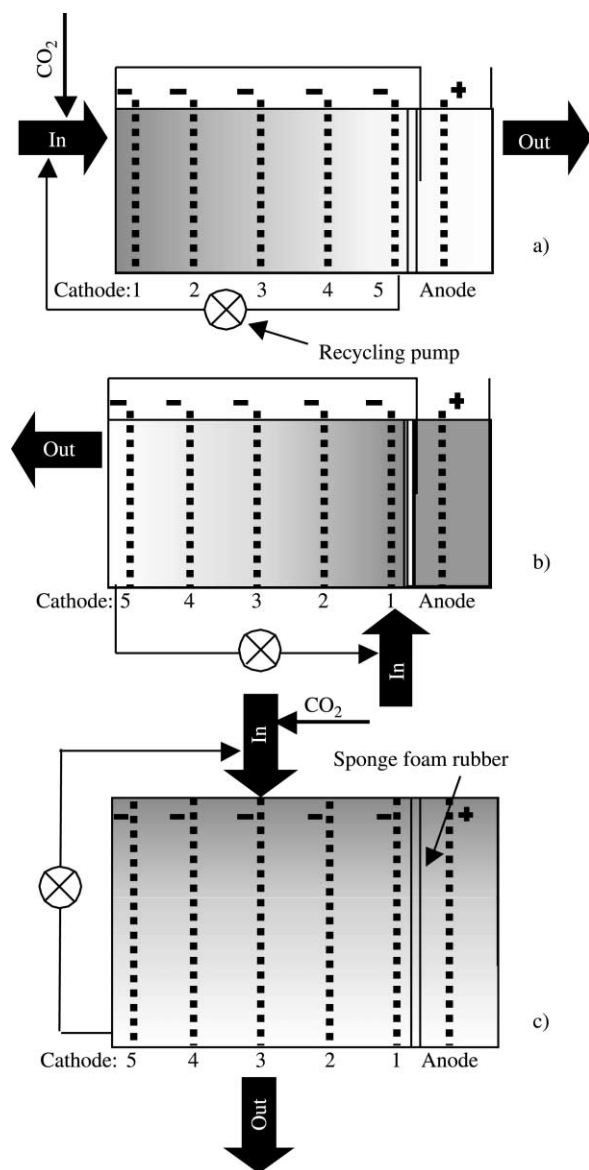


Figure 1 Illustration of three multi-cathode BERs: a) reactor R1, flow-through configuration of electrodes with downstream anode; b) reactor R2, flow-through configuration of electrodes with downstream anode; and c) reactor R3, flow-by configuration

study are illustrated in Figure 1. Figure 1a shows the multi-cathode BER with a flow-through configuration of electrodes and downstream installation of anode (referred to reactor R1), where nitrate-contaminated water entered the cathode zone and the treated water was discharged from the anode zone. The multi-cathode BER with a flow-through configuration of electrodes and upstream location of anode (reactor R2), where water flowed only through the cathode zone and water in the anode zone was immobile, is illustrated in Figure 1b. Figure 1c presents the multi-cathode BER with a flow-by configuration (reactor R3). Water also flowed only through the cathode zone and water in the anode compartment was also motionless.

All three reactors were composed of five cathodes and one anode. The cathodic and anodic zones were divided by 2 mm thick sponge-foam rubber. The volume of all BERs

was 1.21 with a void volume of 0.61. The effective surface area of each electrode was considered as a cross-sectional area of electrochemical cell ($A = 150 \text{ cm}^2$). The total surface area of the cathode and the anode was 750 cm^2 and 150 cm^2 , respectively.

Continuous experiment

Solution containing 15–40 mg-N/l of nitrate was continuously fed into the reactors. The feeding and discharge points for each reactor are shown in Figure 1. The experiment was conducted in six runs. In each run, for the set values of current density and the influent concentration of nitrate, an appropriate volumetric flow-rate was adjusted according to the overall denitrification reaction (Prošnansky *et al.*, 2002; Prošnansky and Kuroda, 2002). The recycle flow-rate was kept 300 l/day. Owing to the elevated pH in the cathode compartments of reactors R1 and R3, as a consequence of OH^- production during denitrification and electrolysis of water, CO_2 was fed (see Figure 1a, c) (Prošnansky *et al.*, 2002; Prošnansky and Kuroda, 2002). The CO_2 feeding rate is shown in Table 1. The total experimental period was about 8 months.

Analytical methods

Analyses were performed on a daily basis. Nitrate and nitrite concentrations were measured by an ion chromatograph (IC 7000 Series II, Yokogawa Analytical Systems). ORP and pH were measured by an ORP/pH meter (UC-23, Central Kagaku). Dissolved oxygen was analysed by a DO meter (UC 12, Central Kagaku) and the conductivity by a conductivity meter (SE 12, Horiba).

Results and discussion

Efficiency and denitrification rate of applied BERs

Table 1 shows the average values of nitrate and nitrite concentrations in the effluent, current-denitrification efficiency and denitrification rate for each BER related to the

Table 1 Operating conditions, current-denitrification efficiency (ϕ) and denitrification rate (r_D) for applied multi-cathode BERs

	i A/m ²	I_r A	Q l/day	CO_2 feeding ml/hr	NO_3^- - in mg-N/l	NO_3^- - out ⁴ mg-N/l	NO_2^- - out ⁴ mg-N/l	ϕ %	r_D mg-N/day
¹ R1	2.67	0.04	2.4	48	40	2.8	0	89.0	89
	4.00	0.06	6.0	72	25	2.8	0	88.6	133
	4.67	0.07	8.6	96	20	3.5	0	81.0	142
	6.00	0.09	14.4	108	15	3.8	0	71.7	161
	12	0.18	28.8	240	15	5.6	0	60.0	271
	20	0.30	43.2	420	15	9.3	0	33.3	246
² R2	2.67	0.04	2.4	0	40	13.0	1.3	61.5	61.7
	4.00	0.06	6.0	0	25	13.7	0.9	41.5	62.5
	4.67	0.07	8.6	0	20	12.3	0.4	35.6	62.5
	6.00	0.09	14.4	0	15	10.5	1.7	18.2	41.0
	12	0.18	28.8	0	15	11.8	0.4	11.6	52.3
	20	0.30	43.2	0	15	13.1	1.0	5.0	38.4
³ R3	2.67	0.04	2.4	24	40	0.9	0	93.6	94
	4.00	0.06	6.0	30	25	3.2	0.2	86.2	130
	4.67	0.07	8.6	36	20	2.8	0.4	82.4	144
	6.00	0.09	14.4	54	15	2.2	0.3	80.0	180
	12	0.18	28.8	84	15	5.4	0.2	60.3	272
	20	0.30	43.2	120	15	6.8	0.3	45.4	341

¹R1 – flow-through configuration with downstream anode, ²R2 – flow-through configuration with upstream anode, ³R3 – flow-by configuration and ⁴average values.

operating conditions. The current-denitrification efficiency was defined by the following equation:

$$\phi = \frac{Q(C_{NO_3^-}^{in} - C_{NO_3^-}^{out} - C_{NO_2^-}^{out})}{I_T/nF} \quad (1)$$

where Q is the volumetric flow-rate, $C_{NO_3^-}^{in}$ and $C_{NO_3^-}^{out}$ are the influent and effluent concentrations of nitrate, $C_{NO_2^-}^{out}$ is the effluent concentration of nitrite, I_T is the total electric current applied, n is the stoichiometric constant for denitrification ($n = 5$) and F is the Faraday's constant (Prošňanský et al., 2002; Prošňanský and Kuroda, 2002). Denitrification rate was calculated by the following equation:

$$r_D = Q(C_{NO_3^-}^{in} - C_{NO_3^-}^{out} - C_{NO_2^-}^{out}) \quad (2)$$

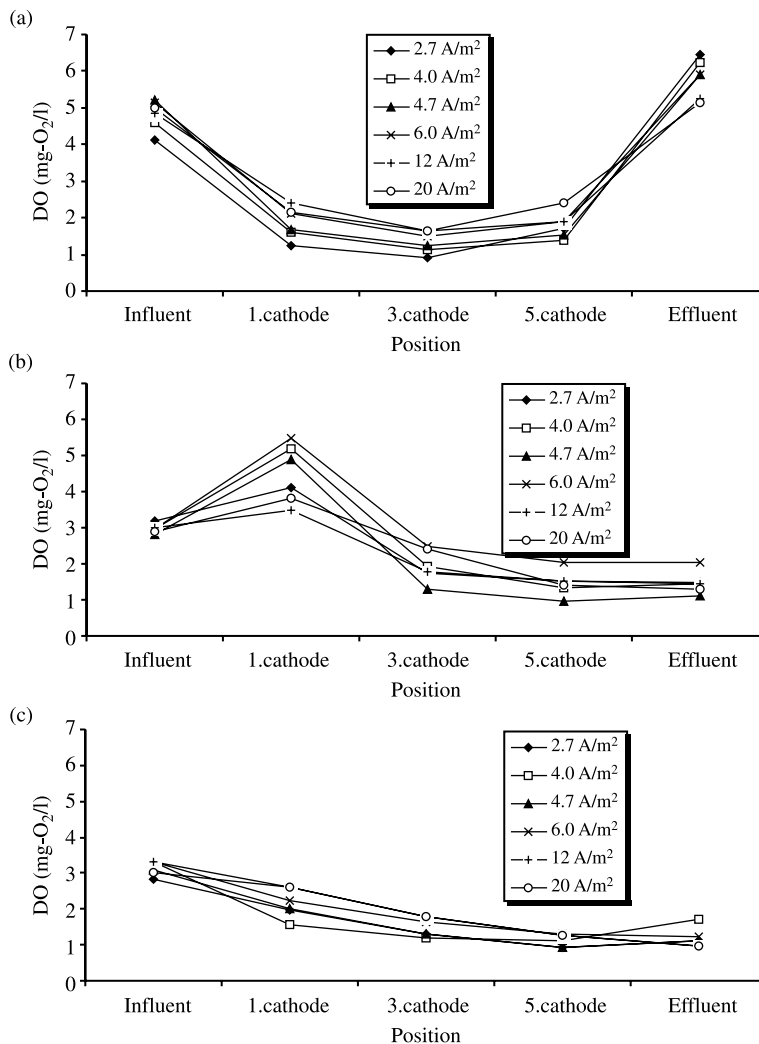


Figure 2 Profile of DO concentration in BERs. a) reactor R1 – flow-through configuration of electrodes with downstream anode; b) reactor R2 – flow-through configuration of electrodes with upstream anode; and c) reactor R3 – flow-by configuration

The poorest efficiency was obtained in the reactor R2, while the highest efficiency achieved the reactor R3. The efficiency in the reactor R1 was comparable with the reactor R3 until the largest current density was applied ($i = 20 \text{ A/m}^2$), then it markedly decreased (see Table 1).

The denitrification rate rose in the reactor R1 due to the enhanced H_2 production with increasing current density. However, when the current density exceeded 12 A/m^2 , denitrification rate dropped. In reactor R2, the denitrification rate was very low and roughly constant until 4.67 A/m^2 . After that it gradually declined. The denitrification rate in reactor R3 was the highest among all applied BERs and was inclining in the whole range of used current densities.

Reactor R1 showed complete and stable denitrification since nitrite was not detected throughout the experiment as nitrification of the produced nitrite probably took place at the downstream located anode before discharge. Hence, possible nitrite accumulating in the effluent was oxidized back to nitrate, which is less health threatening. Nitrite was detected in the effluent from the two reactors.

Effect of dissolved oxygen

Concentration of dissolved oxygen (DO) in the cathode compartment is one factor affecting denitrification. DO appears to regulate synthesis of nitrate reductase enzyme and inhibits denitrification in order that substrate electrons flow to oxygen cytochromes (Jeill and Silverstein, 1999).

DO penetrated all three BERs since the influent contained it. Apart from the influent DO, it also penetrated into the cathode compartment from the anode compartment, where oxygen was produced during the electrolysis of water. Figure 2 shows the measured DO profile for all BERs at different applied electric current densities. DO concentration gradually declined across the cathode region due to its biological and/or electrochemical reduction. DO drop was the sharpest in the cathode zone (1. cathode) during the experiment with the reactor R1 due to no effect of anodic oxygen production. However, at the downstream cathode (5. cathode), the DO concentration slightly increased owing to the back-diffusion of oxygen from the anode compartment.

In the experiment with reactor R2, the DO concentration at the upstream cathode was higher than in the influent due to significant effect of anode. DO produced at the anode diffused into the cathode compartment and then it was transported by advection and diffusion along the reactor. DO in the cathode zone was in the average the highest among all BERs, but the reactor R2 had lower DO concentration at the downstream cathode (5. cathode) than the reactor R1 (Figure 2).

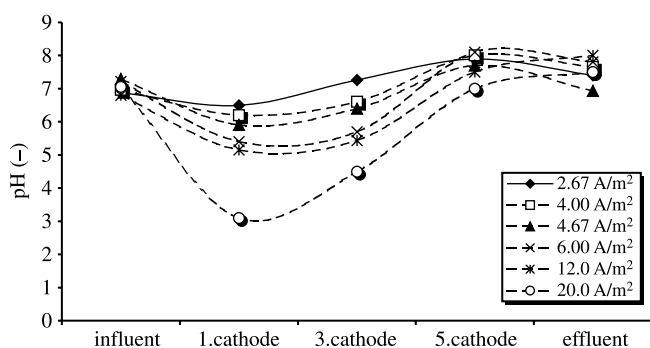


Figure 3 pH distribution in the multi-cathode BER with the flow-through configuration and upstream anode (reactor R2)

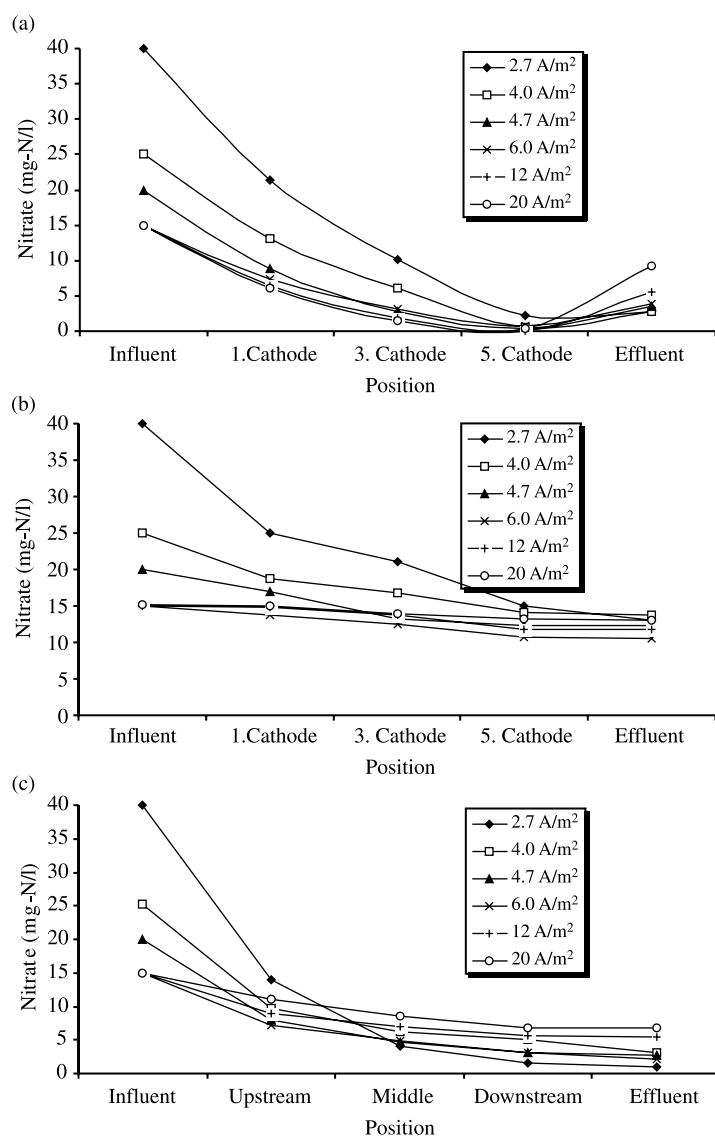


Figure 4 Nitrate distribution in BERS. a) reactor R1, flow-through configuration of electrodes with downstream anode; b) reactor R2, flow-through configuration of electrodes with downstream anode; and c) reactor R3 flow-by configuration

DO concentration in the reactor R3 gradually declined in the direction to the farthest cathode from the anode. However, the decline was slower than in other two reactors since the anode was inserted along the reactor.

There was a strong relationship between DO concentration in the cathode zone and denitrification rate. As the DO concentration was similar for the reactors R1 and R3, denitrification rates were also similar apart from the high rate conditions ($i = 20 \text{ A/m}^2$). The highest DO concentration in the cathode zone of the reactor R2, due to the upstream placement of anode, was the main reason for the lowest denitrification rate (Figure 3).

Effect of pH

The pH in the cathode compartment rose during denitrification as a result of OH^- production (Prošňanský *et al.*, 2002; Prošňanský and Kuroda, 2002). Thus, CO_2 gas was fed

into the reactors R1 and R3 (see Table 1) to maintain pH around neutrality (Prosnansky and Kuroda, 2002). When anode was placed upstream (reactor R2), however, H^+ produced at the anode penetrated the cathode zone and buffered pH reducing operating cost. Also as a result of low denitrification rate in the reactor R2, owing to the significant DO inhibition, the OH^- production was low and CO_2 feeding could be avoided. At $i > 6.0 A/m^2$, pH dropped below 5.5 in the reactor R2 (data not shown) and started to inhibit the activity of denitrifying bacteria (Koenig and Liu, 2002) causing further decline in the denitrification rate (see Table 1).

Effect of electric field

Since nitrate is an ionic constituent, it migrates in the electric field. In the reactor R1, the migration of nitrate ion and water flow advection had the same direction (see Figure 1). On the other hand, the migration had an opposite direction from the advection in the reactor R2 and nitrate migrated perpendicular to the water flow in the reactor R3.

Distribution of nitrate in BERs is presented in Figure 4. It demonstrates a significant effect of the electric field on the nitrate distribution. Negative effect of migration was observed in the reactor R1, where nitrate accumulated in the anode zone. Moreover, it was boosted with increasing current density. Hence, it is not recommended to operate this reactor at high current densities.

Conclusions

In this study, the effect of electrode configuration and flow direction on bio-electrochemical denitrification was investigated through a laboratory-scale continuous experiment.

The electrode configuration and flow direction affected the distribution of nitrate, DO and pH in reactors causing variation of performance among applied BERs. Flow-through configuration with the downstream anode appears to be suitable for denitrification since nitrite was not detected in the effluent. However, low current densities should be maintained as denitrification rate declines rapidly with increasing current density.

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