



DENITRIFICATION AND NEUTRALIZATION WITH AN ELECTROCHEMICAL AND BIOLOGICAL REACTOR

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ABSTRACT

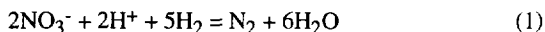
Denitrifying microorganisms were immobilized with a sodium alginate gel on a cathode electrode, and electric current was applied using a carbon electrode as the anode. Biological reductions of nitrate through the use of H₂ at the cathode and formations of inorganic carbons at the anode were observed. Experimental results showed that oxidation of carbon electrode to CO₂ was favorable for developing anoxic conditions and to neutralize alkalinity formed during denitrification. Several volts of potential was needed to operate the reactor.

KEYWORDS

Denitrification; electrochemical bioreactor; nitrate contamination; carbon electrode; electric current.

INTRODUCTION

Nitrate contamination in groundwater has been observed in many countries (Follett, 1989). Feasibility of an electrode-biofilm reactor to reduce nitrate to N₂ gas has been demonstrated experimentally and theoretically (Sakakibara *et al.*, 1993, 1994). The principal mechanism of the electrode-biofilm reactor is that denitrifying microorganisms are immobilized on the cathode utilizing H₂ produced by the electrolysis of water and subsequently reduce nitrate to N₂ gas as follows,



In the electrode-biofilm reactor, carbon electrode was used as the anode, so that the CO₂ formation seems to occur instead of O₂ formation (Kinoshita, 1988). An overall electrochemical reaction occurring in the reactor is,



The formation of CO₂ instead of O₂ formation seems to be advantageous in developing the anoxic condition. Furthermore, the standard electric motive force of Eq. (2), e_{mf} , is 0.207V which is about one sixth of the corresponding potential for water electrolysis to produce O₂ and H₂ (Kinoshita, 1988). This indicates the carbon electrode is also advantageous from a view point of energy consumption.

In this study, denitrifying microorganisms were immobilized on a stainless steel cathode and electric current was passed using a carbon electrode as the anode. The formation of inorganic carbons, gas production, liquid pH and the electric energy requirements to operate the reactors with and without the immobilized cells were observed and the role of carbon electrode was investigated experimentally.

MATERIALS AND METHODS

Fig. 1 shows an illustration of the experimental apparatus used in this study. A carbon rod and a stainless pipe were used as an anode and a cathode, respectively, and were set up concentrically in a cylindrical reactor. The reactor liquid volume is 205 cm³ and the effective surface area is 160 cm² at the anode and 251 cm² at the cathode. The liquid in the reactor was withdrawn from the upper part at a flow rate of 0.3 l/min and fed back tangentially into the bottom.

Denitrifying microorganisms cultivated in our laboratory were enriched using a mixture of glucose, acetate and formate as hydrogen donors, and were immobilized with a sodium alginate gel onto the inner surface of the stainless cathode. The reactor was kept in a room whose temperature is 25°C.

A synthetic groundwater was prepared by dissolving sodium nitrate at 1 mM in tap water, the source of which is groundwater. After dissolved oxygen was purged with N₂ gas, the synthetic groundwater (containing about 1 mM inorganic carbons originally) was fed continuously into the reactor. The pH of the groundwater fed was 7.6. Adjusting the electric current to a constant value, measurements were made for time course changes of gas production, effluent concentrations of nitrate and inorganic carbon, pH and potential differences between the electrodes (ΔE).

Nitrates were measured photometrically using a modified standard method (TNP set, Central Kagaku). Inorganic carbons were measured by using a TN-TC Analyzer (Shimadzu, GC-12NA). The gas composition was analyzed using TCD gas chromatography (Shimadzu, GC-3BT).

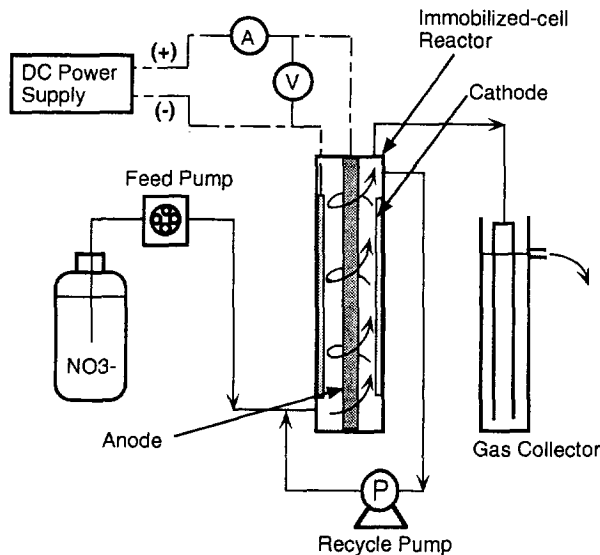


Fig. 1. Schematic diagram of experimental apparatus.

EXPERIMENTAL RESULTS AND DISCUSSION

Response to Applied Electric Current

When electric current is applied, H_2 evolution and CO_2 formation will occur according to Eq.(2). Fig. 2 is a typical result of a carbon-electrode reactor without the immobilized-cells. The liquid HRT is 1 hour and the electric current is 10 mA (the current density is 0.04 mA/cm^2 at the cathode).

The liquid ORP in the reactor declined from a positive (about 160 mV measured by $Ag/AgCl/KCl(3.3M)$ electrode) to negative values after several tens of minutes of operation and thereafter approached a steady-state value. Similar responses were obtained in the HRT range of about 10 min to 1 day. At steady-state conditions, ORP values were less than -200 mV, where increasing HRT tended to decrease the ORP. These results demonstrate that carbon-electrode systems are effective in developing anoxic conditions suited for denitrification. Conductivity in the reactor was nearly the same to the feed liquid.

On the other hand, pH increased up to about 8.5 and then decreased to about 7.0. Because of higher mobility of NO_3^- than Na^+ , it is considered that more NO_3^- will migrate toward the anode, resulting in an increase in OH^- concentration in the bulk liquid to maintain electroneutrality. The formations of CO_2 and carbonate ions, however, lower the pH until their production rates are balanced to discharging rates from the reactor.

Segall and Bruell (1992) reported that NO_3^- ions were reduced to NH_4^+ in electroosmotic processes used for soil treatments. However, nitrate concentrations in this study were almost the same between the influent and effluent. Besides pH difference, the electric energy applied is roughly 2 to 3 orders of magnitude smaller than the power consumptions in the electroosmotic processes. These differences seem to affect the reduction rates of nitrate to ammonium.

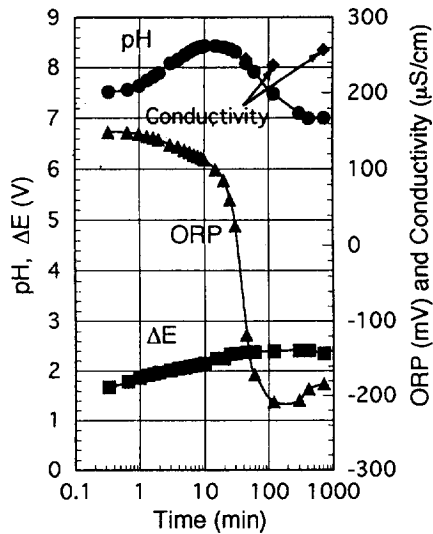


Fig. 2. Response of electrode reactor without immobilized cells.

Nitrate Reduction and Neutralization

Fig. 3 shows an experimental result for the continuous treatment with the immobilized-cell reactor. The electric current applied was 2.5 mA (corresponding to the current density of 0.01 mA/cm^2 at the cathode) and the liquid HRT was 9 hours. Concentrations of nitrite and ammonium in effluent were less than 1 mg-

N/l. Effluent nitrate concentration decreased with time, and gas production increased up to about 1 ml/h and then decreased to about 0.2 ml/h or less. Components of the produced gas were H_2 , N_2 , and CO_2 . Effluent concentrations of inorganic carbons were about 5 to 10 mg-C/l higher than influent.

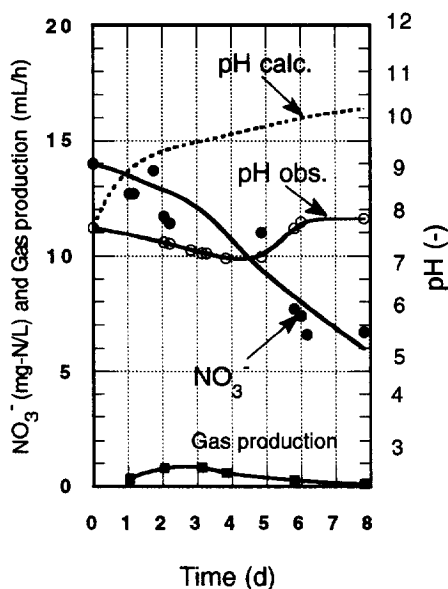


Fig. 3. Response of the electrode-immobilized cells reactor.

The dotted line is a calculated result of pH assuming that no production of CO_2 occurs and hence the alkalinity produced during denitrification is balanced to OH^- ions and carbonate ions in the feed. From a comparison of calculated and observed results, it is shown that the pH values observed were nearly equal to the feed pH and 2 to 3 magnitude smaller than the dotted line. This demonstrates that carbon electrode is effective in developing anoxic conditions and to serve as a source of the carbonate buffer to neutralize the water treated.

With regard to energy consumption, a potential difference (ΔE) of at least 0.8 V was needed to pass the electric current in the stainless-carbon electrodes system. However, this potential was reduced when carbon-carbon electrodes were used. The ΔE applied in Fig. 3 was 2.2 V, which corresponds to an energy consumption of about 0.22 kWh/m³ to remove 10 mg-N/l nitrate.

CONCLUSION

In the electrochemical and biological reactor, carbon electrode was effective to develop anoxic conditions and to supply carbonate ions which neutralize the liquid treated. Electric energy requirement to remove 10 m-N/l nitrate was about 0.22 kWh/m³ when the carbon-stainless electrodes were employed.

ACKNOWLEDGEMENT

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