Analysis of nitrate removal rate in a continuous column denitrification reactor using hydrogen generated by electrolysis

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学 位 論 文 要 旨

ABSTRAC

An autotrophic continuous denitrification process, using hydrogen generated by electrolysis with activated carbon anodes, were experimentally demonstrated to be an effective nitrate removal process. Several fixed bed columns with polypropylene packing and honey-comb shaped activated carbon anodes and stainless rod cathodes were set in thermostat chamber of 30 °C, and then potassium nitrate enriched tap water, nitrogen concentration of 30 mg-N$\cdot l^{1}$, was supplied at various flow rates and electric currents (1.5~6 mA).   Although the anode is in the same column where microbes grow, sufficient nitrate removal was observed. For example, 94 % of nitrate was removed at the HRT of as short as 1.8 h for an electrical current of 6 mA.   A model assuming successive   nitrate and nitrite reductions and plug-flow process, nitrate reduction rate = k_1 [NO$_3^-$][H$_2$], and nitrite reduction rate = k_2 [NO$_2^-$][H$_2$]$^{1.5}$ was constructed.   Calculated results with k_1=1.3 $l\cdot$mmol$^{-1}\cdot$h^{-1} and k_2=3.3 $l^{1.5}\cdot$mmol$^{-1.5}\cdot$h^{-1} agreed well with the all the experimental results.

The effect of increasing electric current on the denitrification rate was investigated in the same columns run at 0.55 hr and 1.1 hr hydraulic retention time (HRT). At the electric current of 20 mA, 76% of the nitrogen was removed for HRT of 0.55 hr and 91% for 1.1 hr. By fitting the results with model previously constructed, we got values of k_1=3.95, k_2=4.00 for 0.55 hr HRT, and k_1=0.95 and k_2=0.60 for 1.1 hr HRT. Also, by using the model, we estimated the necessary electric currents for 95% removal of nitrogen is 25 mA for 0.55 hr HRT, and 16 mA for 1.1 hr HRT. Although the parameters describing the system, k_1, k_2 are different from those obtained for electric currents ranging 1.5~6mA, the estimated necessary HRT for 95% removal of nitrogen was in good agreement with the trend estimated by the 1.5~6mA experiments.

INTRODUCTION

During the last decade, the presence of nitrate in ground and surface waters has become of increasing concern in many part of the world. Nitrate in itself is not a health problem, but when ingested it can be converted into nitrite. In turn, nitrite can lead to "blue baby syndrome" (methemoglobinemia), a blood disorder primarily affecting infants under six months of age. The drinking water standard of Japan and The World Health Organization (WHO) have set the maximum contaminant level at 10 mg· l^{1} for nitrate-nitrogen (NO$_3$-N).

Autotrophic biological treatment that utilizes hydrogen gas as an electron donor is one of the treatment methods for removal of nitrates from water resources. This method has several advantages: no need for an external organic carbon source, the substrate used is hydrogen, which is completely harmless to potable water, and less sludge production. Sakakibara and Kuroda proposed a method for removing nitrate using a denitrifying biofilm-electrode reactor (BER), which utilizes immobilization of autotrophic denitrifying

microorganisms on the surface of the carbon electrode. Hydrogen gas produced by electrolysis of water in the cathode is used as an electron donor. It has been experimentally demonstrated that simultaneous denitrification by hydrogen gas produced in the cathode and neutralization by CO_2 produced in the anode occurred when an electric current was applied.

In this study, the mechanism of reaction in autotrophic biological treatment for removal of nitrate using hydrogen gas produced by electrolysis of water as an electron donor was examined. A fix bed reactor with polypropylene sponges as carrier material for microbial biomass was used. Honeycomb carbon and stainless wire were used as anode and cathode respectively, and placed at the bottom of the reactor. To express the relationship between denitrification reaction rate, nitrate and nitrite concentration and electric current, a kinetic model was also developed.

MATERIAL AND METHOD

Schematic diagram of the experimental apparatus used in this study is shown in Fig. 1. The system consists of cylindrical reactor with a height of 120 mm and an internal diameter of 27.5 mm, DC power supply, electrodes and peristaltic pump. The 50-mm height of the reactor was filled with polyurethane sponges, which allow accumulation of the microbial biomass. Since the size of the reactor is small, polyurethane sponge, which has light weigh and wide surface area, is appropriate for this study. The effective liquid volume was 25 ml and surface area of the packing-bed was 10.5cm^2·cm^{-3}-reactor. A honeycomb activated carbon anode (12mm x 12mm x 30mm) and three stainless cathodes were used for the electrodes and placed at the bottom of the reactor. The surface area of the anode and cathode were 1440 mm^2 and 108 mm^2, respectively. The feed solution (influent) was prepared by dissolving 30 mg-N l^1 potassium nitrate in tap water. Other inorganic substances or growth nutrients such as phosphate were not added to the solution.

Before starting the experiment, for establishment of the microbial biomass in the carrier material, the feed solution mentioned above was fed into the reactor continuously with flow rate of 250 ml·d^{-1} and a constant electric current (3 mA) was applied for a period of about two months. Samples were taken from the effluent of the reactor for twice a week. The nitrate and nitrite concentrations were measured with Ion Chromatography.

The experiments were started after constant nitrate removal rate was obtained. In the experiments, hydraulic retention time (HRT) was shortened in stepwise manners. The details of the experimental conditions are shown in Table 1. At first, 3 mA of electric current was applied to Col. 1~4. After that, 1.5 mA and 6 mA of electric current were applied to Col. 2,4 and Col. 1,3, respectively, and HRT were shortened in stepwise. The changes of concentration of components in the effluent were investigated. Here, hydraulic retention time is defined as dividing flow rate with the effective liquid volume of column (25 ml). The effluent nitrate and nitrite concentration and pH were measured with Ion and pH Meter, respectively.
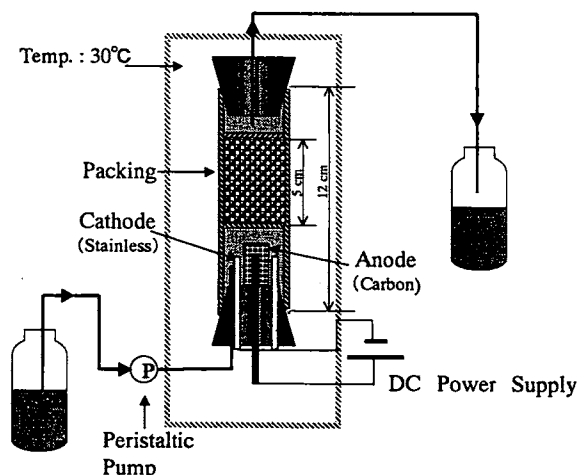

Fig. 1 Illustration of experimental apparatus

Table 1 Experimental condition

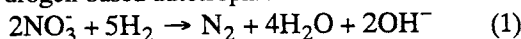| Exp. No.	Col. No.	Current [mA]	HRT [h]	H_2 prod.(theor.) [mmol/h]
1	1	3.0	1~5	0.056
	2	3.0		
	3	3.0		
	4	3.0		
2	2	1.5	2~10	0.112
	4	1.5		
	1	6.0	0~2	0.224
	3	6.0		

RESULTS AND DISCUSSION

Figure 2 shows the experiment results with step decreases in HRT at electric current of 3 mA. In the figure, HRT is showed by solid line. At low HRT, almost complete reduction of nitrate was achieved. However, slight production of nitrite was occurred. With the decrease of HRT caused a rapid rise in nitrate and nitrite. The same results were obtained in each column and different electric current. In the same figure, the changes of pH in the effluent are shown. Influent pH is almost stable around 7.5. As shown in equation (1), because of denitrification activity, the effluent pH is higher than the influent pH. The effluent pH is around 8~9.

From Fig. 2, it is known that although cathode and anode are placed in the same column, denitrification activity has occurred. It is considered that anode almost does not produce the oxygen, which was experimentally confirmed. The same result was reported by Kinoshita (1988) that in the carbon anode, carbon dioxide is produced instead of oxygen. The same reactions as Kinoshita reported might be occurred in this study.

Fig. 2 Change in pH, nitrate and nitrite concentration with stepwise decrease in HRT (3 mA).

Effect of electric current and HRT on nitrate and nitrite concentration

In order to get the plot of concentrations against HRT, the average of effluent nitrate and nitrite concentration in every step of HRT was calculated and shown in Fig. 3.

The stoichiometric reaction of the hydrogen-based autotrophic denitrification is as follows:

$$2NO_3^- + 5H_2 \rightarrow N_2 + 4H_2O + 2OH^- \quad (1)$$

Based on Faraday's law and the stoichiometry in Eq. (1), the minimum HRT was calculated and shown by broken line in the Fig. 3. From the figure, both of nitrate and nitrite concentrations remain in the effluent when the HRT is smaller than the minimum HRT. Therefore, in order to reduce nitrate and nitrite completely, the value of HRT must be higher than the minimum HRT. These results suggest that denitrification occurred in the reactor is controlled by the amount of hydrogen gas.

In several type denitrification processes, the nitrite accumulations are usually detected. The reason for the accumulation of nitrite in the effluent in this study is not clear. The relationship between accumulation of nitrite and HRT or electric current could be seen in the Fig. 3, however, correlation to other data, i.e. DO, temperature and pH, are not unknown. It is assumed that the steps of reduction from nitrate to nitrite and from

Fig. 3 Effect of HRT on nitrate and nitrite concentration, broken lines show the theoretical HRT to remove all the nitrate

nitrite to nitrogen are done by different enzymes or microorganisms and the secretion of nitrate reductase is taken priority.
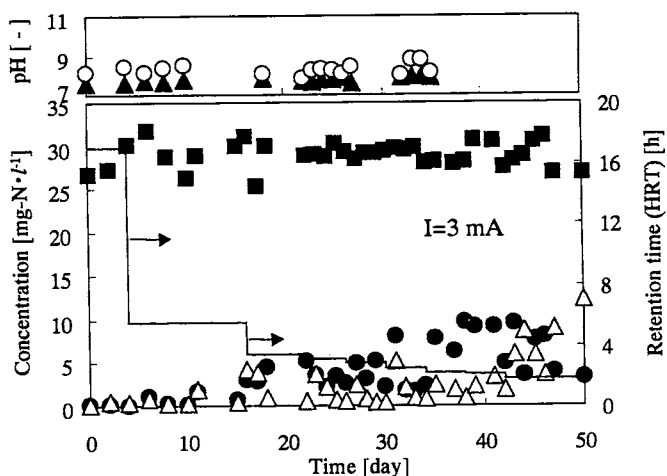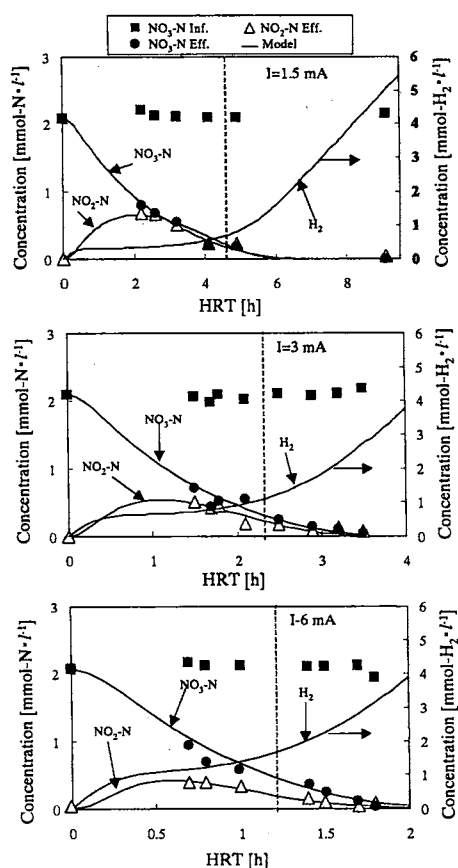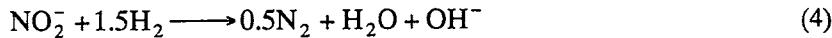
DENITRIFICATION MODEL

In this study the denitrification process is assumed as consecutive reaction, and the reactor is assumed as plug flow reactor (PFR) with constant density. Denitrification model was derived as follows:

$$NO_3^- + H_2 \longrightarrow NO_2^- + H_2O \qquad (3)$$

$$NO_2^- + 1.5H_2 \longrightarrow 0.5N_2 + H_2O + OH^- \qquad (4)$$

Here, the reaction rates are approximated by assuming that rate equations correspond to a stoichiometric equation. The nitrate reduction rate $= k_1 [NO_3^-][H_2]$, and nitrite reduction rate $= k_2 [NO_2^-][H_2]^{1.5}$ are written as: $r_{NO3}= k_1 [NO_3^-][H_2]$ and $r_{NO2}= k_2 [NO_2^-][H_2]^{1.5}$, respectively, where k_1 and k_2 are reaction rate constants for nitrate ion reduction and nitrite ion reduction, respectively. From the calculation by numerical method found that $k_1=1.3$ $l \cdot mmol^{-1} \cdot h^{-1}$ and $k_2=3.3$ $l^{1.5} \cdot mmol^{-1.5} \cdot h^{-1}$ conformed very well to the experiment data ini this study. results. The calculation results are shown in Fig. 3 by solid lines.

Studies of the nitrate removal rate using hydrogen as an electron donor have been very limited. Kurt et al. (1987) and Sakakibara et al. (1994) reported that model calculated by Michaelis-menten equation adequately conformed to the experimental results. Nitrate reduction rate (r_{NO3}) and nitrite reduction rate (r_{NO2}) obtained by Kurt et al. are 1.21~1.64 [mmol-N l^{-1} h^{-1}] and 0.86~1.29 respectively. Ginocchio (1980) studied denitrification in the reactor with indirect H_2 input and recirculation of water. With an influent concentration of 16 mg-N l^{-1} and a residence time of 20 minutes, a denitrification rate of 2.38 mmol-N l^{-1} h^{-1} was reached. The maximum nitrate and nitrite reduction rate obtained from the present study at the electric current of 6 mA are 2.02 mmol-N l^{-1} h^{-1} and 1.66 mmol-N l^{-1} h^{-1}, respectively. The results from the present study are almost equal comparing with the results mentioned above.

Performance of the reactor in the high electric current

In order to increase performance of treatment in removing nitrate and miniaturizing the reactor, it is desirable to reduce HRT. However, the value electric current should be increased when the HRT is low. Since hydrogen solubility in water is low, increasing electric current does not always increase the rate of nitrate removal.

The effect of increasing electric current on the denitrification rate was investigated in the same

Fig. 4 Dependence of HRT on the electric current under condition of 95% nitrogen removal rate

columns run at 0.55 hr and 1.1 hr hydraulic retention time (HRT). At the electric current of 20 mA, 76% of the nitrogen was removed for HRT of 0.55 hr and 91% for 1.1 hr. By fitting the results with model previously constructed, we got values of $k_1=3.95$, $k_2=4.00$ for 0.55 hr HRT, and $k_1=0.95$ and $k_2=0.60$ for 1.1 hr HRT. Also, by using the model, we estimated the necessary electric currents for 95% removal of nitrogen is 25 mA for 0.55 hr HRT, and 16 mA for 1.1 hr HRT.

The relation between applied electric current and HRT needed for obtaining 95% of nitrate reduction rate is shown in **Fig. 5**. From the figure, it is found that although the parameters describing the system, k_1, k_2 are different from those obtained for electric currents ranging 1.5~6mA, the estimated necessary HRT for 95% removal of nitrogen was in good agreement with the trend estimated by the 1.5~6mA experiments. From this, it is known that by increasing the value of the electric current, the column can be operated in low HRT.

A denitrifying biofilm-electrode reactor (BER), which involved direct immobilization of autotrophic denitrifying microorganisms on the surface of the cathode was proposed by Sakakibara and Kuroda. It this system, since the transfer of nitrate ion to the surface of the electrode is driven by the potential gradient, the net denitrification rate reach the limit value with increase the electric current density. Thus, the system has to be operated in the linear zone where the denitrification rate increases linearly with electric current. In the present study, it is considered, since dissolved hydrogen is used and denitrification is done by the microorganism immobilized on the surface of the packed-bed, the effect of the potential gradient is negligible.
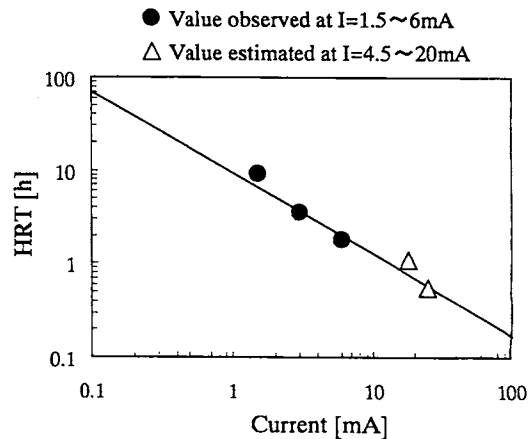
Nitrate removal by continuous column reactors using hydrogen generated by electrolysis is proved to be an effective method. Results show that the necessary HRT and the hydrogen efficiency is a trade-off. For commercial use, we have to consider the trade-off between the HRT and hydrogen efficiency, and also, a low cost, easily exchangeable carbon anode are required to be developed.

CONCLUSSION

A continuous column denitrification reactor using hydrogen generated by electrolysis was developed and satisfactory denitrification was achieved. Effect of hydraulic retention time and electric current to nitrate removal rate was examined, and the following results were obtained:

1) The type of carbon anode used could affect the experimental results
2) Although anode, cathode and packing material were placed in the same column, satisfactory denitrification was achieved. That is, production of oxygen in anode is inhibited.
3) The kinetic model for denitrification reaction was developed and the reaction rate constants were calculated. Calculation results using Runge-Kutta fourth order method show that the value of k_1 and k_2 are $1.3 \text{mmol}^{-1} \cdot \text{h}^{-1}$ and $3.3 \text{mmol}^{-1.5} \cdot \text{h}^{-1}$, respectively. The results predicted by the model agree fairly well with the experimental results.
4) In order to prevent nitrite in the effluent, this system must be operated in the condition where nitrate concentrations approach to zero with sufficient electric current or HRT.
5) In the columns run at the high electric current, although the parameter describing the system k_1 and k_2 are different from those obtained for electric current ranging 1.5~6 mA, the estimated necessary HRT for 95% nitrogen removal was in good agreement with the trend estimated by the 1.5~6 mA experiments.

References

1) Kinoshita, K. (1988) Carbon, electrochemical and physicochemical properties, John Wiley & Son, New York.
2) Sakakibara, Y., Flora, J.V.R., Suidan, M.T. and Kuroda, M. (1994) Modeling of electrochemically-activated denitrifying biofilms, Wat. Res., 28, 1077-1086.

学位論文審査結果の要旨

平成 13 年 8 月 7 日に第 1 回学位論文審査会を開催して本論文の内容を検討し，8 月 9 日の口頭発表，同日開催の第 2 回審査会における最終審査により，下記の通り判定した。

本研究は，電気分解を用いて水素を発生させ，それを電子供与体として，水中の硝酸態イオンを脱窒除去する手法に関する研究である。近年，飲料水源の硝酸態窒素の汚染が進行し，その対策が必要となっているが，本研究で提案されている方法は，電気分解により水素を供給するため，処理水量，濃度に応じた水素供給量の制御が容易であるという特徴がある。本論文の成果はつぎの点に要約される。(1) アノードに炭素電極を用いることにより，アノードとカソードが同一槽内にあっても，槽内の酸素濃度が上昇せず，脱窒が生ずることを明らかにした。(2) カラムを用いた実験的検討により，滞留時間および供給電流量が硝酸態窒素除去率，亜硝酸態窒素残存率に及ぼす影響について定量的に明らかにした。(3) 装置内の反応をモデル化し，実験結果との比較から，反応が逐次反応プラグフローモデルで説明できることを明らかにした。(4) 実験とモデルから，十分な窒素除去を達成するに必要な滞留時間および供給電流量を明らかにし，電流供給量を増やせば滞留時間を短くできるものの水素利用効率が低下することを明らかにした。

以上のように，本論文は，飲料水源からの新たな窒素除去法について，開発，設計の基礎となる反応速度について明らかにしており，工学的な価値は十分に高く，博士（工学）の学位を授与するに値する。