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원추형 유동층 반응기에서 Pseudomonas Denitrificans를 이용한 탈질소 반응

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Biological Denitrificationb by Pseudomonas denitrificans in a Tapered Fluidized Bed Reactor

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요 약

원추형 유동층반응기에서 박테리아 Pseudomonas denitrificans(ATCC 13867)을 25/35mesh의 활성탄에 부착시켜 생물학적 탈질소시키는 반응에 대하여 연구하였다. 탈질화 반응에서 최적 pH 및 온도는 7—8.5 및 25—35°C였으며 nitrate의 환원속도는 nitrate의 농도와 무관한 0 차 반응이었다. 반응기 설계를 위한 수학적 모델은

$$S_0^{0.55} = -K\bar{l} + S_i^{0.55}$$

였으며, 여기에서

$$K = 1.657(1-\epsilon_a)(\rho k)^{0.55} D^{0.45} r_p^{-0.9}$$

였다. 본 실험에는 K는 0.024의 값을 가졌다.

ABSTRACT

A tapered fluidized bed reactor was employed for biological denitrication, in which a facultative and heterotrophic denitrifier Ps. denitrificans(ATCC 13867) adhering on 25/35

mesh activated carbon was used. It has been found that optimum pH was in 7 – 8.5, and optimum temperature in 25 – 35°C. The rate of nitrate reduction was almost constant irrespective of nitrate concentration and zero order. A mathematical model was developed for the design of reactor

$$S_0^{0.55} = -K\bar{t} + S_i^{0.55}$$

where

$$K = 1.657(1 - \epsilon_a)\ (\rho k)^{0.55}\ D^{0.45}\ r_p^{-0.9}$$

In the experiments, K value was 0.024.

I. Introduction

The wastewater containing nitrate accelerates eutrophication of lakes and streams. Nitrate concentration exceeding 10 ppm may cause methemoglobinmia, vitamin A deficiency and various health hazards. Therefore, the anticipated discharge limit will not allow the continued release of the wastewater nitrate.

In order to remove nitrate from wastewater. various processes are being developed. Three basic designs in biological denitrification process have been developed and tested in bench scale and pilot operations. They are modified activated sludge reactor,[1~3] packed bed reactor[4,5] and fluidized bed reactor.[6~11] The fluidized bed has advantages over two other reactors such as (i) utilization of small particles with high specific surface allowing greater specific reaction rate, (ii) easy replacement of the active particles even during operation and (iii) no danger of clogging and very small head loss.

There are two kinds of fluidized bed reactors: cylindrical and tapered fluidized beds. The latter has an advantage of relative stability for the inlet velocity of fluid, which allows a wide range of flow rates without loss of support media since the fluid decreases with reactor height.

In this work, tapered fluidized bed reactor is used for the denitrification with activated carbon as support media and Pseudomonas denitrificans as a micro-organism. A mathematical model is developed and analyzed by the experiments.

II. Mathematical Model Development

1. Reaction within the Biofilm

In biological denitrification, the reaction rate follows intrinsic zero order kinetics and is limited by the diffusion of substrate within the biofilm. The internal mass transfer resistance is such that the substrate penetrates only partially into the biofilm The continuity equation for nitrate within the beioparticle canbe described in the following form if the bioparticle is assumed to be spherical as shown in *Fig. 1.*[12]

$$\frac{D}{r^2}\ \frac{d}{dr}\left(r^2\frac{ds}{dr}\right) = \rho k \qquad (1)$$

The boundary conditions are

$$S = S_b \quad at\ r = r_p$$

$$\frac{dS}{dr} = 0\ or\ S = 0\ at\ r = r' \qquad (2)$$

The reaction rate per unit volume of reactor, $\bar{R}$, is obtained approximately when the

above equations are solved

$$\bar{R} = (1-\epsilon)\rho k\{1-(r'/r_p)^3\}$$
$$= 3.012(1-\epsilon)\ (\rho k)^{0.55}\ D^{0.45} r_p^{-0.9}\ S_b^{0.45} \quad (3)$$

2. Continuity Equation in Tapered Fluidized Bed

The material balance of nitrate within a differential element at the reactor height z may be expressed as below

$$\frac{Q}{A\epsilon}\ \frac{dS_b}{dz} + \bar{R} = 0 \quad (4)$$

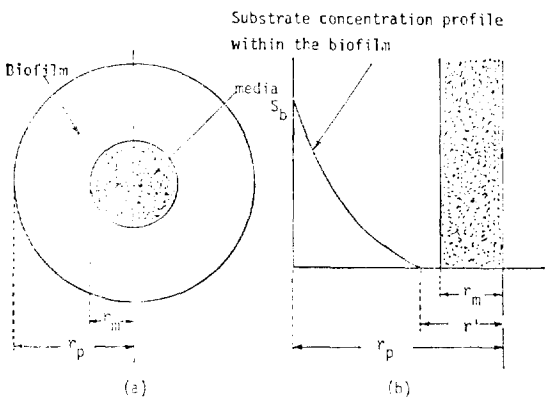

Fig. 1. Bioparticle (a) and Substrate Penetration into Biofilm (b)

Here the biomass growth that is not attached to particles is neglected. The boundary conditions are

$$S_b = S_i \quad at\ z = 0$$
$$S_b = S_0 \quad at\ z = z_t \quad (5)$$

The coordinates of tapered fluidzed bed is shown in *Fig. 2.* By the introduction of a variable $\xi = z/z_0$ and area $A = \pi R_0^2(1+\xi)^2$, the equation (4) becomes

$$\frac{Q}{R_0^2(1+\xi)^2 z_0 \epsilon}\ \frac{dS_b}{d\xi} + 3.012(1-\epsilon)$$
$$(\rho k)^{0.55} D^{0.45} r_p^{-0.9} S_b^{0.45} = 0 \quad (6)$$

By the introduction of new variable

$$t = \frac{\pi R_0^2\{(1+\xi)^3 - 1\} z_0 \epsilon}{30} \quad (7)$$

the equation (6) is transformed into the following form if the void fraction of liquid is assumed to be uniform and inde pendent of reactor height

$$\frac{dS_b}{dt} + 3.012\ (1-\epsilon_a)\ (\rho k)^{0.55} D^{0.45} r_p^{-0.9}$$
$$S_b^{0.45} = 0 \quad (8)$$

It will be shown later that the void fraction is uniform along the bed height and ϵ can be replaced by ϵ_a.

The boundary conditios are

$$S_b = S_i \quad at\ t = 0$$

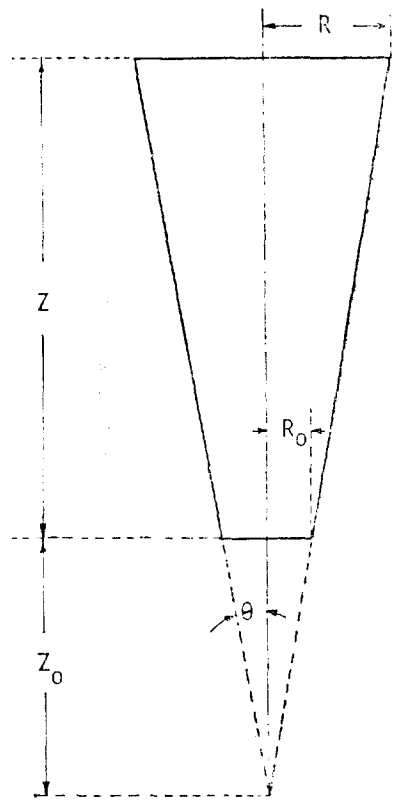

Fig. 2. Schematic Description of Tapered Coordinates

$$S_b = S_0 \quad at\ t = \bar{t} \quad (9)$$

where $\bar{t}$ corresponds to the residence time of liquid in a tapered fluidized bed. Integration (8) with boundary conditions yields in

$$S_0^{0.55} = -K\bar{t} + S_i^{0.55} \quad (10)$$

where $K = 1.657\ (1-\epsilon_a)\ (\rho k)^{0.55} D^{0.45} r_p^{0.9}$

III. Experimental Materials and Methods

Pseudomonas denitrificans (ATCC 18367) was used for the biological denitrification throughout the experiments. The medium composition is shown in *Tabld 1*. The pH was adjusted with 1N-H_3PO_4 or 1N-N_aOH solution. Batch culture was performed in 500 ml Erlenmeyer flask at 30°C and pH 7. The initial nitrate concentration was changed from 50 to 980 ppm.

The experiments in tapered fluidized bed were carried out in a glass reactor, which had 2.5 cm diameter at the bottom, 6.4 cm at the top and 106 cm height, as shown in *Fig. 3*. The inlet at the bottom of the reactor was designed to induce the uniform distri bution of liquid velocity.[13] Activated carbon particles of 25/35 mesh filled 630cm^3 volume of reactorand void fraction was 0.38

During early stage after inoculation, the feed with 0.097 (W/V%) KNO_3 concentration was supplied from the feed tank to the reactor, and the liquid and solid discharged from the reactor were separated in separator. Some liquid was returned to the reactor by the recy-cling pump and produced gas was vented through wet-test meter. The temperature and pH were kept at 30°C and 7, respectively. After microorganisms were attached to activated carbons f-orming a stable bacteria population bed, the liquid recycling was stopped and the experiments were performed leaving the reactor open to contamination.

The effects of pH and temperature on denitrfication were observed in the range of pH value 6-10 at 30°C and 10-45°C at pH 7, respectively. The feeding flow rate was fixed at 4cc/sec and KNO_3 concentration at 0.097 (w/v%) for both effects observations. When the steady state was reached, samples were collected.

Table 1. Medium Composition for Biological Denitrification (W/V%)

	Maintenance	Incocuum	Batch and continuous Denitrification
Glucose	1	—	—
Yeast Extract	0.5	0.1	0.0194
$FeCl_3$	0.03	—	—
Agar	1.5	—	—
Peptone	—	1	0.194
lNaCl	—	1	0.194
KH_2PO_4	—	0.15	0.0291
K_2HPO_4	—	0.5	0.097
KNO_3	—	0.5	*
NH_4Cl	—	0.1	0.0194
$NgSO_4 \cdot 7H_2O$	—	0.02	3.88×10^{-3}
$CaCl_2$	—	0.002	3.88×10^{-4}
Na_2SO_3	—	—	0.02
Trace Metal Solution	—	one drop	one drop

Trace Metal Solution	
$MnCl_2$	0.5
$CuSO_4$	0.5
$FeCl_3$	0.5
$Na_2Mo_4 \cdot 2H_2O$	0.5

* Changed for different experiments

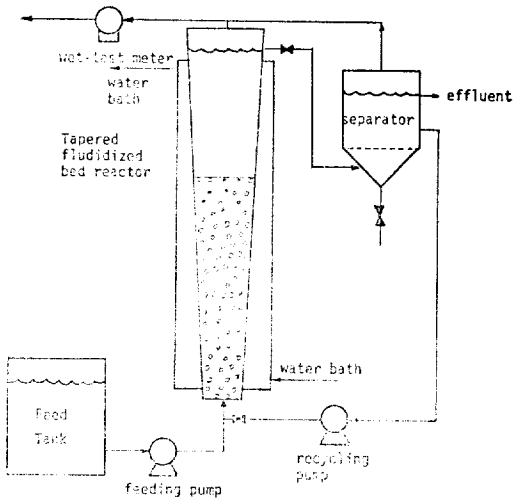

Fig. 3. Tapered Fluidized Bed Experimental Apparatus

The experiments on the effects of nitrate concention and residence time were operated at pH 7 and 30°C. The liquid flow rate changed from 1 to 5cc/sec and the inlet nitrate concentration from 50 to 120 ppm. Sampling was done at steady state.

Nitrate concentration was determined by measuring the absorbence of Beckman 2400 Spectrophotometer at 220 nm and then substracting the reading at 275 nm from the 220 nm result to correct for interference by dissolved organic compounds.[14]

IV. Results and Discussion

1. Effect of pH, Temperature and Reaction Rate

The pH effect on bological denitrification has been measured in tapered fluidized bed and the result is shown in *Fig. 4*. Removal efficiency is plotted as a percentage of conversion ratio at pH 7. Since the maximum removal is obtained over the range of pH 7 to 8.5, pH 7 was chosen for the optimal condition.

The temperature efficiency is shown as a percentage of conversion ratio at 25°C in *Fig. 5*. The maximum conversion occurs between 25 and 35°C. The supplement heating above 25°C would be uneconomical but for the safe control, the temperature of 30°C was selected as an operating condition.

To find the reaction rate in the biological denitrification, the change of nitrate concentration in batch culture is plotted in time in *Fig. 6*. The results turn out to be that the reaction rate is zero order. This indicates that the assumption in the deriva tion of mathematical model is correct. It is considered that the same assumption may be applied in the modelling if the reaction is zero order around the exponential growth of cell.

2. Uniform Void Fraction

A force balance in a differential element at a height z of tapered fluidized bed gives the following equation[15]

$$\frac{dp}{d\xi} = (\rho_s - \rho_f)(1-\epsilon)\{1 + 2/(1+\xi)^3\} \quad gz_0/3 \qquad (11)$$

If ξ approaches to zero, the equation is reduced to the equation of pressure drop in

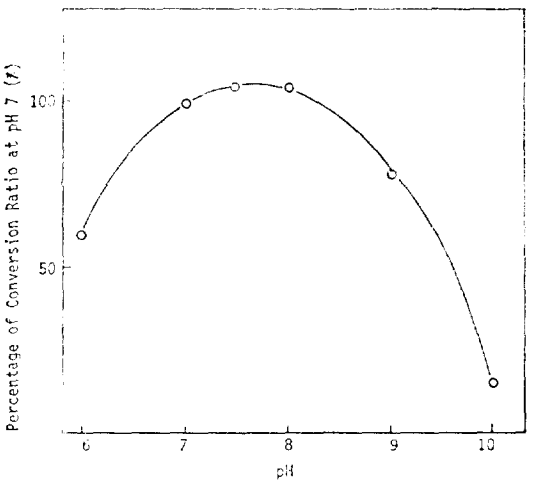

Fig. 4. Effect of pH on Denitrification

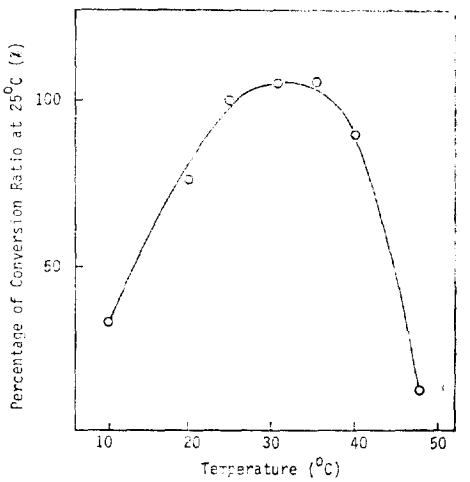

Fig. 5. Effect of Temperature on Denitrification

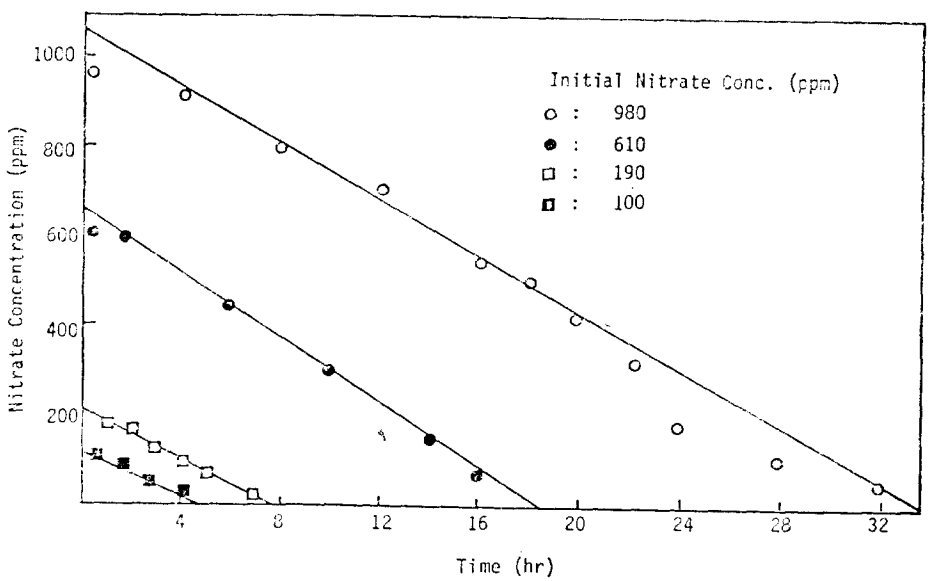

Fig. 6. Effect of Nitrate Concentration on Denitrificatien

cylindrical fluidized bed reactor.[16] If the void fraction is uniform along the bed height and the average void fraction is substituted into the equation (11), the difference of pressure from the bottom can be calcul ated. It is shown in *Fig. 7* that the deviation of calculated pressure drop from the experimental value is very small in the experimental range of flow rate. Hence, the assumption that the void fraction is uniform is considered reasonable in the modelling. It seems that as the flow rate increases, the deviation becomes larger. For high flow rate, application of equation (11) may be in doubt. Further research may be required to invest-igate the characteristics of fluidizat-

ion.

3. Rate Coefficient

In the experiment, all activated carbon particles were fluidized when residence time was less than 200 sec. As rational basis for design of tapered fluidized bed reactor in biological denitrification, a mathematical model was proposed in the equation (10). The nitrate removal amount was almost constant irrespective of inlet nitrate concention. The relation between $S_0^{0.55}$ and $\bar{t}$ is linear as shown in *Fig. 8*. The rate coefficient, K, is found with slope in *Fig. 9*. The value of K is about 0.024 which is constant for denitrification no matter what concentration and residence time are. It is important to note that a rate coefficient is actually a parameter rather than a constant. Although the effluent contains biomass removed from particles and biomass not attached to particles, it may be reasonable to neglect them in mathematical modelling. It

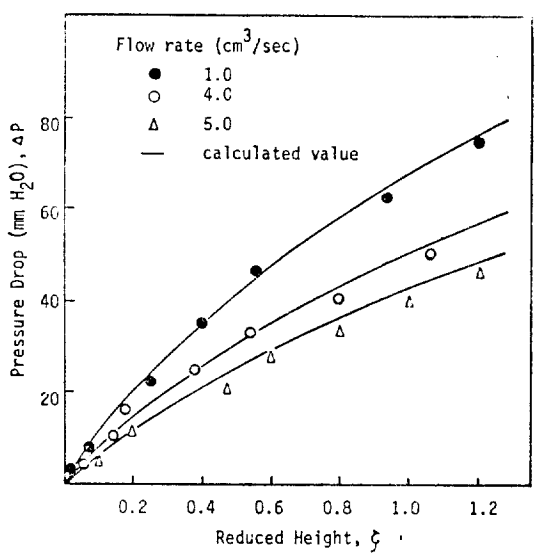

Fig. 7. Pressure Drop Versus Reduced Height in Tapered Fluidized Bed

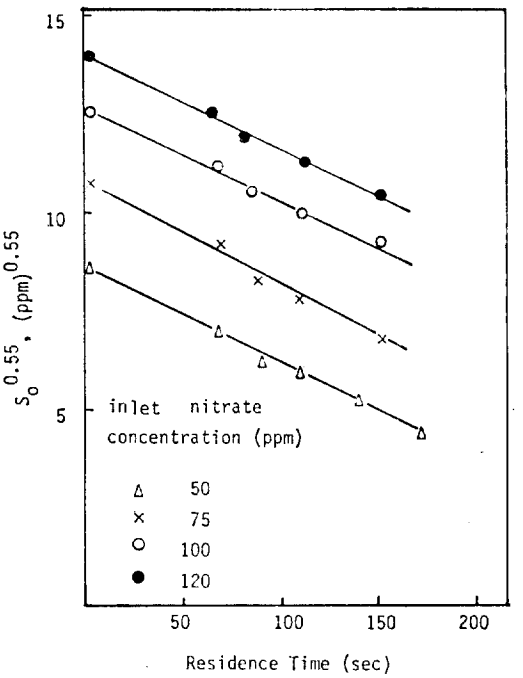

Fig. 8. Outlet Nitrate Concentration Change with Residence Time

is believed that the biomass in the biofilm plays a major role for the denitrification because the cell mass in effluent is very small. Further research on biofilm may bring some understanding on the magnitude of rate coefficient.

V. Conclusions

The optimal operating conditions of pH and temperature in biological denitrification by Pseudomonas denitrificans(ATCC 13867) were 7-8.5 and 25~35°C, respectively. The reaction rate is zero order and the void fraction in tapered fluidized bed is uniform laong the hegiht. Based on these results, a mathemtical model is derived in the following form

$$S_0^{0.5} = -K\bar{t} + S_i^{0.55}$$

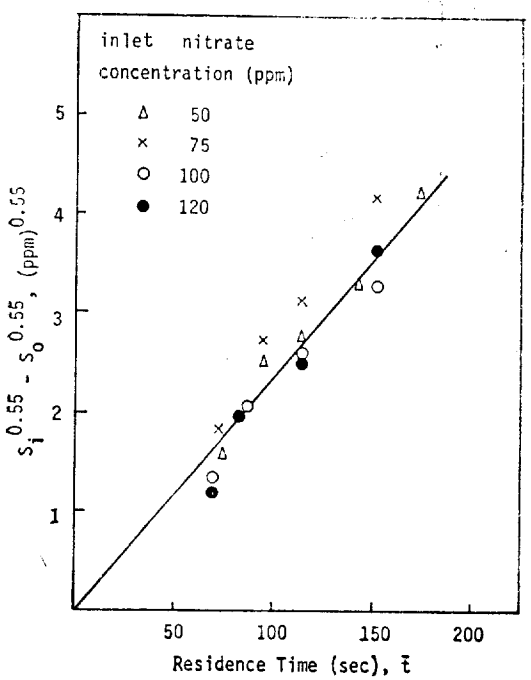

Fig. 9. Pot of $S_i^{0.55} - S_0^{0.55}$ versus$\bar{t}$

where $K = 1.657\ (1-\epsilon_a)\ (\rho k)^{0.55} D^{0.45} r_p^{-0.9}$ K value is about 0.024. This model may be used for the design of a tapered fluidized bed bioreactor.

Nomenclature

A: cross sectional area of tapered reactor at height z (cm²)
D: effective diffusivity of substrate within biofilm (cm²/sec)
g: acceleration of gravity (cm/sec²)
k: intrinsic rate constant (sec⁻¹)
K: rate coefficient
p: pressure (mm H_2O)
Q: volumentric flow rate (cm³/sec)
R: radius of tapered reactor at a height z (cm)
$\bar{R}$: reaction rate per unit volume of reactor (g/cm³ sec)
R_0: redius of tapered reactor at the inlet of reactor bottom (cm)
r: radial distance from the center of bioperticle (cm)
r_m: radius of support medium (cm)
r': radius at which no flux of substrate (cm)
r_p: radius of bioparticle (cm)
S: ubstrate concentration within the biofilm (g/cm³)
S_b: substrate concetration in the bulk of liquid (g/cm³)
S_i: inlet substrate concentration of reactor (g/cm³)
S_0: outlet substrate concention of reactor (g/cm³)
t: variable defined in Eq. (7)
$\bar{t}$: residence time (sec)
z: height of tapered fluidized bed (cm)
z_0: axial distance from the bottom of reactor to the hyperthetical apex of the inverted cone (cm)
z_t: total height of tapered fluidized bed (cm)

Greek Symbols

ϵ: local void fraction
ϵ_a: average void fraction
ξ: reduced reactor height, z/z_0
ρ: biofilm dry density (g/cm³)
ρ_f: fluid density (g/cm³)
ρ_s: solid particle density (g/cm³)

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