g_1 = function defined by (63)
g_2 = function defined by (64)
k = Boltzmann constant
k_o = minimum number of monomers in a stable nucleus
Kn = Knudsen number
$m(\tilde{v}, t)$ = size distribution density of the small condensing nuclei, μm^{-3} cm^{-3}
M = constant monomer number density, cm^{-3}
$M_o(t)$ = total number of particles at any time, cm^{-3}
$M_1(t)$ = total volume of particles at any time, μm^3 cm^{-3}
$n(v, t)$ = aerosol size distribution density, μm^{-3} cm^{-3}
n_k = number density of particles containing k monomers, cm^{-3}
$\bar{n}$ = Laplace Transform of $n(v, t)$ with respect to v
$n_o(v)$ = aerosol size distribution density at $t = 0$, μm^{-3} cm^{-3}
N_o = total number of particles at $t = 0$, cm^{-3}
p_k = frequency of collision of k-mer with a monomer, s^{-1}
q_k = frequency of escape of monomer from a k-mer, s^{-1}
Q = function defined by (65)
R = function defined by (66)
$r_o(t)$ = rate of formation of stable clusters containing k_o monomers from homogeneous nucleation, cm^{-3} s^{-1}
s = Laplace transform variable, μm^{-3}
s_o = starting value of the s characteristic, μm^{-3}
t = time, s
T = reduced time
v = particle volume, μm^3
v_m = largest volume of the condensing species, μm^3

Greek Letters

$\alpha_o(v)$ = rate of change of the volume of a particle of size v, μm^3 s^{-1}
$\alpha_1(v)$ = diffusion coefficient for the aerosol size spectrum, μm^6 s^{-1}
$\alpha_o{}^*$ = α_o/v_o
$\beta(v, \tilde{v})$ = coagulation constant, cm^3 s^{-1}
β_o = coagulation constant, cm^3 s^{-1}
β_1 = coefficient in the linear coagulation constant, cm^3 μm^{-3} s^{-1}
β_2 = coefficient in the quadratic coagulation, cm^3 μm^{-6} s^{-1}
$\beta_{i,j}$ = collision rate between particles of sizes i and j, cm^3 s^{-1}
γ = exponent in the condensation growth law, $0 \leq \gamma \leq 1$
γ_1 = Euler's constant
Γ = incomplete Gamma function
δ = Kronecker delta function
ϵ = defined as v_1/v_o
η = dimensionless particle volume v/v_o
θ = absolute temperature, °K
λ = mean free path of air molecules, μm
Λ = dimensionless group: ratio of characteristic times of condensation and coagulation
μ = viscosity of air, $g\ cm^{-1}$ s^{-1}
ν_o = mean volume of the initial size distribution, μm^3
σ = constant in condensation growth law, $\mu m^{3(1-\gamma)}$ s^{-1}
σ_o = condensation constant for uniform growth, μm^3 s^{-1}
σ_1 = condensation constant for linear growth, s^{-1}
τ = dimensionless characteristic time for condensation
χ = reduced time defined as $(1 + T)$
ω = function defined by (43)

Superscript

$\bar{\ }$ = Laplace transform variable

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Denitrification Kinetics in Packed Beds

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Bench scale packed columns were used to study the kinetic behavior of biological denitrification. After tracer studies were run to determine flow characteristics, steady state nitrate profiles were determined. A first-order rate expression with an Arrhenius temperature dependence is an adequate model of the reaction for nitrate-nitrogen concentrations of < 100 mg/l and temperatures of 5° to 20°C. The rate constants are proportional to the packing surface area.

SCOPE

Nitrate discharges from municipal and septic tank sewage systems, agricultural runoff, and some food industries are pollution hazards for aquatic environments. Nitrogen is a primary nutrient for microbiological growth; concentrations of only a few milligrams per liter of nitrate-nitrogen ($NO_3{}^-$-N) may result in the eutrophication of surface waters. Moreover, nitrate is toxic to human infants. A maximum of 10 mg/l of $NO_3{}^-$-N has been specified for

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drinking water supplies by the U.S. Public Health Service (1962).

Of the processes proposed for removal of nitrogenous compounds from these waste streams, the most popular is aerobic nitrification followed by anaerobic denitrification. The latter is accomplished by facultative heterotrophic bacteria, which utilize nitrate as the terminal hydrogen acceptor in the oxidation of a soluble organic energy source such as methanol. The nitrate is reduced primarily to elemental nitrogen:

$$NO_3^- + 5/6\,CH_3OH \rightarrow 1/2\,N_2 + 5/6\,CO_2 + 7/6\,H_2O + OH^- \qquad (1)$$

The energy source (for example, CH_3OH) is normally present in excess. This process is economical (Seidel and Crites, 1970), compatible with phosphorus removal (Barth et al., 1968), and does not introduce any additional pollutants (McCarty et al., 1969). For the denitrification, packed columns are preferred; they show much higher denitrification rates than continuous stirred-tank reactors (Barth, 1970). Even though biological denitrification has been an industrial practice for many years, there have only been a few studies of the reaction kinetics. Requa and Schroeder (1973) measured denitrification in packed beds and developed a rate expression which was zero order in nitrate concentration and first order in microbe concentration. In denitrification system design, it can be hypothesized that the steady state microbe concentration is directly proportional to the nitrate concentration, so that their conclusion leads to a rate expression with first-order dependence on nitrate concentration. The present study was planned to provide experimental confirmation of this hypothesis and to establish a kinetic model showing the effects of concentration, temperature, and surface area on the rate of denitrification in packed beds.

Nitrate removal systems normally operate at ambient air temperatures, making temperature a critical variable in system operation, especially in northern climates. For packed columns, packing surface area is also important. After the experimental residence time distributions were determined, steady state concentration profiles for two identical small scale packed columns were obtained at 20°, 13°, and 5°C. Two additional columns packed with different packing media were studied at 20°C to determine surface area effects. Measurements were confined to low concentrations of nitrate, which are of interest in waste treatment.

CONCLUSIONS AND SIGNIFICANCE

For denitrification in packed beds, with steady state microbe populations and at influent nitrate-nitrogen concentrations of less than 100 mg/l, a rate expression with a first-order dependence on nitrate concentration is suitable:

$$r_N = \mu Y C_N \qquad (2)$$

For a dolomite packed column, the Arrhenius equation successfully models the temperature dependence over the range of temperatures considered (0 to 20°C) but is based on only three temperatures and should not be extrapolated:

$$\mu Y = A e^{-u/RT} \qquad (3)$$

For glass bead packing, the measured rate constants at 20°C are directly proportional to the packing surface area. However, in our experiments the overall rates for glass beads were approximately one-fifth those for dolomite of equivalent nominal surface area. Therefore, recommended values of the constants are

$u = 7\,500$ cal/gm mole

$A/a \simeq 40\,400$ cm/hr for Dolomite (~ 1 cm)

$\approx 8\,800$ cm/hr for glass beads (3 to 6 mm)

This project was concerned with finding a kinetic expression which is applicable to denitrification systems. The effects of temperature and packing surface area on that expression were also investigated.

Microbial kinetics are generally described by the Monod equation

$$r_N = \frac{\mu C_N X}{K_s + C_N} \qquad (4)$$

Requa and Schroeder (1973) found that K_s for denitrification is small compared to the NO_3^--N concentration. When K_s is negligible, and the steady state concentration of biomass and nitrate are assumed to be proportional, Equation (4) reduces to a first-order expression in NO_3^--N concentration.

McCarty *et al.* (1969) tried to investigate surface area effects by comparing the extent of denitrification attained in identical anaerobic filters using different packing media. Unfortunately, the experiments were run at a single residence time, which was sufficient for complete denitrification in all cases. Therefore, no conclusion about surface area effects can be drawn from these data. Smith *et al.* (1972) also compared the performance of identical packed columns using different sized packing media. Their data indicate an increase in reaction rates with increased specific surface areas but give no information about the actual form of the dependence.

METHODS AND EQUIPMENT

Two systems were employed in the study, each consisting of two identical columns. The type A columns were of Plexiglas, 64 cm in length with an internal diameter of 10.2 cm. Liquid sampling ports were located 14, 34, and 54 cm from the top of the columns, with gas relief and sampling provided by water displacement through a port at the top of the columns. Dolomite chips averaging 1 cm in diameter were used as packing. The columns were equipped with refrigeration jackets for temperature control. Influent and effluent flow rates from the columns and methanol addition to the influent were controlled by a peristaltic pump.

The type B columns were also of Plexiglas construction, 45.75 cm in length with an internal diameter of 5.1 cm. Sampling ports, which also provided gas relief, were located 0., 15.25, and 30.5 cm from the top of the column. Packing consisted of 3 mm glass beads in column I and 6 mm glass beads in column II, each mixed with approximately 5% of the 1 cm dolomite chips by volume in order to control *p*H. Refrigeration and methanol addition were accomplished as in the type A columns, but effluent flow rates were controlled by Nupro micrometering valves.

Residence time distributions for system A were determined through the use of a 100 p.p.m. chloride step function input. In system B, a 25 ml 1 000 p.p.m. chloride

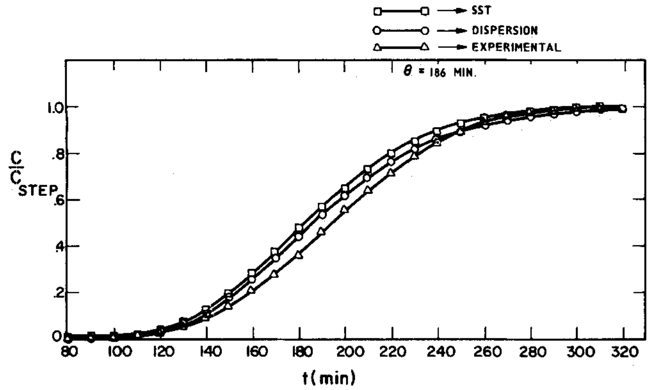

Fig. 1. Comparison of SST and dispersion models with experimental residence time distribution.

pulse was used. Effluent samples were analyzed by using a Buchler-Cotlove chloridometer. The experimental residence time distributions were compared to both the series of stirred-tanks (SST) model and the dispersion model. For system A, the number of tanks in the SST model was determined by making a least-squares fit of the experimental data. A series of eighteen tanks was found to best describe the flow characteristics. For system B, the number of tanks was found to be seventeen by using the method described by Levenspiel (1967). For the dispersion model, the axial dispersion coefficients were evaluated for system A by using the method described by Levenspiel and Smith (1957) for low dispersion systems. Axial dispersion coefficients for system B were evaluated by using the output curve variance (Levenspiel, 1967). Figures 1 and 2 show comparisons of the two models with the experimental residence time distributions for systems A and B, respectively.

During continuous flow operation, tap water containing 5 to 10% mechanically aerated septic tank effluent plus sufficient nitrate to bring NO_3^--N concentrations to desired levels was fed to the columns. Methanol at twice the stoichiometric amount from Equation (1) was added to the feed. Data were taken daily until steady state had been attained and sufficient steady state data collected (Table 1). More data were taken in some cases owing to larger variations in the data. Steady state was defined as less than a 10% NO_3^--N concentration change per day at every port for a period of at least 3 days. Steady state as defined was not attained in system B owing to a variety of factors, but it was felt that portions of the data collected adequately represented steady state operation. Samples were analyzed for NH_4^+-N and NO_3^--N plus NO_2^--N by the steam distillation method of Bremner and Keeney (1965).

Data from system A were used for rate model discrimination and to evaluate temperature effects. Both systems were used in examining surface area effects. Since the SST and dispersion models compared equally well with the experimental residence time distributions, the SST model was used for system modeling in order to simplify the necessary calculations.

RESULTS AND DISCUSSION

For low inlet NO_3^--N concentrations, a first-order rate expression models the system well. Figure 3 shows a typical plot of the least-squares residuals for a first-order model with inlet NO_3^--N concentrations of less than 100 mg/l. The standard deviation of an observation was calculated from replicate runs and indicated in Figure 3 by a dotted line. The residual plots exhibited two important features. The residuals appeared to be randomly distributed around zero, and 67% of the total residuals were smaller than the standard deviation of an observation which compared well

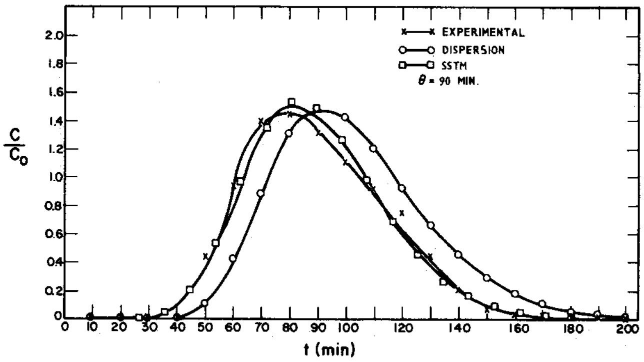

Fig. 2. Comparison of dispersion and SST models with experimental residence time distribution for a type B column.

TABLE 1. EXTENT OF DATA COLLECTED

Column	Temperature (°C)	Days of steady state operation	Data points
A	20	5	25
A	13	4	20
A	5	3	15
B-I	20	6	24
B-II	20	6	24

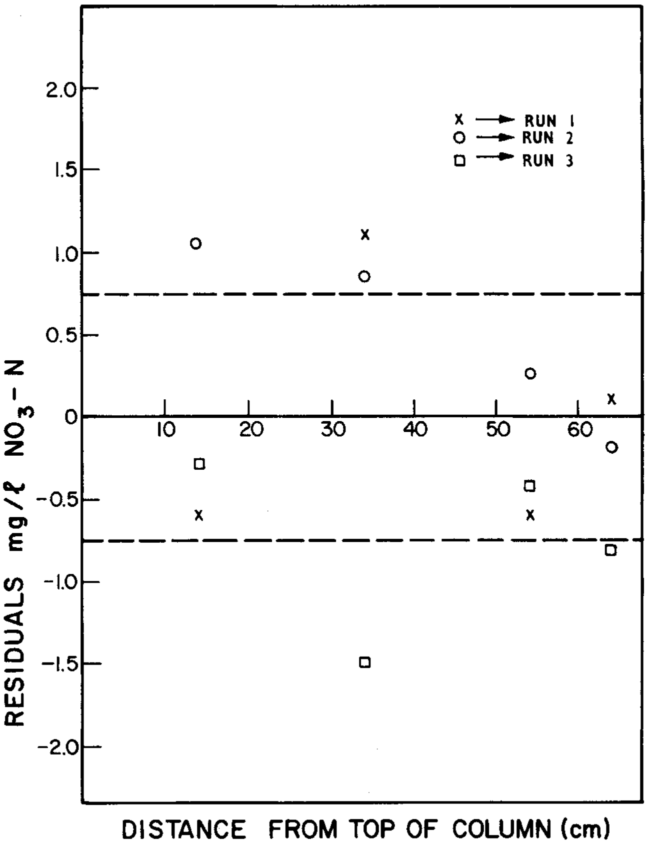

Fig. 3. Residuals at 5°C as a function of distance along the column.

TABLE 2. MODELING OF LOW NO_3^--N DATA WITH A FIRST-ORDER KINETIC MODEL

Column	Temperature (°C)	μY (hr^{-1})	Res. stnd. error (mg/l)	Obs. stnd. dev. (mg/l)
A	20	0.463	7.73	7.95
A	13	0.311	3.34	3.11
A	5	0.236	0.80	0.73
B-I	20	0.309	4.24	4.21
B-II	20	0.175	7.43	7.30

TABLE 3. COMPARISON OF FIRST-ORDER AND MONOD MODELS FOR HIGH NO_3^--N DATA (20°C)

		First	Monod
μY	hr^{-1}	0.666	1.70
K_s	mg/l	—	129
s_R	mg/l	12.23	7.90

TABLE 4. RATE CONSTANTS PER SURFACE AREA

Column	Packing* specific S.A. (cm^2/cm^3)	Wall S.A. (cm^2)	Total specific S.A. (cm^2/cm^3)	$\mu Y/a$ ($cm^3/cm^2 \cdot hr$)
A	4.00	2 050	4.39	0.105
B-I	13.28	730	14.06	0.0220
B-II	6.64	730	7.42	0.0236

* Corrected for observed deviation from assumed packing arrangement in type B columns.

with the 68% expected for normally distributed experimental error. Table 2 is a summary of these results.

When inlet NO_3^--N concentrations were raised to approximately 200 mg/l, the first-order model was no longer adequate (Table 3). The calculated standard deviation of an observation for this data was 7.59 mg/l, much less than the residual standard error of 12.23 in Table 3. Two factors led to the rejection of the first-order model in this case. First, a F test on the hypothesis that the variance of the residuals was representative of experimental variance showed that this would be true less than 5% of the time. Second, the residuals had a tendency to be either all positive or all negative at a sampling port, also indicating model inadequacy. In this high NO_3^--N region, it was necessary to use the Monod model to obtain acceptable modeling.

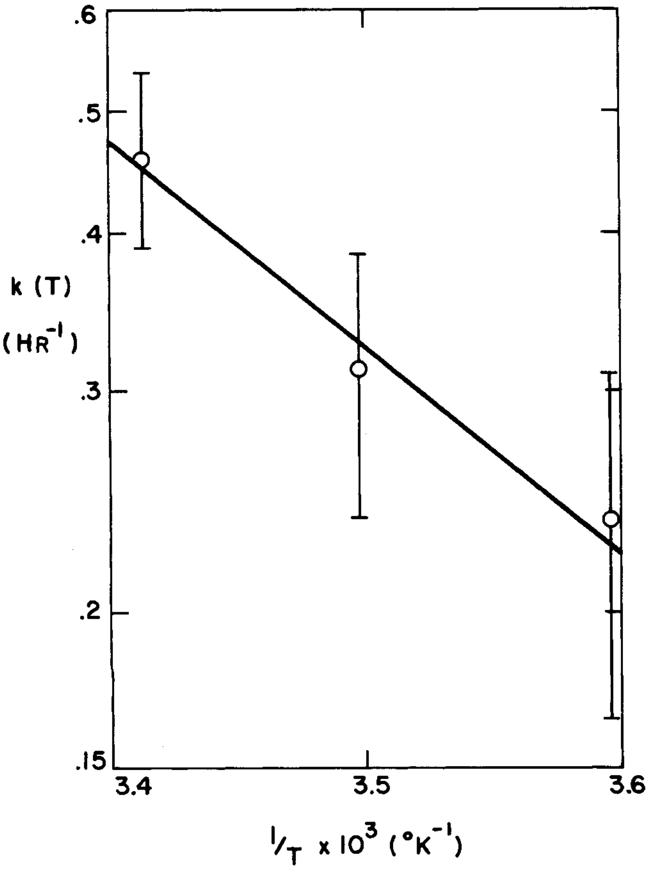

Fig. 4. Arrhenius plot for denitrification with 90% confidence intervals.

The NO_3^--N concentration range of interest here lies between 0 and 70 mg/l because the influent NO_3^--N concentrations which are anticipated in the practical application of this work are below 70 mg/l (Balakrishnan and Eckenfelder, 1969; Bouma et al., 1972; and Tamblyn and Sword, 1969). Therefore, the first-order rate constants were chosen for the examination of temperature and surface area effects.

In considering temperature effects, t tests were run in order to establish the existence of significant differences between the rate constants. The difference between μY_5 and μY_{13} was significant at the 10% level and the difference between μY_{13} and μY_{20} at the 2.5% level.

Several investigators (Muck and Grady, 1974; Novak, 1974; and Sutton et al., 1975) have obtained good results by modeling the temperature dependence of biological rate constants with the Arrhenius equation [Equation (3) above]. Figure 4 is an Arrhenius plot for our system showing the 90% confidence intervals for the rate constants. Least-squares analysis gave values of $A = 177\,500$ hr^{-1} and $u = 7\,500$ cal/gm mole with a residual standard error of 0.025 hr^{-1}. The u value falls within the range normally encountered in biological systems (Muck and Grady, 1974). The Arrhenius equation models the observed temperature dependence quite well. However, owing to the use of only three points and to the large observed variability, extrapolation of the equation would yield unreliable results.

The surface area for system A was estimated by using specific surface area data from Smith et al. (1972). Their data were used because they pertained to packing particles which were similar in shape to those used in system A. It should be noted that their data estimate only the external surface area of the packing.

For system B, it was assumed that the glass beads were arranged in a face centered cubic packing arrangement (Van Vlack, 1970). This assumption was supported by experimental porosity measurements (Parker, 1975). Specific surface areas were then calculated from known unit cell parameters.

The results (Table 4) indicate that the rate constant is proportional to the estimated specific surface area in system B, but values from systems *A* and *B* do not agree. The recommended coefficients A/a for Equation (3) are based on the values $\mu Y/a$ from this table. The most probable explanation for the discrepancy between the dolomite and glass bead columns is that the specific surface area in system *A* was grossly underestimated. Since dolomite is a rough, porous material, and only the external surface area was considered, any microbial penetration of the pores would lead to the observation of an enhanced reaction rate as seen in system **A**.

NOTATION

A = preexponential empirical constant, hr^{-1}
a = specific surface, cm^2/cm^3
C_N = nitrate-nitrogen concentration, mg/l
K_s = saturation constant, mg/l
$k(T)$ = kinetic constant expressed as a function of temperature, hr^{-1}
R = gas law constant, cal/(gm·mole·°K)
r_N = specific rate of removal of nitrate-nitrogen, mg/l·hr
s_D = standard deviation of the experimental rate constants, mg/l
s_R = residual standard error from the least-squares fit of concentration profiles, mg/l

T = temperature, °K

u = temperature characteristic of biological reaction rate constants, cal/gm·mole

X = biomass concentration, mg/l

Y = biological yield coefficient, mg biomass/mg NO_3^--N

μ = specific nitrate-nitrogen removal rate, mg NO_3^--N removed/mg biomass·hr

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Process Design in a Dynamic Environment:

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Part I. A Decomposition Technique to Study the Stability of Chemical Engineering Systems

The stability of various chemical engineering systems is studied through the use of vector Lyapunov functions. A decomposition technique is employed which reduces the problem to small, independent, free subsystems that can be analyzed through Lyapunov's second method. The stability characteristics of the overall system are then related to the behavior of a linear system which is easily analyzed.

SCOPE

The aim of the stability analysis of a system is to determine the number of steady states in the system and to understand the effect of disturbances on these states. Regions of stability are developed which guarantee the stable operation of the system once the operating conditions fall into this region.

The chemical engineering systems, being nonlinear in their majority, cannot be effectively analyzed through the popular approaches of the eigenvalue structure analysis or Lyapunov's second method. All the reported methods

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