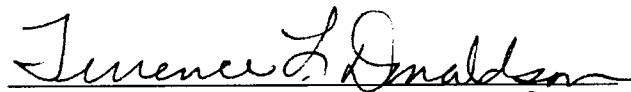


To the Graduate Council:

I am submitting herewith a thesis written by Joseph F. Walker, Jr. entitled "Modeling of Fixed-Film, Fluidized-Bed Bioreactors for Biological Denitrification." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.


Terrence L. Donaldson, Major Professor

We have read this thesis
and recommend its acceptance:




Accepted for the Council:


Vice Provost
and Dean of The Graduate School

MODELING OF FIXED-FILM, FLUIDIZED-BED BIOREACTORS
FOR BIOLOGICAL DENITRIFICATION

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Joseph F. Walker, Jr.

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ACKNOWLEDGMENTS

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ABSTRACT

Nitrate containing wastewaters are produced in many industries. These nitrates impact the environment by promoting eutrophication of lakes, streams, and coastal waters and may produce toxic effects in humans. Nitrates may be biologically degraded with nitrogen and carbon dioxide gases produced as by-products. The use of fixed-film, fluidized bed bioreactors (FBBRs) for biological denitrification has advantages over other continuous reactors which may result in larger volumetric reaction rates, smaller reactor volumes, and potentially lower capital costs. In order to utilize these FBBRs for denitrification, a model which predicts nitrate concentration as a function of axial position within the reactor is useful for sizing the reactor and for optimizing the FBBR process.

A steady state kinetic model was developed to predict the concentration of nitrate as a function of axial position for FBBRs. The model, which utilized Monod kinetics with pH inhibition, was compared with the operating data from several FBBRs which operated at Oak Ridge National Laboratory (ORNL) for periods during 1980-1986. These FBBRs ranged from 10 to 50 cm in diameter and from 6 to 12 meters in height. The model developed agrees with the experimental data from these reactors very well for inlet nitrate concentrations up to ~10,000 mg/L and for pHs within the FBBRs ranging from ~6.5 to 9.

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LIST OF SYMBOLS

- A - Total surface area normal to direction of diffusion, $[L^2]$
 C - Dimensionless concentration, $[S/S_b]$
 C_L - Concentration of inhibition, $[mole/L^3]$
 D_e - Effective diffusivity of substrate in biofilm, $[L^2/t]$
 k_A - Monod reaction velocity constant, $[m/L^3 \cdot t]$
 K_s - Monod constant, $[m/L^3]$
 K_i - Inhibition constant $[moles/L^3]$
 k_o - Intrinsic zero order rate constant, $[1/t]$
 L - Thickness of biofilm on support particle, $[L]$
 N - Substrate flux into biofilm, $[m/L^2 \cdot t]$
 n - Moles of substrate, $[moles]$
 Q - Volumetric flowrate, $[L^3/t]$
 R - Rate of substrate utilization $[m/(L^3 \cdot t)]$
 R_v - Observed conversion rate per unit reactor volume $[m/L^3 \cdot t/L^3]$
 r - Distance in the radial direction, $[L]$
 r_i - Substrate penetration depth, $[L]$
 r_m - Radius of support media, $[L]$
 r_p - Radius of bioparticle, $[L]$
 S - Substrate concentration, $[m/L^3]$ or $[moles/L^3]$
 S_b - Substrate bulk liquid concentration, $[m/L^3]$
 S_i - Inlet substrate concentration, $[m/L^3]$
 t - Time, $[t]$
 U - Axial fluid velocity, $[L/t]$
 V_B - Volume of differential shell within the biofilm, $[L^3]$
 V_R - Reactor volume, $[L^3]$
 X - Dimensionless distance, r/r_p
 x - Distance measure in the direction of diffusion, $[L]$
 X_m - Dimensionless distance, r_m/r_p
 X_i - Dimensionless distance, r_i/r_p
 X_b - Biomass concentration in the reactor, $[m/L^3]$
 y - Distance into the biofilm layer, $[L]$
 z - Distance in the axial direction, $[L]$

LIST OF SYMBOLS
(continued)

- ϵ - Fraction of reactor bed occupied by liquid
 ρ - Biofilm density, [m/L₃]
 ϕ - Thiele modulus
 ϕ_0 - Zero order Thiele modulus
 ϕ_{om} - Modified zero order Thiele modulus
 η - Effectiveness factor
 η_0 - Effectiveness factor for zero order kinetics
 τ - Reactor hydraulic residence time, [t]

1. INTRODUCTION

Nitrate-containing wastewaters are produced in many industries including paper manufacturing, metal finishing, fertilizer production, and the nuclear industry. These nitrates impact the environment by promoting eutrophication of lakes, streams, and coastal waters and may produce toxic effects in humans.

Due to concerns about the quantity of liquid nitrates produced in the nuclear fuel cycle and the nitrate discharge limits which were being considered by many states, Oak Ridge National Laboratory (ORNL) developed a fluidized-bed bioreactor (FBBR) process for treatment of wastewater streams containing up to 10,000 mg/L of nitrate. The initial bench scale work on this process was conducted in the mid-1970s. This was followed by pilot-scale tests and the start-up of full scale treatment systems in the 1980s.^{1,2,3,4,5}

In the studies conducted at ORNL, FBBRs ranging from bench scale to 50-cm in diameter and to 12-m in height have been used. Global denitrification rates, based on the inlet and effluent nitrate concentrations, were utilized to model the denitrification FBBRs. No effort has been made to utilize these models to compare the predicted nitrate concentrations as a function of height with the actual nitrate profiles along the axis of the FBBRs or to compare the performance of the various FBBRs operated

at ORNL using the same model. The purpose of this study is to develop a kinetic model to predict the concentration of nitrate as a function of bioreactor height in the axial direction and to compare model predictions with the nitrate concentrations of various FBBRs used during pilot studies at ORNL.

2. DISCUSSION OF RELEVANT LITERATURE

The removal of nitrogen in the form of nitrate by conversion to nitrogen gas can be accomplished biologically under anoxic (without oxygen) conditions. The nitrogen from the nitrate serves as the terminal electron acceptor for microbial respiration in the absence of molecular oxygen. The bacteria responsible for denitrification are facultative and utilize the same basic biochemical pathways during both aerobic and anaerobic respiration; the major differences are in the enzymes which catalyze the terminal electron transfer and the sites of those enzymes in the electron transport chain.⁶

A carbon source must also be present to act as an electron donor. Several studies have been performed evaluating different carbon sources.⁶⁻⁹ McCarty and St. Amant studied sugar, acetate, methanol, ethanol, and acetone, before selecting methanol as the most desirable for denitrification.⁷ Francis and Hancher reported that acetate concentrations greater than 2.0 - 2.5 kg C/m³ appeared to inhibit denitrification, while no inhibitory effects were observed with methanol at concentrations of 7.5 kg C/m³.⁸ However, Grady reported that methanol acts as an inhibitory substrate at concentrations >1.1 kg C/m³.⁶ Skrindel and Bhagat found that industrial waste products including whey, corn silage derivative, yeast, and spent sulfite liquor were suitable carbon source alternatives to methanol for denitrification.⁹

Denitrification reactors fall into two categories: slurry reactors and fixed-film reactors. The slurry reactors are similar to those used for activated sludge, except the mixing systems are designed to minimize oxygen transfer while maintaining the sludge in suspension. There is a great deal of variation among fixed-film reactors. This variation includes differences in the type of media employed, as well as the flow regime (from downward to upflow at a velocity sufficient to fluidize the support particles). The advantages of the fluidized-bed bioreactors is evident when compared to other continuous bioreactors. Packed-bed reactors must have large support particles, or microbial growth quickly clogs them. Therefore, the surface area of microbial film per unit reactor volume is low, resulting in a reduction of the volumetric productivity.¹⁰ In a fluidized-bed, the particles can be much smaller because the bed can expand to accommodate microbial growth resulting in a higher biomass concentration. This higher biomass concentration produces greater volumetric reaction rates resulting in a reduction in the required reactor volume and, therefore, potentially lower capital costs.

In order to model fixed-film, fluidized-bed reactors, two approaches may be taken: (1) empirical or (2) mechanistic. Empirical models simply relate input and output operating variables with no effort to represent individual phenomena. These models are useful for design from pilot plant data and are used extensively in environmental engineering. Mechanistic

models express the influences and interrelationships of individual mechanistic phenomena in a manner which allows investigators to determine how the system might respond under differing conditions. Therefore, the primary purpose of a mechanistic model is to further understanding. This review will be limited to mechanistic models.

The starting point for modeling a bioreactor is writing the mass balance equation for a differential element of biofilm. A mass balance performed around a differential element of a steady-state film of constant microbial composition results in the following equation:

$$- D_e A \left(\frac{dS}{dx} \right)_x + D_e A \left(\frac{dS}{dx} \right)_{x+\Delta x} - RA\Delta x = 0 \quad (1)$$

This equation is used almost universally to model reactions within biofilms. In the above equation, x is the distance measured in the direction of diffusion, A is the total surface area normal to the direction of diffusion, R is the reaction rate expression for consumption of substrate, D_e is the effective diffusivity, and S is the substrate concentration within the biofilm. The key elements which are to be inserted into the above equation are the effective diffusivity (D_e) and an expression for the reaction rate (R). In addition to this equation for intrafilm phenomena, mechanistic models of fixed-film biochemical processes require information on the mass transport of reactants from the bulk liquid to the biofilm surface (external mass transfer) and methods for solving the resulting equations.

In examining the effects of external mass transfer (EMT) in modeling fixed-films Chen and Bungay¹¹ utilized a microprobe for measuring the concentration of dissolved oxygen up to and through biofilms. These experiments were conducted on a system typical of trickling filters. The results indicated that the dissolved oxygen concentration at the liquid/biofilm interface can be substantially less than in the bulk liquid. This indicates that EMT may be important in fixed-film systems. In other studies it was found that the EMT was dependent on the liquid velocity past the biofilm.^{12,13,14} These studies suggest that at lower velocities EMT limits the reaction rate. As the velocity is increased the effect of EMT becomes less pronounced and as the velocity exceeds some limiting value the effects of EMT on the reaction rate becomes negligible. This limiting value is dependent on the concentrations of substrates in the bulk liquid and the potential reaction rates in the biofilm.¹⁵ In systems utilizing fixed-film fluidized-bed bioreactors Shieh and Keenan utilized an empirical equation developed by Mulcahy and LaMotta to demonstrate that the errors in the observed reaction rate which resulted if EMT effects were neglected ranged from 2.6% to 7.1%. In these studies by Shieh and Keenan the bulk liquid nitrate-nitrogen ($\text{NO}_3\text{-N}$) concentrations ranged from 6 to 43 mg/L, and as the bulk liquid nitrate concentration increased the effects of EMT decreased.¹⁶ One might therefore assume that EMT would be negligible in fluidized-bed bioreactors treating concentrated wastes as was the case in the pilot FBBRs operated at ORNL.

Once the substrates reach the biofilm surface they must be transported into the cell where the reaction will occur. It is believed that attached microorganisms secrete a polysaccharide material which holds the microorganisms together. The bacteria in the interior of the film are enmeshed in the polysaccharide material and as a result do not experience direct contact with the bulk liquid which contains the substrates. These substrates must therefore reach the bacteria by diffusion through the biofilm. This diffusion is typically characterized by Fick's law:^{15,17}

$$N = -D_e \, dS/dx \quad (2)$$

where N is the flux (mass of substrate transported per unit area per unit time). The other parameters have been previously defined.

Using direct techniques for measuring the concentration gradient and flux of oxygen through biofilms, Bungay and associates found the effective diffusivity to be 80% of the value in water for laboratory-grown films and 35% for field-grown films.^{11,18} In studies by Williamson and McCarty the measured diffusion of oxygen through the biofilm was in excess of 80% of the values in water while Wang found it to be only 10%.^{19,20} As can be seen, the values of the effective diffusivities found by direct measurement differ greatly. This can be attributed to the differences in the biofilms of the various microorganisms used in the studies, as

well as the different techniques used to measure the diffusivity. Due to the difficulties associated with the direct measurement of the effective diffusivity, most models utilize assumed values. This value is typically 80% of the value measured in water for a large number of substances.¹⁵

After diffusing into the cell the substrates are utilized by the microorganisms to carry out various cell functions. The rates at which these substrates are utilized is an important parameter in modeling fixed-film biological systems. In all cases two soluble, transporting substrates are necessary for the reaction to occur. These substrates are the electron donor and the electron acceptor. The reaction rate within the biofilm may be controlled by either of these or by both. Most models identified in the literature assumed that reaction rate was controlled by either the electron donor or the electron acceptor and the reaction rate was written in terms of a single substrate. Many equations have been used to characterize the reaction rate in terms of the electron donor and/or the electron acceptor concentration. The most common of these rate expressions are the (1) Monod equation^{19,21,22,23,24,25} and (2) the Blackman equation.¹⁵ Other equations used included: (1) zero order kinetics^{16,26,27,28,29}, (2) first order kinetics^{16,26}, (3) variable order kinetics³⁰, and (4) double substrate limited kinetics.^{31,32}

Three methods have generally been employed to solve the equations in the overall model:¹⁵

1. A direct approach where numerical methods are employed to solve equation 1.

2. An indirect approach where equation 1 is solved for various concentrations of reactants in the bulk liquid and the result is expressed as the flux of material into the biofilm (which is equal to its removal rate from the bulk fluid) as a function of the bulk fluid concentrations, transport characteristics, etc. This flux relationship can then be used during solution of the process equation in an iterative manner, i.e., the concentration leaving the control volume by fluid flow is assumed and the corresponding reaction rate is determined from the flux/bulk concentration relationship. The flux is then used to calculate the concentration leaving the control volume and the procedure is repeated until the two concentrations agree. Even though an iterative procedure is used, the indirect technique is more efficient than the direct approach because the second-order differential equation resulting from equation 1 needs to be solved only once to establish the flux/bulk concentration relationship and then the relationship can be used with any process model.¹⁵

3. An effectiveness factor which is similar to the indirect approach, but results in a more general solution, may also be used. The effectiveness factor is defined as the ratio of the actual, observed reaction rate in the presence of mass transport limitations to the theoretical rate in their absence (i.e., the intrinsic reaction rate).¹⁵ It can be used as a correction factor that can be applied to the reaction rate as calculated from the intrinsic kinetics at the bulk substrate concentration, thereby

converting the rate into the actual rate occurring in the presence of mass transport limitations both up to and through the biofilm. The second-order differential equation resulting from equation 1 is solved with the appropriate boundary conditions to obtain the concentration gradients through the biofilm associated with various bulk substrate concentrations. The average reaction rate is then obtained by integrating over the entire biofilm depth and is divided by the intrinsic reaction rate at the corresponding bulk substrate concentration to get the value of the effectiveness factor. By doing this for a large number of conditions, an effectiveness factor can be obtained as a function of the various parameters describing transport to and through the film. Once this effectiveness factor relationship has been determined it can be used with any type of process model and the second-order differential equation resulting from equation (1) need not be solved again to solve the process model. Details of the procedure required to obtain effectiveness factor relationships have been published by Grady and Lim.⁶

3. PREVIOUS MODELING OF ORNL FLUIDIZED BED BIOREACTORS

The most extensive modeling of the ORNL fluidized bed bioreactor system to date was performed by Hancher and Perona.²¹ In the model developed by Hancher and Perona the following assumptions were made: (1) the effects of external mass transfer were negligible, (2) internal mass transfer followed Fick's law, (3) the reaction rate (R) followed Monod kinetics [$R = k_A S / (K_S + S)$, where k_A and K_S are constants] and (4) the effective diffusivity equaled $0.815 \times 10^{-9} \text{ m}^2/\text{s}$. The resulting equations were solved utilizing an effectiveness factor approach. Data from the operation of two 20 cm-diam, 6-m-high fluidized bed bioreactors which were operated in series during 1979 were used to verify the model. These reactors were used to denitrify aqueous wastewaters containing nitrate concentrations up to ~15,000 mg/L. The results of 148 sets of samples were divided into 14 groups covering nitrate feed concentrations ranging from 474 to 16,450 mg/L. The average feed and effluent nitrate concentrations for each group were calculated and used to search for a set of Monod constants (k_A and K_S) which caused the model to represent the experimental data. It was found that the data were well represented up to nitrate feed concentrations of 7000 mg/L with $k_A = 795 \text{ mg}/(\text{L min})$ and $K_S = 350 \text{ mg/L}$, where k_A is the reaction velocity constant and K_S is the so-called Monod, or half-saturation, constant. Above nitrate feed concentrations of 7000 mg/L the model deviated from the data by more

than 50%. Also, in all cases the effectiveness factor was >0.9 indicating minimal mass transfer limitations both up to and through the biofilm.

It should be noted that in this study the researchers were only concerned with the reactor inlet and effluent nitrate concentrations. The model was not tested against the nitrate concentration as a function of axial position within the bioreactor.

4. MODEL DEVELOPMENT

The mathematical model used here to study the denitrification kinetics of the fixed-film, fluidized-bed bioreactors at ORNL is divided into two submodels: (1) the Biofilm Model and (2) the Reactor Flow Model. The Biofilm Model examines the effects of internal mass transfer and simultaneous biochemical nitrate conversion by microorganisms within the fixed-films attached to the fluidized support particles within the bioreactor. The Reactor Flow Model describes the hydraulic transport of the nitrate through the FBBR. These submodels are coupled with a reaction rate equation, the fluidization mechanics, and the biofilm bulk liquid boundary conditions to yield an overall kinetic model for the FBBRs.

The literature survey revealed that most researchers modeling similar systems used either zero-order kinetics or Monod kinetics in the Biofilm Model and plug-flow in the Reactor Flow Model. In the previous modeling of the ORNL bioreactors by Hancher and Perona, Monod kinetics and plug-flow hydraulic transport were also used. As a result, both zero-order and Monod kinetics will be examined in this study.

4.1 Plan of Attack

In developing the model used in this study the following plan of attack was utilized:

1. The first model derived, the Zero-Order Model, coupled intrinsic zero-order kinetics in the Biofilm Model and plug-flow in the Reactor Flow Model. The resulting differential equations were solved for two

sets of boundary conditions: (a) the case in which the entire biofilm was penetrated by substrate (nitrate) and (b) the case in which the biofilm was only partially penetrated by the substrate.

2. The second model derived, the Monod Model, coupled Monod kinetics and plug-flow hydraulic transport. The parameters (Monod constants and effective diffusivity) used in this model were the same constants used by Hancher and Perona in their previous modeling of the ORNL FBBR which operated in 1978.²¹

3. Both the Zero-Order Model and the Monod Model were compared with operational data taken from a 50-cm-diam., 6-m-high FBBR which operated at ORNL from August through October 1980.

4. The saturation constant K_s in the Monod Model was changed from the value used by Hancher and Perona (350 mg/L) to 800 mg/L. This Modified Monod Model was then also compared with the operational data taken from the 50-cm-diam., 6-m-high FBBR which operated at ORNL during August through October 1980.

5. The Modified Monod Model was compared with operational data from a 10-cm-diam., 6-m-high FBBR which operated at ORNL from September through December 1985 and in a 10-cm-diam., 12-m-high FBBR which operated during April and May 1986.

6. A pH-inhibition function was added to the Monod rate equation to further improve the model.

4.2 The Biofilm Model

Presented in Fig. 1 is a schematic diagram of a typical bioparticle (support particle + attached biofilm) within a fluidized-bed bioreactor. The development of the Biofilm Model will proceed under the following simplifying assumptions:

1. Homogeneous biofilm of uniform thickness.
2. Spherical support particle of uniform size.
3. Negligible external mass transfer.
4. Internal transport of substrate characterized by Fick's law
5. Steady-state conditions.

A mass balance may be performed on the differential element in Fig. 1 as follows:

$$\text{input} - \text{output} + \text{generation} = \text{accumulation, or} \quad (3)$$

$$\left(n \right)_{r+\Delta r} - \left(n \right)_r - RV_B = \frac{d}{dt} (V_B S) \quad (4)$$

where

n = the moles of substrate entering or exiting the differential shell within the biofilm, per unit time

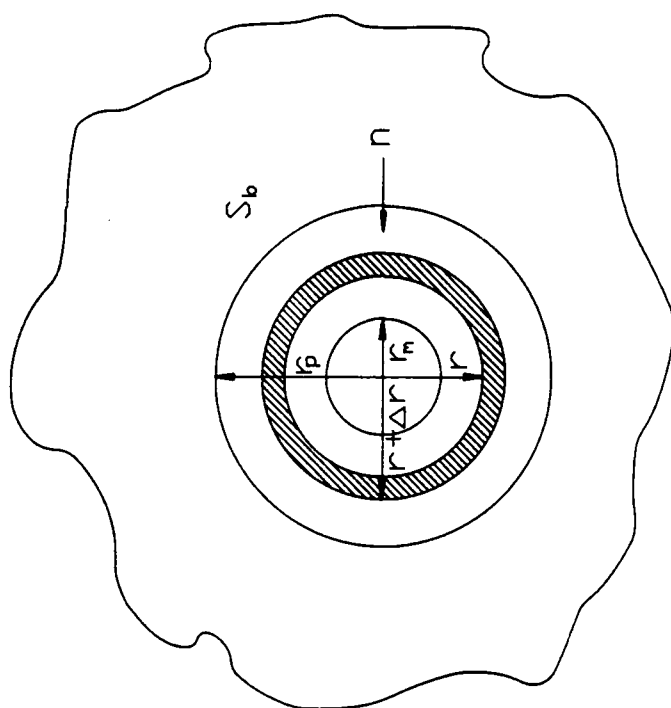
R = the rate of substrate utilization,

V_B = the volume of the differential shell within the biofilm,

r = radial direction in the biofilm,

t = time, and

S = the molar concentration of substrate within the differential shell of the biofilm.



r = Distance in radial direction
 r_m = Radius of support media
 r_p = Radius of bioparticle
 S_b = Substrate bulk liquid concentration
 n = Moles of substrate
 Δr = Differential element of biofilm

Fig. 1. Schematic diagram of a typical bioparticle (support particle + attached biofilm).

Fick's law of diffusion is presented in equation 5,

$$N = n/A = -D_e \, dS/dr \quad (5)$$

where

N = the diffusive molar flux in the radial direction (r),

D_e = the effective diffusivity, and

A = the surface area of the differential element.

By combining equations (4) and (5) and assuming steady-state operation the following is obtained:

$$\frac{r^2 D_e \left(\frac{dS}{dr} \right)_{r+\Delta r} - r^2 D_e \left(\frac{dS}{dr} \right)_r}{\Delta r} = r^2 R \quad (6)$$

Now taking the limit as Δr approaches zero and recalling the definition of a derivative, one obtains the following equation which is used to model the biofilm within the FBBR.

$$\frac{D_e}{r^2} \frac{d}{dr} \left(r^2 \frac{dS}{dr} \right) = R \quad (7)$$

4.2.1 Zero-Order Kinetics. For intrinsic zero-order kinetics the reaction rate may be written as follows:

$$R = \rho k_0 \quad (8)$$

where,

ρ = the biofilm dry density, and

k_0 = the intrinsic zero-order rate constant.

By combining equations (7) and (8) the biofilm model becomes

$$\frac{D_e}{r^2} \frac{d}{dr} \left(r^2 \frac{dS}{dr} \right) = \rho k_0 \quad (9)$$

The assumption of negligible external mass transfer fixes the biofilm bulk liquid boundary condition of equation (9) as:

$$S = S_b \text{ at } r = r_p \quad (10)$$

where

S_b = the nitrate concentration in the bulk liquid and

r_p = the bioparticle radius.

For the other boundary conditions two possibilities exist: (1) the nitrate is able to fully penetrate the biofilm as shown in Fig. 2 and (2) the nitrate only partially penetrates the biofilm as shown in Fig. 3. The boundary conditions for full and partial penetration, respectively, are presented below:

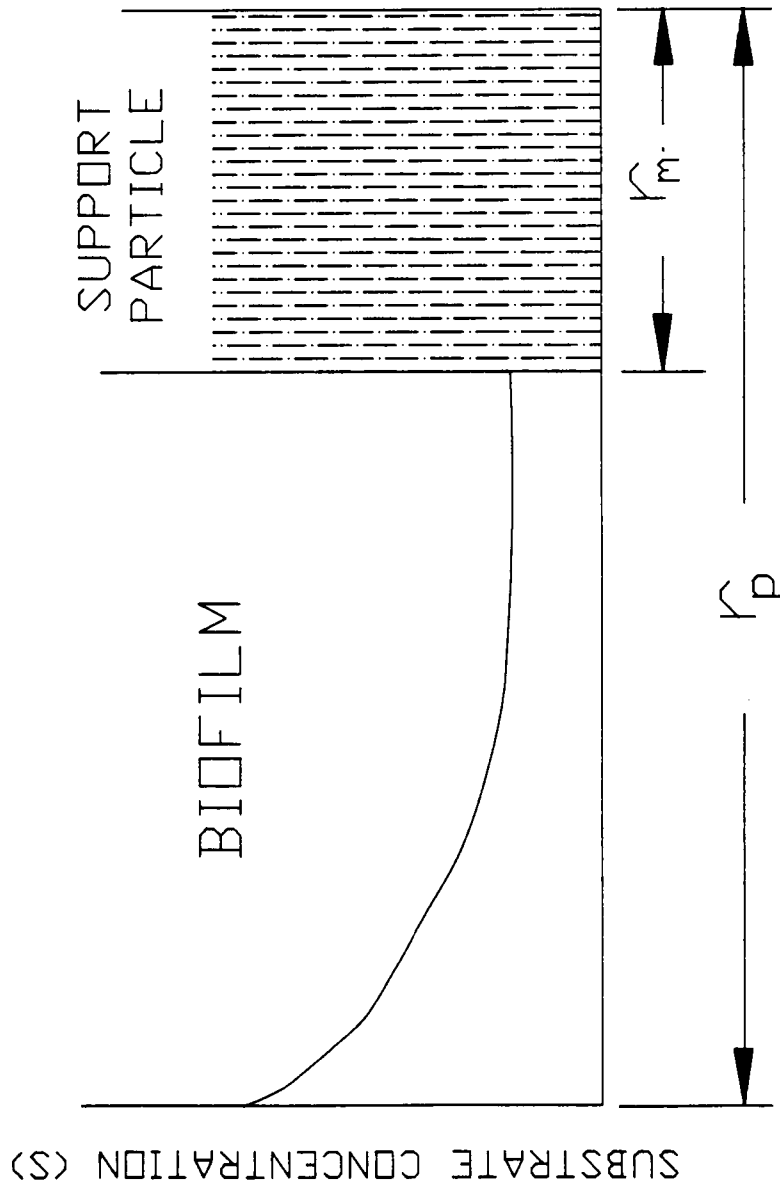


Fig. 2. Schematic diagram showing full penetration of the biofilm by the substrate.

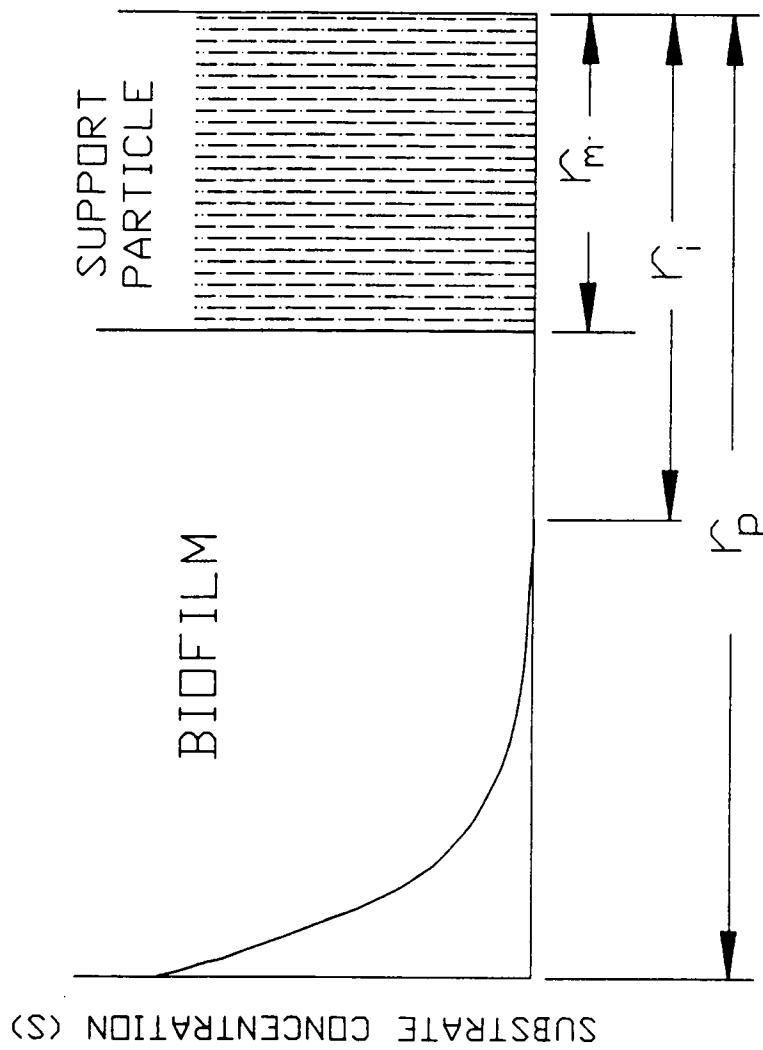


Fig. 3. Schematic diagram in which the substrate only partially penetrates the biofilm.

$$dS/dr = 0 \text{ at } r = r_m \quad (11)$$

and

$$dS/dr = S = 0 \text{ at } r = r_i \quad (12)$$

where

r_m = the support media radius and

r_i = the nitrate penetration depth.

In the case of partial penetration, the substrate penetrates only part of the biofilm. The position at which S becomes zero in the biofilm is defined as r_i , as indicated in equation 12.

Equation (9) may be written in dimensionless form as:

$$\frac{1}{X^2} \frac{d}{dX} \left(X^2 \frac{dC}{dX} \right) = \phi^2 \quad (13)$$

where

$$C = S/S_b$$

$$X = r/r_p$$

$$\phi = r_p \left(\frac{\rho k_o}{S_b D_e} \right)^{1/2}, \text{ the Thiele modules}$$

The dimensionless boundary conditions then become

$$C = 1 \text{ at } X = 1, \text{ for the biofilm bulk liquid} \quad (14)$$

$$dC/dX = 0 \text{ at } X = X_m, \text{ for full penetration} \quad (15)$$

$$dC/dX = 0 \text{ at } X = X_i, \text{ for partial penetration} \quad (16)$$

where

$$X_m = r_m/r_p$$

$$X_i = r_i/r_p$$

For the case of partial penetration, integration of equation (13) subject to boundary conditions (14) and (16) yields the following equation²⁷:

$$\phi_o^2 = \frac{6}{2X_i^3 - 3X_i^2 + 1} \quad (17)$$

The dimensionless nitrate penetration depth, X_i , can be related to the bioparticle effectiveness factor (η). For intrinsic zero-order kinetics the effectiveness factor is the ratio of biofilm volume with substrate concentrations greater than zero to the total biofilm volume:

$$\eta_o = \frac{1 - X_i^3}{1 - X_m^3} \quad (18)$$

For incorporation into an overall kinetic model it would be useful to express η_o as an explicit function of X_m and ϕ_o . To accomplish this a modified zero-order Thiele modulus (ϕ_{om}) can be defined as:

$$\phi_{om} = \bar{r} \left(\frac{\rho k_o}{S_b D_e} \right)^{1/2} \quad (19)$$

where

$$\bar{r} = \left(\frac{r_p^3 - r_m^3}{3r_p^2} \right) \quad (20)$$

Numerical solution of equations (18), (19), and (20) by Shieh et al.²⁸ produced the following explicit relationship for the intrinsic zero-order reaction in partially penetrated biofilms:

$$\eta_o = 1.2712 \phi_{om}^{-1} - \left[\frac{3.814}{1 - \left(\frac{r_m}{r_p} \right)^3} \right] \left(\frac{D_e}{\rho k_o r_p^2} \right)^{1/2} S_b^{1/2} \quad (21)$$

This equation indicates that the effectiveness factor is proportional to the bulk-liquid substrate concentration to the 0.5 power. The value of the modified Thiele modulus at which transition from partial to full penetration occurs can be found by setting $\eta_o = 1$ in Equation (21). For $\phi_{om} \leq 1.27$, the entire biofilm is active and intrinsic zero order kinetics are observed. For $\phi_{om} > 1.27$, the inner portion of the biofilm is inactive and the observed reaction rate is proportional to $S_b^{0.5}$.

4.3 The Reactor Flow Model

The Reactor Flow Model will be developed according to the following simplifying assumptions:

1. Axial dispersion is negligible.
2. Bioparticle characteristics are independent of position within the bioreactor.
3. No nitrate conversion occurs within the liquid phase.
4. Steady-state conditions exist within the bioreactor.

Dispersion measurements on ORNL FBBRs were reported by Walker, Hancher, and Genung². Values for the dispersion peclet number were of the order of 10, indicating that axial dispersion was negligible. Since the axial dispersion within the bioreactor is assumed to be negligible, the reactor may be modeled as a plug flow reactor (PFR). A schematic diagram of a PFR is presented in Fig. 4. A mass balance across an axial reactor element of the PFR may be performed as follows:

$$\text{input} - \text{output} + \text{generation} = \text{accumulation, or} \quad (22)$$

$$\left(SQ \right)_Z - \left(SQ \right)_{Z+\Delta Z} + A \Delta Z R_V = \frac{d}{dt} SA \Delta Z \quad (23)$$

where

S - bulk nitrate concentration,

Q - volumetric flowrate,

A - reactor cross sectional area

R_V - observed nitrate conversion rate per unit reactor volume,

Z - distance in the axial direction.

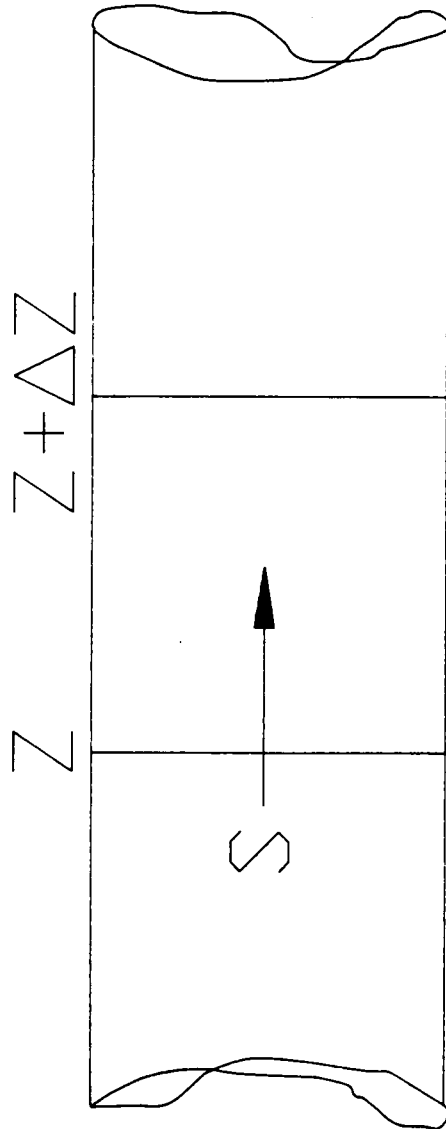


Fig. 4. Schematic diagram of a plug flow reactor (PFR).

Assuming steady-state operation and noting that Q = cross sectional area multiplied by the axial fluid velocity (U) through the bioreactor, one may obtain the following equation:

$$\frac{\left(US\right)_Z - \left(US\right)_{Z+\Delta Z}}{\Delta Z} + R_v = 0 \quad (24)$$

Taking the limit as ΔZ approaches zero and recalling the definition of a derivative, one obtains the following differential equation which is used to describe the hydraulic transport of nitrate through a FBBR.

$$U \frac{dS}{dZ} + R_v = 0 \quad (25)$$

Equation (25) is subject to the following boundary condition:

$$S = S_i \text{ at } Z = 0 \quad (26)$$

The observed nitrate conversion rate per unit fluidized bed volume (R_v) in equation (25) can be expressed as:

$$R_v = RX_b \quad (27)$$

where X_b is the biomass concentration in the FBBR.

4.3.1 Overall Model: Zero-Order Kinetics. For intrinsic zero-order kinetics:

$$R_v = RX_b = \eta_o k_o X_b \quad (28)$$

For the case of partial penetration of the biofilm by the substrate, the overall reactor model for FBBR denitrification kinetics may be developed by combining equations (21) and (28) to produce:

$$R_v = \left[\frac{3.814}{1 - \left(\frac{r_m}{r_p} \right)^3} \right] \left(\frac{k_o D_e}{\rho r_p^2} \right) X_b S_b^{1/2} \quad (29)$$

Integration of equation (25) subject to equations (26) and (29) yields:

$$S^{0.5} = S_i^{0.5} - K_o Z \quad (30)$$

where

$$K_o = \frac{1.907}{1 - \left(\frac{r_m}{r_p} \right)^3} \left(\frac{k_o D_e}{\rho r_p^2} \right) \left(\frac{X_b}{U} \right)$$

For the case of partial penetration of the biofilm, the square root of the nitrate concentration is predicted to be linear with axial position (Z). The value of K_o will vary with the operating conditions of the bioreactor.

For the case of full penetration of the biofilm by the substrate ($\phi \leq 1.27$) the overall reactor model may be developed by combining equations (25) and (28), with $\eta_0 = 1$, and integrating subject to the boundary condition, Equation 26, to yield the following:

$$S = S_i - k_o X_b Z/U \quad (32)$$

For the case of full penetration of the biofilm, the nitrate concentration profile is linear with respect to the axial position (Z) within the bioreactor. Equations 30 and 32 combined describe the nitrate concentration profile through a FBBR for the Zero-Order Model.

4.4 Overall Model: Monod Kinetics

The previous modeling of the ORNL FBBRs by Hancher and Perona assumed Monod kinetics. Hancher and Perona also stated that the biofilm thickness was small compared to the support particle diameter; therefore, slab geometry could be assumed without excessive error. With these assumptions the Biofilm Model becomes

$$D_e \frac{d^2 S}{dy^2} + k_A \left(\frac{S}{K_s + S} \right) = 0 \quad (33)$$

with the following boundary conditions:

$$S = S_b \text{ at } y = 0 \quad (34)$$

$$dS/dy = 0 \text{ at } y = L \quad (35)$$

where

y - the distance into the biofilm layer

L - the thickness of the biofilm on the support particle.

k_A - the reaction velocity constant for nitrate, and

K_S - the saturation constant for nitrate.

Hancher and Perona also used the effectiveness factor and Thiele modulus approach to solve these equations. For Monod kinetics the following Thiele modulus was used:

$$\phi = L(k_A / D_e K_S)^{0.5} \quad (36)$$

Equation (33) can then be written in dimensionless form as:

$$\frac{d^2 C}{dY^2} - \phi^2 \frac{C}{1 + \beta C} = 0 \quad (37)$$

where $C = S/S_b$, $Y = y/L$ and $\beta = S_b/K_S$. The boundary conditions may then be written in dimensionless form as:

$$C = 1 \text{ at } Y = 0 \quad (38)$$

$$dC/dY = 0 \text{ at } Y = 1 \quad (39)$$

The effectiveness factor for Monod kinetics is defined as

$$\eta_m = R \left(k_A \frac{S V_B}{K_S + S} \right)^{-1} \quad (40)$$

The concentration gradient at the biofilm surface can be written in dimensionless form as

$$\left(\frac{dC}{dY}\right)_{Y=0} = -\phi^2 \frac{1}{1+\beta} \eta_m \quad (41)$$

Hancher and Perona solved Equation (41) along with Equations (37) to (39) numerically. For given values of ϕ and β , the computer searched for a value of η_m that allowed the boundary condition (Eqn. 39) to be satisfied. The following parameters were used: $D_e = 0.815 \times 10^{-9} \text{ m}^2/\text{s}$, $k_A = 795 \text{ mg}/(\text{L min})$ and $K_S = 350 \text{ mg/L}$. Hancher and Perona found that at nitrate concentrations $>130 \text{ mg/L}$ the effectiveness factors approached unity.

For Monod kinetics the Reactor Flow Model becomes

$$U \frac{dS}{dZ} + \eta_m F k_A \left(\frac{S}{K_S + S} \right) = 0 \quad (42)$$

The constant F in Equation (42) contains volumetric factors for converting the reaction term to a basis of rate per unit volume of liquid phase. Therefore,

$$F = \frac{(1 - \epsilon)}{\epsilon} \left[1 - \left(\frac{r_m}{r_p} \right)^3 \right] \quad (43)$$

where ϵ = the fraction of the bed occupied by the liquid (void volume).

The other parameters have been previously defined.

Since Hancher and Perona verified that the effectiveness factor is near unity in modeling the ORNL FBBRs, Eqn. (42) can be integrated to yield the overall model for Monod kinetics:

$$\tau = \frac{Z}{U} = \frac{1}{Fk_A} \left[K_s \ln \left(\frac{S_{Z=0}}{S_{Z=Z}} \right) + S_{Z=0} - S_{Z=Z} \right] \quad (44)$$

where τ is the hydraulic residence time within the FBBR. Equation 44 describes the nitrate concentration profile through the FBBR for the Monod Model.

5. MODELING RESULTS

The Zero-Order Model and the Monod Model may be compared with experimental data taken during the operation of a FBBR. This was done for a 50-cm-diam., 6-m-high FBBR which was operated continuously at ORNL from August through October, 1980. The reactor was operated at relatively constant conditions of temperature (27 to 31°C), inlet pH (6.8 to 7.2), and superficial liquid velocity (0.9 cm/s). For evaluation of these models the data was divided into 7 groups, with the group depending on the nitrate feed concentration to the bioreactor. A summary of the data from the operation of this bioreactor is presented in Table 1. The nitrate feed concentrations varied from 460 to 2900 mg/L and the average nitrate concentration for each group was calculated as a function of the distance from the inlet of the bioreactor. The average bacterial loading on the support particles varied from 12 to 30 weight percent on a dry basis. In all cases, S_i for the model prediction was taken to be the experimental value of the nitrate feed concentration.

5.1 Zero-Order Model

Graphs of the nitrate concentration as a function of reactor height, along with the nitrate profiles predicted by the zero-order model, are presented in Figs. 5-11. The Zero-Order Model predicts that the nitrate concentration through a FBBR is described by a linear profile with respect to axial position within the FBBR (Eqn. 32) when the nitrate is able to fully penetrate the biofilm. When the nitrate is able to penetrate only

Table 1. The average nitrate concentration, as a function of height, taken from the operation of the 50-cm-diam., 6-m-high FBBR from August through October, 1980.

Group	Nitrate Feed Range (g/m ³)	<u>Distance from Reactor Inlet (m)</u>					Average Biomass on Dry Particles (wt. %)
		<u>0</u>	<u>0.90</u>	<u>2.74</u>	<u>3.96</u>	<u>5.79</u>	
		Average Nitrate Concentration (mg/L)					
A	460-640	536	405	155	75	33	30
B	660-990	823	721	273	113	47	27
C	1050-1400	1145	1037	519	222	100	26
D	1600-1660	1630	1460	770	683	703	25
E	1700-2100	1935	1935	1283	905	722	20
F	2190-2410	2250	2330	1454	1202	1454	18
G	2610-2900	2717	2697	2025	1582	1647	12

ZERO ORDER MODEL 50-CM-DIAM X 6-M-HIGH FBRR

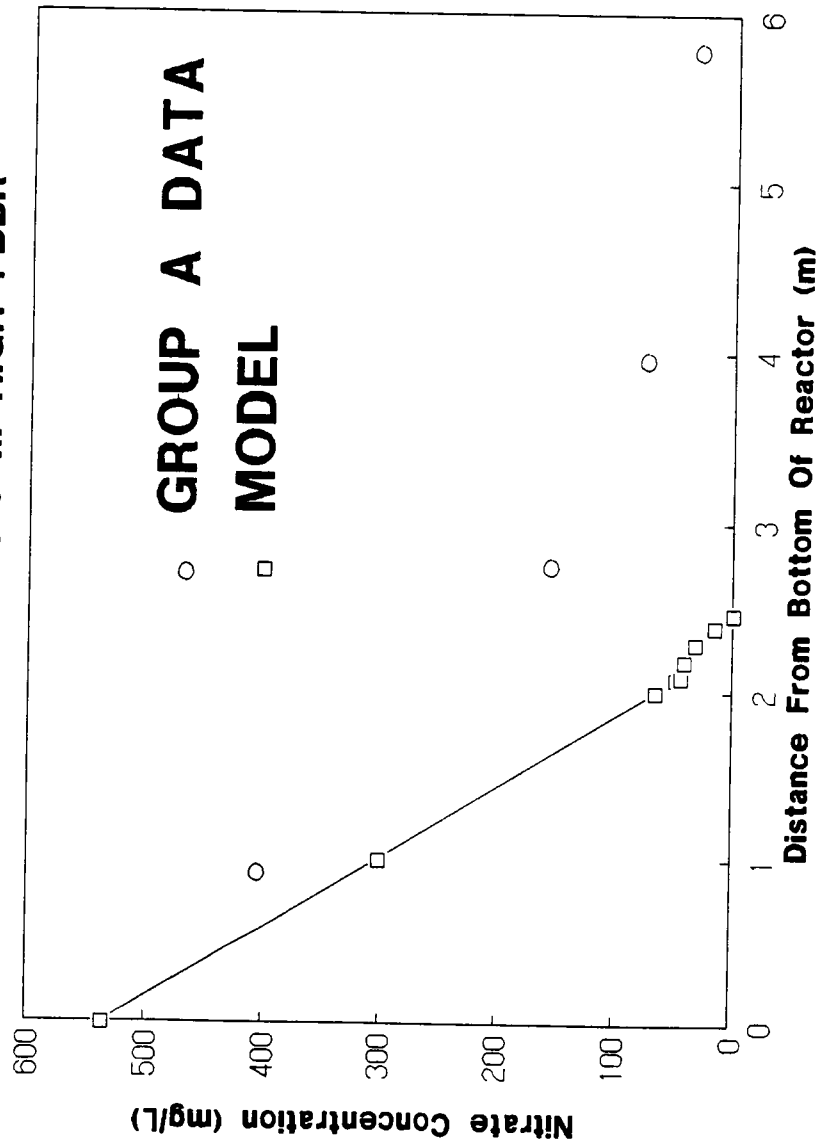


Fig. 5. Comparison of the nitrate profile from Group A data taken from the operation of a 50-cm-diam., 6-m-high FBRR from August through October 1980 with the zero-order model.

ZERO ORDER MODEL

50-CM-DIAM X 6-M-HIGH FBRR

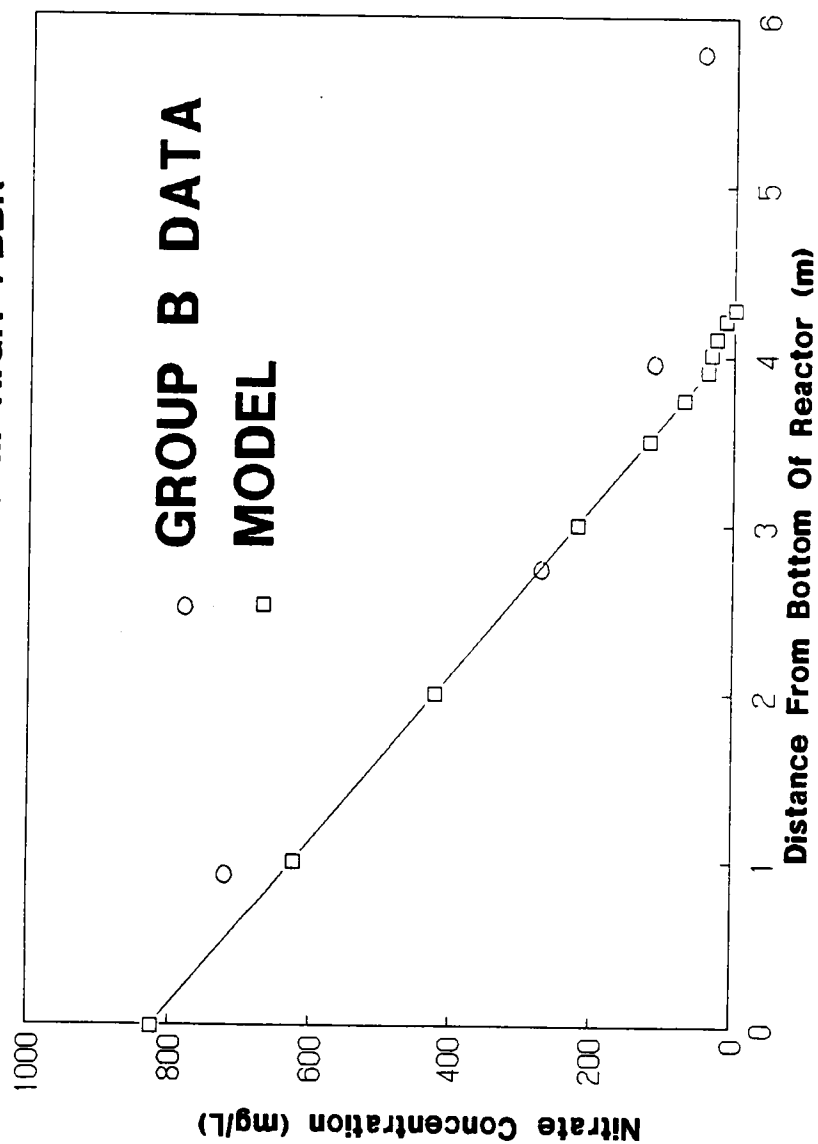


Fig. 6. Comparison of the nitrate profile from Group B data taken from the operation of a 50-cm-diam., 6-m-high FBRR from August through October 1980 with the zero-order model.

ZERO ORDER MODEL 50-CM-DIAM X 6-M-HIGH FBFR

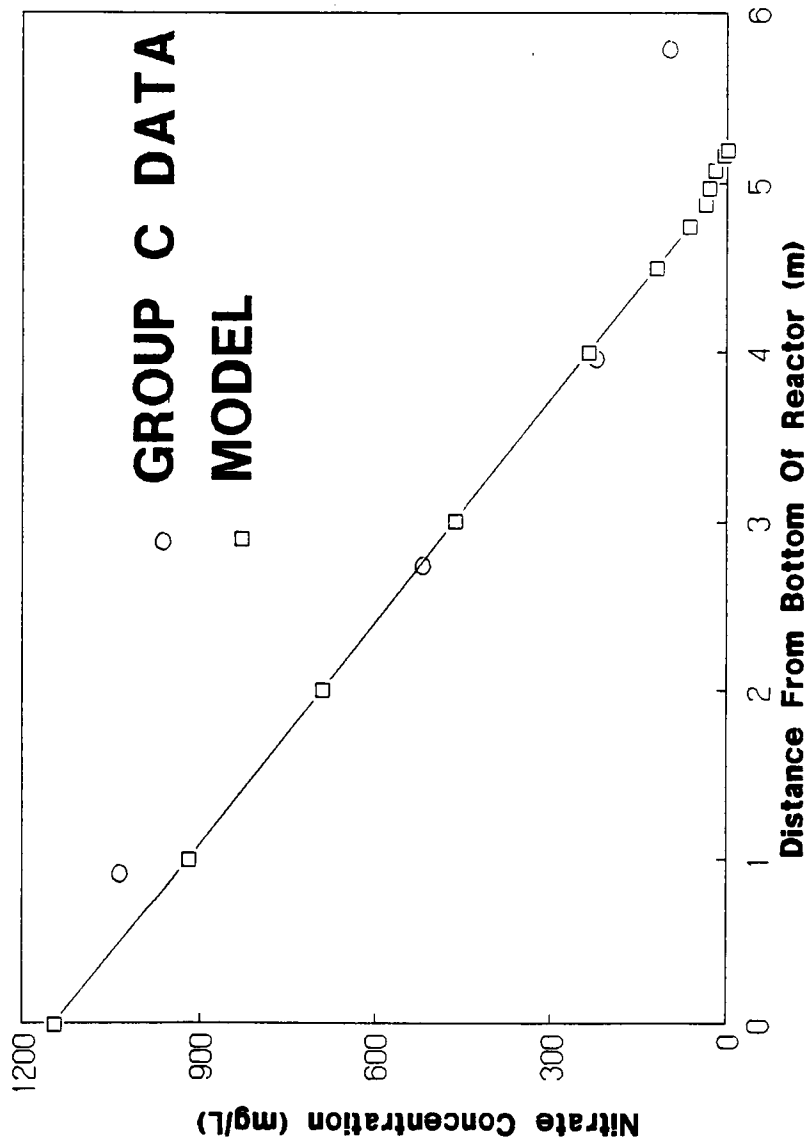


Fig. 7. Comparison of the nitrate profile from Group C data taken from the operation of a 50-cm-diam., 6-m-high FBFR from August through October 1980 with the zero-order model.

ZERO ORDER MODEL

50-CM-DIAM X 6-M-HIGH FBRR

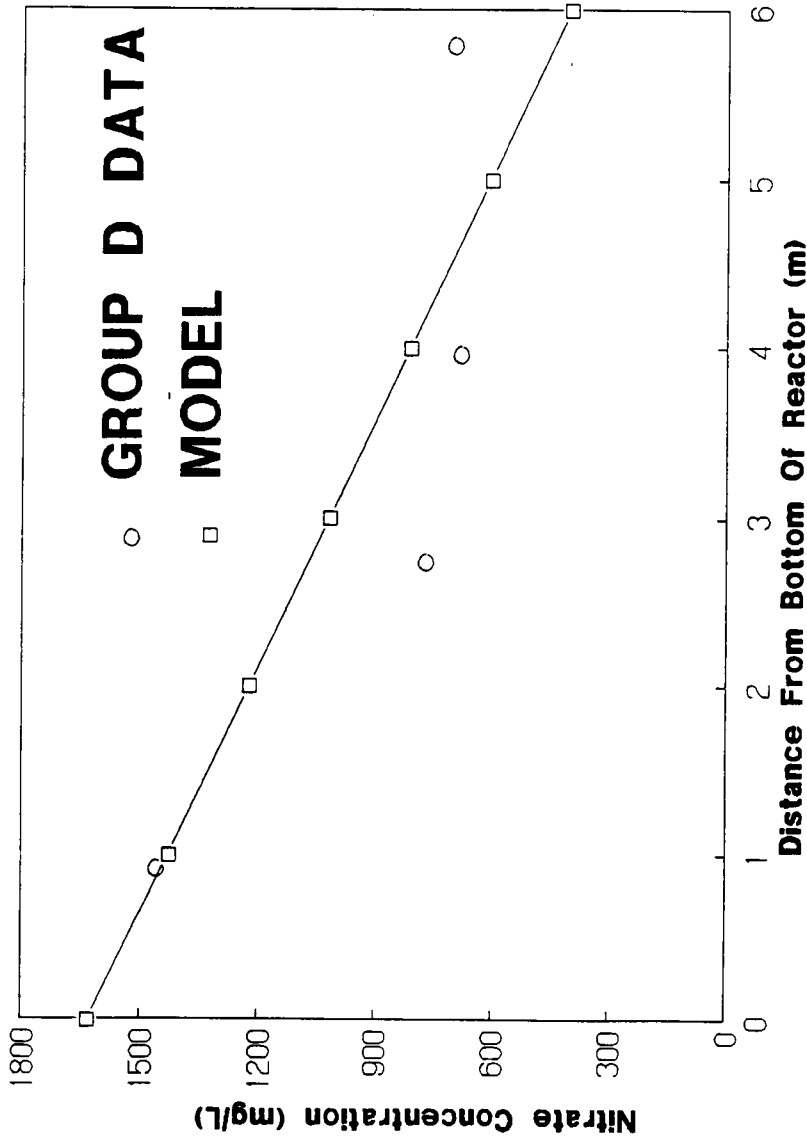


Fig. 8. Comparison of the nitrate profile from Group D data taken from the operation of a 50-cm-diam., 6-m-high FBRR from August through October 1980 with the zero-order model.

ZERO ORDER MODEL 50-CM-DIAM X 6-M-HIGH FBRR

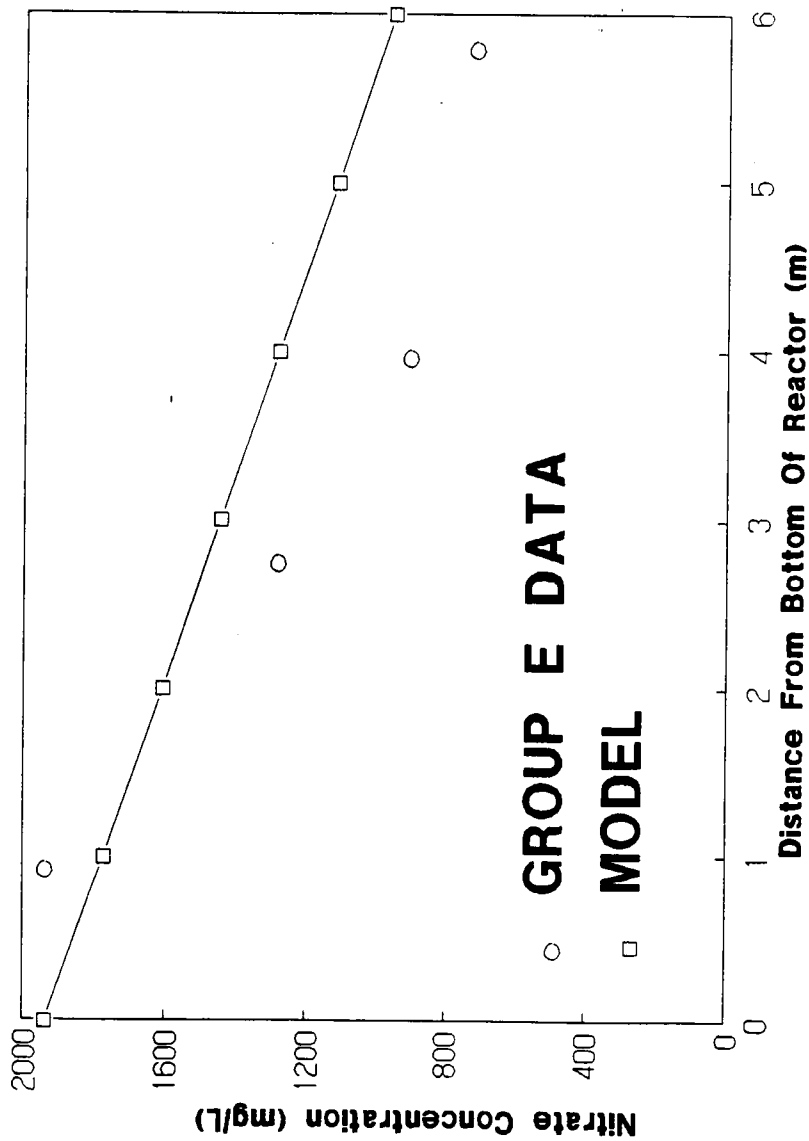


Fig. 9. Comparison of the nitrate profile from Group E data taken from the operation of a 50-cm-diam., 6-m-high FBRR from August through October 1980 with the zero-order model.

MONOD KINETICS

50-CM-DIAM X 6-M-HIGH FBFR

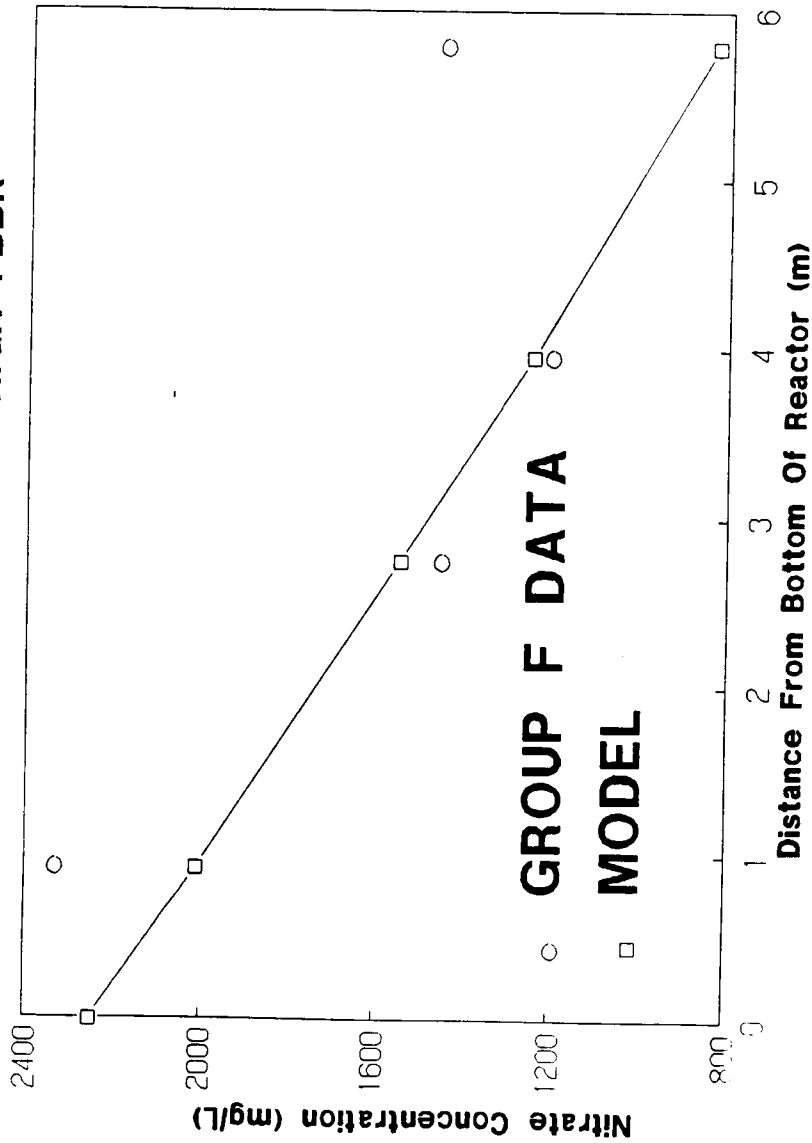


Fig. 10. Comparison of the nitrate profile from Group F data taken from the operation of a 50-cm-diam., 6-m-high FBFR from August through October 1980 with the zero-order model.

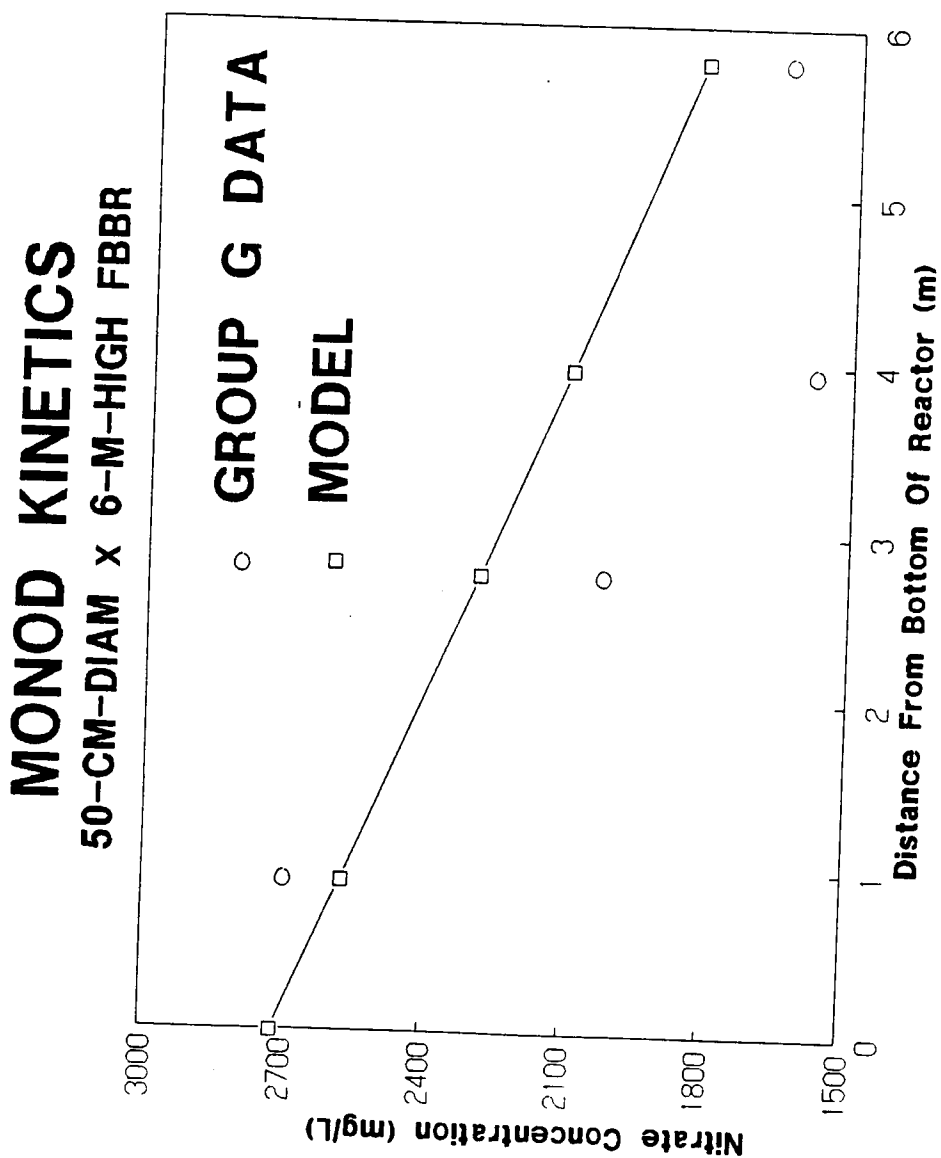


Fig. 11. Comparison of the nitrate profile from Group G data taken from the operation of a 50-cm-diam., 6-m-high FBFR from August through October 1980 with the zero-order model.

part of the biofilm the square root of the nitrate concentration is proportional to the axial position (Z) within the FBBR (Eqn. 30). In Figs. 5-7, the model predicts that majority of the bed is described by a first-order equation and that transition to equation 30 occurs only at very low nitrate concentrations. The nitrate concentration at which the transition is calculated to occur as a function of bacterial loading is presented in Table 2. In Figs. 8-11 the inlet nitrate concentration is such that the effluent nitrate concentration is >400 mg/L; therefore, the nitrate concentration within the bioreactor was not low enough for the transition to equation 30 to occur. In Figs. 8-11 the Zero-Order Model predicts that the nitrate profile within the entire bioreactor is described by equation 32.

In comparing the fit of the Zero-Order Model with the experimental data taken from the operation of the 50-cm-diam. bioreactor from August through October, 1980, it can be seen that, in general, the linear equation which describes the full penetration of the nitrate into the biofilm represents the experimental data fairly well. However, equation 30, which should describe the nitrate profile at low concentrations, does not represent the experimental data well. It is interesting to note in Figs. 5-7 that at the low concentrations the experimental data does deviate from the linear equation (Eqn. 32), but does not follow Eqn. 30 as predicted by the Zero-Order Model.

Table 2. The nitrate concentration at which transition from full to partial penetration occurs as a function of bacterial loading.

Bacterial Loading (wt. %)	Nitrate Concentration at Transition (mg/L)
10	9.0
15	16.6
20	25.0
25	34.2
30	44.1
35	54.8

5.2 Monod Model

Using the Monod Model (Eqn. 44) with $k_A = 795 \text{ mg}/(\text{L min})$ and $K_S = 350 \text{ mg/L}$, Hancher and Perona were able to predict the hydraulic residence times for a two reactors system, which operated in series for ~7 months, within 13% provided the nitrate feed concentration was $<7000 \text{ mg/L}$. In their study Hancher and Perona did not utilize the model to predict the nitrate profile within the reactor; therefore, it is not known if the model fit the experimental data within the reactors or simply predicted the effluent nitrate concentration from the reactors.

Graphs of the nitrate concentration as a function of reactor height, along with the nitrate profiles predicted by the Monod Model developed by Hancher and Perona, are presented in Figs. 12 to 18 for the 50-cm-diam., 6-m-high bioreactor operated at ORNL from August through October, 1980. In Figs. 12, 13, 14, 16, and 18 the Monod Model does an adequate job of predicting the effluent nitrate concentration from the bioreactor but does not necessarily represent the nitrate profile data within the bioreactor. In Figs. 15 and 17 the Monod Model does not predict the effluent nitrate concentration from the reactor.

In comparing the fit of the Monod Model with the experimental data taken during the operation of the 50-cm-diam., 6-m-high bioreactor it can be seen that, in general, the model predicts the effluent nitrate concentration from the bioreactor but does not necessarily fit the experimental nitrate profile data within the bioreactor. This might be expected because Hancher and Perona used only data from the reactor inlet and effluent in developing and testing the model. This suggests that different values for the constants in the Monod Model may improve the performance of the model in predicting the nitrate profile within the bioreactor. This is verified in Figs. 19-25, where the value of K_s is changed to 800 mg/L and the nitrate profile predicted by the Monod Model with this new value of K_s is compared with the experimental data taken from the operation of the 50-cm-diam. reactor. The nitrate profile predicted by the previous Monod Model is also included in Figs. 19-25 for comparison.

MONOD KINETICS

50-CM-DIAM X 6-M-HIGH FBRR

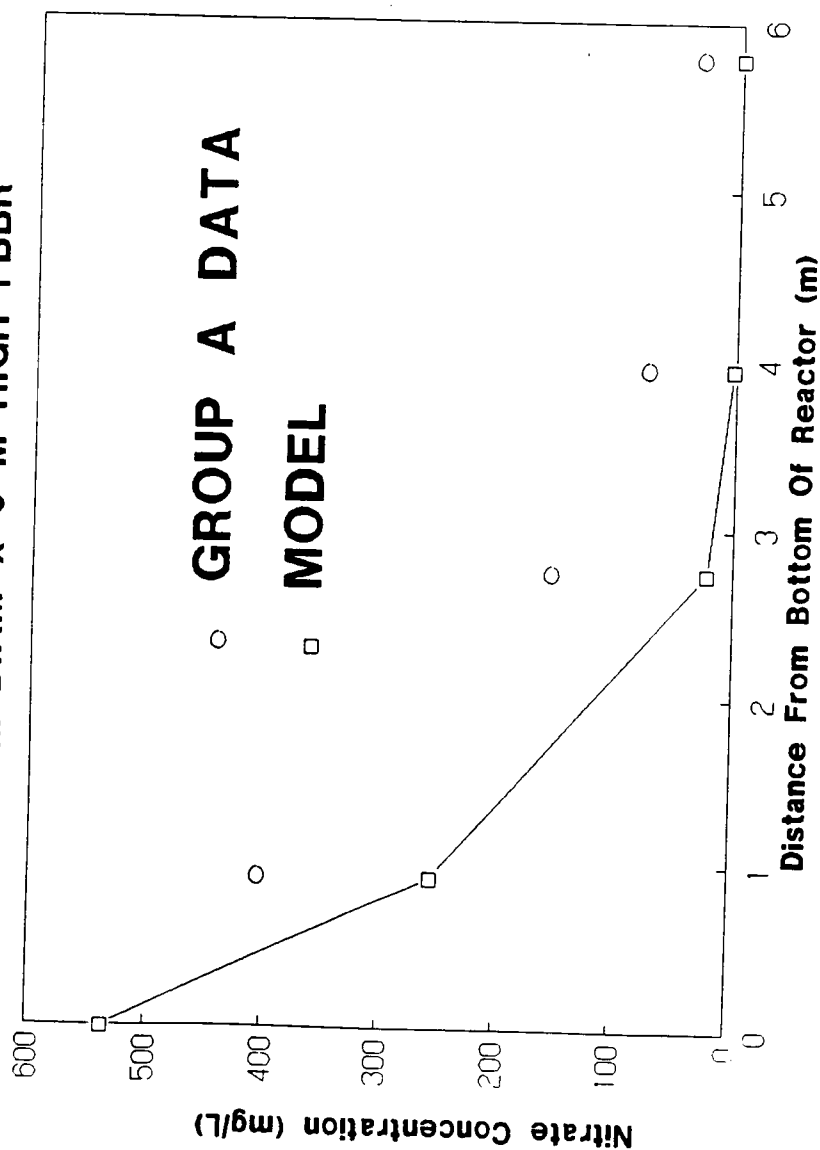


Fig. 12. Comparison of the nitrate profiles from Group A data with the Monod Model.

MONOD KINETICS **50-CM-DIAM x 6-M-HIGH FBRR**

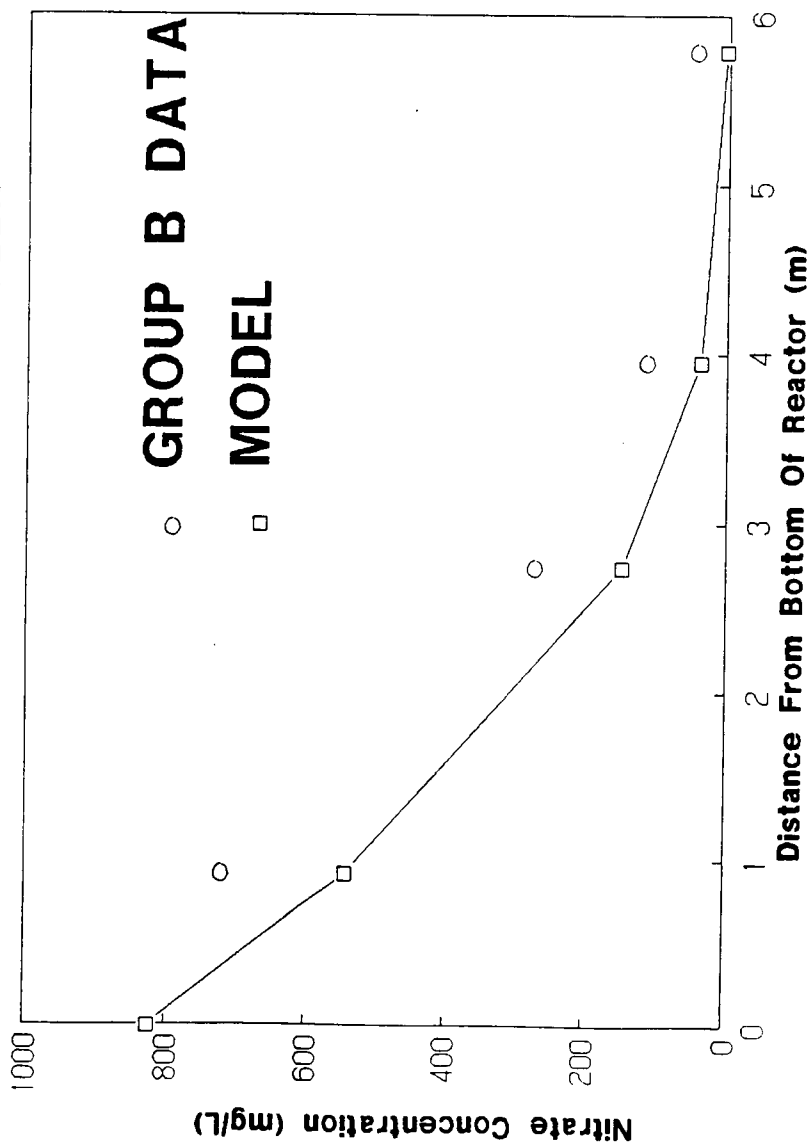


Fig. 13. Comparison of the nitrate profiles from Group B data with the Monod Model.

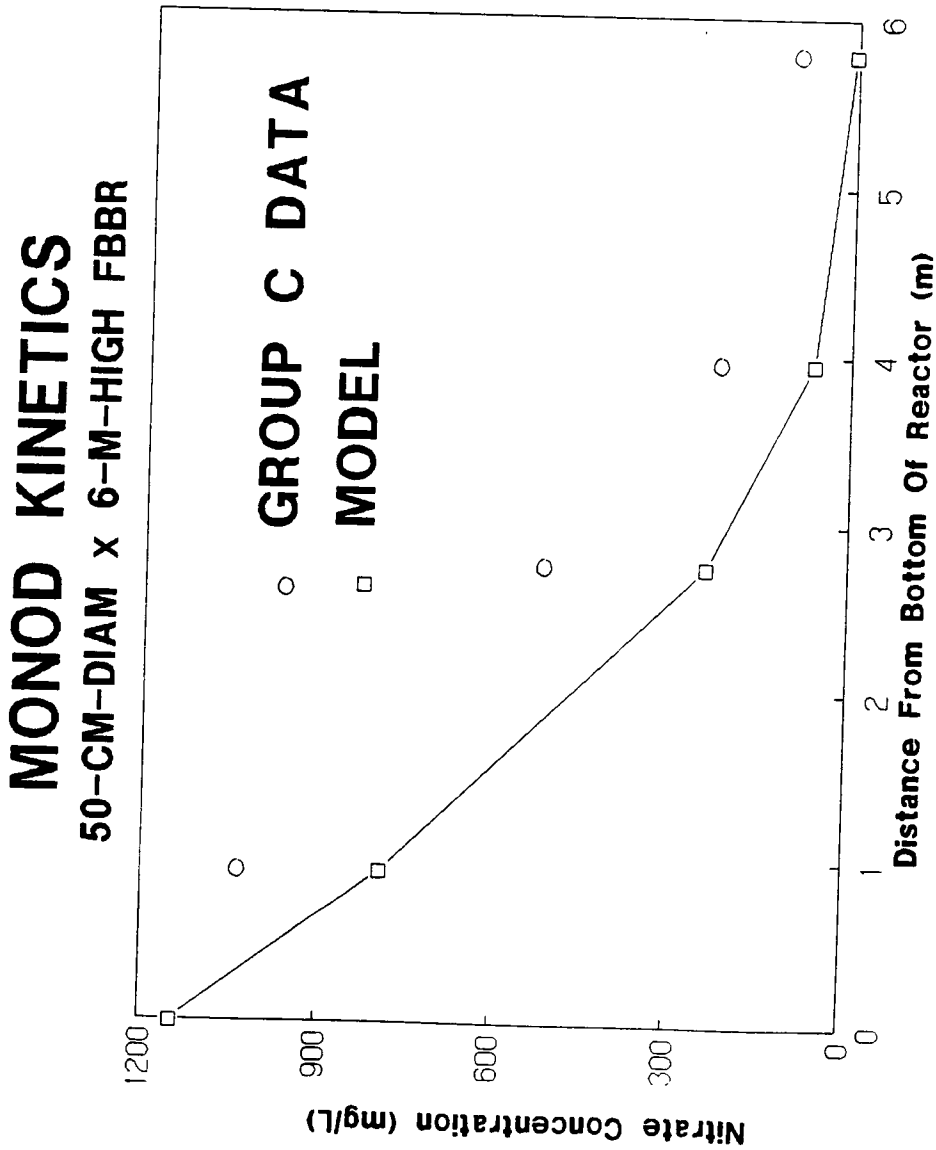


Fig. 14. Comparison of the nitrate profiles from Group C data with the Monod Model.

MONOD KINETICS

50-CM-DIAM X 6-M-HIGH FBRR

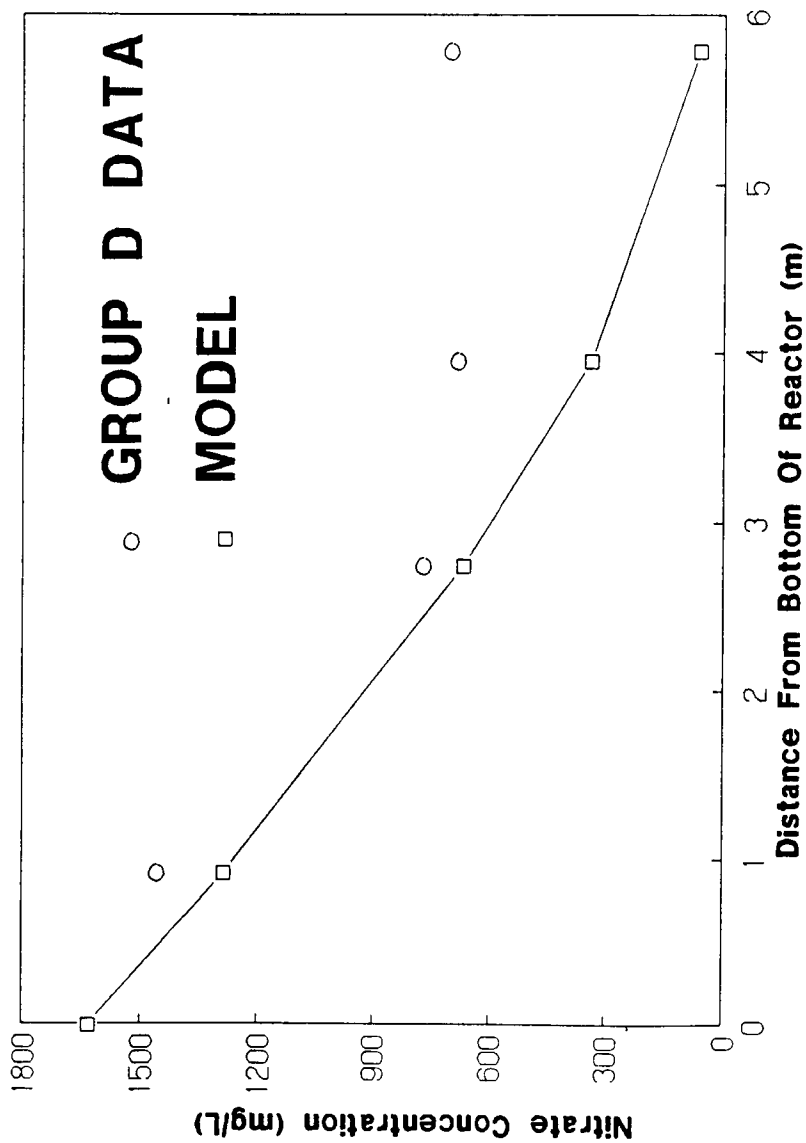


Fig. 15. Comparison of the nitrate profiles from Group D data with the Monod Model.

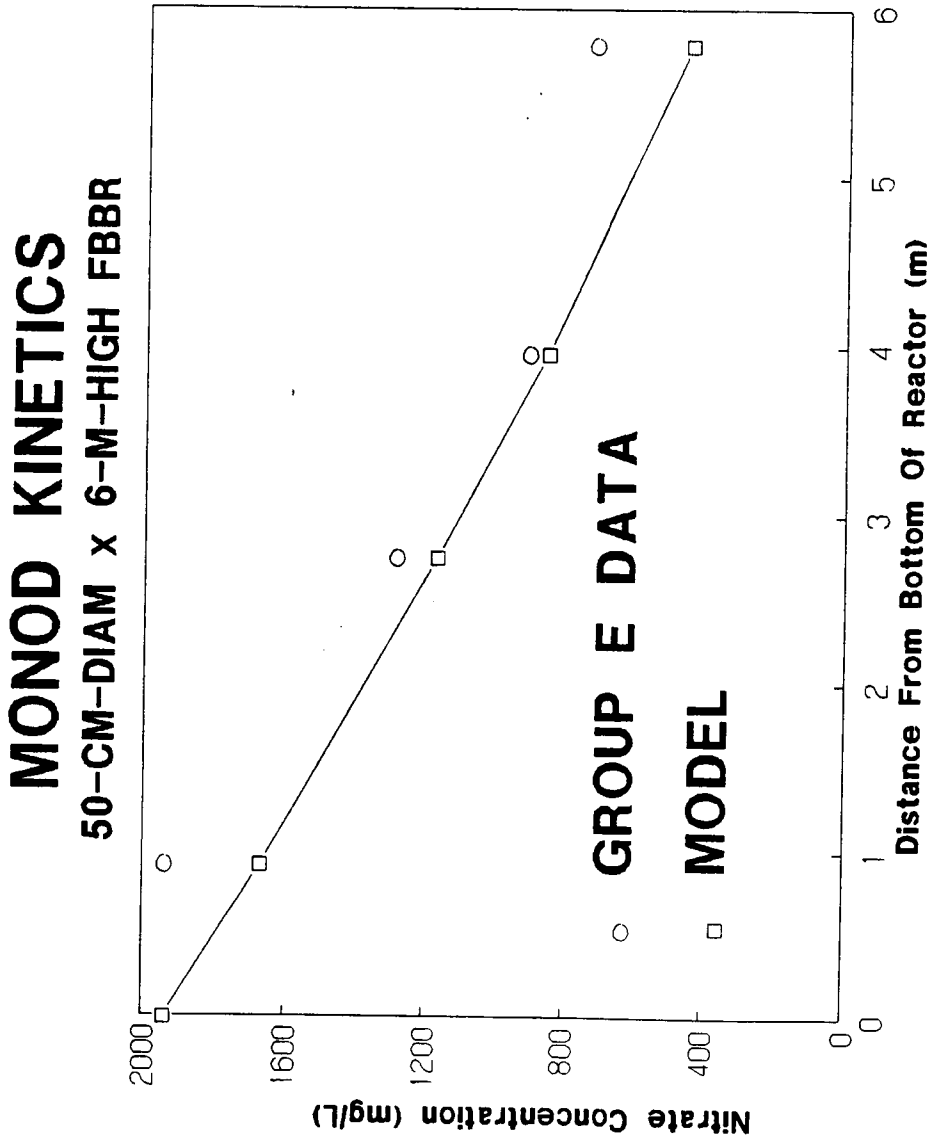


Fig. 16. Comparison of the nitrate profiles from Group E data with the Monod Model.

MONOD KINETICS

50-CM-DIAM X 6-M-HIGH FBFR

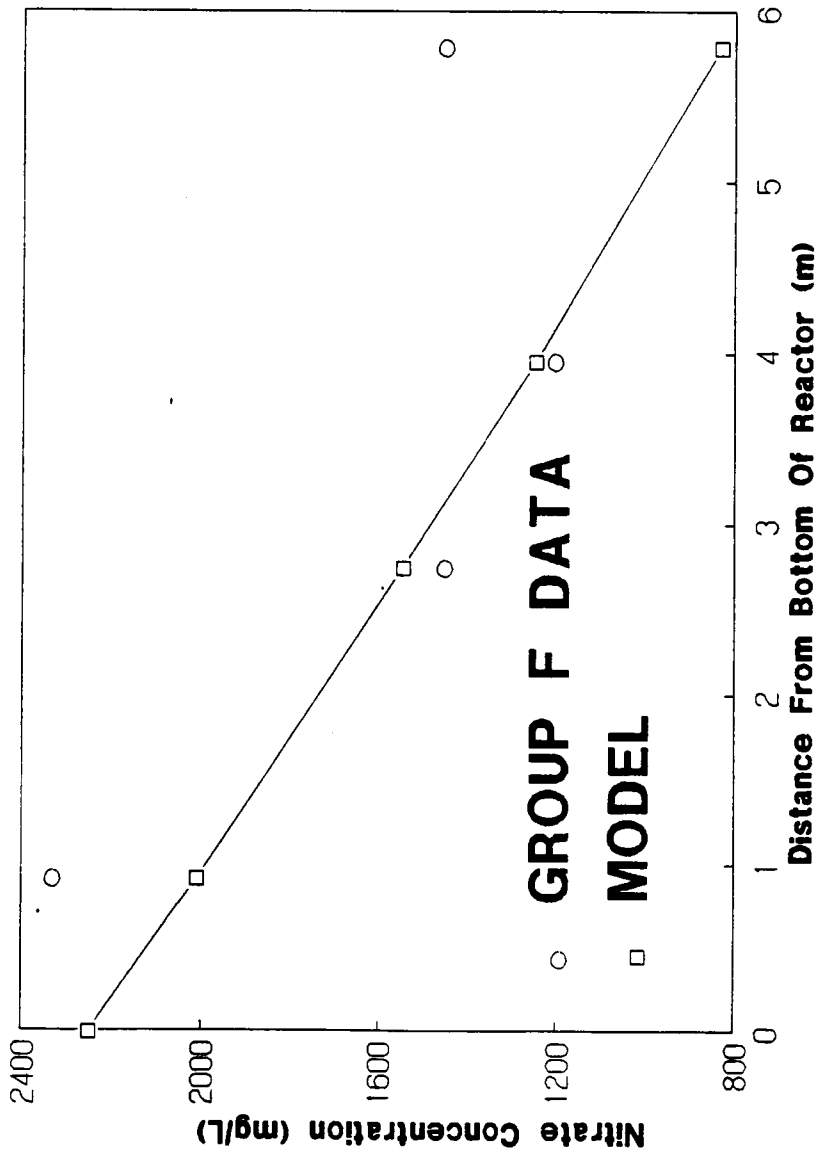


Fig. 17. Comparison of the nitrate profiles from Group F data with the Monod Model.

MONOD KINETICS **50-CM-DIAM X 6-M-HIGH FBRR**

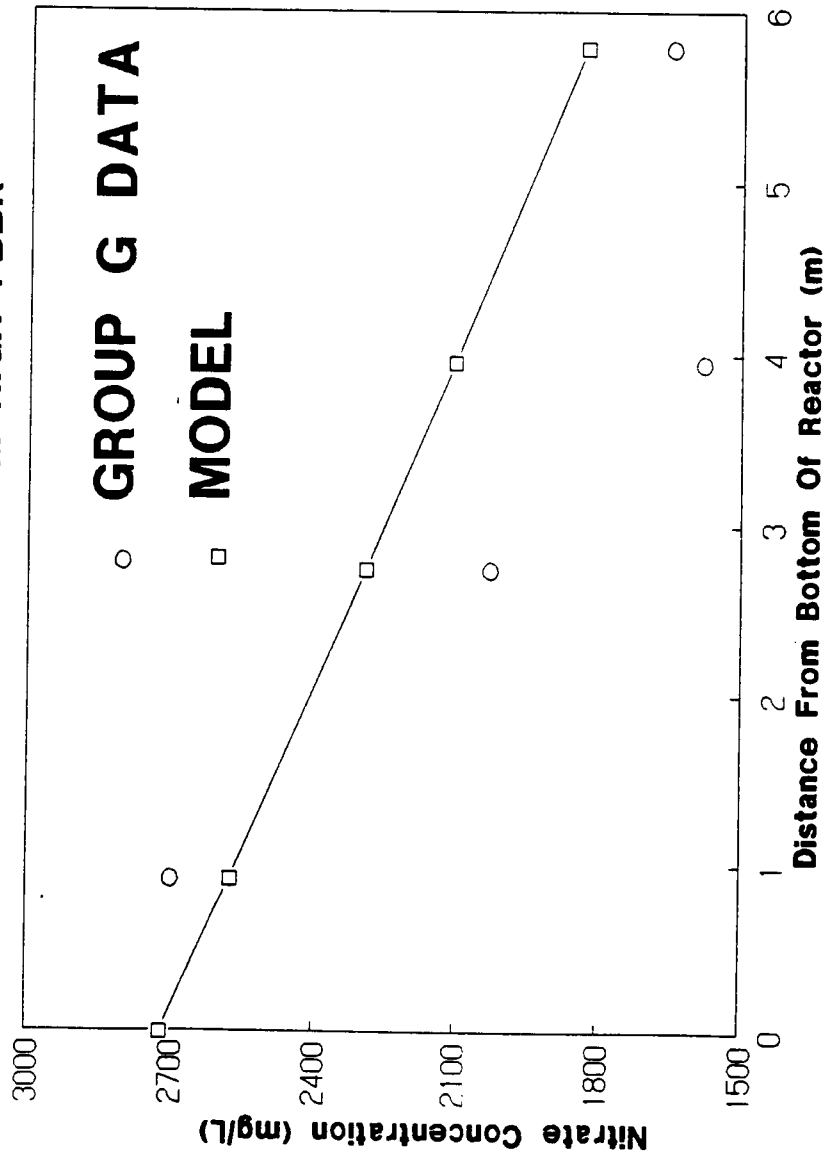


Fig. 18. Comparison of the nitrate profiles from Group G data with the Monod Model.

MONOD KINETICS **50-CM-DIAM X 6-M-HIGH FBRR**

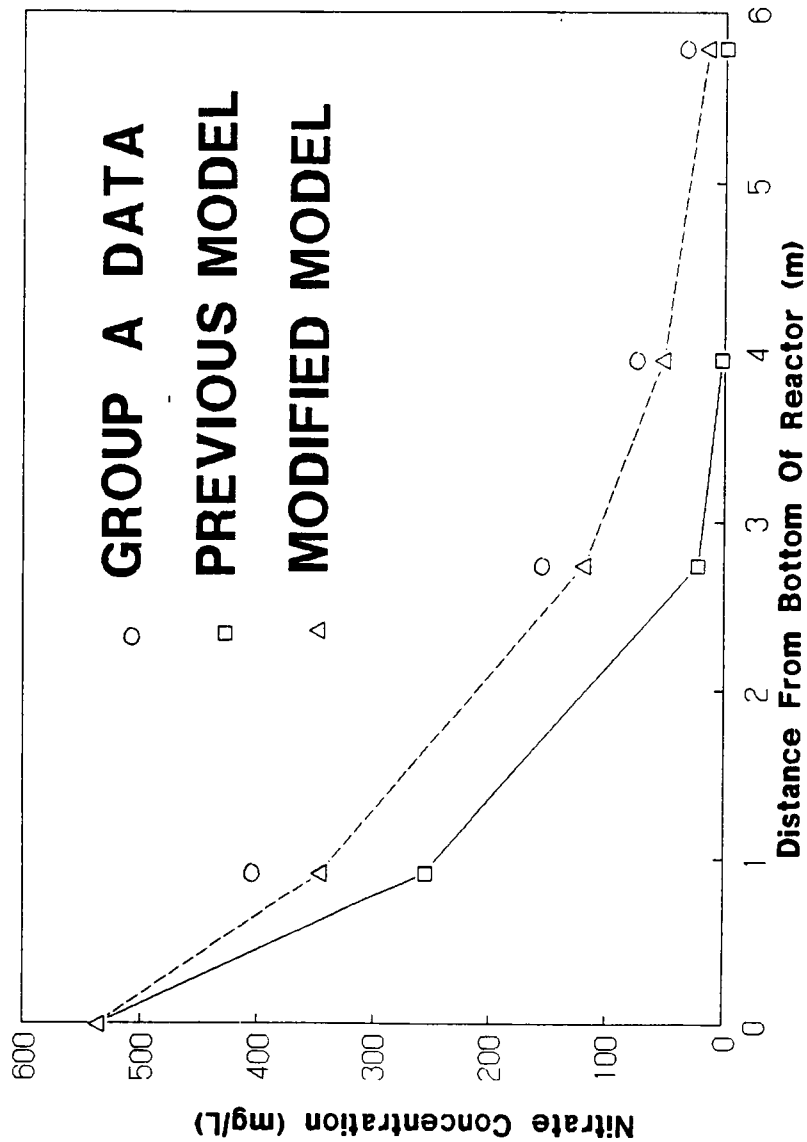


Fig. 19. Comparison of the nitrate profiles from Group A data with the Monod Model and the Modified Monod Model.

MONOD KINETICS

50-CM-DIAM X 6-M-HIGH FBRR

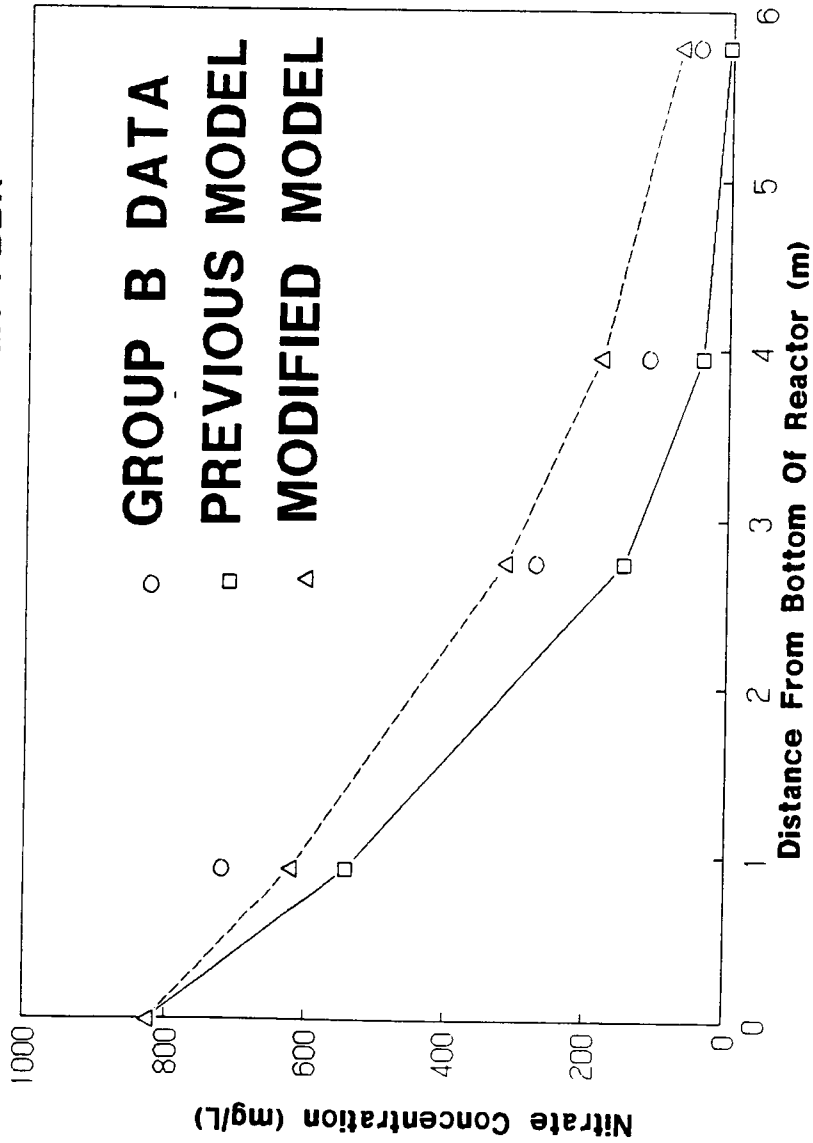


Fig. 20. Comparison of the nitrate profiles from Group B data with the Monod Model and the Modified Monod Model.

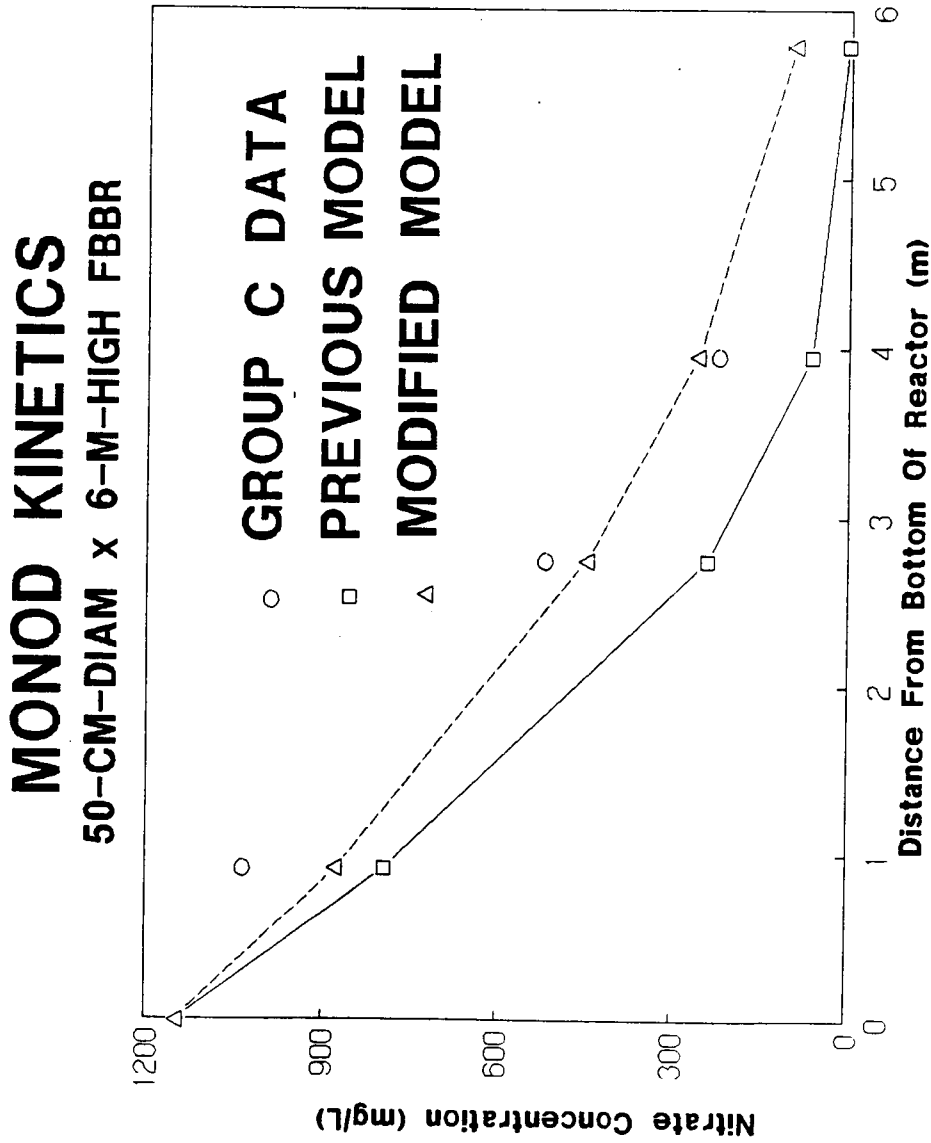


Fig. 21. Comparison of the nitrate profiles from Group C data with the Monod Model and the Modified Monod Model.

MONOD KINETICS **50-CM-DIAM X 6-M-HIGH FBRR**

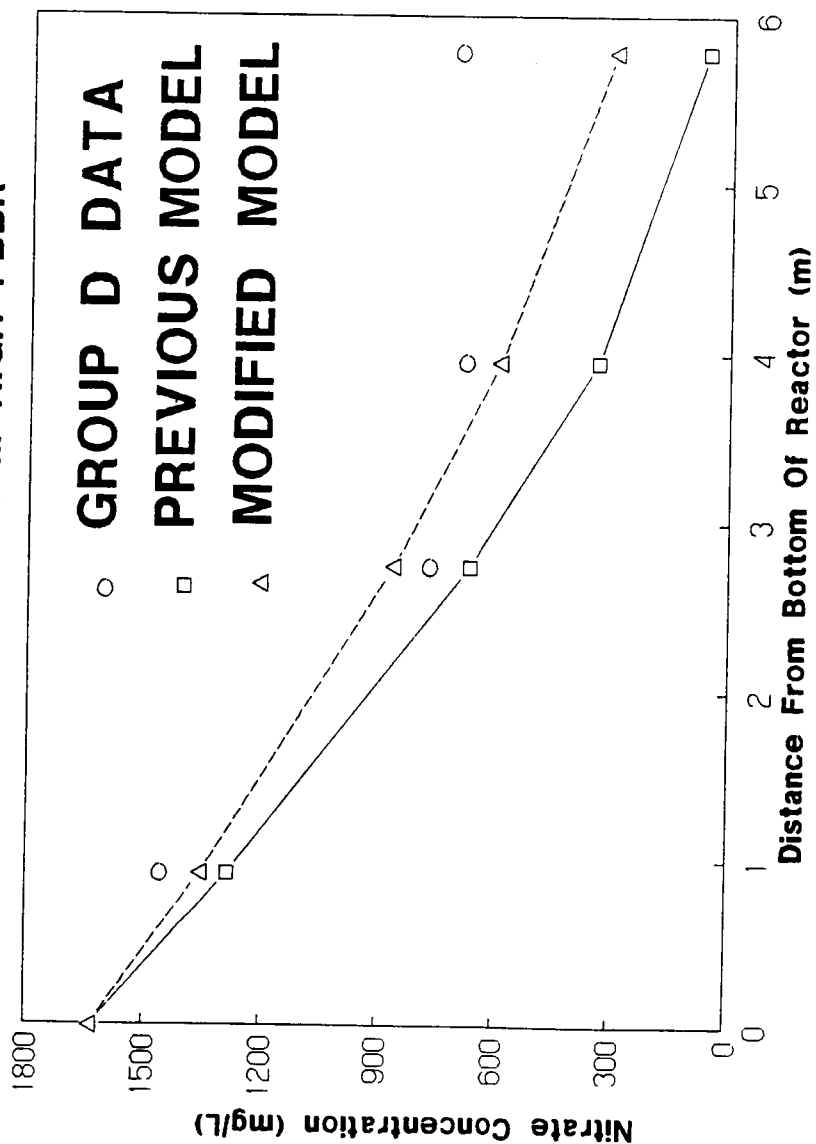


Fig. 22. Comparison of the nitrate profiles from Group D data with the Monod Model and the Modified Monod Model.

MONOD KINETICS

50-CM-DIAM X 6-M-HIGH FBRR

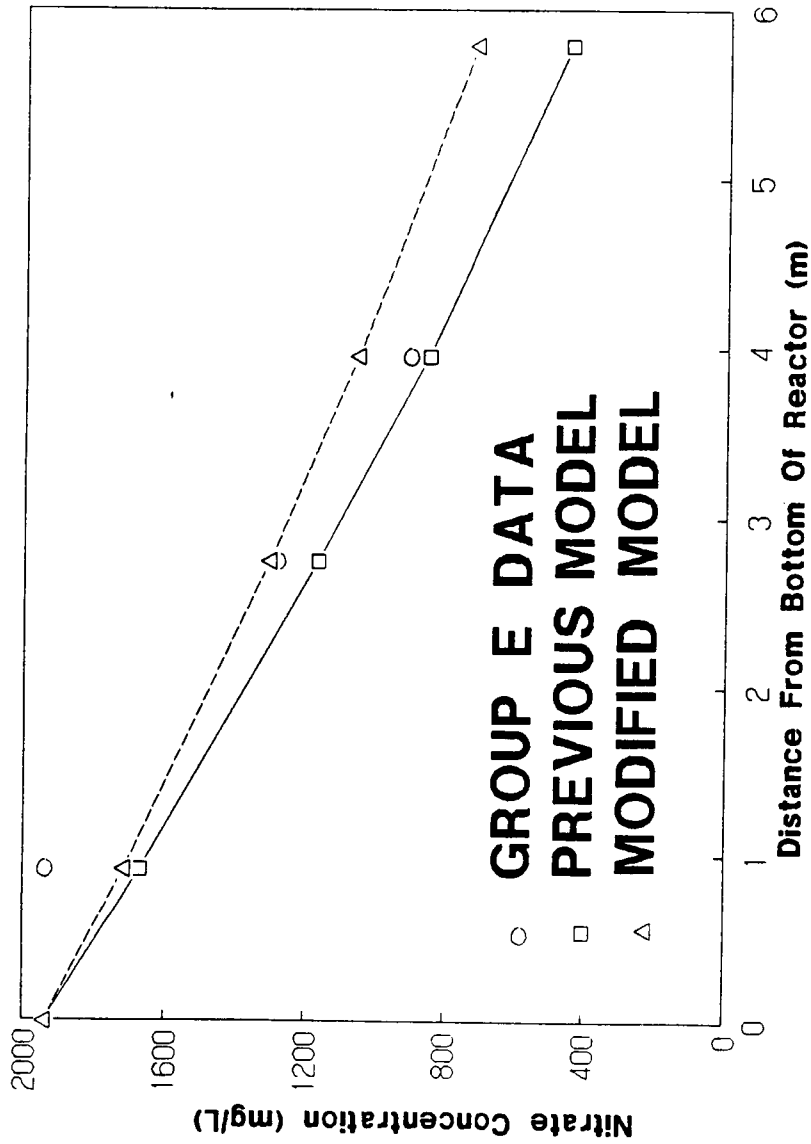


Fig. 23. Comparison of the nitrate profiles from Group E data with the Monod Model and the Modified Monod Model.

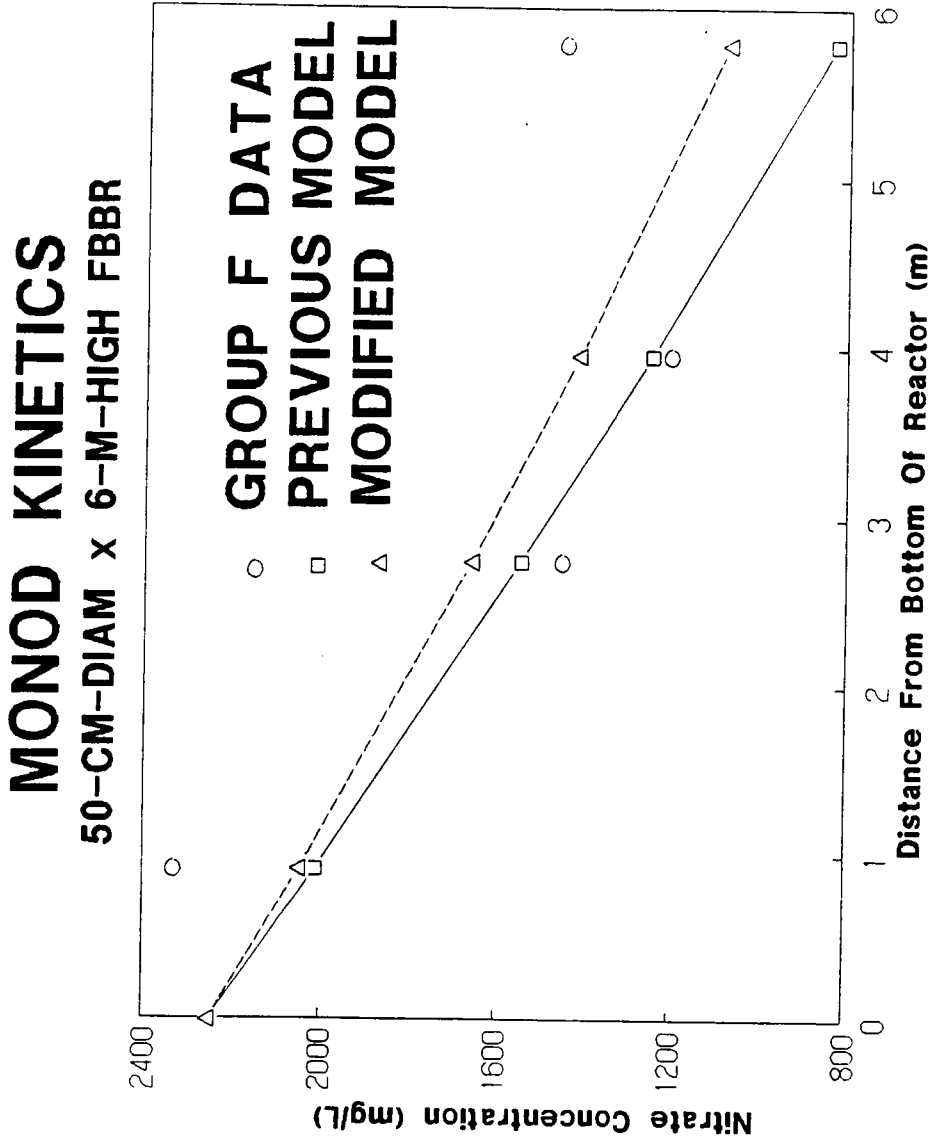


Fig. 24. Comparison of the nitrate profiles from Group F data with the Monod Model and the Modified Monod Model.

MONOD KINETICS

50-CM-DIAM X 6-M-HIGH FBRR

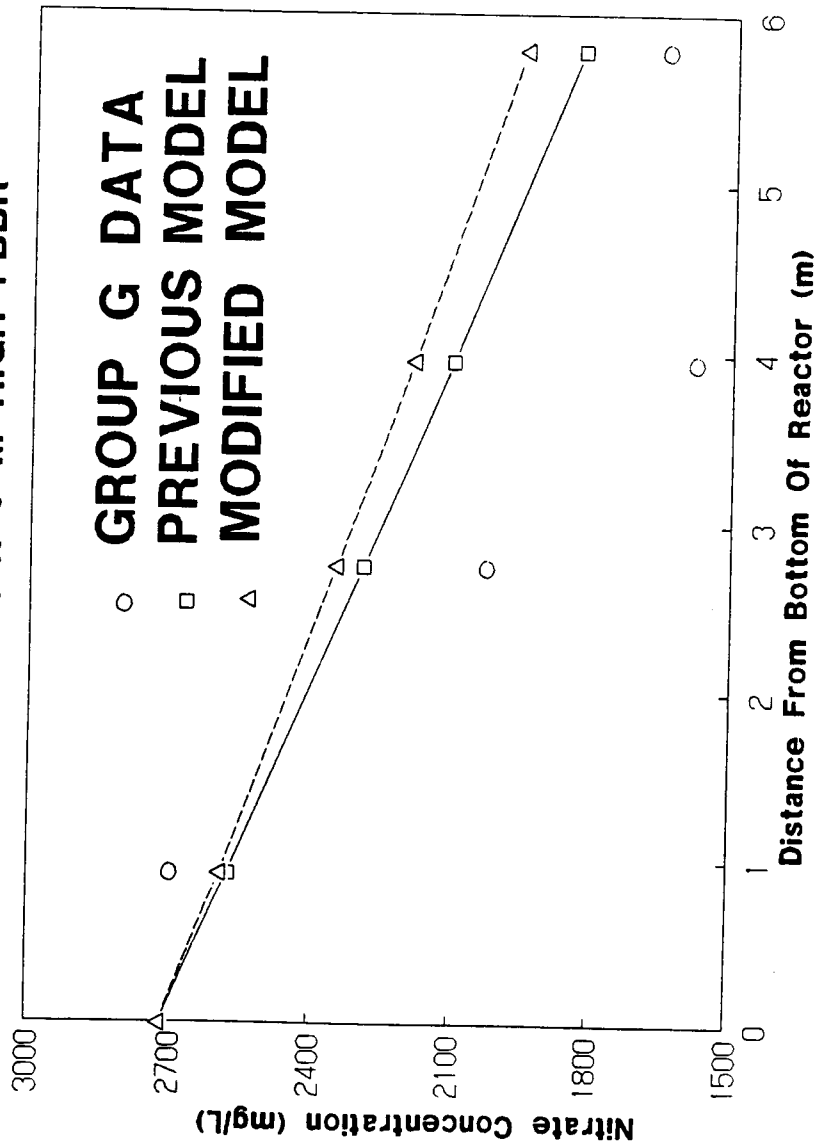


Fig. 25. Comparison of the nitrate profiles from Group G data with the Monod Model and the Modified Monod Model.

With $k_A = 795 \text{ mg}/(\text{L min})$ and $K_S = 800 \text{ mg/L}$ the Modified Monod Model, in general, represents the nitrate profiles within the 50-cm-diam., 6-m-high bioreactor very well. In Figs. 22 and 24, the Modified Monod Model represents the data well in the bottom 4 m of the reactor but not in the upper 2 m of the reactor. This indicates that some fundamental change may have occurred within the top portion of the bioreactor which caused the experimental data in these two operational groups to deviate from the model. In Fig. 25 the Modified Monod Model does not represent the data well.

In comparing the nitrate profiles predicted by the Zero-Order Model and the Modified Monod Model (with $K_A = 795 \text{ mg}/(\text{L min})$ and $K_S = 800 \text{ mg/L}$), with the data taken during the operation of the 50-cm-diam., 6-m-high bioreactor, both models adequately fit the data in the higher nitrate concentration range. As the nitrate concentration in the reactor falls below $\sim 200 \text{ mg/L}$ the Zero-Order Model no longer represents the experimental data; however, the Modified Monod model still represents the data well. This may be due to the fact that the Monod Model is more versatile and covers both zero and first order kinetics depending on the substrate concentration. Because the Monod model is more versatile and represents the experimental data at both high and low nitrate concentrations, the remainder of this paper will be limited to the Modified Monod model with $k_A = 795 \text{ mg}/(\text{L min})$ and $K_S = 800 \text{ mg/L}$.

The next step in evaluating the Modified Monod Model is to compare the nitrate profile predicted by the model with operational data from a second bioreactor. This was done for a 10-cm-diam., 6-meter-high bioreactor which operated at ORNL from September through December, 1985. The operating conditions of temperature, inlet pH, and superficial liquid velocity were similar to the operating conditions of the 50-cm-diam. reactor to which the model was previously compared. The bacterial loading for the 10-cm bioreactor was ~15% on a dry weight basis. For evaluation of the model the data was divided into 4 groups, depending on the nitrate feed concentration to the bioreactor. A summary of the data from the operation of this bioreactor is presented in Table 3. The nitrate feed concentrations varied from 2700 to 9500 mg/L and the average nitrate concentration for each group was calculated as a function of the distance from the inlet of the bioreactor.

Graphs of the nitrate concentration as a function of reactor height, along with the nitrate profiles predicted by the Modified Monod Model, are presented in Figs. 26-29. In each of these figures the nitrate profile predicted by the Modified Monod Model represents the experimental data extremely well for approximately the bottom 4 m of the bioreactor. In the top 2 m of the bioreactor the actual nitrate concentration is substantially larger than that predicted by the Modified Monod Model. This indicates that some fundamental change may be occurring within the bioreactor which is limiting the rate of denitrification.

Table 3. Data from the operation of a 10-cm-diam., 6-m-high FBBR which operated from September through December, 1985.

	Height (m)					
	0	0.94	2.21	3.48	4.75	5.89
Group	Nitrate Concentration (mg/L)					
A	2733	2505	2361	2279	2189	2120
B	5305	5026	4816	4740	4781	4498
C	6993	6796	6479	6390	6246	6238
D	9511	8902	8934	8706	8655	8620

MONOD KINETICS

10-CM-DIAM X 6-M-HIGH FBRR

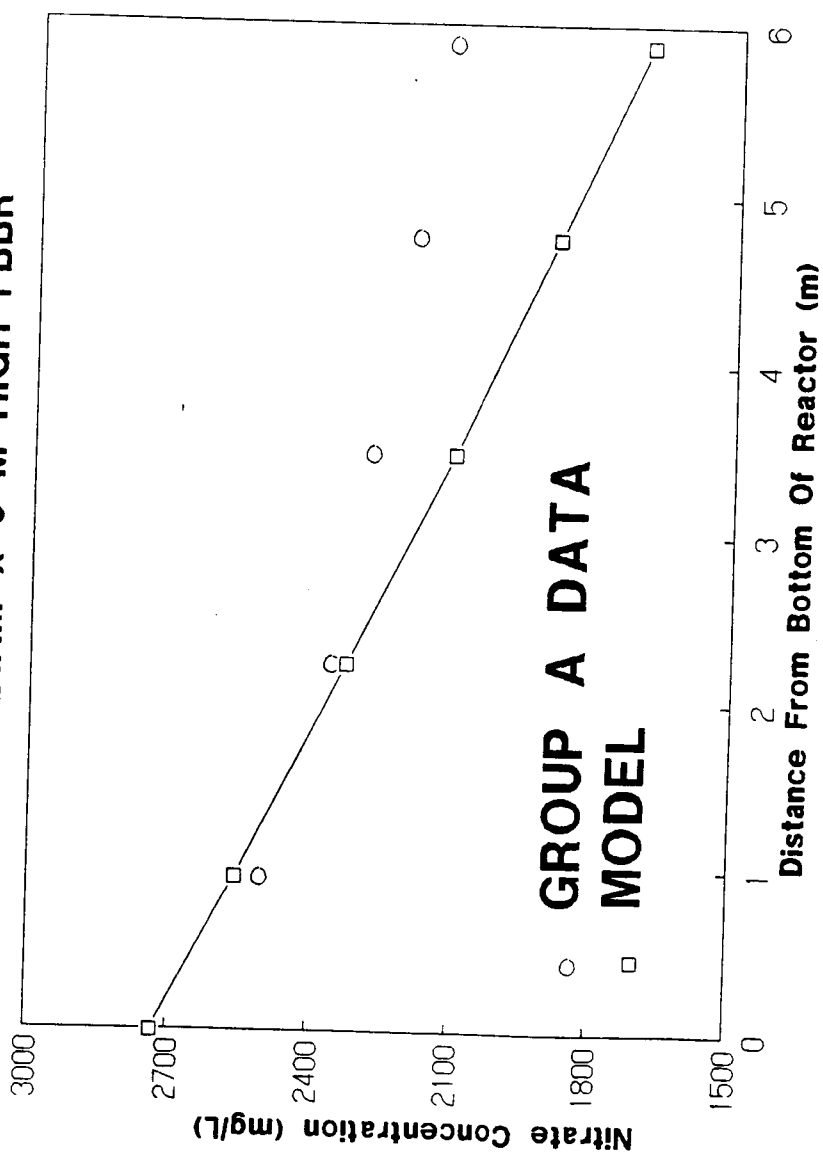


Fig. 26. Comparison of Group A data taken from the operation of a 10-cm-diam., 6-m-high FBRR, which operated at ORNL from September through December 1985, with the Modified Monod Model.

MONOD KINETICS

10-CM-DIAM X 6-M-HIGH FBRR

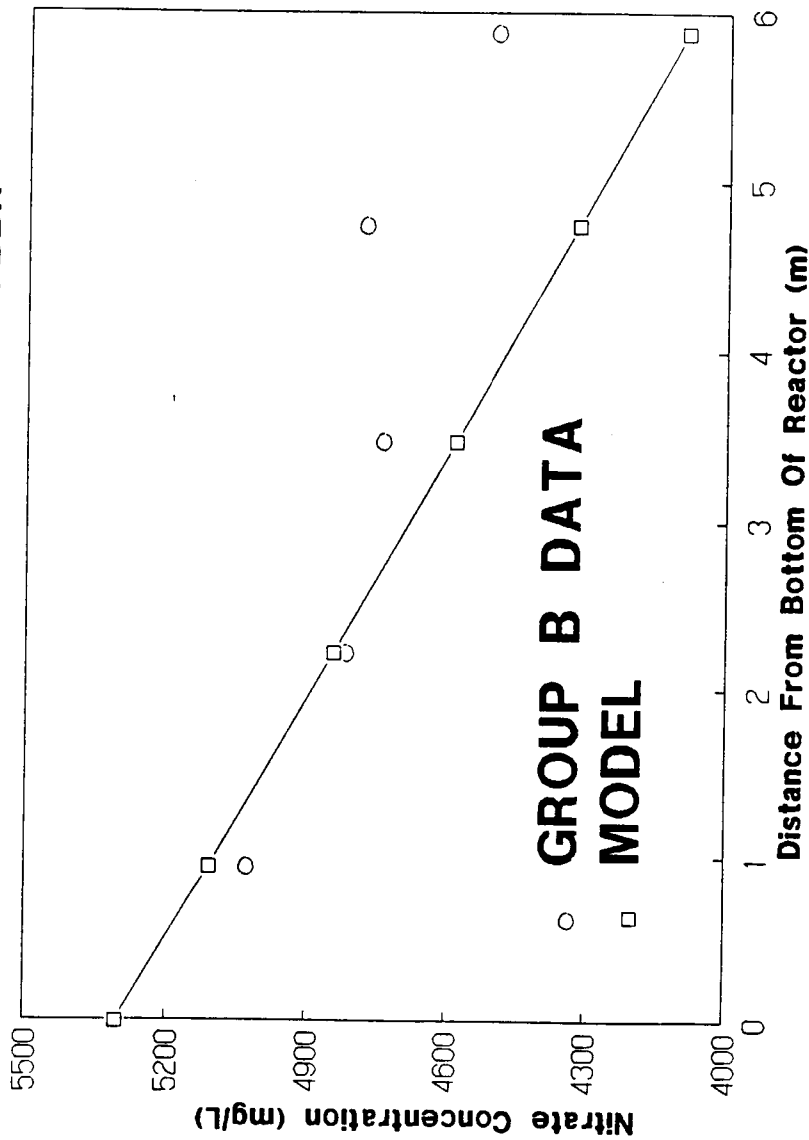


Fig. 27. Comparison of Group B data taken from the operation of a 10-cm-diam., 6-m-high FBRR, which operated at ORNL from September through December 1985, with the Modified Monod Model.

MONOD KINETICS

10-CM-DIAM X 6-M-HIGH FBRR

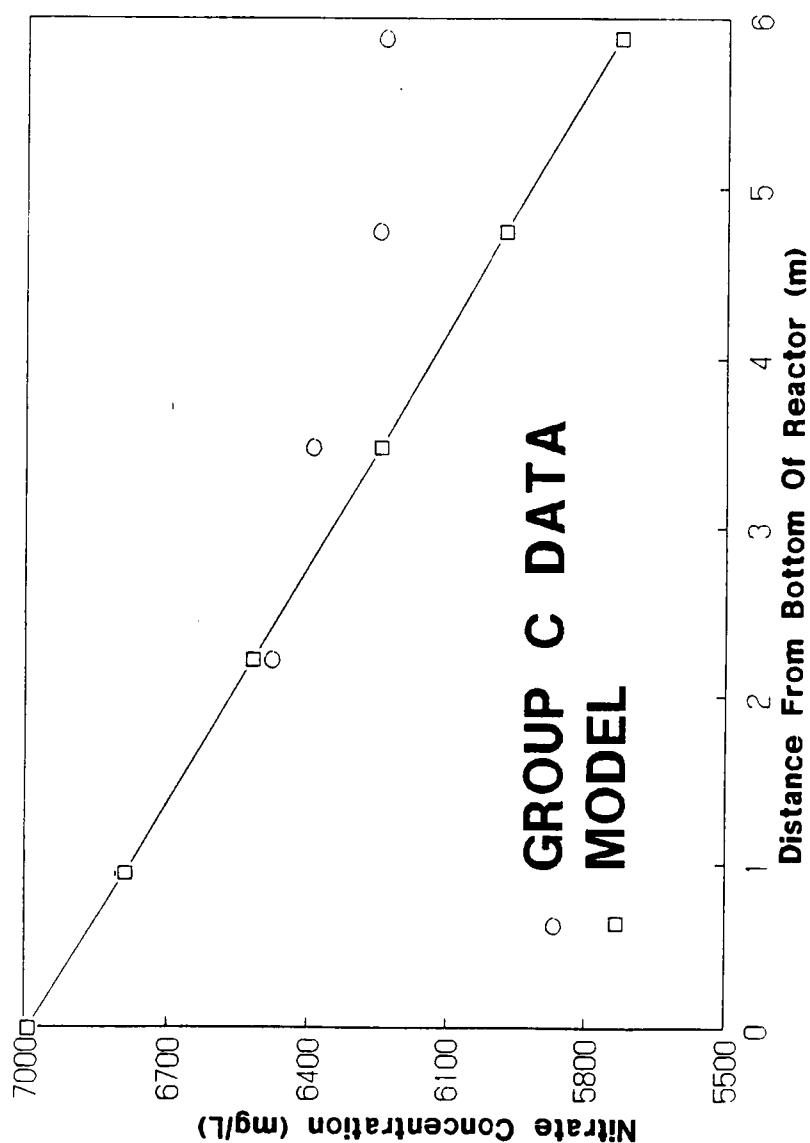


Fig. 28. Comparison of Group C data taken from the operation of a 10-cm-diam., 6-m-high FBRR, which operated at ORNL from September through December 1985, with the Modified Monod Model.

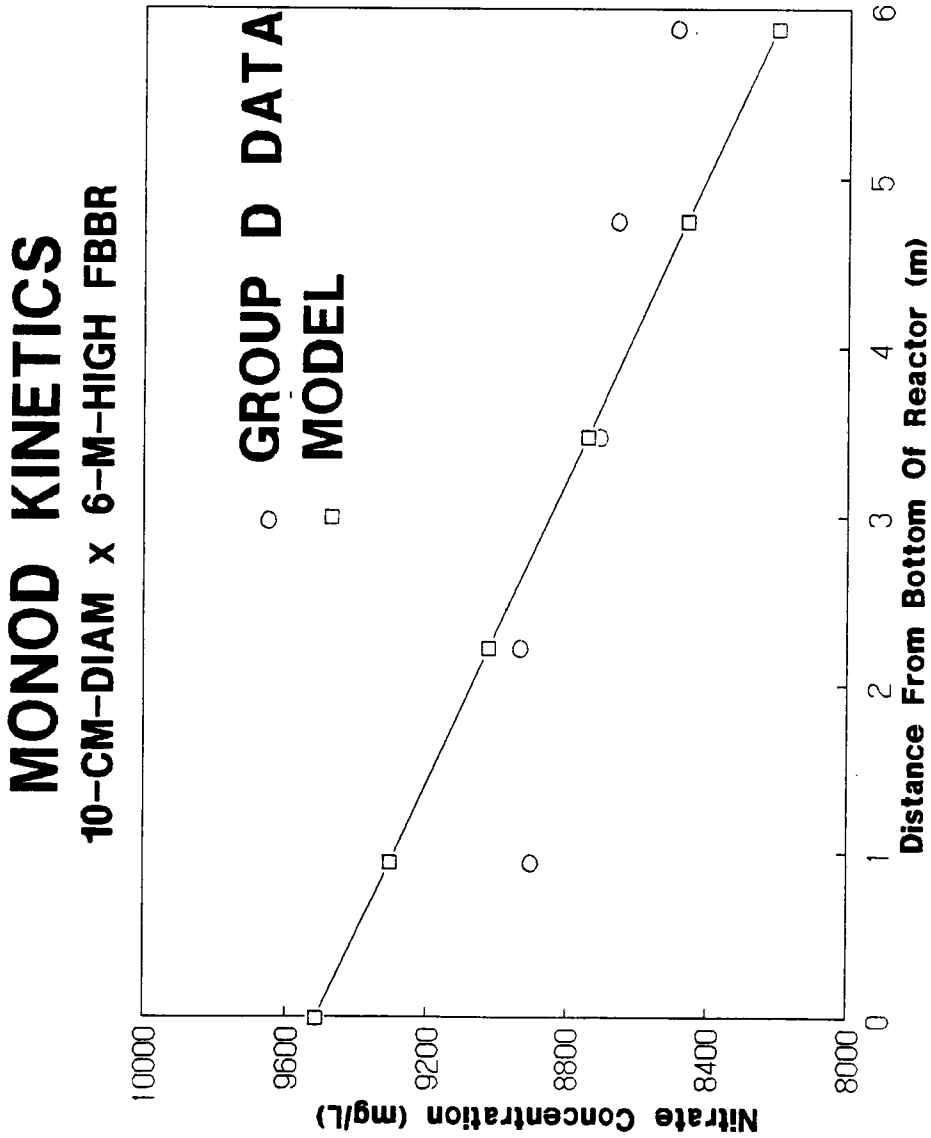


Fig. 29. Comparison of Group D data taken from the operation of a 10-cm-diam., 6-m-high FBRR, which operated at ORNL from September through December 1985, with the Modified Monod Model.

Many researchers have indicated that the denitrification rate is a function of pH and that the pH of the reactor rises during the denitrification process. Therefore, a potential explanation is that the pH within the bioreactor is rising enough to inhibit degradation of the nitrate. The pH profile for each of these operational groups was examined and a typical pH profile is presented in Fig. 30. For each group the pH rose above ~8.5 at ~4 m from the reactor inlet. This corresponds to the reactor height at which the nitrate profile predicted by the Modified Monod Model deviates from the experimental data. From this one may hypothesize that at a pH of ~8.5 the denitrification process is being inhibited. There is some disagreement in the literature as to optimum pH for denitrification. In general, the literature indicates that denitrification rates are depressed at a pH below 6 and above 8.⁶ Therefore, the value of 8.5 for pH inhibition is consistent with other literatures.

One could test this hypothesis by holding the pH within a FBBR to <8.5 and comparing the nitrate profile predicted by the Modified Monod Model with the actual nitrate concentrations along the length of the bioreactor. This was done in a 10-cm-diam., 12-m- high bioreactor that operated at ORNL during 1986. The operating conditions for this bioreactor were similar to those listed for the previous bioreactors. During a period from April-May 1986, this reactor was operated with the actual wastewaters from the Fernald Feed Materials Production Center. The Fernald wastewater

AVERAGE pH VERSUS REACTOR HEIGHT

Col 1, 10-cm-diam x 6-m high

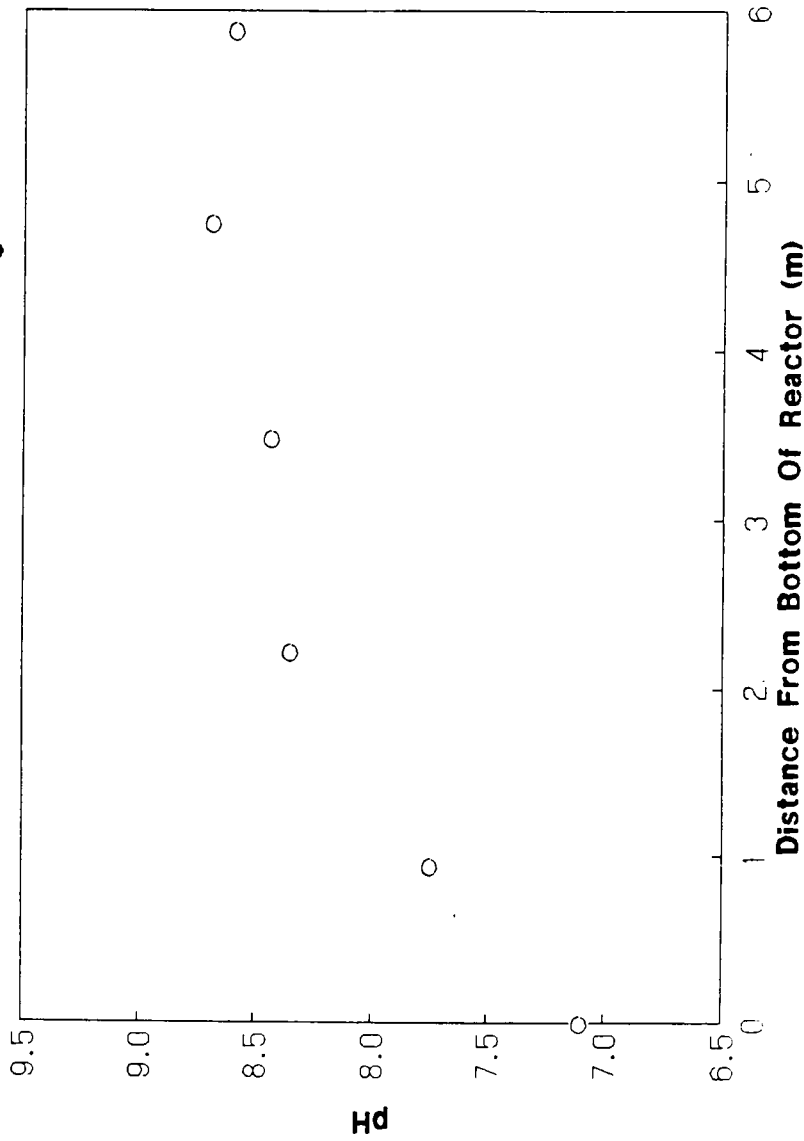


Fig. 30. Typical pH profile taken from the operation of the 10-cm-diam, . 6-m-high FBFR which operated at ORNL from September through December 1985.

had a buffering capacity which prevented the pH within the bioreactor from climbing as rapidly as it did when synthetic wastewater was used. Also during this period acid was slowly injected at various points along the reactor height. With the combined effect of these two events the pH within the 12-m-high bioreactor was held under 8.3, whereas in the typical operation with a synthetic wastewater the pH usually climbed to ~9 within a 6-m-high bioreactor.

The pH profile for this period of operation with the 10-cm-diam., 12-m-high FBBR is presented in Fig. 31. The nitrate concentration as a function of reactor height, along with the nitrate profile predicted by the Modified Monod Model, is presented in Fig. 32. As can be seen, the Modified Monod Model represents the experimental data very well along the entire length of the bioreactor as long as the pH within the bioreactor is kept between 6.8 and 8.5.

The final item necessary for completion of this mathematical model is to include the effects of inhibition. Inhibition occurs when a chemical species acts to reduce the rate of an enzymatically-catalyzed reaction by binding with either the free enzyme or the enzyme-substrate complex. By reducing the rate of one reaction in a long series of reactions necessary for life, small quantities of inhibitors can effectively alter the rate of substrate utilization by microorganisms.

AVERAGE pH VS. REACTOR HEIGHT

12-METER-HIGH BIOREACTOR

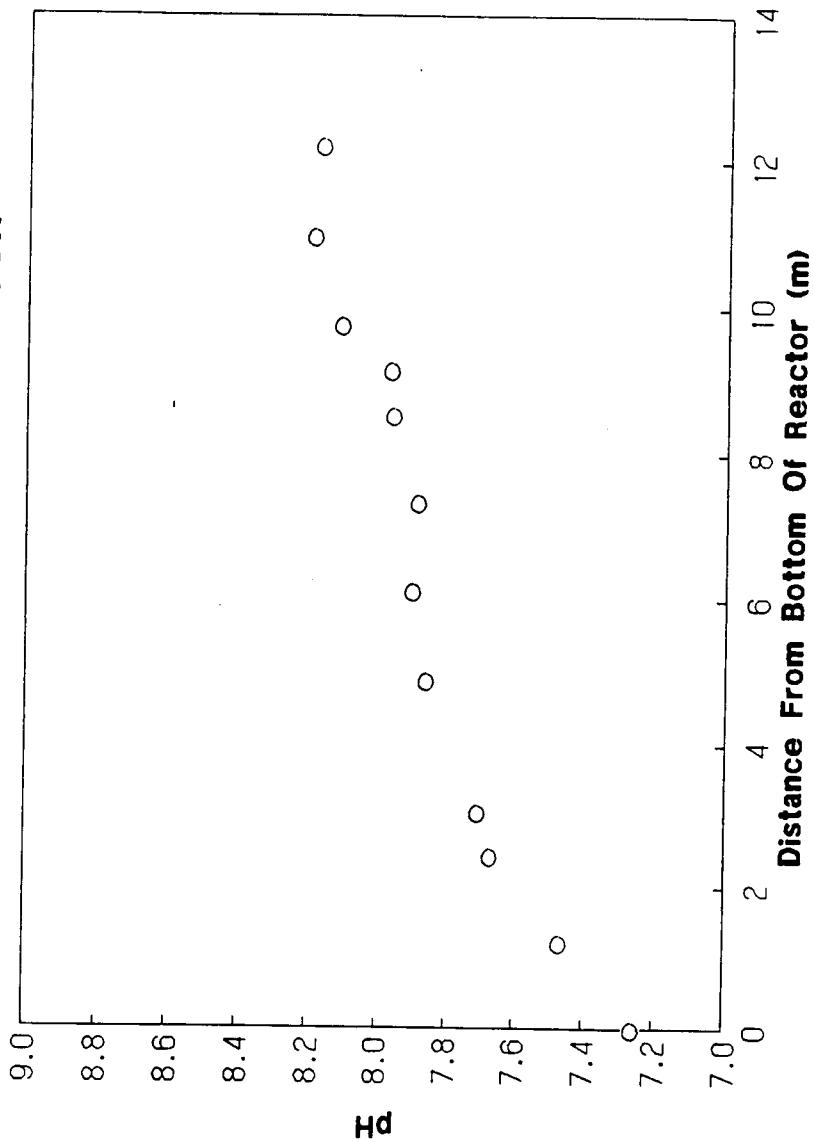


Fig. 31. Typical pH profile taken from the operation of a 10-cm-diam., 12-m-high FBRR, during a period in April through May 1986, when the pH in the reactor was kept below 8.3.

NITRATE CONCENTRATION VS HEIGHT 12-METER-HIGH BIOREACTOR

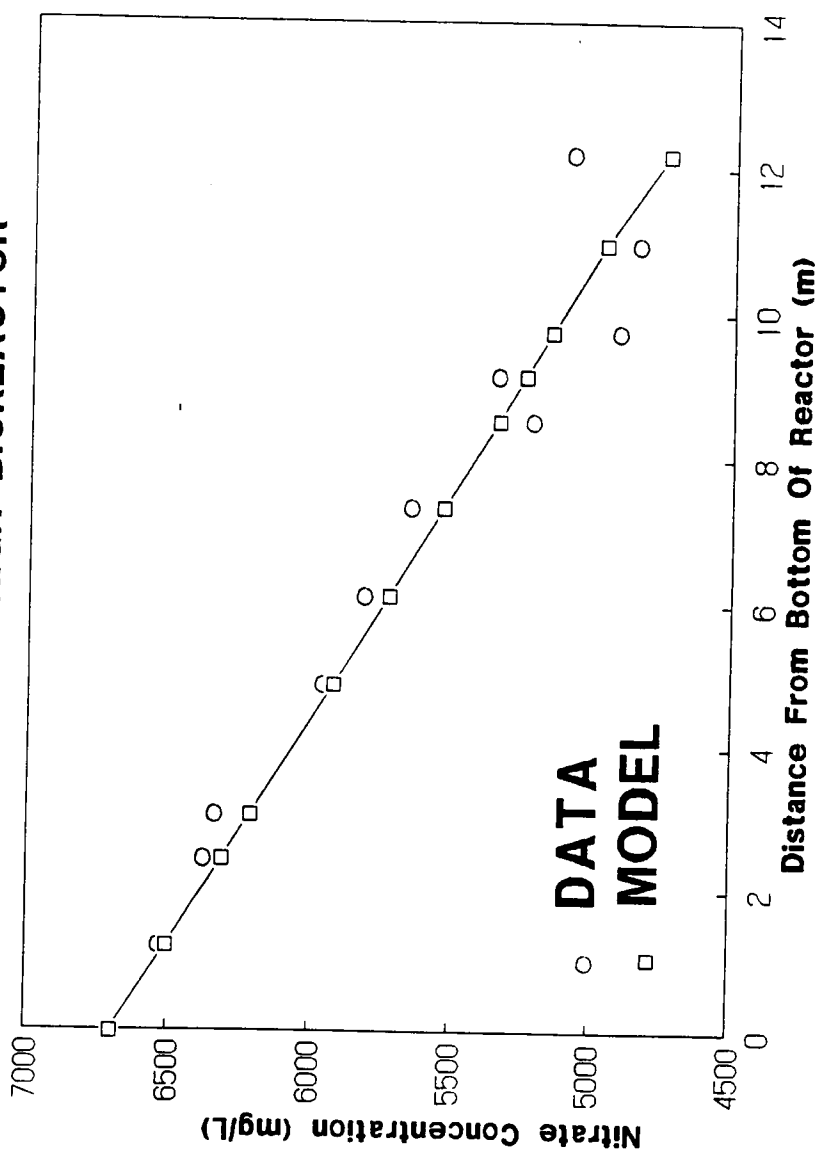


Fig. 32. Comparison of the nitrate profile taken during the operation of 10-cm-diam., 12-m-high reactor during April and May, 1986, with the Modified Monod Model.

Inhibitors are generally classified as competitive or noncompetitive. A competitive inhibitor binds at the same active site as the substrate and therefore competes with the substrate for a site on the enzyme. The effect of a competitive inhibitor can be countered or reversed by increasing the substrate concentration. A noncompetitive inhibitor renders the enzyme or enzyme-complex inactive; therefore, increasing the substrate concentration cannot produce as great a substrate utilization rate as with the uninhibited enzyme.

In Figs. 26-29, it can be seen that as the inlet substrate (nitrate) concentration is increased from 2700 to 9500 mg/L the effect of the inhibitor is not countered or reversed as would be expected with a competitive inhibitor. It is therefore reasonable to assume that the hydroxide ions (pH) are acting as a noncompetitive inhibitor. The Monod equation is typically modified as follows to account for noncompetitive inhibition:³³

$$R = \left(\frac{k_A S}{K_S + S} \right) \left(\frac{1}{1 + I_i/K_i} \right) \quad (45)$$

where I_i = the concentration of inhibitor and K_i = the inhibition constant.

The Monod Model With Inhibition, using different values of K_i , was compared with the experimental data taken during the operation of the 10-cm-diam., 6-m-high bioreactor which operated from September - December, 1985 and the 10-cm-diam., 12-m-high bioreactor, during the operation in

1986, when the pH within the bioreactor was held under 8.5. The data were best represented by the Monod Model With Inhibition with $K_i = 10^{-5}$. The results for $K_i = 10^{-5}$ are presented in Figs. 33-36 for the 6-m-high bioreactor and in Fig. 37 for the 12-m-high bioreactor. The results for the Modified Monod Model (without inhibition) are also presented in these figures for comparison. In Figs. 33-36, both the model with inhibition and without inhibition fit the experimental data well as long as the pH within the bioreactor is < 8.5 . As the pH climbs above ~ 8.5 the model with inhibition continues to fit the experimental data while the model without inhibition deviates from the experimental data. In Fig. 37, with the pH in the reactor kept below 8.5, both the model with and without inhibition fit the experimental data well along the entire height of the bioreactor.

The above comparisons (Figs. 33-37) indicate that if the pH remains below 8.5 (and above ~ 6.8) the substrate utilization rate remains essentially constant. As the pH climbs above ~ 8.5 some fundamental change occurs within the bioreactor which limits the rate of substrate utilization. This rate change is independent of substrate concentration and reactor height. The experimental evidence is consistent with the hypothesis that the change in substrate utilization rate is a result of pH/hydroxide inhibition. The Monod Model With Inhibition represents the operational data from both the 10-cm-diam. x 6-m-high FBBR and the 10-cm-diam. x 12-m-high FBBR very well.

MONOD KINETICS

10-CM-DIAM X 6-M-HIGH FBRR

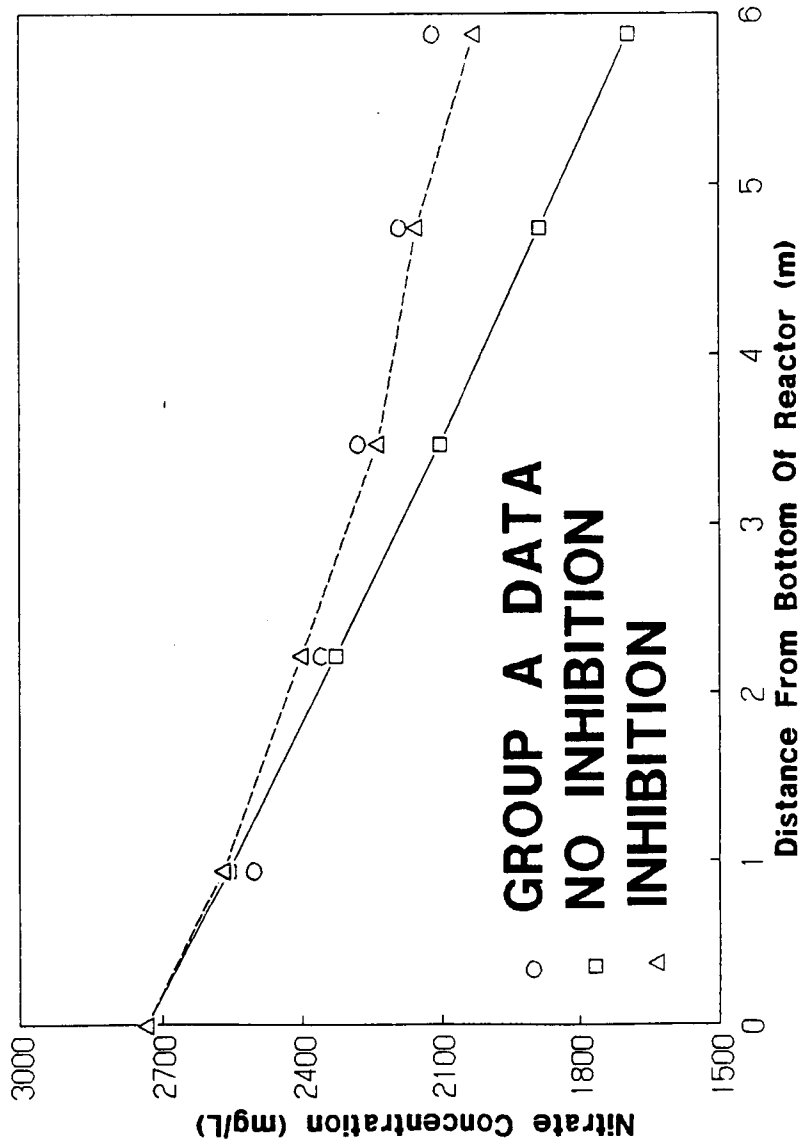


Fig. 33. Comparison of the Monod Model, with and without inhibition, with Group A data taken from the operation of the 6-m-high ORNL FBRR.

MONOD KINETICS

10-CM-DIAM X 6-M-HIGH FBFR

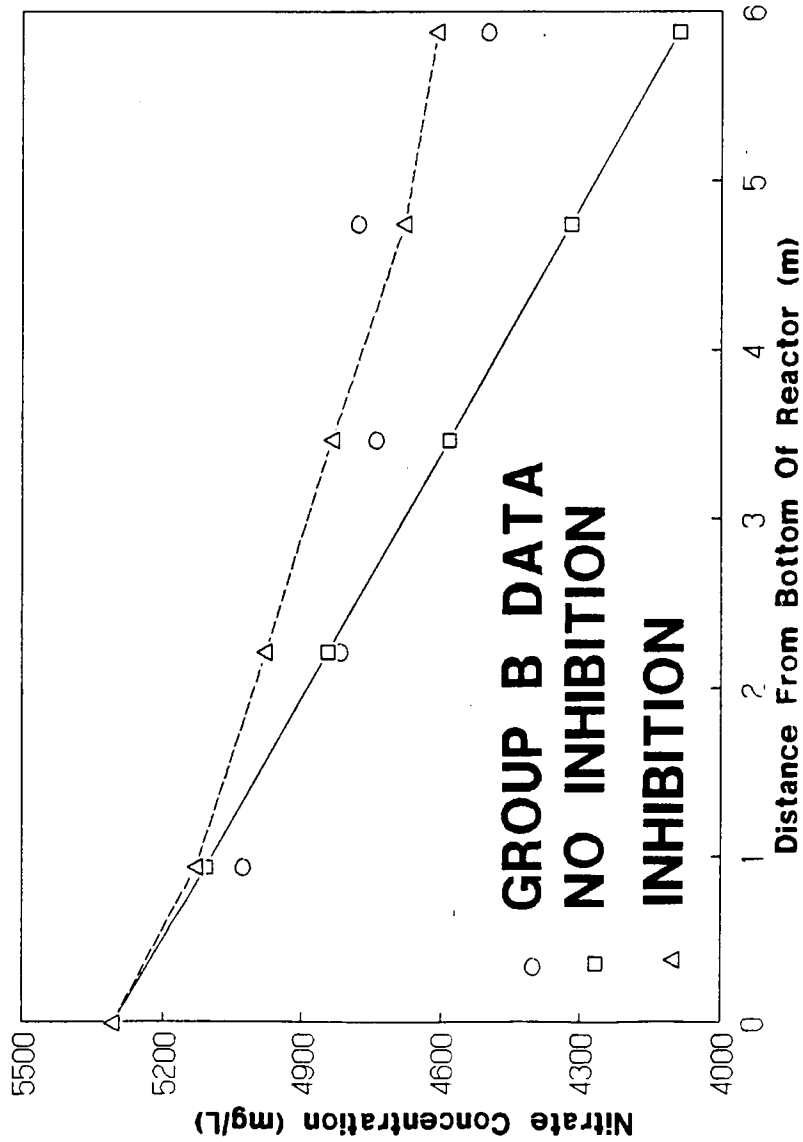


Fig. 34. Comparison of the Monod Model, with and without inhibition, with Group B data taken from the operation of the 6-m-high ORNL FBFR.

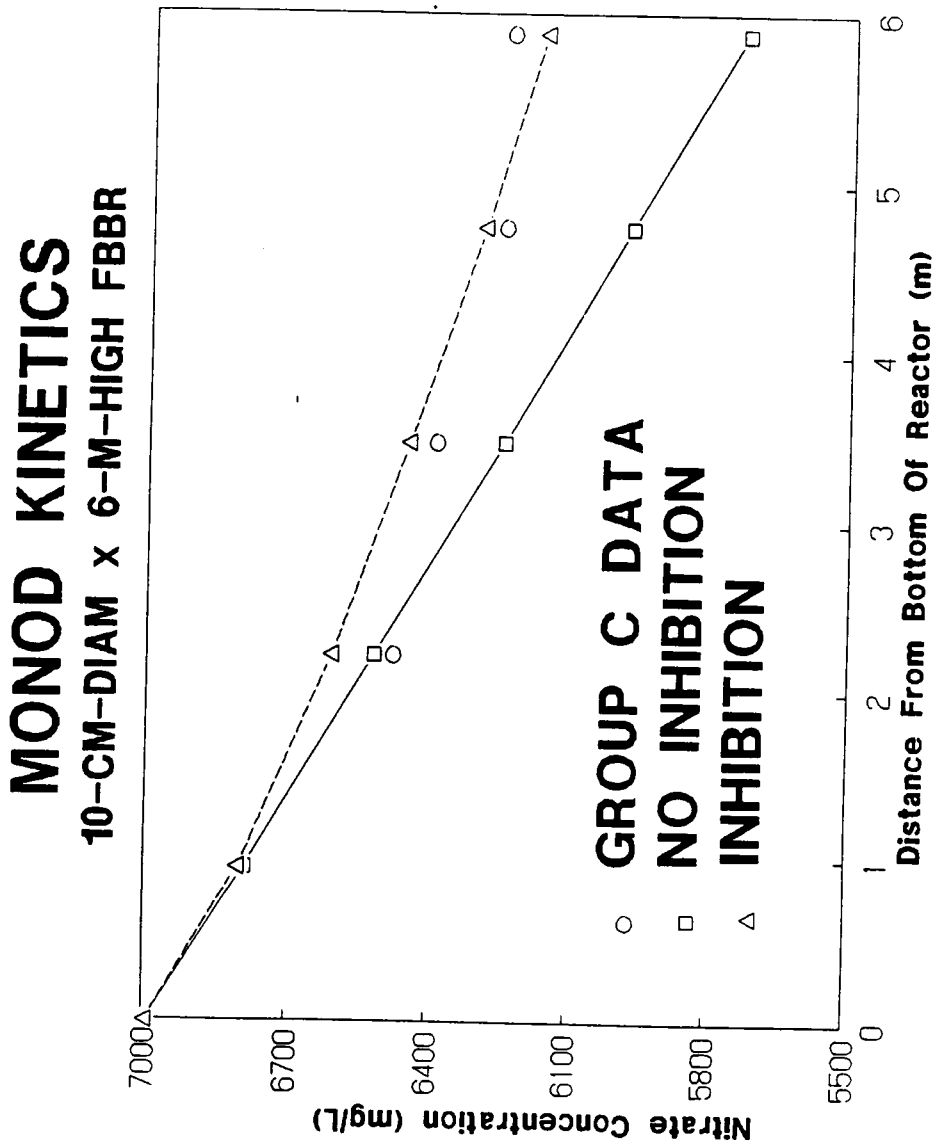


Fig. 35. Comparison of the Monod Model, with and without inhibition, with Group C data taken from the operation of the 6-m-high ORNL FBRR.

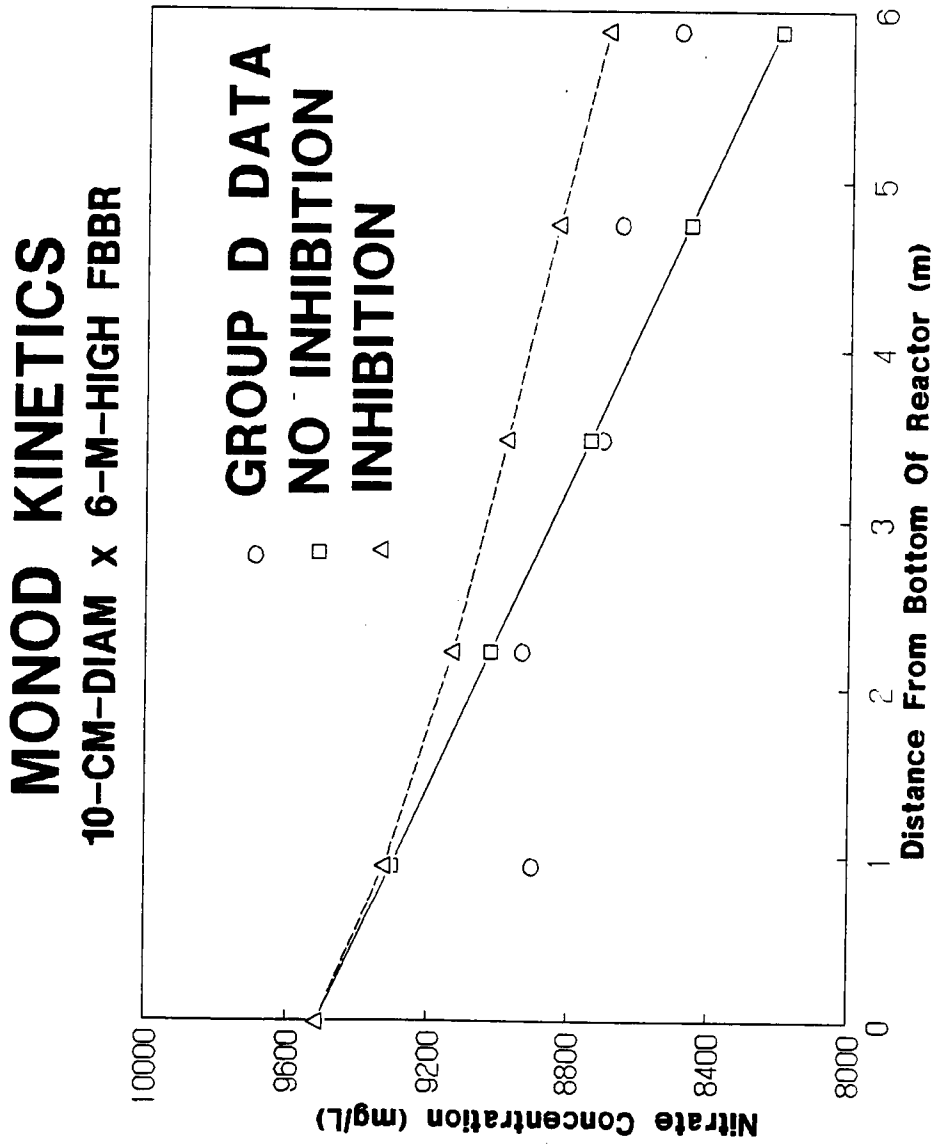


Fig. 36. Comparison of the Monod Model, with and without inhibition, with Group D data taken from the operation of the 6-m-high ORNL FBRR.

NITRATE CONCENTRATION VERSUS HEIGHT **10-CM-DIAM X 12-M-HIGH BIOREACTOR**

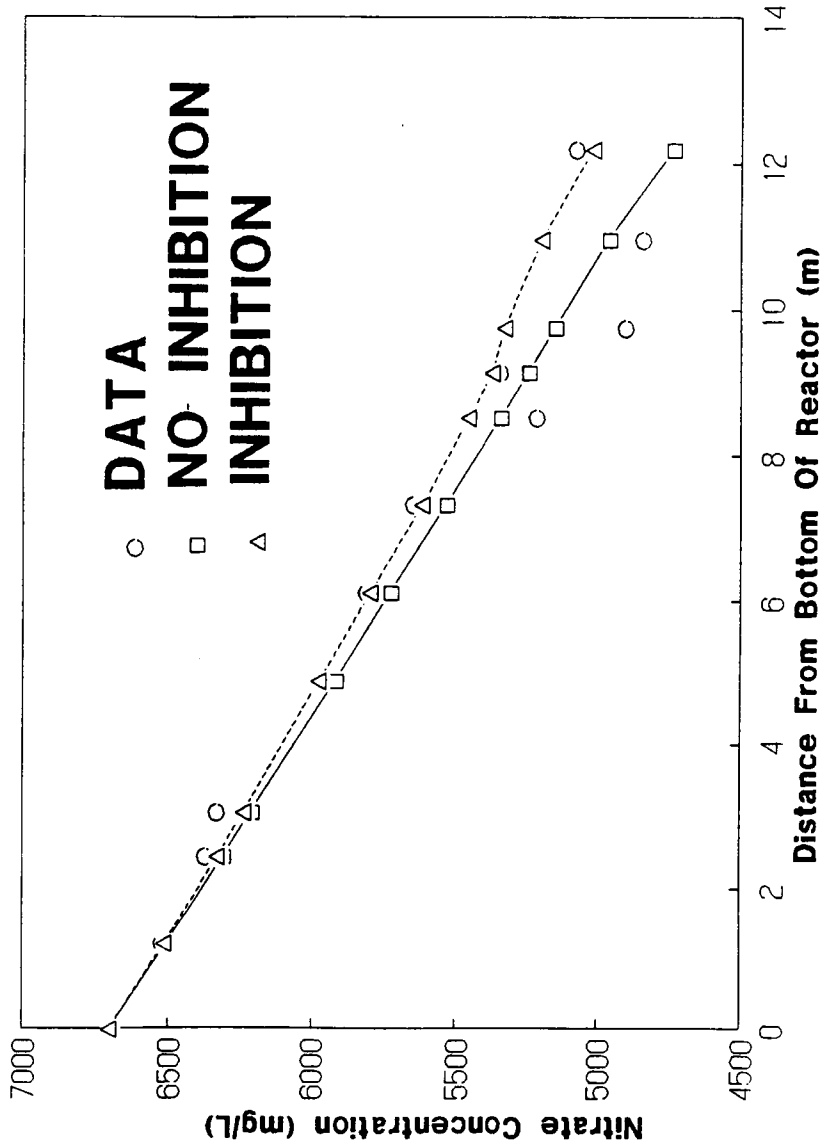


Fig. 37. Comparison of the Monod Model, with and without inhibition, with Group A data taken from the operation of the 12-m-high ORNL FBFR.

6. SUMMARY

Two steady-state kinetic models were developed and compared with operational data from several different FBBRs that operated at ORNL from 1980 to 1986. These FBBRs covered a large range of inlet nitrate concentrations (500 to 10,000 mg/L), different carbon sources (ethanol, methanol, and acetate), and different reactor sizes (10 to 50-cm-diam., 6 to 12-m-height). All other operational parameters were similar.

The first of these two models coupled zero-order reaction kinetics and plug-flow hydraulic transport. The resulting model predicted a linear relationship between nitrate concentration and reactor height at high nitrate concentrations (>50 mg/L). At lower nitrate concentrations the square root of the nitrate concentration was proportional to the reactor height. When compared with operational data from FBBRs operated at ORNL the Zero-Order Model agreed well at high nitrate concentrations as described by the linear equation; however, the model did not agree well at the lower nitrate concentrations. For the majority of cases the FBBRs at ORNL were operated at inlet nitrate concentrations too high for the square root dependence to be observed (i.e., the nitrate concentration from the exit of the reactor was >50 mg/L).

The second model coupled Monod reaction kinetics and plug-flow hydraulic transport. When compared with operational data taken from the FBBRs at ORNL, it was found that this Monod Model, with $k_A = 795$ mg/(L·min) and $K_S = 800$ mg/L, agreed well with the operational

data if the pH within the FBBR did not rise above ~8.2. If the pH in the reactor rose above ~8.2, the two constants in the Monod rate equation, K_S and k_A , were not sufficient to model the operational data.

At pH above 8.2, the hydroxide ions present in the reactor are believed to act to inhibit the denitrification process. The addition of a term for noncompetitive inhibition to the Monod rate equation was used to account for the hydroxide inhibition. The Monod Model With Inhibition was compared with operational data from ORNL FBBRs at inlet nitrate concentrations up to ~10,000 mg/L and at pH ranges within the FBBRs from ~6.5 to 9. The Monod Model With Inhibition agreed well with the operational data from these FBBRs.

This study indicates that a model combining Monod kinetics with a noncompetitive inhibition term in the Biofilm Model and plug-flow in the Reactor Flow Model can be successfully used to predict the nitrate concentration as a function of axial position within FBBRs of different heights and diameters. This model is applicable to inlet reactor concentrations up to ~10,000 mg/L and to pH values within the reactor ranging from ~6.5 to 9. The model was not tested outside of these limits.

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VITA

Joseph F. Walker, Jr. was born in Hampton, South Carolina on August 10, 1954. He attended elementary school in Barnwell, South Carolina and graduated from Barnwell High School in May 1973. The following September he entered the University of South Carolina. He received a Bachelor of Science Degree in Biology in May 1977 and a Bachelor of Science Degree in Chemical Engineering in May 1980. In June 1980 he accepted a position in the Chemical Technology Division of Oak Ridge National Laboratory. In the fall of 1981 he enrolled at the University of Tennessee and began study toward a Master's degree while still a full-time employee at Oak Ridge National Laboratory. He received his Master of Science Degree in Chemical Engineering in December 1989. Mr. Walker will continue his employment with Oak Ridge National Laboratory after receiving his Master's degree.