THE ACTIVATED SLUDGE PROCESS—3

SINGLE SLUDGE DENITRIFICATION

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Abstract—The general aerobic bi-substrate active-site death-regeneration activated sludge model including nitrification of Dold et al. (Prog. Wat. Technol. 12, 47–77, 1980) is extended to include the kinetic behaviour of the denitrification process in single sludge systems. The extension requires a change in the value of only one of the kinetic constants (K'_{mp}) in the expression for the particulate substrate utilization rate when the environment becomes anoxic. The extended model simulates very closely the response of the multi-reactor nitrification–denitrification process configurations under both constant and cyclic flow and load conditions. Under constant flow and load conditions, the denitrification response predicted can be reduced to that approximated by a zero order reaction $dN/dt = -KX_a$ with two rates in the primary and one in the secondary anoxic reactor respectively.

NOMENCLATURE

a = recycle ratio

b_h = endogenous respiration rate constant for heterotrophs (mg $X_a \cdot$ mg $X_a^{-1} \cdot d^{-1}$)

b'_h = death rate constant for heterotrophs (mg $X_a \cdot$ mg $X_a^{-1} \cdot d^{-1}$)

b_n = death rate constant for nitrifiers (mg $X_n \cdot$ mg $X_n^{-1} \cdot d^{-1}$)

f = inert residue fraction in endogenous respiration approach (mg VSS $\cdot$ mg VSS^{-1})
= 0.2

f' = inert residue fraction in death regeneration approach (mg VSS $\cdot$ mg VSS^{-1})

f_{ca} = ratio easily biodegradable (S_{bsi}): total biodegradable (S_{bi}) COD concentration in influent (mg COD $\cdot$ mg COD^{-1})

f_n = nitrogen/VSS ratio in sludge
= 0.1 mg NH$_3$–N $\cdot$ mg VSS^{-1}

f_{us} = unbiodegradable soluble COD fraction in influent (mg COD $\cdot$ mg COD^{-1})

f_{up} = unbiodegradable particulate COD fraction in influent (mg VSS $\cdot$ mg COD^{-1})

t = time (d or h)

t_p = duration of primary phase in a pre-denitrification reactor (h)

A = specific rate of utilization of easily biodegradable material (mg COD $\cdot$ mg $X_a^{-1} \cdot d^{-1}$)

B = specific rate of adsorption of slowly biodegradable material (mg COD $\cdot$ mg $X_a^{-1} \cdot d^{-1}$)

C = specific rate of utilization of stored biodegradable material (mg COD $\cdot$ mg $X_a^{-1} \cdot d^{-1}$)

D = specific rate of release of COD due to lysis (mg COD $\cdot$ mg $X_a^{-1} \cdot d^{-1}$)

E = specific rate of utilization of ammonia for nitrification (mg NH$_3$–N $\cdot$ mg $X_n^{-1} \cdot d^{-1}$)

F = specific death rate of nitrifiers (mg $X_n \cdot$ mg $X_n^{-1} \cdot d^{-1}$)

K = denitrification rate constant (mg NO$_3$–N $\cdot$ mg VSS$^{-1} \cdot$ h^{-1})

K_1 = denitrification rate constant in primary phase (mg NO$_3$–N $\cdot$ mg $X_a^{-1} \cdot$ h^{-1})

K_2 = denitrification rate constant in secondary phase (mg NO$_3$–N $\cdot$ mg $X_a^{-1} \cdot$ h^{-1})

K_3 = denitrification rate constant in post denitrification reactor (mg NO$_3$–N $\cdot$ mg $X_a^{-1} \cdot$ h^{-1})

K_a = specific adsorption rate constant (l mg $X_a^{-1} \cdot d^{-1}$)

K_m = maximum specific utilization constant (mg COD $\cdot$ mg $X_a^{-1} \cdot d^{-1}$)

K_n = Monod half saturation concentration for nitrification (mg NH$_3$–N $\cdot$ l^{-1})

K_s = Monod half saturation concentration for biodegradable organic material (mg COD $\cdot$ l^{-1})

N_a = ammonia concentration (mg N $\cdot$ l^{-1})

N_n = nitrate concentration (mg N $\cdot$ l^{-1})

O_c = oxygen uptake rate for carbonaceous energy removal (mg O $\cdot$ l$^{-1} \cdot$ h^{-1})

O_n = oxygen uptake rate for nitrification (mg O $\cdot$ l$^{-1} \cdot$ h^{-1})

O_t = total oxygen uptake rate (mg O $\cdot$ l$^{-1} \cdot$ h^{-1})

P = COD/VSS ratio (mg COD $\cdot$ mg VSS^{-1})

R = nominal reactor retention time (h or d)

R_a = actual retention time (h or d)

R_h = hydraulic retention time (h or d)

R_s = sludge age (d)

S = general parameter for COD concentration (mg COD $\cdot$ l^{-1})

S_b = biodegradable COD concentration (mg COD $\cdot$ l^{-1})

S_t = total COD concentration (mg COD $\cdot$ l^{-1})

T = temperature

X = general parameter for sludge concentration (mg VSS $\cdot$ l^{-1})

X_a = active sludge concentration (mg VSS $\cdot$ l^{-1})

X_e = concentration of endogenous residue (mg VSS $\cdot$ l^{-1})

X_n = concentration of nitrifiers (mg VSS $\cdot$ l^{-1})

X_s = concentration of stored material (mg VSS $\cdot$ l^{-1})

Y_h = yield coefficient for heterotrophs (mg VSS $\cdot$ mg COD^{-1})

Y_n = yield coefficient for nitrifiers (mg $X_n \cdot$ mg NH$_3$–N^{-1})

α = proportionality constant

ΔN = nitrogen requirement for sludge synthesis (mg N $\cdot$ l^{-1})

ΔN_a = reactor nitrate removal (mg NO$_3$–N $\cdot$ l^{-1})

ΔN_s = system nitrate removal (mg NO$_3$–N $\cdot$ l^{-1})

μ_{nm} = maximum specific growth rate of nitrifiers (mg $X_n \cdot$ mg $X_n^{-1} \cdot d^{-1}$)

θ = Arrhenius temperature dependency coefficient

INTRODUCTION

In the single sludge nitrification–denitrification process organic material in the influent is utilized as electron donor in the denitrification reaction. Procedures for determining the mass of nitrogen removed have been, in the main, empirically based. One approach has been to model the observed denitrification response as one additional to and largely independent of the aerobic response—the aerobic phase produces the volatile mass which in turn is accepted as the basic parameter in formulating the denitrification phase. Under constant flow and load conditions development of this approach has resulted in a remarkable close description of the denitrification behaviour. However when flow and load varies daily cyclically this empirical approach has failed completely—an approach taking cognisance of the basic kinetics governing the system is needed.

Modelling of nitrification–denitrification systems has been limited to the 3 and 2 sludge systems. In the 3 sludge system complete separation of the respective carbonaceous energy removal, nitrification and denitrification phases is achieved by having 3 separate reactor systems with settlers in series, 1 for each phase. In the 2 sludge system the energy removal and nitrification phases take place in 1 reactor and that of denitrification in a second. Modelling of energy removal and nitrification in one reactor has not presented any serious difficulties, the reason for this is that the 2 reactions are mediated by two entirely different groups of organisms—the auto-trophic nitrifiers and heterotrophic energy removers. Their respective kinetic behaviour can be modelled virtually independently of each other; the process response of the two are linked only insofar as the reactor and the process parameters (sludge age, temperature) are common to both, and that ammonia is abstracted from the wastewater for growth by both groups of organisms.

In both the 3 and 2 sludge systems the denitrification phase is entirely divorced from the preceding energy removal and nitrification phases. The only common feature is the nitrate in the effluent/influent flow link. The denitrification reactor develops its own sludge mass under very specific conditions—a simple soluble easily biodegradable energy source is added to the reactor in which nitrate is the sole electron acceptor. Consequently, the denitrification reactor organism mass also is very specific. The denitrification process in the denitrification reactor has been successfully

modelled by Stensel *et al.* (1973) on lines very similar to the activated sludge model of Lawrence & McCarty (1970).

In the single sludge process the same mass of sludge accomplishes aerobic energy removal, nitrification and denitrification. Nitrification and denitrification is achieved either by imposing sequentially anoxic and aerobic conditions on the mixed liquor in a single reactor, or, by having a minimum of 2 reactors of which one is maintained anoxic and the other aerobic and recycling the sludge between the 2 reactors.

Modelling of the single sludge process requires description of a complex system of intereacting reactions: energy removal for heterotrophic growth takes place from the same substrate source under both aerobic and anoxic (denitrification) conditions by the same organism mass, i.e. the same organism mass must react alternately to oxygen and nitrate as electron acceptors; nitrification is affected by anoxic conditions in that growth of nitrifiers can take place only in an aerobic environment, but endogenous respiration takes place under both aerobic and anoxic conditions. The main problem area however is the behaviour of the heterotrophic organisms under alternating anoxic and aerobic conditions. Despite the complexity of the behaviour of the single sludge nitrification–denitrification process, because denitrification, like aerobic energy removal, is mediated by heterotrophic facultative organisms, one can hypothesise that modelling of their respective behaviour under sequential aerobic–anoxic conditions should not be qualitatively dissimilar even though quantitatively their response may differ. In this paper it will be shown that in the single sludge nitrification–denitrification process when the organisms are in the anoxic phase it is necessary to change the value of only one of the kinetic constants in order to model the nitrification–denitrification single sludge system in terms of the bi-substrate active-site death-regeneration model of Dold *et al.* (1980).

NITROGEN REMOVAL IN THE ACTIVATED SLUDGE PROCESS

In municipal wastewaters nitrogen is present principally in the form of amino compounds (organic nitrogen) and ammonia. In the activated sludge process nitrogen is removed wholly or partially from the wastewater by biological activities of the microorganisms, through (1) incorporation into the sludge, and (2) reduction of nitrate (or nitrite) to nitrogen gas when nitrate (or nitrite) serves as electron acceptor.

Nitrogen incorporation into the sludge mass

Fractions of the influent nitrogen mass are removed by incorporation into the active bio-mass, endogenous residue mass generated, and inert organic particulate mass in the influent enmeshed in the sludge mass, respectively. In terms of the synthesis-endogenous respiration kinetic theory for the activated sludge pro-

cess, Marais & Ekama (1976) developed the following equation to determine the concentration of nitrogen removed from the influent flow under constant flow and load conditions:
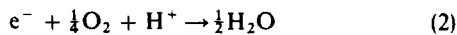
$$\Delta N = f_n \cdot \left[\frac{Y_h(1 + f \cdot b_{hT} \cdot R_s)}{1 + b_{hT} \cdot R_s} \right.$$

$$\left. \times (1 - f_{us} - P \cdot f_{up}) + f_{up} \right] S_{ti}. \quad (1)$$

From equation (1), for sludge ages longer than 10 days the concentration of influent nitrogen removed per mg influent COD ($\Delta N/S_{ti}$) is less than 0.03. Raw domestic sewage generally has a TKN/S_{ti} ratio of 0.07–0.10; it follows that only a minor part of the influent nitrogen is removed by incorporation in the sludge (20–30%).
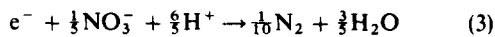
Nitrogen removal by reduction of nitrate

This biochemical reaction is known as dissimilative reduction of nitrogen or denitrification and involves the reduction of nitrate or nitrite, present in the wastewater, to gaseous nitrogen which escapes to the atmosphere. The removal of nitrogen is a consequence of biological redox reactions wherein biodegradable organic material serves as electron donor and nitrate or nitrite serves the same function as oxygen, i.e. as electron acceptor. The equivalence is evident in the following half-reactions:
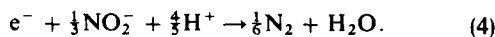
Oxygen

$$e^- + \tfrac{1}{4}O_2 + H^+ \rightarrow \tfrac{1}{2}H_2O \quad (2)$$

Nitrate

$$e^- + \tfrac{1}{5}NO_3^- + \tfrac{6}{5}H^+ \rightarrow \tfrac{1}{10}N_2 + \tfrac{3}{5}H_2O \quad (3)$$

Nitrite

$$e^- + \tfrac{1}{3}NO_2^- + \tfrac{4}{3}H^+ \rightarrow \tfrac{1}{6}N_2 + H_2O. \quad (4)$$

In transferring electrons from the organic material to the electron acceptor (oxygen, nitrate or nitrite) there are approximately equal changes of free energy per electron transferred irrespective of the donor or acceptor (McCarty, 1964)*. From equations (2) and (3) it can be noted that the transfer of 1 electron equivalent involves the reduction of $\tfrac{1}{4}$ mol of oxygen, or $\tfrac{1}{5}$ mol of nitrate, i.e. $\tfrac{32}{4}$ g $O_2 \equiv \tfrac{14}{5}$ g NO_3-N, or, 1 mg NO_3-N $\equiv 2.86$ mg O_2 (or COD). Nitrite usually is present only in insignificant amounts in nitrification–denitrification systems and will not be considered further.

Nitrate readily replaces oxygen as electron acceptor because the pathway for the transfer of electrons from

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* This is the basis of the COD test as a means for estimating free energy change in terms of oxygen.

† An environment wherein neither oxygen nor nitrate is present is called anaerobic. Differentiation between anoxic and anaerobic states is necessary because the establishment of an anaerobic state is one of the necessary (but not sufficient) prerequisites for inducing excess biological uptake of phosphorus.

the organic substrate to the final electron acceptor is similar (Christensen & Harremoës, 1972), but the presence of dissolved oxygen acts as a strong inhibitor on denitrification as it prevents the formation of the enzyme necessary for the final electron transfer to nitrate (Chong & Morris, 1962).

From the above it can be concluded that there are 4 conditions that are necessary for denitrification:

1. Presence of nitrate
2. Absence of dissolved oxygen
3. Bacterial mass that can accept nitrate and oxygen as electron acceptor
4. Presence of a suitable electron donor (energy source).

With regard to (1), in the treatment of municipal wastes, the presence of nitrate implies that nitrification is a prerequisite for denitrification. With regard to (2) and (3), an environment that satisfies both is called anoxic†. With regard to (3), the ability to denitrify is widespread among bacteria; dissimilative denitrification with end products N_2, NO and NO_2 has been established in numerous cases (Christensen & Harremoës, 1977). The bulk of the bacterial mass in wastewater treatment systems is facultative and a significant fraction is capable of dissimilative denitrification. With regard to (4), a variety of carbonaceous organic substances have been investigated as energy sources for denitrification; these can be categorized as follows:

(a) Energy source not present in wastewater, i.e. an external carbonaceous energy source (e.g. methanol).

(b) Energy source present in the influent wastewater, i.e. internal (influent) energy source.

(c) Energy source generated within the system by the release of substrate by organisms death and lysis, i.e. self-generated energy source.

The external energy source is associated with the 2 and 3 sludge systems, wherein the energy source is added at the denitrification stage. Internal and self-generated energy sources are associated with the single sludge nitrification–denitrification system, wherein the same biological mass is placed alternately in anoxic and aerobic environments. Only the single sludge nitrification–denitrification system will be discussed in this paper.

Process configurations

There are two basic configurations for the single sludge nitrification–denitrification system depending on the type of energy source, i.e. (1) internal or (2) self-generated.

(1) *Internal (influent) energy source.* Ludzack & Ettinger (1962) were first to propose a process configuration utilizing the biodegradable material in the influent as the main energy source for denitrification. Their configuration is given in Fig. 1(a). The anoxic reactor is in partial communication with the aerobic
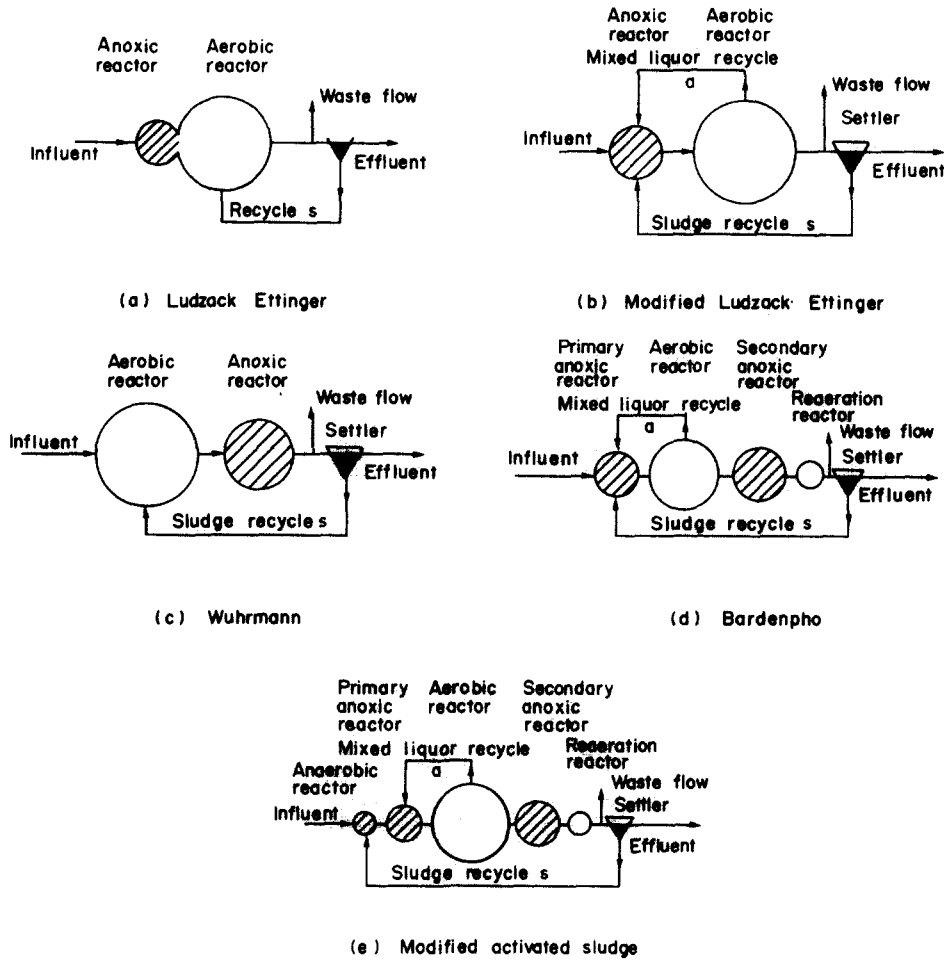
Fig. 1. Single sludge nitrification–denitrification activated sludge process configurations. (a) Ludzack Ettinger: (b) Modified Ludzack Ettinger: (c) Wuhrmann: (d) Bardenpho: (e) Modified activated sludge.

reactor. The influent is discharged to the anoxic reactor and the underflow recycle from the settling tank is discharged to the aerobic reactor. Nitrification takes place in the aerobic reactor and nitrified mixed liquor is cycled to the anoxic reactor in a rather indeterminate fashion by the mixing action in the two reactors. As a consequence the denitrification performance of the process is very variable.

Barnard (1973) in developing the Bardenpho system proposed (1) complete separation of the anoxic reactor (also called the pre-denitrification reactor). and (2) the introduction of controlled recycle from the aerobic to the anoxic reactor and (3) discharge of the underflow recycle to the anoxic reactor (Fig. 1b). We can apply this modification to the Ludzack–Ettinger system and for identification call the process the Modified Ludzack–Ettinger (MLE) process. Compared with the original process the modified process has given improved and more consistent performance.

The MLE process cannot reduce the effluent nitrate concentration to zero because the net concentration of nitrate established in the aerobic reactor (under the concentrations generated in that reactor and removed

by the denitrification recycles) is the source for both the recycle and the effluent flows.

(2) Self-generated energy source. The nitrification–denitrification configuration in which endogenous death and lysis provides the energy for denitrification was first proposed by Wuhrmann (1964). A schematic representation of this process is shown in Fig. 1(c). The first reactor, which is aerobic, receives the influent flow and sludge return flow from the settling tank; nitrification of the influent TKN occurs in this reactor. The contents of the aerobic reactor discharge to the anoxic reactor (also called the post-denitrification reactor) where denitrification takes place.

The rate of energy release due to organism death and lysis is low, resulting in a low rate of denitrification. Hence a high degree of denitrification requires a large anoxic sludge mass fraction, but experience has shown that this may affect the nitrification efficiency of the process: the nitrifiers are obligate aerobes, consequently they can multiply only in the aerobic zone of the process. If the organism retention time in the aerobic zone is too short, the nitrifiers cannot reproduce and nitrification ceases. Therefore, in a design it

is possible that, in order to obtain complete denitrification, the required anoxic sludge fraction is so great that nitrification does not take place. Usually for any sludge age the nitrification requirement places a lower limit on the aerobic mass fraction and thereby, an upper limit on the anoxic sludge mass fraction; the latter in turn places a limit on the mass of nitrate that can be denitrified.

The two basic configurations described above have been combined to (a) obtain higher denitrification efficiencies, or (b) create conditions necessary for luxury uptake of phosphorus.

(a) Barnard (1973) proposed combining the MLE and Wuhrmann configurations to obtain a low nitrate in the effluent, called the Bardenpho process (see Fig. 1d). He added a flash aeration reactor before the final settling tank to strip nitrogen gas bubbles from the flocs and to nitrify ammonia released in the post-denitrification reactor.

(b) In 1976 Barnard noted that enhanced biological phosphorus removal is induced if, at some point in the process, the mixed liquor is maintained in an anaerobic condition such that phosphorus is released from the organism mass. To obtain this condition efficiently an "anaerobic reactor" was included ahead of the pre-denitrification reactor to receive the influent and the underflow recycle (see Fig. 1e). Due to the relatively low mass of nitrate in the underflow recycle it was hypothesized that the capacity for denitrification of the anaerobic reactor will be greater than the mass of nitrate introduced and hence anaerobic conditions sufficient to cause release of phosphorus will be assured. This configuration is called the Phoredox system.

The design of these processes has been largely empirical, based on pilot plant behaviour. The problem with this approach is that, because the basic mechanisms are not quantitatively delineated, it is almost impossible to predict the denitrification behaviour once the temperatures, sludge ages or sewage characteristics differ from those in the pilot plant investigation. For this reason a wide-ranging experimental investigation was initiated to enquire if there is a basic pattern of behaviour that does allow a general design approach.

EXPERIMENTALLY BASED DENITRIFICATION MODEL

Carlson (1971) and Christensen & Harremoes (1972) suggested that the kinetic reaction describing denitrification by the activated sludge mixed liquor can be expressed by:

$$dN/dt = -KX_v \qquad (5)$$

* At all sludge ages >4 days under constant flow and load conditions the concentration of active sludge, X_a, given by equation (6) (endogenous-respiration approach) is virtually identical to the value calculated from the death-regeneration approach of Dold et al. (1980). The reason for this is that the two approaches are linearly related and give the same response once the stored biodegradable and easily biodegradable COD concentrations are negligible.

where

N = nitrate concentration, mg $(NO_3-N) \cdot l^{-1}$
(dN/dt) = denitrification rate, mg $N \cdot l^{-1} \cdot time^{-1}$
t = time in hours or days
X_v = volatile solids concentration, mg $\cdot l^{-1}$
K = specific denitrification constant, mg $N \cdot$ mg $VSS^{-1} \cdot time^{-1}$.

Equation (5) was developed from batch tests. It indicates that the nitrate-time relationship is linear and independent of the nitrate concentration, i.e. the denitrification rate is a zero order reaction with respect to the nitrate concentration, and a function only of the volatile solids concentration. Although the denitrification reaction may exhibit zero order characteristics in batch tests such a relationship does not signify a basic biological relationship. When batch experiments are done with aerobic sludge, linear oxygen time profiles are always obtained and can be described by a relationship such as equation (5), but an activated sludge theory cannot be developed only from such a behavioural pattern, as it is the consequence of a number of mechanisms operating in the process. However, it is possible that in a multi-reactor nitrification-denitrification system, the reaction in the anoxic reactors may exhibit characteristics that can be modelled empirically by a linear relationship such as equation (5). If, for example, K in equation (5) shows reasonable constancy and is independent of the influent COD in different nitrification-denitrification configurations, it would serve adequately as a design tool even though it is empirical.

Experimental background

In order to evaluate equation (5) as a basis for describing denitrification behaviour, Marais and a number of co-workers (Stern & Marais, 1974; Wilson & Marais, 1976; Marsden & Marais, 1976) undertook an extensive investigation into the kinetic behaviour of the Modified Ludzack-Ettinger and Wuhrmann systems using plug-flow régimes for the respective anoxic reactors. By sampling the nitrate concentration along the length of an anoxic plug-flow reactor the denitrification kinetic behaviour could be determined by plotting time profiles of the nitrate concentration. Experiments were carried out using only raw and settled municipal influents, over a range of sludge ages, sludge concentrations, influent COD concentrations and recycle ratios between 14 and 20°C.

Under constant flow and load conditions the nitrate concentration-retention time profiles typically exhibited shapes as indicated in Fig. 2(a) and 2(b) for pre- and post-denitrification reactors respectively. The post-denitrification profiles all exhibited a single phase linear decrease of the nitrate concentration with time, i.e. behaviour that can be described by equation (5). The pre-denitrification profiles however, all indicated a two phase denitrification response, i.e. (1) a fast primary phase of short duration (1-9 min) followed by (2) a slower secondary phase that persisted for the balance of the time in the plug-flow reactor.

Analysis of the experimental data over a range of sludge ages (10-20 days) indicated that the rate of denitrification was directly proportional to the concentration of the active fraction of the sludge, X_a, not to the total volatile sludge concentration, X_v, as suggested by Christensen & Harremoes (1972). The concentration X_a was estimated utilizing the equation proposed by Marais & Ekama (1976) (based on the synthesis-endogenous respiration approach to activated sludge kinetics) for constant flow and load conditions, i.e.

$$X_a = \frac{Y_h S_{bi}}{1 + b_{hT} R_s} \cdot \frac{R_s}{R_h} \qquad (6)*$$

where

$$b_{hT} = 0.24(1.029)^{T-20}.$$

With regard to the applicability of equation (6) to anoxic–aerobic systems, experimental data indicate that, provided the anoxic volume fraction is less than 40%, the production of sludge does not appear to be significantly different from that generated in a completely aerobic system (Stern & Marais, 1974; Heide, 1977). One can infer from this that both Y_h and b_{hT} are not significantly affected by the anoxic zone (when it is not too large) and, that organism death and lysis takes place in both the aerobic and anoxic zones.

Experimentally based model

In a plug-flow reactor in a nitrification–denitrification system, if the rate of denitrification is constant over the actual hydraulic retention time of the anoxic reactor, R_a, a denitrification rate constant can be defined by equation (5), except that X_a replaces X_v, i.e.

$$K = \Delta N_a / (R_a X_a) \qquad (7)$$

where

ΔN_a = difference between influent and effluent nitrate concentrations ($N_i - N_e$) in the plug-flow reactor.

If the rate of flow through the plug-flow reactor is $Q \cdot (1 + a)$ (where Q = average influent flow rate to the plant and a = recycle ratio) the flow passes ($a + 1$) times through the reactor and the system removal ΔN_s is given by:

$$\Delta N_s = (a + 1) \cdot \Delta N_a = (a + 1)(N_i - N_e). \qquad (8)$$

The nominal retention time R is defined by V/reactor)/Q and is related to the actual retention time, R_a, by

$$R = R_a(a + 1). \qquad (9)$$

Substituting equations (8) and (9) in equation (7):

$$\begin{aligned} K &= \Delta N_s / (R X_a) \\ &= \Delta N_a(1 + a)/(R_a(1 + a)X_a) \\ &= \Delta N_a / (R_a X_a). \end{aligned} \qquad (10)$$

Equations (7)–(9) are valid only if the nitrate is not reduced to zero somewhere before the end of the plug-flow reactor flow path. From the development of equation (10) [from equation (7)], it is evident that K is independent of the recycle ratio, a.

Considering the plug-flow post-denitrification reactor, (Fig. 2a), the conditions are identical to those stated for the formulation of equation (7) (Fig. 2b). Consequently, the system removal of nitrate, ΔN_{3x}, can be written directly,

$$\Delta N_{3x} = K_3 X_a R_3 \qquad (11)$$

where the index 3 refers to the post-denitrification reactor.

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* The value of K_3 at 20°C was determined in a completely mixed reactor.

Considering the pre-denitrification reactor (Fig. 2), equation (7) cannot be applied directly. In this reactor two rate phases are observed (Fig. 2a). In order to determine a denitrification rate constant for each phase, it was assumed that in the first phase the high rate is due to two simultaneous processes: a primary rate with a denitrification rate constant, K_1, that persists only over the period of the primary phase, t_p, and a secondary rate with a denitrification rate constant, K_2, that persists for the total time in the anoxic reactor (interrupted lines in Fig. 2a). (Later it will become evident that there is good reason for this assumption.) Consequently, the system removal ΔN_x can be expressed as:

$$\Delta N_x = \Delta N_{1x} + \Delta N_{2x}$$
$$= K_1 X_a \cdot t_p(a + 1) + K_2 X_a R_1 \qquad (12)$$

where

ΔN_{1x} = system removal due to denitrification with rate constant K_1
ΔN_{2x} = system removal due to denitrification with rate constant K_2
R_1 = nominal retention time in the pre-denitrification reactor
t_p = duration of the primary phase in h.

From numerous experimental nitrate profiles the values of K_1, K_2 and K_3 were calculated over a range of sludge ages, from 10 to 20 days, temperatures from 14 to 20°C and influent COD's from 300 to 800 mg l^{-1}. Figure 3(a) shows a statistical plot for both K_1 and K_2 at 14 and 20°C respectively, and Fig. 3(b) a plot for K_3 at 14°C ($R_x = 20$ days).

Statistical comparisons of the respective mean K_1, K_2 and K_3 values at the same temperature, but at different sludge ages for different influent COD concentrations, showed not significant differences, i.e. the K values appeared to be independent of sludge age, influent COD, sludge concentration and recycle ratios.

Temperature dependency of the mean K_1, K_2 and K_3 values respectively was formulated assuming an Arrhenius type equation:

$$K_{1T} = 0.03(1.20)^{T-20} \text{ mg N} \cdot \text{mg } X_a^{-1} \cdot \text{h}^{-1} \qquad (13)$$

$$K_{2T} = 0.0042(1.08)^{T-20} \text{ mg N} \cdot \text{mg } X_a^{-1} \cdot \text{h}^{-1} \qquad (14)$$

$$K_{3T} = 0.0033(1.03)^{T-20} \text{ mg N} \cdot \text{mg } X_a^{-1} \cdot \text{h}^{-1}.* \qquad (15)$$

The system reduction of nitrate, ΔN_{1x}, due to the reaction with rate constant, K_1, was also calculated. It was found that ΔN_{1x} is proportional to the influent biodegradable COD concentration and independent of the temperature, sludge concentration and recycle ratio (Stern & Marais, 1974).

Hence ΔN_{1x} can be formulated as

$$\Delta N_{1x} = \alpha S_{bi}. \qquad (16)$$
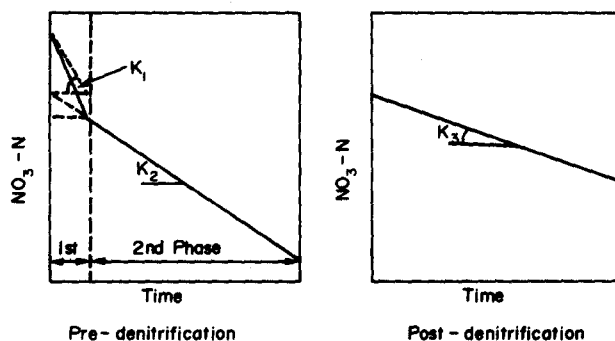

Pre-denitrification   Post-denitrification

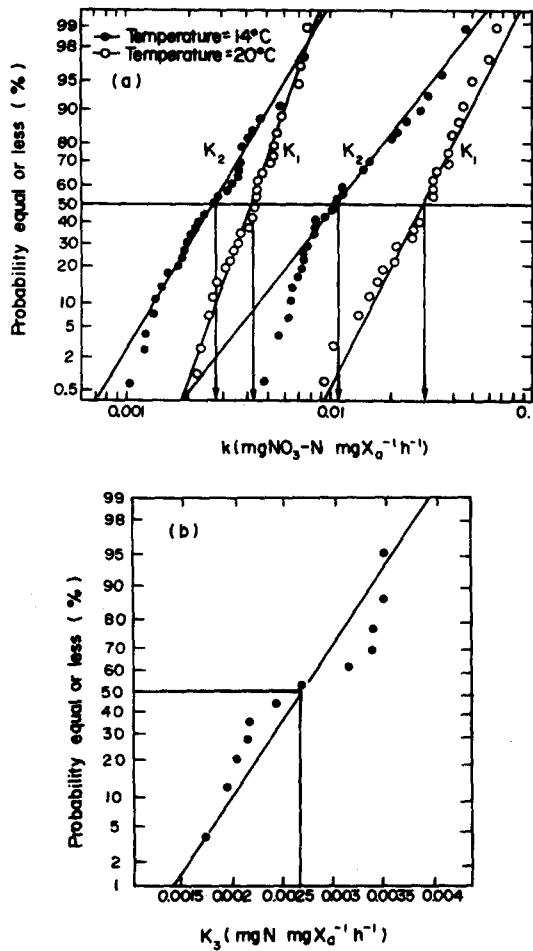Fig. 2. Typical nitrate concentration–retention time profiles in anoxic plug flow reactors.

Fig. 3. (a) Statistical plot of the denitrification rate constants K_1 and K_2 in a pre-denitrification reactor. (b) Statistical plot of the denitrification rate constant K_3 in a post-denitrification reactor.

The mean experimental value of α was found to be 0.028 mg N·mg S_{bi}^{-1}. (See Fig. 4.)

The values of K_1, K_2 and K_3 and in equations (13)–(16) are mean values. The data showed wide variation (see Fig. 3) and although the standard deviation of the mean is small, it should not be inferred that the mean has a corresponding stability; reviewing the data indicates that sequences of low and high values were often obtained. The lengths of these sequences were usually associated with the feed periods of a batch of influent sewage (one batch was used for 1–2 weeks). Variation of $\pm 25\%$ in the values of K_1, K_2, K_3 and α were not uncommon. The changes in these values very evidently were in part due to changes in the sewage characteristics from batch to batch. Identification of some of the causes of change will become possible after modelling the general behaviour of the process later in this paper.

The fact that linear nitrate profiles are obtained in plug-flow reactors indicates that in the particular states present in these reactors the denitrification rate approximates a zero order reaction. Consequently if completely mixed reactors replace the plug flow reactors the nitrogen removal again should be amenable to estimation by means of the equations developed above, all of which implicitly contain the zero order approximation. In experiments where

the plug flow reactors were replaced by completely mixed reactors it was found repeatedly that within experimental error, the denitrification achieved in the completely mixed reactors was in accordance with the predictions of equations (7)–(17) using the experimentally determined values for K_1, K_2 and K_3 [equations (13)–(15)], and α [equation (16)].

The system reduction for a process having both pre- and post-denitrification reactors (Fig. 1d) can now be written:

$$\Delta N_s = \Delta N_{1s} + \Delta N_{2s} + \Delta N_{3s}$$
$$= \alpha S_{bi} + K_2 X_a R_1 + K_3 X_a R_3. \quad (17)$$

An important point to note is that equation (17) is valid only if the nitrate is not reduced to zero in any one of the anoxic reactors. If this condition is satisfied the recycle ratio does not affect the system reduction. However, there must be a minimum recycle; this is determined by the recycle value that just causes the nitrate to be zero at the end of the plug flow reactor. If the recycle is less, the nitrate will become zero before the end of the reactor is reached— the recycle can be increased (with concomitant increase in the nitrate removal) to the point where nitrate just starts to appear in the effluent. Once nitrate appears in the effluent from all the anoxic reactors then theoretically, a further increase in the recycle will have no effect on the system nitrate reduction. Practically, however, it is necessary to take into account the oxygen in the recycles; at high recycles the mass of oxygen introduced may significantly reduce the mass of nitrate denitrified in an anoxic reactor.

Essentially the relationships developed above are empirical; except for the linkage of denitrification with X_a instead of X_v, there is no evident link with the activated sludge process theory. To find such a link attention was directed to the general theory for aerobic processes developed by Dold et al. (1980).

INTEGRATION WITH THE GENERAL THEORY

In the general theory by Dold et al. (1980) it is stated that the biodegradable material in municipal sewage expressed as COD is divided into two fractions, (a) easily biodegradable (about 24% of the total biodegradable COD), and (b) particulate slowly bio-
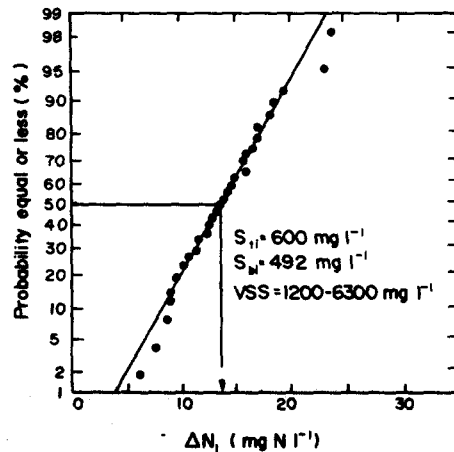

Fig. 4. Statistical plot of the system nitrate removal due to high rate denitrification.
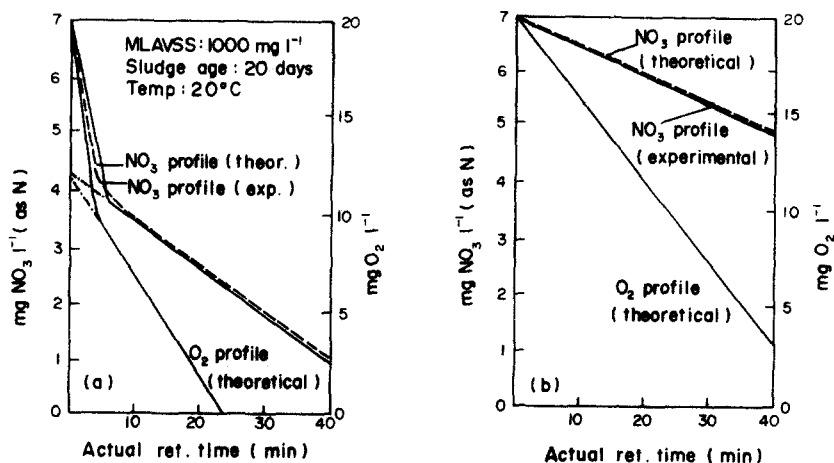
Fig. 5. Experimental and simulated NO_3-time profiles in an anoxic plug flow reactor and DO-time profile in an aerobic plug flow reactor.

degradable (76%).* To incorporate denitrification kinetics into the aerobic kinetic model it was hypothesized that the two phase behaviour observed in the pre-denitrification reactor arose from the response of the organisms to the two substrate character of the influent feed. If this is correct, then theoretically the two phase behaviour should be predicted also if the plug-flow anoxic reactors are replaced by plug-flow aerobic reactors, and the process operated under constant load and flow conditions. Accordingly, plug-flow reactor options were incorporated into the general aerobic model, and under constant load and flow conditions oxygen profiles for the pre- and post-aerobic reactors were generated.

The simulated response of the dissolved oxygen profile in the pre- and post-aerobic plug-flow reactors for $X_a = 1000 \cdot l^{-1}$, sludge age = 20 d, temperature = 20°C is shown in Fig. 5(a) and (b) respectively. Also shown are the nitrate profiles based on the experimental values of the denitrification rate constants and α [equations (13)–(16)] and plotted as equivalent oxygen†, to allow direct comparison between the respective curves. The simulated aerobic and observed anoxic profiles are strikingly similar: the two phase behaviour in the pre-anoxic reactor and the single phase behaviour in the post-anoxic reactor, is clearly reproduced in the aerobic simulations, except that the simulated slopes corresponding to the K_2 and K_3 rate phases differ from the observed anoxic slopes. Furthermore, the concentration of nitrate (or equivalent oxygen) removed due to the high rate in the primary phase of the anoxic reactor is the same as the corresponding concentration of oxygen removed in the aerobic reactor (see extrapolation to $t = 0$ in

Fig. 5a). The similarity of the profiles is so clearly evident that it was accepted that the general aerobic model can provide a basis for modelling the denitrification behaviour. The problem now was what changes and additions needed to be made to the aerobic model to allow a quantitative description of the response of a nitrification–denitrification single sludge system. The following aspects formed the basis for formulating the changes necessary.

1. In the bi-substrate active-site death-regeneration model there is only growth (synthesis) and death, the latter with its associated substrate release by lysis; no endogenous respiration *per se*, is recognized. From comparisons of the oxygen utilization rates in completely mixed reactors, simulated and observed, in different aerobic systems, it appears that the lysed material is slowly biodegradable particulate COD. This material is added to the same material derived from the influent to constitute the energy source of slowly biodegradable particulate material [equation (23)].

2. Growth of the heterotrophs is assumed to take place in both aerobic and anoxic conditions; death and lysis take place irrespective of whether the conditions are aerobic, anoxic or anaerobic. Under anaerobic conditions no heterotrophic growth can take place, but, due to death and lysis there is a corresponding accumulation of lysed slowly biodegradable material.

3. Growth of the nitrifiers can take place only under aerobic conditions; death is assumed to take place irrespective of aerobic, anoxic or anaerobic conditions.

4. The general theory accepts that easily biodegradable and slowly biodegradable material are simultaneously and independently utilized in synthesis [equations (22) and (24)]. This assumption is reasonable, unless the particulate material stored on the active sites are all occupied (a situation possible in the contact reactor of a contact stabilization plant).

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* The composition of COD in municipal sewage is approximately as follows: 5% soluble unbiodegradable; 13% particulate unbiodegradable; 20% easily biodegradable and 62% particulate biodegradable.

† Adjustment on the basis of 1 mg NO_3–N $\equiv$ 2.86 mg O_2.

Normally the organisms remain essentially in a continuous state of stress due to the low food/micro-organism ratio even under cyclic loading conditions, once the sludge age exceeds 4–6 days.

For the general model the differential equations describing the aerobic system have been set out by Dold et al. (1980) and for convenience, are repeated here.

Let

$$A = K_{ms} \cdot S_{bs}/(S_{bs} + K_{ss}) \tag{18}$$

$$B = K_a S_{bp} \cdot (f_{ma} - X_s/X_a) \tag{19}$$

$$C = K'_{mp} \cdot P \cdot X_s/(X_s P + K_{sp} X_a) \tag{20}$$

$$D = P \cdot b'_h. \tag{21}$$

Then the differential equations for energy removal are:

$$dS_{bs}/dt = -A \cdot X_a \tag{22}$$

$$dS_{bp}/dt = (-B + (1 - f')D) \cdot X_a \tag{23}$$

$$dX_s/dt = (B - C)/P \cdot X_a \tag{24}$$

$$dX_a/dt = (Y_h(A + C) - D/P)X_a \tag{25}$$

$$dX_e/dt = f'D/P \cdot X_a \tag{26}$$

$$O_c = (1 - PY_h)(A + C)X_a. \tag{27}$$

Let

$$E = \mu_{nm}/Y_n \cdot N_a/(N_a + K_n) \tag{28}$$

$$F = b_n. \tag{29}$$

Then the differential equations for nitrification are:

$$dN_a/dt = -E \cdot X_n \tag{30}$$

$$dN_n/dt = EX_n \tag{31}$$

$$dX_n/dt = (Y_n E - F) \cdot X_n \tag{32}$$

$$O_n = 4.57 E \cdot X_n. \tag{33}$$

The temperature dependency of the various constants are:

(a) Carbonaceous (energy removal)

$$K_{ms} = 8(1.20)^{T-20} \text{ mg COD} \cdot \text{mg VASS}^{-1} \cdot \text{d}^{-1} \tag{34}$$

$$K_{ss} = 5(1.00)^{T-20} \text{ mg COD} \cdot \text{l}^{-1} \tag{35}$$

$$K'_{mp} = 3.0(1.060)^{T-20} \text{ mg COD} \cdot \text{mg VASS}^{-1} \cdot \text{d}^{-1} \tag{36}$$

$$K'_{sp} = 0.04(1.1)^{20-T} \text{ mg COD} \cdot \text{mg VASS}^{-1} \tag{37}$$

$$K_a = 0.25(1.029)^{T-20} \text{ l} \cdot \text{mg VSS}^{-1} \cdot \text{d}^{-1} \tag{38}$$

$$b'_h = 0.62(1.029)^{T-20} \text{ mg VASS} \cdot \text{mg VASS}^{-1} \cdot \text{d}^{-1} \tag{39}$$

$$f' = 0.08 \text{ mg VSS} \cdot \text{mg VASS}^{-1} \tag{40}$$

$$P = 1.48 \text{ mg COD} \cdot \text{mg VSS}^{-1} \tag{41}$$

$$Y_h = 0.45 \text{ mg VSS} \cdot \text{mg COD}^{-1}. \tag{42}$$

(b) Nitrogeneous (nitrification)

$$\mu_{nm} = (0.3–0.65)(1.123)^{T-20} \quad 7.2 \leqslant \text{pH} \leqslant 8.0 \tag{43}$$

$$b_n = 0.04(1.029)^{T-20} \text{ mg } X_n \cdot \text{mg } X_n^{-1} \cdot \text{d}^{-1} \tag{44}$$

$$Y_n = 0.1 \text{ mg } X_n \cdot \text{mg NH}_3\text{-N}^{-1}. \tag{45}$$

Equation (27) describes the oxygen utilization rate and needs adjustment for an anoxic environment in order to express the utilization rate of nitrate instead of oxygen:

$$(dN_n/dt) = -(1 - PY_h)(A + C) \cdot X_a/2.86. \tag{46}$$

The fact that the observed rate of nitrate removal (as equivalent oxygen) in the anoxic reactors was not so rapid as the simulated decrease of dissolved oxygen in the aerobic reactors (Fig. 5a and b) indicated that the rate of utilization of particulate substrate in the anoxic environment is lower. The degree in which the rate is reduced was estimated by considering first the post-denitrification reactor.

In the post-denitrification reactor the concentration of easily biodegradable nutrient is virtually zero and the rate of nitrate removal is associated only with the utilization of slowly biodegradable material. It was possible to simulate the experimental nitrate profile in a post-denitrification reactor at 20 C accurately when the value of the maximum specific substrate utilization rate constant, K'_{mp}, for slowly biodegradable material was reduced to a fraction, 0.38, of the value this constant has in an aerobic environment. Figure 5(b) shows the simulated nitrate profile in a post-denitrification plug-flow reactor for $T = 20$ C, $R_s = 20$ d, $X_a = 1000$ mg·l^{-1} and an anoxic sludge fraction of 25%, when the maximum specific substrate utilization rate for slowly biodegradable substrate, K''_{mp}, is set at a value:

$$K''_{mp} = 0.38 K'_{mp} = 1.14 \text{ mg COD} \cdot$$

$$\text{mg } X_a^{-1} \cdot \text{d}^{-1} \text{ (at 20 C).} \tag{47}$$

When this same value for K''_{mp} was used to simulate denitrification in a pre-denitrification reactor under the same conditions of temperature, sludge age and anoxic volume fraction, again a very close correspondence between simulated and experimental nitrate profiles in the secondary phase was obtained (see Fig. 5a).

With regard to the maximum specific utilization rate constant for easily biodegradable material, Dold et al. (1980) could not determine K_{ms} accurately in an aerobic environment from the completely mixed reactor response under square wave cyclic flow and load conditions. The utilization of easily biodegradable substrate is an extremely rapid reaction and all that could be established was a lower limit for the constant—any value greater than the minimum, predicted a behaviour in conformity with the observation. The lower limit was determined as $K_{ms} = 5$ mg COD·mg X_a^{-1}d^{-1} at 20 C. However, in anoxic plug flow reactors it was possible to derive a value for
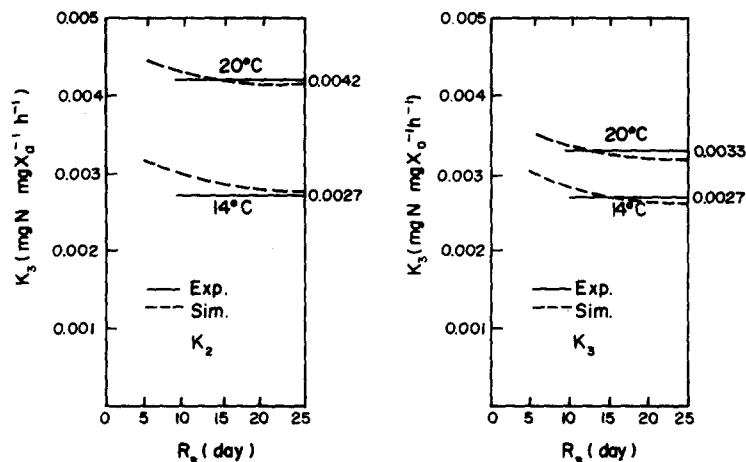
Fig. 6. Simulated and experimental denitrification rate constants K_2 (a) and K_3 (b) vs sludge age.

K_{ms} from fitting simulated and experimental nitrate profiles in the plug flow reactor. This gave $K_{ms} = 8$ mg COD·mg $X_a^{-1}d^{-1}$ at 20°C. This value, because it also satisfies the observed aerobic response, was adopted for both aerobic and anoxic conditions. Uncertainty of the values of K_{ms} in both aerobic or anoxic states, in fact, is not important, because the rate of utilization of easily biodegradable material is so high that invariably the reaction is complete well within the actual retention times normally provided.

Once the values of K'_{ms} and K''_{mp} at 20°C were established for a sludge age $= 20$ d and an anoxic volume fraction $= 25\%$, simulations were done for different sludge ages and anoxic sludge fractions. From the simulated slopes of the nitrate profiles in the secondary phase of the pre-denitrification plug flow reactor and in the single phase of the post-denitrification reactor, the values of K_2 and K_3 were calculated. The simulated response data indicated that (1) the magnitudes of the anoxic volume fractions have virtually no effect on the simulated K values, neither in the pre- nor in the post-denitrification reactors. (2) In the range of sludge ages from 10 to 20 days the respective K values remain substantially constant (see Fig. 6a and b). The constancy of the K values over this range of sludge ages has been noted experimentally earlier in this paper.

In order to establish the temperature dependency for the constant K''_{mp} the simulations were repeated for a temperature of 14°C using pre- and post-denitrification plug flow reactors. The value of K''_{mp} was varied until close correspondence between experimental and observed nitrate profiles was obtained. As for the aerobic model, an Arrhenius type of temperature dependency was assumed, i.e.

$$K''_{mpT} = K''_{mp20}\,\theta_p^{T-20}. \qquad (48)$$

It was found that at 14°C the best correspondence between the experimental and simulated K_2 and K_3 values was obtained when K''_{mpT} was given a tempera-

ture dependency of $\theta_p = 1.06$. In Fig. 6(a) and (b) the experimental and simulated values of K_2 and K_3 for a temperature of 14°C are shown plotted as a function of the sludge age. By using $\theta_p = 1.06$ it is possible therefore to obtain good correlation of the observed and theoretical K values over the range $T = 14-20$°C. Dold *et al.* (1980) accepted a temperature dependency of $\theta_p = 1.029$ for K'_{mp} in their analysis of aerobic systems. However, when the temperature dependency $\theta_p = 1.06$ was inserted for K'_{mp} to simulate experimental data of aerobic systems at 12°C, it was found that the predicted response was fractionally closer to the observed one than in the case where $\theta_p = 1.029$ was used. The value of $\theta_p = 1.06$ therefore seems to be acceptable for both aerobic and anoxic environments. The temperature dependency of K_{msT} for the process was determined also by fitting the simulated to the observed profile in the reactor. Similarly from the slope of the nitrate profiles in the primary phase of a pre-denitrification plug flow reactor the temperature dependency of K'_{ms} could be established when again an Arrhenius type of temperature dependency was assumed, i.e.

$$K'_{msT} = K_{ms20}\cdot\theta_s^{T-20}. \qquad (49)$$

The closest correlation was obtained with $\theta_s = 1.20$.

Once the temperature dependencies of K_{mp} and K_{ms} were known, simulations were done over the temperature range between 12 and 22°C. In Fig. 7 the simulated values of K_1, K_2 and K_3 are shown plotted as a function of the temperature for sludge ages $R_s = 10$ d and $R_s = 20$ d. The experimentally observed K values are also indicated.

Having calibrated the model it is now of interest to inquire if there is a simple quantitative link between the K values and the kinetic constants for substrate utilization. This can be done as follows: The rate of nitrate utilization as expressed in equation (46) can be divided into a rate associated with the utilization of easily biodegradable material, dN_1/dt, and a rate as-
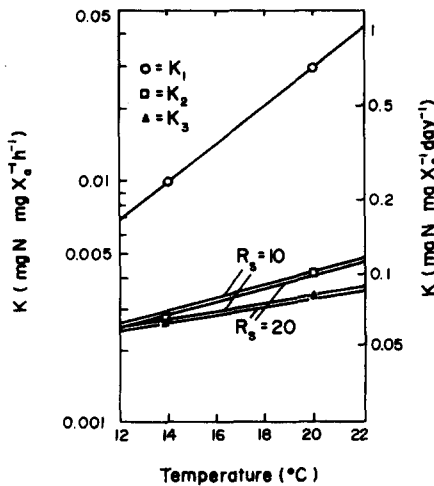
Fig. 7. Simulated and experimental denitrification rate constants K_1, K_2 and K_3 vs temperature for $R_s = 10$ and $R_s = 20\,d$.

sociated with the utilization of slowly biodegradable material, dN_2/dt, where

$$dN_1/dt = -\left[(1 - PY_h)\cdot\frac{A}{2.86}\right]\cdot X_a \qquad (50)$$

and

$$dN_2/dt = -\left[\left(\frac{1 - PY_h}{2.86}\right)C\right]\cdot X_a \qquad (51)$$

i.e.

$$dN_n/dt = dN_1/dt + dN_2/dt. \qquad (52)$$

Substituting for A from equation (18), one obtains:

$$dN_1/dt = -(1 - PY_h)\,K_{ms}\cdot S_{bs}\cdot X_a/((S_{bs}$$
$$+ K_{ss})2.86). \qquad (53)$$

As the half saturation value, K_{ss}, is very small, $(K_{ss} = 5\,mg\,COD\cdot l^{-1})$ the expression $K_{ms}\cdot S_{bs}/(K_{ss} + S_{bs})$ remains virtually constant and equal to K_{ms} until S_{bs} falls to very low values. Consequently, the function in square brackets in equation (50) remains virtually constant and hence equation (7) applies:

$$dN_1/dt = \Delta N_1/t_p \simeq -K_1 X_a \qquad (54)$$

where

$$K_1 = (1 - PY_h)\cdot K_{ms}\cdot S_{bs}/(K_{ss} + S_{bs})/2.86$$

as

$$S_{bs}/(K_{ss} + S_{bs}) \simeq 1$$

hence,

$$K_1 \simeq (1 - PY_h)\cdot K_{ms}/2.86. \qquad (55)$$

The mass of denitrified nitrate, from equation (46), is directly proportional to the mass of substrate utilized in the denitrification reaction, the proportionality constant being $(1 - PY_h)/2.86$. In a pre-denitrification

reactor normally all the influent easily biodegradable substrate is completely utilized and hence the nitrate removal associated with the utilization of easily biodegradable material can be expressed as

$$\Delta N_{1s} = (1 - PY_h)\cdot S_{bsi}\cdot/2.86. \qquad (56)$$

Substituting for $Y = 0.45$ and $P = 1.48$:

$$\Delta N_{1s} = 0.1168\,S_{bsi}. \qquad (57)$$

Now in unsettled and approximately so in settled municipal waste flows

$$S_{bsi} = 0.24\,S_{bi}. \qquad (58)$$

Substituting in equation (57)

$$\Delta N_{1s} = 0.028\,S_{bi} \qquad (59)$$

giving the same value as that experimentally observed, in equation (16). This reaction applies only in the pre-denitrification reactor, in the post-denitrification reactor S_{bs} is essentially zero.

With regard to the slowly biodegradable COD fraction, the nitrate utilization rate can be expressed by substituting equation (20) in equation (37):

$$dN_2/dt = (1 - PY_h)K''_{mp}\cdot P\cdot X_s\cdot X_a/(PX_s$$
$$+ K_{sp}X_a)/2.86. \qquad (60)$$

Considering the pre-denitrification reactor, X_s is large and due to the slow rate of the reaction there is only a small change in X_s between the beginning and the end of the plug flow reactor. Consequently, again it is possible to write

$$\Delta N_2/R_{1a} = K_2 X_a \qquad (61)$$

even though the constancy exhibited by K_2 arises from a different cause from that for K_1. Considering the post-denitrification reactor, X_s generally is very small arising principally from storage of lysis products. The concentration of X_s hardly changes from the beginning to the end of the reactor and consequently again the slope, dN_3/dt, can be expressed as in equation (60):

$$\Delta N_{3a}/R_{3a} = K_3 X_a.$$

The behavioural patterns described above have been observed elsewhere. Heideman (1979) analysed the denitrification behaviour in batch experiments, using mixtures of sludge and influent municipal sewage. By observing the change of nitrate and soluble COD with time he found that (1) the nitrate time profile was very similar to that observed by Marais & Ekama (1976) in pre-denitrification plug flow reactors, i.e. there was a high denitrification rate in the primary phase followed by a lower rate in the secondary phase. (2) Cessation of the primary phase occurred when the soluble COD concentration attained a constant value, i.e. when all the easily biodegradable substrate was utilized. (3) The ratio between the nitrate removal due to the high rate, i.e. ΔN_{1s}, and the decrease in the soluble COD concentration, i.e. S_{bsi}, was
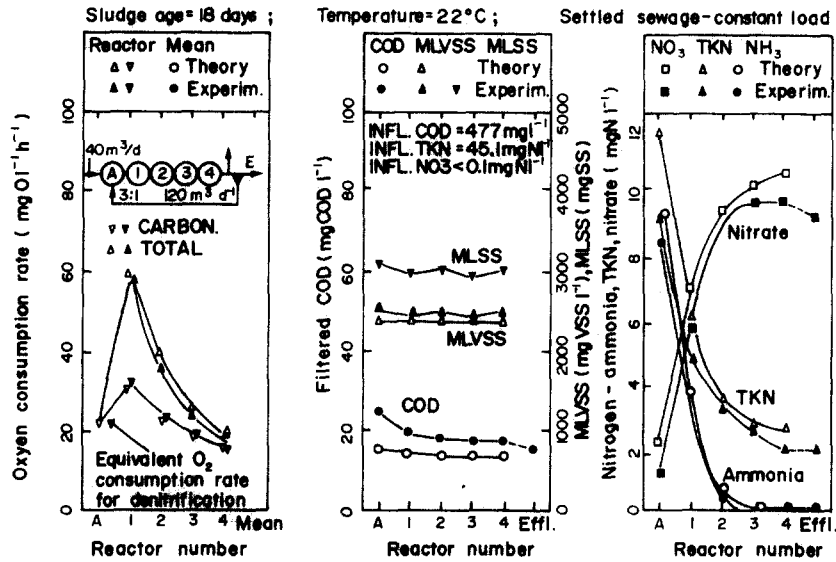
Fig. 8. Experimental and simulated response of series reactor anoxic/aerobic system under constant flow and load conditions. (Plant design parameters in Table 1.)

repeatedly found to be in the range 0.11–0.12 mg N · mg COD^{-1}, the same as determined above [equation (57)]. Furthermore, the two phase behaviour was observed only when sludge and influent sewage were mixed; batch denitrification tests with sludge only yielded linear profiles akin to the post-denitrification plug flow nitrate profiles. Unfortunately, it was not possible to calculate the active sludge concentration from the data supplied by Heideman, so that the denitrification rate constants (in terms of mg N · mg X_a^{-1} · d^{-1}) could not be determined.

From the analysis above the denitrification "constants" K_1, K_2, K_3 have no fundamental kinetic significance; they are a result of a combination of kinetic reactions which, fortuitously, show little variation with sludge age (in the range from 10 to 20 days) at any selected temperature in the range 12–22°C. Both from an experimental and a practical point of view it would appear that for design, the acceptance of constant values for K_1, K_2 and K_3 at any selected temperature is not unreasonable and hence suitable for estimating the denitrification achievable under constant flow and load conditions.

MODEL VERIFICATION

The plug flow experiments allowed calibration of the general nitrification-denitrification model. It now remains to check if the calibrated model applies to completely mixed reactors under more general conditions of flow and load.

The predictive power of the calibrated model was tested by comparing the simulated data with those observed in completely mixed series reactor nitrification-denitrification systems under a variety of flow and load conditions. In addition, tests were carried

out in a single reactor system where the environment was made sequentially aerobic and anoxic.

The series reactor systems were all space dependent (Ekama & Marais, 1978) and time dependency could be superimposed by cyclicly varying the flow and/or load conditions. An experimental investigation was carried out at pilot plant level under both time independent and time dependent conditions at Daspoort Sewage Works, Pretoria. The process configuration is shown in Fig. 8. It consists of a series of 5 equal-sized reactors each of 5 m³ capacity, the first reactor anoxic, the remainder aerobic, with an underflow recycle to the anoxic zone of 3:1. Sewage characteristics and design parameters are listed in Table 1. Two series of tests were carried out.

The first series was carried out under time independent and space dependent conditions by having a constant influent flow and load. In Fig. 8 the averages of 27 daily measurements of the process variables, i.e. oxygen uptake rate, VSS, COD, TKN, ammonia and

Table 1. Anoxic/aerobic pilot plant design parameters and sewage characteristics (see Fig. 8)

Parameters	Constant load	Cyclic load
Configuration	Series	Series
No. of reactors	5 × 5 m³	5 × 5 m³
Total volume (m³)	25	25
Sludge age (d)	18	18
Influent flow (m³·d^{-1})	40	60
Influent COD (mg l^{-1})	477	mean 363
Influent TKN (mg N·l^{-1})	45.1	mean 33.5
μ_{mn}	0.41	0.41
pH	7.8	7.8
Temperature	22°C	22°C
Underflow recycle ratio	3:1	2:1

nitrate concentrations are shown plotted. Also shown are the predictions by means of the model.

The second series was carried out under time and space dependent conditions by imposing a daily cyclic load as follows: A constant influent flow was drawn directly from the discharge of a primary settling tank of a full scale works, so that the natural diurnal variations of the COD, TKN and ammonia concentrations of the waste flow was imposed on the process.

The same process variables as in the first series were measured at regular intervals over a number of 24 h test periods. The results of one 24 h test are shown in Fig. 9(a), the simulated results in Fig. 9(b).

The simulations of Figs 8 and 9 were obtained assuming values of all the kinetic constants [equations (34–45)] to be identical to those reported by Dold et al. (1980), for aerobic systems and calculating K_{mp}'' from equation (48). With regard to the maximum growth rate of nitrifiers, μ_{nm20}, Dold et al. (1980) found repeatedly that its value is dependent on the waste flow source and can vary from 0.15 to 0.65 d^{-1}. Its value must therefore be determined by fitting the simulated nitrate profiles to the experimental for every individual waste flow.

In the first series of tests, i.e. under constant flow and load conditions, (Fig. 8), there was good correspondence between simulated and the mean experimental data, for all the measured variables, in each reactor. In the second series of tests, i.e. under cyclicly varying load conditions (Fig. 9) it was not possible to obtain the same close correspondence. A problem here was that the reproduceability of experimental response between different runs was rather poor. The imposition of cyclic flow and load conditions exerts severe demands on the predictive power of the model and from a theoretical point of view this system should be the most satisfactory for checking the validity of the general model. Unfortunately, the quasi plug flow conditions in the series system tend to cause unstable response if a perturbation appears either in the value of a kinetic constant or in the flow and load conditions. Such effects can be averaged out if the cyclic test is repeated a number of times and a mean effect calculated but the magnitude of work involved makes this approach rather impractical.

At laboratory scale, Wilson & Marais (1976) tested a two reactor process under cyclic conditions (Fig. 10). The process consisted of a pre-denitrification

At laboratory scale, Wilson & Marais (1976) tested a two reactor process under cyclic conditions (Fig. 10). The process consisted of a pre-denitrification reactor (1.0 l.) and an anaerobic reactor (6.4 l.) in series with an underflow recycle ratio of 1.5:1 with respect to the mean daily influent flow. A square wave flow and load pattern (12 h constant feed, 12 h no feed) was imposed with a flow of 151 d^{-1} of settled municipal sewage from the Athlone-Cape Town outfall (COD = 570 mg·l^{-1}; TKN = 54 mg·l^{-1}). This waste flow contained a high proportion of industrial discharge. Figure 10 shows the simulated and ob-

served concentrations of nitrate and TKN in the anoxic and aerobic reactors and the oxygen uptake rate in the aerobic reactor for one experiment over a period of 26 h. The average values of effluent COD and volatile solids concentration are also indicated (Fig. 10c).

To obtain the best correlation between the experimental and simulated data it was necessary to assume that the fraction of easily biodegradable material was only 10% of the biodegradable influent COD concentration (instead of the average fraction of 24% reported by Ekama and Marais) and that the maximum specific substrate utilization rate constant for slow biodegradable material had to be reduced from 3.0 to 2.3 mg COD·mg X_a^{-1}·d^{-1}, still keeping $K_{mp}'' = 0.38 K_{mp}'$ [equation (48)]. In addition a maximum specific growth rate of nitrifiers $\mu_{nm20} = 0.17$ d^{-1} had to be used to describe the nitrification behaviour. The lower values can be ascribed to the high proportion of industrial waste in the influent sewage. With these adaptions it was possible to simulate very closely the experimental data (see Fig. 10).

In all the test series reported experience indicated that instability, i.e. poor reproduceability in response arose either from series configurations operation, or cyclic variation load, or hydraulic effects due to precipitous changes in flow rate, or a combination of these. Consequently, in a third investigation it was sought specifically to find a system in which severe demands would be imposed on the predictive power on the model but the factors inducing instability would not be present. A system found to satisfy these requirements was a single reactor system operating under constant flow and load, but with alternate periods of aerobic and anoxic conditions. A reactor of 6 l. was operated at a sludge age of 6 days and a temperature of 20°C. Sewage was obtained from the Strandfontein outfall, Cape Town. The influent flow was kept at a constant value of 20 l d^{-1} and the influent concentrations of COD and TKN as near as possible to 500 and 45 mg·l^{-1} respectively. During an experiment the oxygen supply to the mixed liquor was interrupted for certain time periods each day and the concentrations of TKN, ammonia, nitrate, COD and VSS were observed over both the anoxic and the aerobic periods. During the aerobic periods the oxygen uptake rate was measured. A short sludge age of 6 days was selected as this assures a high rate of denitrification per unit sludge mass. By varying the lengths of the anoxic periods the possible effects of these periods on nitrification and denitrification also could be evaluated.

Figure 11 shows the experimental and simulated response for an anoxic period of 5 h, followed by an aerobic period of 19 h. The oxygen uptake rate (and equivalent oxygen uptake rate during the anoxic period, Fig. 11a), volatile solids and filtered COD concentrations (Fig. 11b), TKN, ammonia and nitrate concentrations (Fig. 11c, d and e respectively) are plotted vs time. In addition, the alkalinity time profile
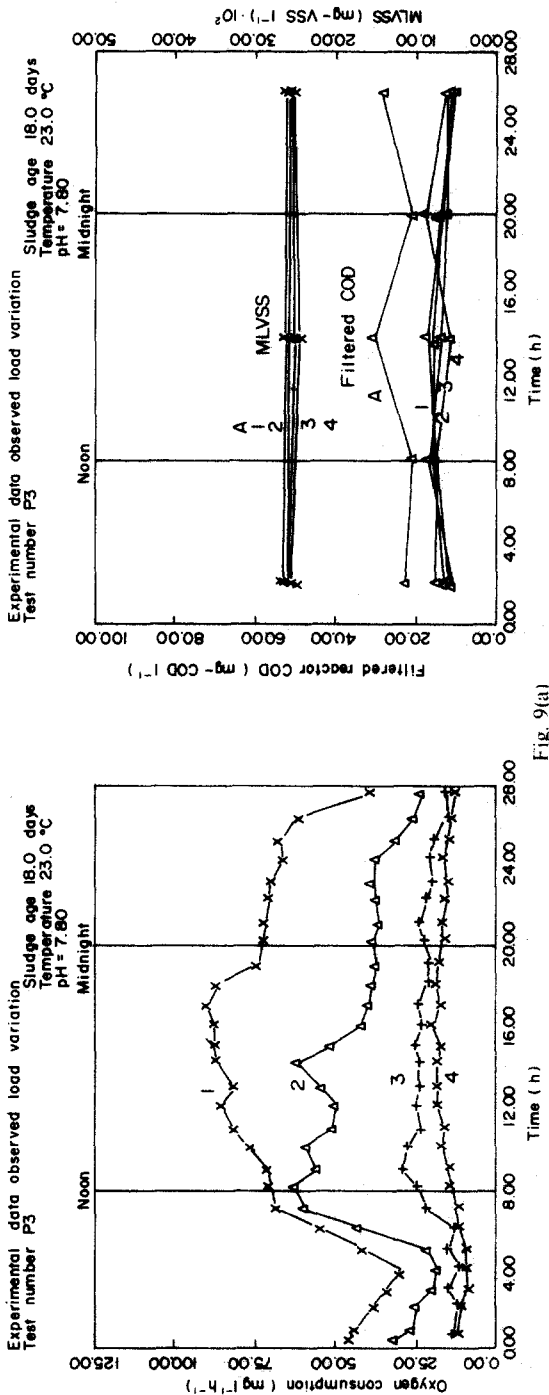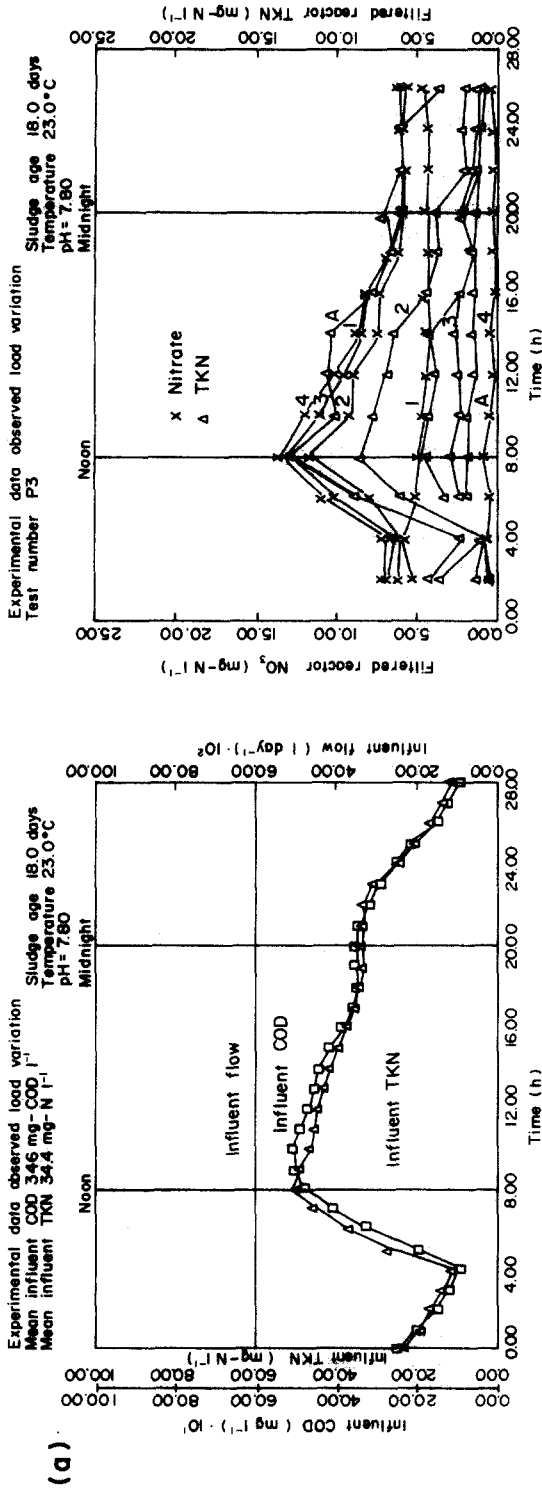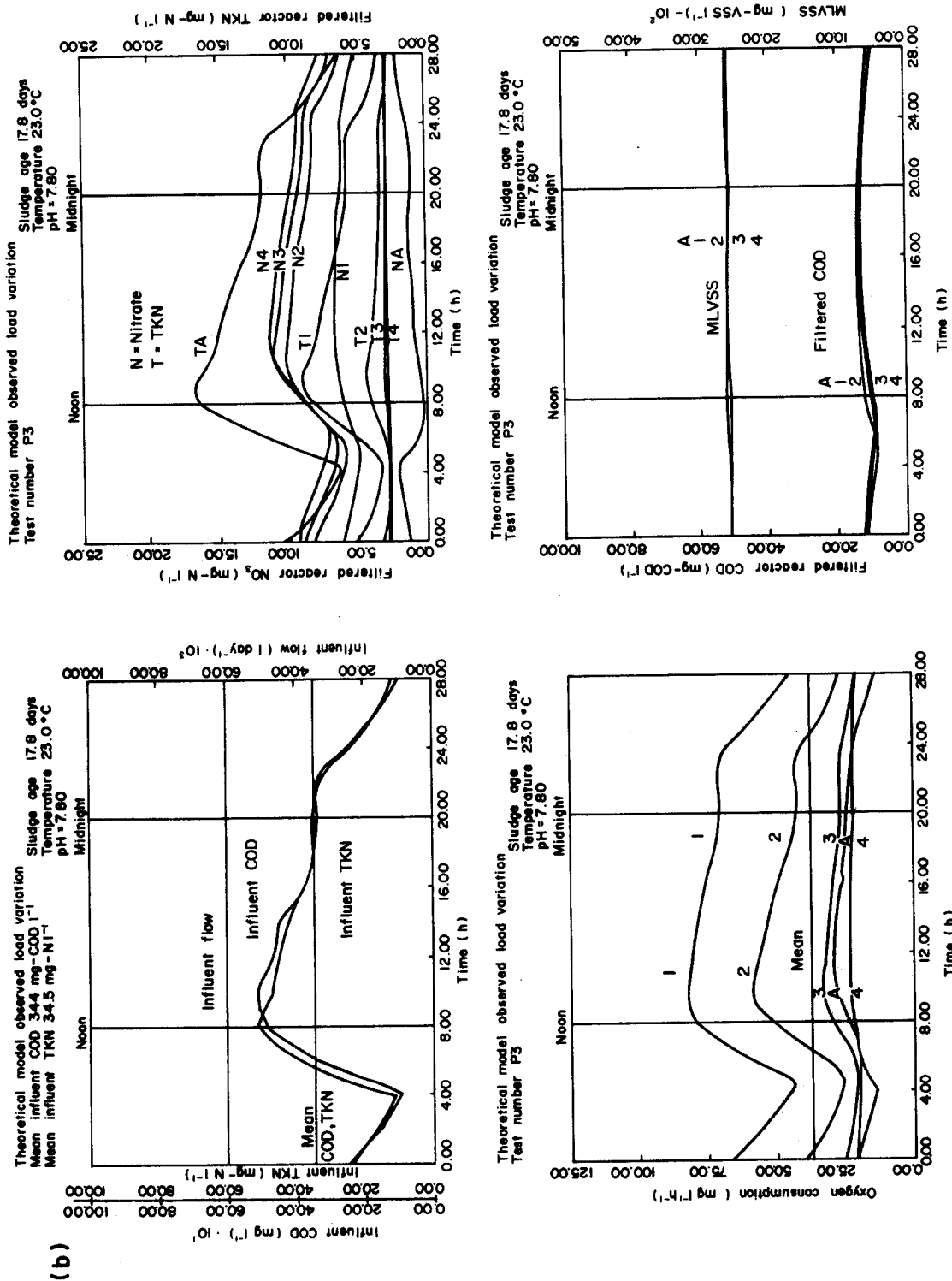
Fig. 9(a)

Fig. 9. Experimental and simulated response of an anoxic/aerobic series reactor system under cyclic load conditions (configuration shown in Fig. 8; plant design parameters in Table 1). (a) Experimental response. (b) Simulated response.
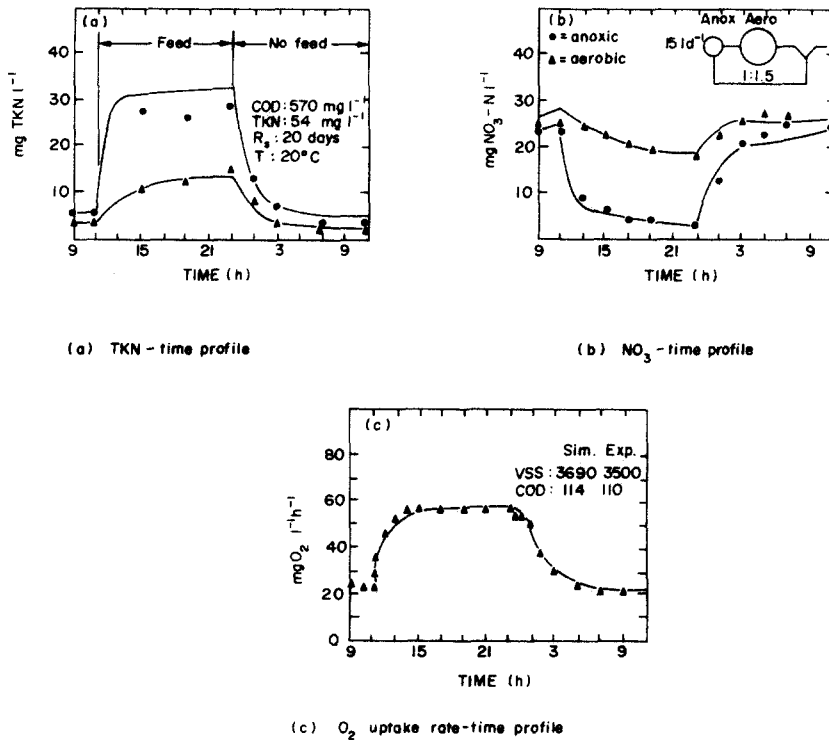
(a) TKN - time profile

(b) NO$_3$ - time profile

(c) O$_2$ uptake rate-time profile

Fig. 10. Experimental and simulated response of TKN, NO$_3$ and O$_2$ uptake rate in a Modified Ludzack Ettinger system under cyclic (square wave) flow and load conditions.

was measured and simulated (Fig. 11f) assuming stoichiometric changes due to nitrification and denitrification and taking into account the effect of ammonification (Scearce et al., 1980).

The following values were obtained for the fits shown in Fig. 11: $f_{cu} = 0.0$; $K'_{mp} = 2.2$; $K''_{mp} = 0.66$; $\mu_{nm20} = 0.45$. Note that the value for K'_{mp} is lower than the mean value found by Dold et al. (1980) and that the value of K'_{mp} is lower than that calculated by equation (48). The fraction of easily biodegradable COD, f_{cu}, was zero instead of the mean value of 24%$_0$ of the biodegradable COD. Because these constants deviated from the mean values derived by Dold et al. (1980) from their accumulated data, the validity of the experimental procedure with the single reactor system was checked by carrying out experiments during the same time, utilizing four modified Ludzack Ettinger systems each with different anoxic volume fractions, treating the same sewage as the single reactor system. Simulation of these systems utilizing the constants derived from the single reactor system gave excellent correspondence with the experimental data. It was therefore concluded that the very low values of K'_{mp} and K''_{mp} and f_{cu} were due to the sewage characteristics and could not be ascribed to the experimental set up using a single reactor system.

An interesting observation from the nitrification behaviour at 20°C was that the close correspondence between the experimental and simulated nitrate profile (Fig. 11e) implies that the imposed anoxic period of five hours did not appear to have any noticeable influence on the nitrification behaviour subsequently; no lag phase was apparent, and the rate of nitrification attained its maximum value immediately on reimposing aerobic conditions. This conclusion is substantiated by the good correspondence between simulated and experimental profiles of TKN, ammonia, oxygen uptake rate and alkalinity during the aerobic period.

Even though the cyclic changes of all the variables (except the VSS and filtered COD concentrations) were substantial, reproducibility in experimental response was excellent. Changes in simulated response on changing the values of the kinetic constants in the expressions for nitrification and denitrification indicated that the response is very sensitive to the values assigned to these constants. Hence, by means of the experimental method described above in conjunction with the simulated model it was possible not only to obtain reliable experimental data but also accurate estimates of the kinetic constants for a particular waste flow and constitutes a most convenient and time saving method to determine the kinetic constants for substrate utilization, nitrification and denitrification.

Taking all the experimental work into account it would appear that the model characterized by the differential equations (18)–(33) and (46) gives a good description of all the nitrification–denitrification systems with the proviso that the numerical values of
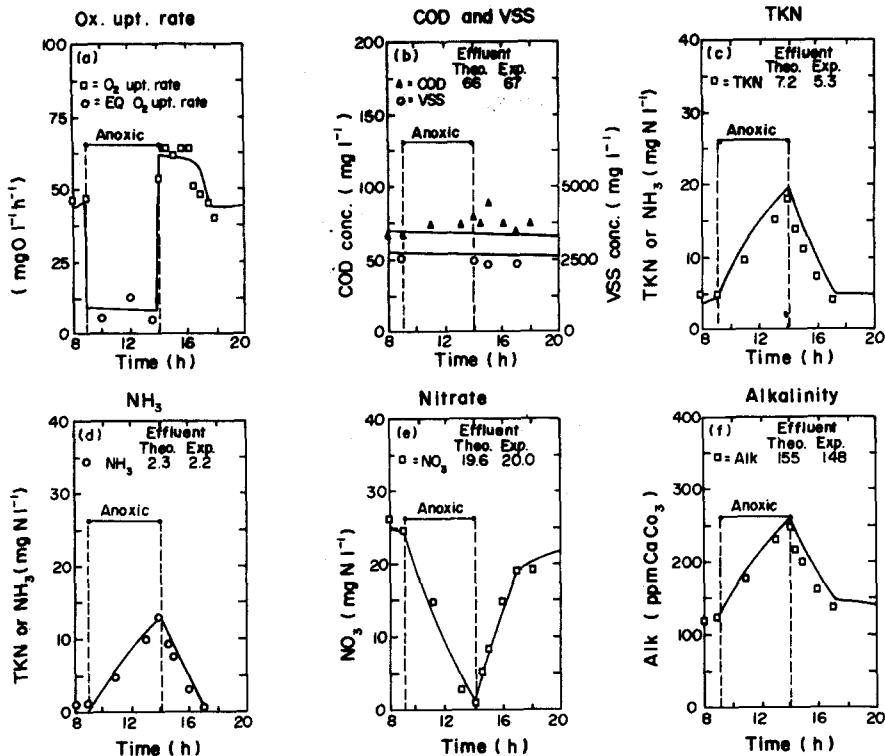
Fig. 11. (a) Oxygen uptake rate; (b) VSS and filtered COD; (c) TKN; (d) NH₃; (e) NO₃; and (f) Alkalinity as a function of time in a single reactor anoxic/aerobic system under constant flow and load conditions.

some of the kinetic constants are affected by the characteristics of the influent sewage. The constants that seem to be most sensitive to changes in influent sewage characteristics are the maximum specific growth rate of the nitrifiers (reflected in the maximum nitrification rate) and to a lesser extent the maximum specific utilization rate constant for slowly bio-degradable material (reflected in the utilization rate of dissolved oxygen and the denitrification rate). Also it was found that the fraction of easily biodegradable material in sewage is subjected to considerable variations. This implies that the numerical values of the empirical denitrification rate "constants" K_1, K_2, K_3 and α also depend on the sewage characteristics and that accurate values for a particular waste flow can only be determined by experiment, most conveniently by utilizing the single reactor constant flow and load-sequential aerobic/anoxic procedure outlined above. In such an investigation it is preferable to use fresh sewage every day rather than to store a batch and to feed it over a longer period. In the latter case the possibility of an atypical response of the system due to a coincidental singularity in the characteristics of the influent is greater.

CONCLUSIONS

(i) The bi-substrate active-site death-regeneration model developed by Dold et al. (1980) to describe the

aerobic activated sludge system, can be extended to provide a reliable description of the kinetics of the nitrification–denitrification single sludge process under both constant and daily cyclic conditions of flow and load.

(ii) The extension requires no change in the basic equations describing the aerobic process, only a change in the value of one of the constants in the expression defining the substrate utilization rate for slowly biodegradable particulate material when an anoxic environment is required. Nitrification is affected only in so far that growth of the nitrifiers takes place only in an aerobic environment but death in both aerobic and anoxic environments.

(iii) Under constant load and flow conditions the denitrification kinetics can be adequately described by the empirical equation $\Delta N_s = K X_a$. Depending on the position of the denitrification reactor in the process configuration K has different values. These K values have no fundamental kinetic significance; they are only apparent constants, the result of a combination of kinetic reactions which fortuitously show little variation under normal operational conditions.

(iv) The fundamental kinetic constants in the expressions for substrate utilization and nitrification are affected by the wastewater characteristics. The variability of the constants for nitrification is greater than that for substrate utilization.

(v) A single reactor system operated under sequential anoxic and aerobic periods constitutes a convenient experimental set up for the determination of the values of the kinetic constants of nitrification and substrate utilization and of denitrification in the anoxic phases.

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