

A TECHNIQUE TO DETERMINE THE SIMULTANEOUS NITRIFICATION AND DENITRIFICATION RATES IN AN INTERMITTENT AERATION TANK

Hong W. Zhao and Terry J. Mah
US Filter/Kruger Products
401 Harrison Oaks Blvd., Suite 100
Cary, NC 27513

Donald S. Mavinic, William K. Oldham, and Frederic A. Koch
University of British Columbia

ABSTRACT

This paper reports on a technique to determine potential specific nitrification and denitrification rates (SNR and SDNR) in an oxidation-reduction potential (ORP) controlled, intermittent aeration (IA) tank, in which nitrification and denitrification occurred simultaneously. In addition, potential SNRs in the aerobic zone of a three-stage (anaerobic, anoxic and oxic) and potential SDNRs in its anoxic zone were determined using this technique. The technique involves a steady-state run and two additional transient-state phases: one created by ammonia shock loading and the other by nitrate shock loading. The technique is flexible and generates data relating rate to substrate concentration in one steady-state run. Data analysis was performed using the integral method; an excellent agreement between predicted and experimental data was found. Zero-order kinetics could describe nitrification in an ammonia concentration range of 10-30 mgN/L and denitrification in a nitrate concentration range of 10-30 mgN/L. The potential SNRs in the IACM tank ($0.39\text{-}1.69 \text{ mgNH}_4\text{-N/gMLVSS h}^{-1}$) were considerably lower than those in the aerobic zone of the three-stage process ($3.4\text{-}8.1 \text{ mgNH}_4\text{-N/gMLVSS h}^{-1}$); the potential SDNRs in the IACM tank were in a range of $0.16\text{-}1.26 \text{ mgNO}_x\text{-N/gMLVSS h}^{-1}$, which were also considerably lower than that in the anoxic zone of the three-stage process ($2.5 \text{ mgNO}_x\text{-N/gMLVSS h}^{-1}$).

KEYWORDS

Denitrification, intermittent aeration, kinetics, nitrification

NOMENCLATURE

α , β = regression constants in the equation representing the influent (to the IACM tank) ammonia-N concentration during a transient-state phase created by ammonia-N shock loading.

a , b , c , m = coefficients in the differential equation describing both ammonia-N and $\text{NO}_x\text{-N}$ dynamic changes in the IACM tank during a transient-state phase.

A_{DN} = average amount of $\text{NO}_x\text{-N}$ denitrified in the IACM tank during a steady-state phase (mg per liter feed).

A_N = average amount of ammonia-N nitrified in the IACM tank during a steady-state phase (mg per liter feed).

S_{NH}^o = average ammonia-N concentration in the IACM tank during a steady-state phase (mg/L).

S_{NH-in}° = average influent (to the IACM tank) ammonia-N concentration during a steady-state phase (mg/L).

S_{NO}° = average NO_x -N concentration in the IACM tank during a steady-state phase (mg/L).

S_{NO-in}° = average influent (to the IACM tank) NO_x -N concentration during a steady-state phase (mg/L).

S_{NH} = ammonia-N concentration in the IACM tank during a transient-state phase created by ammonia-N shock loading (mg/L).

$S_{NH}(0)$ = initial ammonia-N concentration in the IACM tank during a transient-state phase created by ammonia-N shock loading (mg/L).

S_{NH-in} = influent (to the IACM tank) ammonia-N concentration during a transient-state phase (mg/L) created by ammonia-N shock loading.

S_{NO} = NO_x -N concentration in the IACM tank during a transient-state phase created by NO_x -N shock loading (mg/L).

$S_{NO}(0)$ = initial NO_x -N concentration in the IACM tank during a transient-state phase created by NO_x -N shock loading (mg/L).

S_{NO-in} = influent (to the IACM tank) NO_x -N concentration during a transient-state phase created by NO_x -N shock loading (mg/L).

HRT = nominal hydraulic retention time of the IACM tank (h).

$IACM$ = Intermittently aerated, completely mixed.

k_{DN} = Potential specific denitrification rate ($mgNO_x$ -N/gMLVSS \times h $^{-1}$).

k_N = Potential specific nitrification rate ($mgNH_4$ -N/gMLVSS \times h $^{-1}$).

Q = actual flow rate through the IACM tank (L/h).

r_{DN} = denitrification rate ($mgNO_x$ -N/L \times h $^{-1}$).

r_G = ammonia-N assimilation rate ($mgNH_4$ -N/L \times h $^{-1}$).

r_N = nitrification rate ($mgNH_4$ -N/L \times h $^{-1}$).

r_O = ammonification rate ($mgNH_4$ -N/L \times h $^{-1}$).

$SDNR$ = specific denitrification rate ($mgNO_x$ -N/gMLVSS \times h $^{-1}$).

SNR = specific nitrification rate ($mgNH_4$ -N/gMLVSS \times h $^{-1}$).

t = time (h).

V = volume of the IACM tank (L).

X = mixed liquor volatile suspended solids (MLVSS) concentration in the IACM tank (mg/L).

INTRODUCTION AND BACKGROUND

Many studies (Bishop et al., 1976; Ip et al., 1987; Brink et al., 1993; Huang, 1993) have reported that intermittent aeration (IA) processes are effective in nitrogen removal. The aeration cycle times used in these studies were usually controlled in a range of 0.5 to 3 hours. In this type of IA process, ammonia-N is converted to nitrate-N during the air-on period, and the nitrate-N produced is used to remove organic substrate during the subsequent air-off period. Therefore, the nitrification and denitrification rates can be determined in-situ, based on the nitrate production rate during the air-on period and the nitrate reduction rate during the air-off period (Huang, 1993). However, Batchelor (1982) predicted that an IA reactor would behave just like a continuous-aeration reactor, if the cycle time ratio (CTR , the ratio of aeration cycle time to reactor HRT) is less than 0.1; this suggested that the nitrate concentration in the IA reactor could become constant, if aeration cycles are short enough. As such, the in-situ determination of

nitrification and denitrification rates based on nitrate profiles would become difficult, if not impossible.

Recently, the phenomenon of simultaneous nitrification and denitrification (SND) has frequently been reported in the aeration tank of both lab-scale and full-scale biological nutrient removal (BNR) processes (U.S. EPA, 1987; Kugelman et al., 1991; Kshirsagar et al., 1995). Significant SND (up to 50% of the influent TKN) was observed in an oxidation-reduction potential (ORP) controlled, IA tank and in the aerobic zone of a three-stage (anaerobic, anoxic, and aerobic) process (Zhao et al., 1999). Due to SND, the method used by Huang 1993 (*i.e.*, based on in situ $\text{NO}_x\text{-N}$ profile) could significantly underestimate both nitrification and denitrification rates.

For estimating reaction rates, the simplest and most frequently used method is a batch reactor, operated at constant temperature and volume. However, a simple batch reactor cannot simulate a continuous-flow process. When a continuous-flow reactor is used to obtain the rate data, a number of steady-state runs are required to obtain data relating reaction rate to concentration. In other words, one steady-state run is unable to assess the reaction order. Furthermore, as a substrate becomes limiting, such as close to zero, the rates obtained are less than the potential rate.

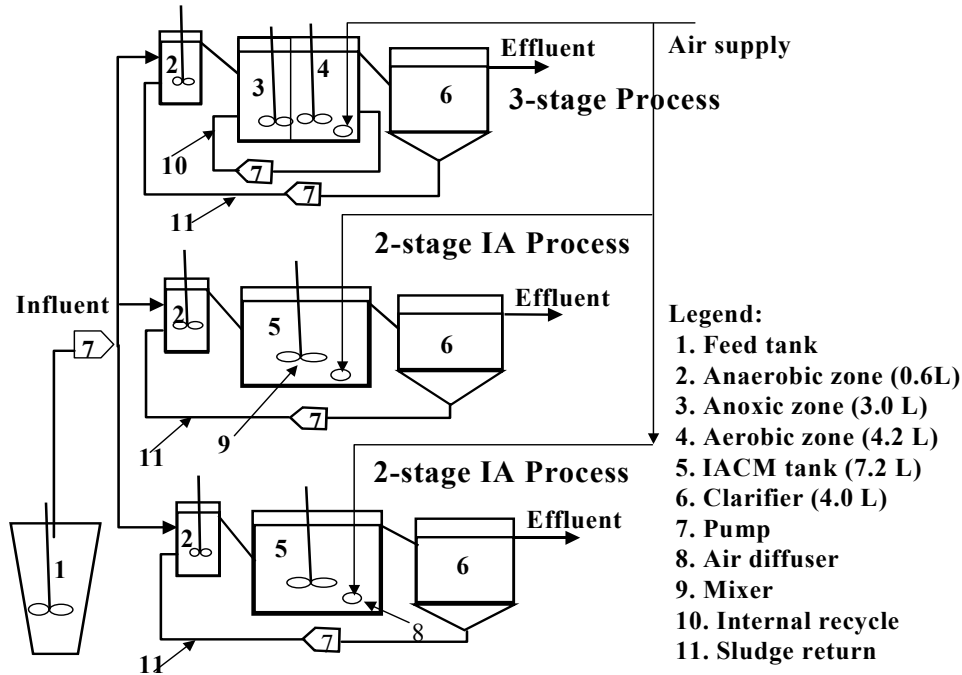
This paper introduces a technique that allows reaction kinetics (e.g., potential rate and order) to be studied in a continuous-flow reactor. For each studied reaction, the technique requires a steady-state run with an additional transient-state phase. The transient state is created by a shock loading, using the substrate of the studied reaction, after the steady state has been reached. Such a technique can eliminate the influence of side reactions, which involve the substrate, on the rate determination of the studied reaction. For example, nitrate is a substrate of denitrification (studied reaction), as well as a product of nitrification (side reaction). Therefore, the determination of denitrification rate, based on nitrate reduction rate, in a reactor involving SND, is subject to the influence of nitrification. However, such influence can be eliminated, if the reactor's response to a nitrate shock loading, is used to determine the denitrification rate. To the knowledge of these authors, this technique has not been used in the area of wastewater treatment.

In the current study, this technique was applied to determine potential specific nitrification and denitrification rates (SNR and SDNR in $\text{substrate-mass} \times \text{bio-mass}^{-1} \times \text{time}^{-1}$) in an ORP controlled, IA tank, involving significant SND. In addition, the technique was applied to determine potential SDNR and SNR in the anoxic and aerobic zones, respectively, of a three-stage process.

MATERIALS AND METHODS

A total of five series of experiments were conducted under various controlled conditions in three bench-scale reactor systems: a three-stage process (control system) and two identical, two-stage, IA processes. Each series of experiments consisted of one steady-state run and two additional transient-state phases, one created by an ammonia-N shock load and the other by a nitrate-N shock load. [Figure 1](#) presents a schematic diagram of the three reactor systems. The two-stage IA process consisted of an anaerobic selector and an intermittently-aerated, completely-mixed (IACM) tank, in which aeration was controlled by absolute ORP measurement.

Figure 1 A Schematic Diagram Of The Three Reactor Systems



Steady-State Phase

The three experimental systems were primarily fed with domestic sewage at a rate of 19.2 L/d and supplemented with sodium acetate or methanol at various dosages. The characteristics of the sewage are presented in Table 1. Sodium acetate was continuously added into the anaerobic zone of each system. Methanol was added into the two IACM tanks, during air-off periods only, and into the anoxic zone of the three-stage process continuously. Details of the controlled conditions, such as the external substrate dosages and the ORP control ranges, are summarized in Table 2. The three systems were operated with a system SRT of 15 days. The details regarding the system HRTs and the recycle flow rates are given in Table 3.

Table 1 Characteristics Of The Influent Sewage.

| TCOD, mg/L | SCOD, mg/L | TSS, mg/L | TKN, mg/L | NH ₄ , mg/L | TP, mg/L |
|------------|------------|-----------|-----------|------------------------|----------|
| 300-360 | 132-152 | 120-160 | 23-32 | 11.5-19.6 | 4.6-5.9 |

Transient-State Phase

After the completion of each steady-state run, an instantaneous ammonia-N shock load, followed two days later by a nitrate-N shock load, was imposed on the three systems under continuous flow conditions. To provide the ammonia-N shock load, ammonia chloride was added into the two IACM tanks and the aerobic zone of the three-stage process instantaneously. The amount added was equivalent to an additional 30 mg/L ammonia-N in the IACM tanks. After the

systems returned to the steady state from the ammonia shock loading (a stabilization period of two days was usually used), a nitrate-N shock load was imposed on the three systems by adding sodium nitrate into the two IACM tanks and the anoxic zone of the three-stage process; this gave an additional 30 mg/L of nitrate-N in the IACM tanks.

To prevent the added chemical from being short-circuited, the outlets of the reactors were closed just before pouring the chemical solution and reopened after a two-minute wait. Finally, it should be noted that except for the shock loading, experimental conditions for each additional transient-state phase were identical to those of the corresponding steady-state phase.

Table 2 Variable Experimental Conditions For Each Steady-State Phase.

| Series No | External Substrate | A Three-stage Process | | B Two-stage IA Process | | C Two-stage IA Process | |
|-----------|--------------------|--------------------------|-----------|---------------------------|-----------|---------------------------|----------|
| | | Dose (mgCOD/h) | DO (mg/L) | Dose (mgCOD/h) | ORP (mV) | Dose (mgCOD/h) | ORP (mV) |
| 1 | Acetate | 24 | 3.0 | 24 | -25--25 | 24 | -100—100 |
| 2 | Acetate | 40 | 1.0 | 40 | -25--0 | 24 | -25--0 |
| 3 | Methanol | 12 | 3.0 | 12 | -50--0 | 12 | 0—50 |
| 4 | Methanol | 12 | 3.0 | 12 | -100--100 | 12 | -25—25 |
| 5 | Acetate | 80 | 3.0 | 0 | -25--0 | 40 | 0—25 |

Table 3 Fixed Experimental Conditions.

| | Three-stage Process | Two, 2-stage IA Processes |
|--------------------|---------------------|---------------------------|
| FLOW RATE | | |
| Influent | 19.2 (L/d) | 19.2 (L/d) |
| Internal recycle | 57.6 (L/d) | N/A |
| Sludge return | 9.6 (L/d) | 9.6 (L/d) |
| NOMINAL HRT | | |
| Anaerobic | 0.75 (h) | 0.75 (h) |
| Anoxic | 3.75 (h) | N/A |
| Aerobic | 5.25 (h) | 9.0 (h) |
| Total | 9.75 (h) | 9.75 (h) |
| Clarifier | 5.0 (h) | 5.0 (h) |

Sampling and Analytical Methods

Each steady-state run was run for about a month. Sampling was conducted every other day. Samples were taken from all bioreactors, the influent and the three effluents in order to perform nitrogen balances. For transient-state phases, an intensive monitoring program (sampling once every 30 minutes) started immediately, after shock loading was imposed, and continued for up to 6 hours. The samples were taken from the reactors, in which shock loading was added (*e.g.*, IACM tank), and from the preceding reactors (*e.g.*, the anaerobic zone).

The analytical parameters involved in the determination of reaction rates were total Kjeldahl nitrogen (TKN), ammonia-N, nitrate + nitrite ($\text{NO}_x\text{-N}$). All three parameters were analyzed using the methods outlined in the Methods Manual for the QuikChem Automated Ion Analyzer. Real time ORP and DO data were logged using a data acquisition and control system (DAC) system.

RESULTS

The experimental results presented here provide background information and lay the base for some assumptions made for the determination of reaction rates.

Aeration Cycle

The intermittent aeration (on/off) in the IACM tank was controlled by comparing the ORP measurements in the bulk liquid with the preset upper and lower ORP limits pre-set in the DAC system. It was observed that the intermittent aeration cycle in the IACM tank depended mainly on the breadth of an ORP range. When intermittent aeration was controlled by narrow ORP ranges with breadths of 25 and 50 mV, the aeration cycle time was about 3-5 minutes without a zero-DO period in the cycle. In comparison to the above narrow ranges, the wide ORP range (a breadth of 200 mV) control gave 4 to 5 times longer cycle and a zero-DO period for up to one third of the total cycle time. Furthermore, the DO concentrations in the IACM tank, under control by the narrow ORP ranges, were generally in a low range of 0.0-0.3 mg/L, whereas the DO concentration range, corresponding to the wide ORP range, was 0.0-0.6 mg/L. The DO concentration in the aerobic zone of the three-stage process was manually maintained at approximately 3 mg/L for most of the experimental series.

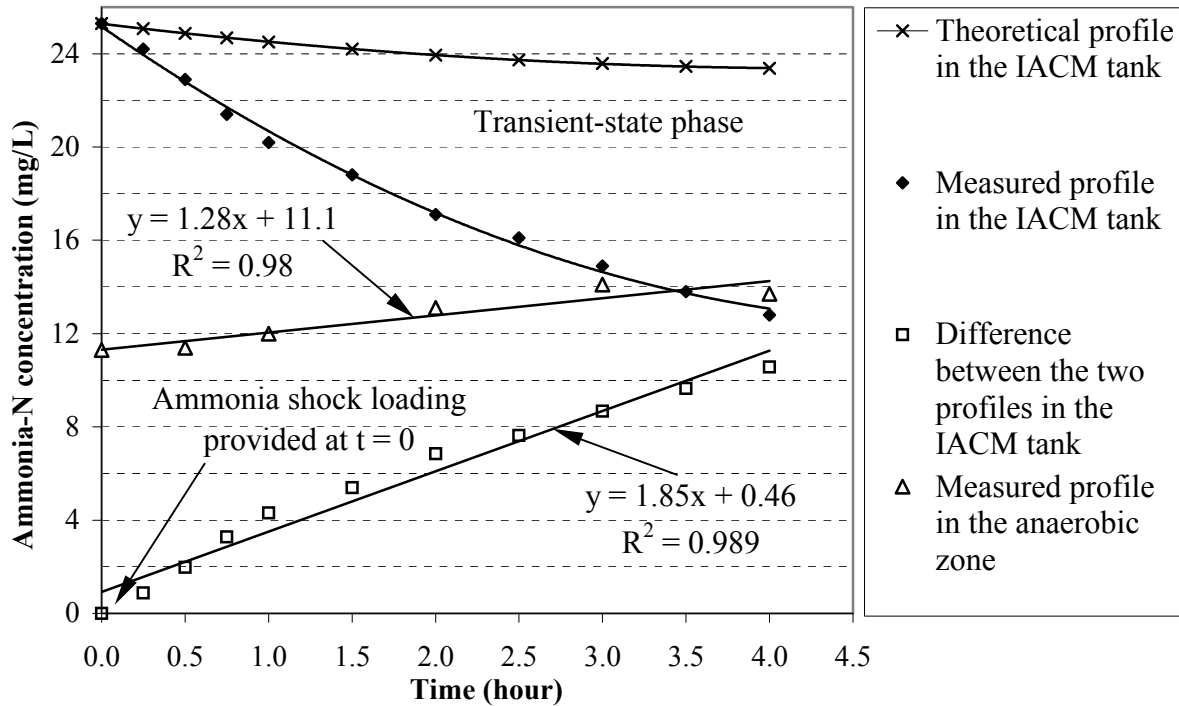
Dynamic Responses to the Shock Loading

Figure 2 presents a typical measured ammonia-N profile in the IACM tank, in response to the ammonia-N shock loading, a corresponding theoretical profile, as well as the difference between these two profiles. The theoretical profile was calculated using Equation 17 (presented later), in which nitrification reaction was not considered. As noted, the measured profile lies well below the theoretical one; this indicates that significant nitrification occurred in the IACM tank. The difference between the two profiles increases linearly with time; this suggests that the nitrification rate followed zero-order kinetics. As noted from the measured ammonia profiles in the anaerobic zone, the ammonia-N shock loading caused a linear increase in the ammonia-N concentration in the preceding anaerobic zone, through the return sludge flow.

Figure 3 presents a typical measured $\text{NO}_x\text{-N}$ profile in the IACM tanks, in response to the nitrate-N shock loading, a corresponding theoretical profile, and the difference between these two profiles. The theoretical profile was calculated using Equation 18 (given later), in which denitrification reaction was not considered. As noted, the measured profile also lies well below the theoretical one; this indicates that significant denitrification occurred in the IACM tank. Furthermore, the linear increase (with time) of the difference between the two profiles suggests that the denitrification rate followed zero-order kinetics. The results in Figure 3, combined with those in Figure 2, clearly show that denitrification occurred simultaneously with nitrification in

the IACM tank. As also shown in Figure 3, the nitrate-N shock loading resulted in a negligible increase in the $\text{NO}_x\text{-N}$ concentration in the preceding anaerobic zone.

Figure 2 Typical Measured And Theoretical Ammonia Profiles In An IACM Tank, As Well As A Typical Measured Ammonia Profile In The Preceding Anaerobic Zone.



ANALYSIS OF REACTION RATES

Steady State

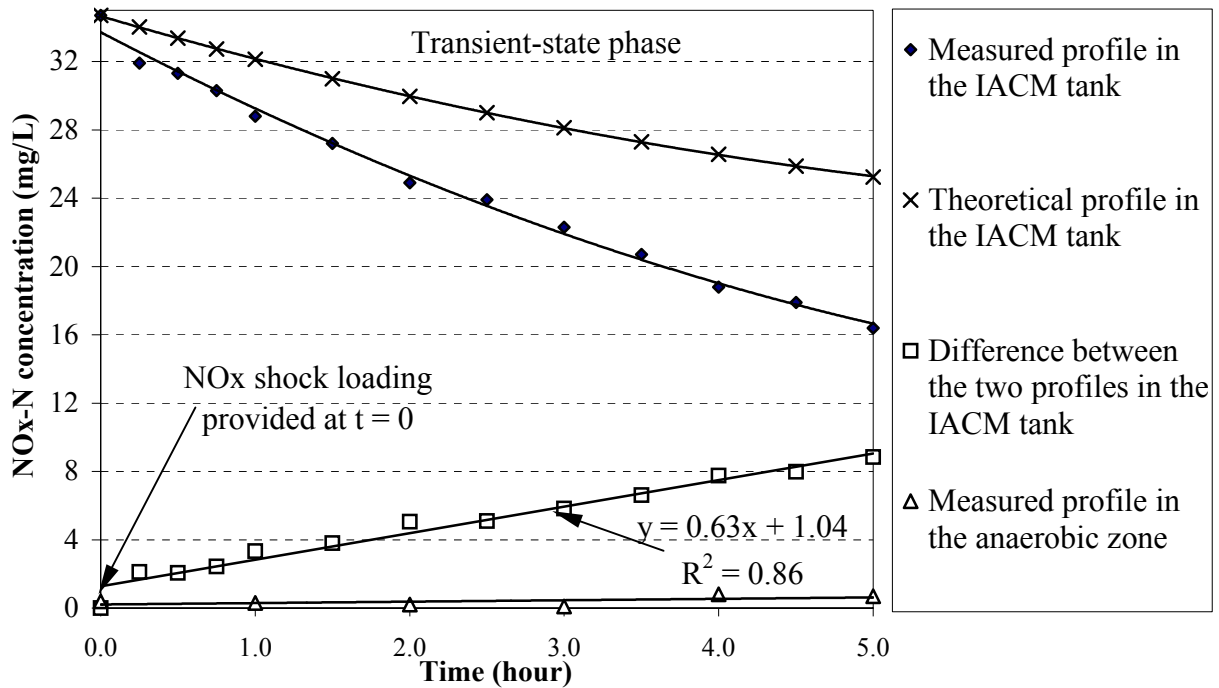
The specific nitrification and denitrification rates in a reactor, under steady-state conditions, are defined as (Randall et al., 1992):

$$SNR \text{ (or } SDNR) = A_N \text{ (or } A_D) / (HRT \times X) \quad (1)$$

where SNR and $SDNR$ are steady-state specific nitrification and denitrification rates, respectively; A_N and A_{DN} are the amounts of ammonia-N nitrified and $\text{NO}_x\text{-N}$ denitrified per liter of the feed, respectively; X is the average mixed liquor volatile suspended solids (MLVSS) level; and HRT is the nominal hydraulic retention time.

In this study, A_N and A_{DN} in the IACM tank were calculated by performing nitrogen balances around the entire process train and each individual reactor. The details on the calculations can be found elsewhere (Zhao, 1998; Zhao et al., 1999).

Figure 3 Typical Measured And Theoretical NO_x-N Profiles In An IACM Tank, As Well As A Typical Measured Nox-N Profile In The Preceding Anaerobic Zone.



Transient State

For simplicity, the equations below generally refer to the IACM tank of the two-stage, IA process (Figure 1). A general mass balance on a substrate around a continuous-flow, complete-mix reactor is written as follows:

$$V(dS/dt) = QS_{in} + QS - r_C V \tag{2}$$

where V is the volume of the reactor; Q is the actual flow rate through the reactor; S and S_{in} are the substrate concentrations in the reactor and in the influent, respectively; and r_C is the sum rate of all reactions involving S .

Nitrification. Generally, ammonia-N concentration change in an activated sludge system involves three reactions: nitrification (r_N), ammonia-N assimilation for bacterial growth (r_G), and ammonification of organic nitrogen (r_O). Volatilization of ammonia-N was ignored due to in-situ operating temperature and pH being less than favorable for it to occur (to any great extent). Therefore, mass balances on ammonia-N concentration around an IACM tank, during steady-state and transient-state phases, can be written as follows:

Steady-state phase:

$$0 = QS_{NH-in} - QS_{NH} - r_N V - (r_G - r_O) V \tag{3}$$

where S_{NH-in}^o and S_{NH}^o are the average ammonia-N concentrations in the influent (*i.e.*, in the anaerobic zone) and in the IACM tanks, respectively, during a steady-state phase; $r_N V$ is the amount of ammonia-N nitrified in the IACM tank and is the same as $Q A_N$.

Transient-state phase:

$$V(dS_{NH}/dt) = QS_{NH-in} - QS_{NH} - r_N(S_{NH})V - (r_G - r_O)V \quad (4)$$

where S_{NH-in} and S_{NH} are the ammonia-N concentrations in the anaerobic zone and in the IACM tanks, respectively, during a transient-state phase; $r_N(S_{NH})$ indicates that the nitrification rate in the IACM tank is a function of ammonia-N concentration.

The base substrate for ammonification is organic nitrogen, hence the rate of ammonification is dependent on the influent organic-N composition and bacterial population. Therefore, the change in ammonia-N concentration would not likely affect the ammonification rate. Ammonia-N assimilation has affinity constants as low as 10 μ -mole (Kleiner, 1985); this means that its rate can reach maximum at very low ammonia-N concentrations. For the current experimental systems treating domestic sewage containing sufficient ammonia-N, it is reasonable to assume that the increase in ammonia-N concentration (*e.g.*, by ammonia-N shock loading) would not affect the assimilation rate, since the maximum rate had already been reached at a very low ammonia-N level (*e.g.*, during the steady-state phase).

As noted earlier, from a steady-state phase to its corresponding ammonia-N transient-state phase, the only change in the experimental systems was an increase in ammonia-N concentration. Therefore, the rates of assimilation and ammonification during the transient-state phase would remain the same as those of the steady-state phase; in other words, r_G and r_O in Equation 4 are identical in value to that in Equation 3.

As shown in Figure 2, the ammonia shock loading also resulted in an ammonia concentration increase in the feed (*i.e.*, in the anaerobic zone) through the return sludge flow. This increase was carefully monitored and described by a quadratic equation as follow (in some cases, a linear regress equation was accurate enough; *i.e.*, $\beta = 0$):

$$S_{NH-in} = S_{NH-in}^o + \alpha t + \beta t^2 \quad (5)$$

where α and β are regression constants.

Subtracting Equation 3 from Equation 4 and taking Equation 5 into account produces Equation 6:

$$V(dS_{NH}/dt) = Q\alpha + Q\beta t^2 - QS_{NH} - r_N(S_{NH})V + Q(S_{NH}^o + A_N) \quad (6)$$

Equation 6 clearly shows that the ammonia-N response (dS_{NH}/dt), to the ammonia-N shock loading, can be used to study nitrification kinetics without the influences of side reactions such as ammonification and assimilation.

Denitrification. The change of nitrate concentration usually involves nitrification (r_N) and denitrification (r_{DN}). The assimilation of nitrate for bacterial growth can be neglected, when the influent feed contains plentiful ammonia-N, since the latter is a primary nitrogen source for bacterial growth. Therefore, mass balances on the $\text{NO}_x\text{-N}$ concentration around the IACM tank, during steady-state and transient-state phases, can be written as follows:

Steady-state phase:

$$0 = QS_{NO-in}^o - QS_{NO}^o - r_{DN}V - r_NV \quad (7)$$

where S_{NO-in}^o and S_{NO}^o are the average $\text{NO}_x\text{-N}$ concentrations in the anaerobic zone and in the IACM tank, respectively; $r_{DN}V$ is the amount of $\text{NO}_x\text{-N}$ denitrified in the IACM tank and is the same as QA_{DN} .

Transient-state phase:

$$V(dS_{NO}/dt) = QS_{NO-in} - QS_{NO} - r_{DN}(S_{NO})V - r_NV \quad (8)$$

where S_{NO-in} and S_N are the $\text{NO}_x\text{-N}$ concentrations in the anaerobic zone and in the IACM tanks, respectively; $r_{DN}(S_{NO})$ indicates that the denitrification rate is a function of $\text{NO}_x\text{-N}$ concentration.

Since the nitrate-N shock loading would not affect nitrification rate, the nitrification rate during the transient-state phase would remain the same as that during the steady-state phase. As shown in [Figure 3](#), nitrate-N shock loading did not increase the $\text{NO}_x\text{-N}$ concentration in the preceding anaerobic zone. Therefore, the term of QS_{NO-in} in Equation 8 is equal to QS_{NO-in}^o in Equation 7, in value (actually both are near zero). Subtracting Equation 7 from Equation 8 gives:

$$V(dS_{NO}/dt) = -QS_{NO} - r_{DN}(S_{NO})V + Q(S_{NO}^o + A_{DN}) \quad (9)$$

Equation 9 indicates that the response to the nitrate-N shock loading (dC_N/dt) can be used to study denitrification kinetics without the influence of nitrification.

Reaction Order

A review of the literature concerning the nitrification process shows diverse opinions regarding the reaction order (Halling-Sensen and Jørgensen, 1993). However, it is generally accepted that nitrification follows zero-order kinetics down to ammonia-N concentrations as low as 5 mg/L. In this study, the shock loading elevated the ammonia-N concentrations in the three systems to a range of 15-40 mg/L. Therefore, zero-order kinetics is assumed for the nitrification reaction during the transient-state phase:

$$r_N = k_N X \quad (10)$$

where k_N is the potential specific nitrification rate.

Several investigators (Moore and Schroeder, 1970; Murphy and Dawson, 1972; Stensel et al., 1973) have all reported zero-order kinetics for the denitrification process, when the nitrate-N concentration is above 1-2 mg/L and insitu organic carbon is not limiting. During the transient-state phase, the ammonia-N concentrations in the three processes were elevated to a level above 30 mg/L; organic carbon was constantly supplied from the influent feed. Therefore, zero-order kinetics (with respect to NO_x concentration) was also assumed for the denitrification reaction during this phase, under such constant organic carbon supply conditions.

$$r_{DN} = k_{DN}X \quad (11)$$

where k_{DN} is the potential specific denitrification rate.

During the steady-state phase, a SRT of 15 days was maintained in the three systems by wasting the mixed liquor from the aeration tank daily. Therefore, the daily variation of MLSS level in the three systems, caused by the sludge wastage, was less than 7%. Considering that the duration of a transient-state phase was less than 6 hours, the variation of MLSS level during this period would be less than 2%. Therefore, solids level X can be considered as a constant during the both steady and transient state phases.

Based on the assumptions of zero-order kinetics for both nitrification and denitrification, Equations 6 and 9 both can be simplified to Equation 12.

$$(dS(t)/dt) + mS(t) = at^2 + bt + c \quad (12)$$

where, in describing an ammonia-N profile, $S(t)$ represents ammonia-N concentration at time t ; $m = Q/V$, $a = m\beta$, $b = m\alpha$, $c = (mS_{NH}^0 + mA_N - k_N X)$.

where, in describing a NO_x -N profile, $S(t)$ represents NO_x -N concentration at time t ; $m = Q/V$, $a = 0$, $b = 0$, $c = (mS_{NO}^0 + mA_{DN} - k_{DN} X)$.

Integration of Equation 12 gives:

$$S(t) - \beta t^2 + (2\beta/m - \alpha)t = C_o e^{-mt} + (2\beta/m - \alpha + c)/m \quad (13)$$

where C_o is an integration constant.

Equation 13 is a two-variable linear equation expressed by:

$$y = C_o x + I \quad (14)$$

where $x = e^{-mt}$; $y = S(t) - \beta t^2 + (2\beta/m - \alpha)t$; and the intercept, $I = (2\beta/m - \alpha + c)/m$.

Based on measured time-concentration profiles, x - y plots with appropriate regression equations were developed according to Equation 14, as shown in Figures 4 and 5. The intercepts I from the linear plots are used to estimate the specific reaction rates (k_N and k_{DN}).

Figure 4 Linear Plots Developed From Measured Ammonia Profiles According To Equation 13 (Data Obtained From The Fourth Series Of Transient-State Experiments).

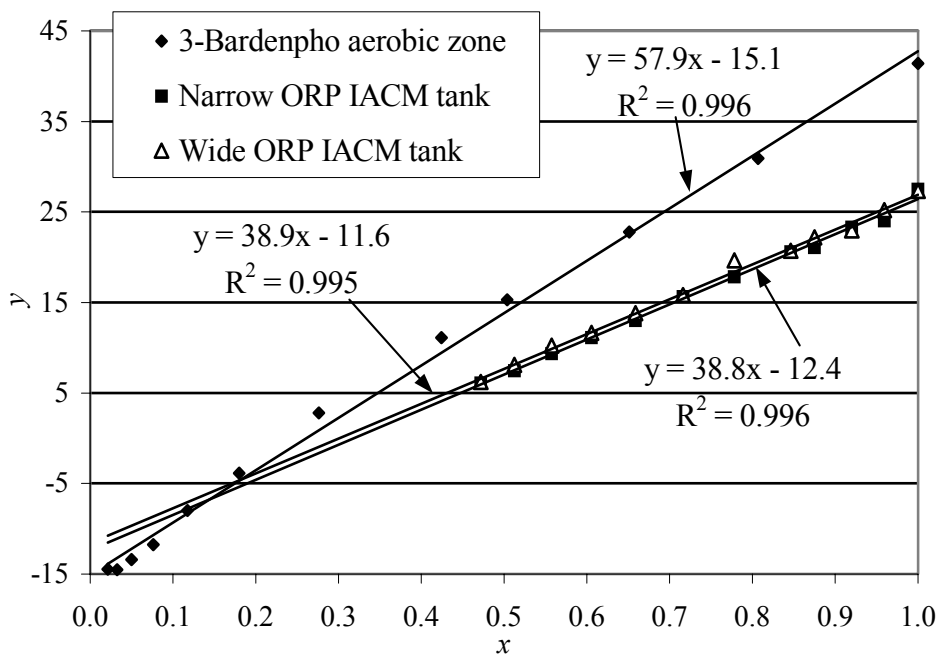
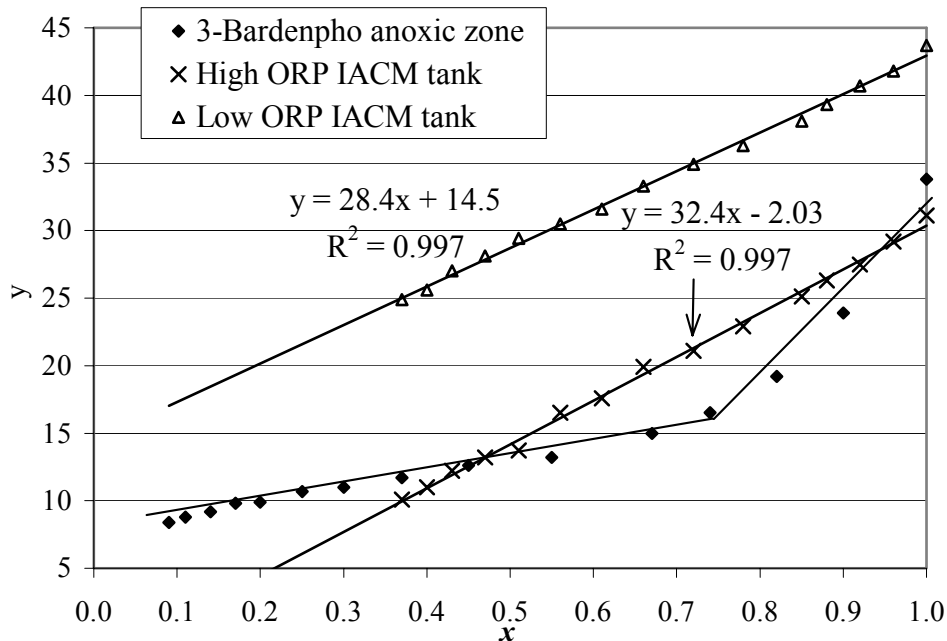


Figure 5 Linear Plots Developed From Measured Nitrate Profiles According To Equation 13 (Data Obtained From The Third Series Of Transient-State Experiments).



$$k_N = [m(S_{NH}^o + A_N - I) - \alpha + 2\beta/m]X \quad (15)$$

$$k_{DN} = m(S_{NO}^o + A_D - I)/X \quad (16)$$

As shown in [Figures 4 and 5](#), the high correlation coefficients of the linear plots suggested that the assumption of zero-order kinetics for both nitrification and denitrification reactions was adequate. However, a non-linear $\text{NO}_x\text{-N}$ plot was observed in the anoxic zone of the three-stage process, in the experimental series with methanol addition. The non-linear plot might result from using different carbon sources for denitrification and could be broken into two linear phases.

Assuming that the reaction terms in Equations 6 and 9 are zero, (*i.e.*, $r_N = 0$ and $r_D = 0$), Following the same procedure used in developing Equation 13, Equations 17 and 18 can be developed to calculate the theoretical profiles, which were presented earlier in [Figures 2 and 3](#), respectively.

Ammonia-N theoretical profile:

$$S_{NH}(t) = \alpha t + (S_{NH}^o + A_N - \alpha/m) + (S_{NH}(0) - (S_{NH}^o + A_N - \alpha/m))e^{-mt} \quad (17)$$

$\text{NO}_x\text{-N}$ theoretical profile:

$$S_{NO}(t) = (S_{NO}^o + A_{DN}) + (S_{NO}(0) - (S_{NO}^o + A_{DN}))e^{-mt} \quad (18)$$

where $S_{NH}(0)$ and $S_{NO}(0)$ are initial ammonia-N and $\text{NO}_x\text{-N}$ concentrations, respectively, in the IACM tank during a transient-state phase.

DISCUSSION

Specific Nitrification Rate (SNR)

The potential, and the steady-state, SNRs are summarized in [Table 4](#). The steady-state SNRs in the aerobic zone of the three-stage process were in a typical range of 1.4-2.0 ($\text{mgNH}_4\text{-N/gMLVSS}\times\text{h}^{-1}$). These values are in good agreement with the literature data under the same conditions: Randall et al. (1992) reported that the SNRs were 1.78, 1.92 and 2.02 ($\text{mgNH}_4\text{-N/gMLVSS}\times\text{h}^{-1}$), at temperatures of 20, 15 and 10°C in a single-sludge BNR process, treating municipal wastewaters, with a total SRT of 15 days and an aerobic SRT of 8 days.

Table 4 Summary Of The Potential And Steady-State SNRs And The Calculation Procedure.

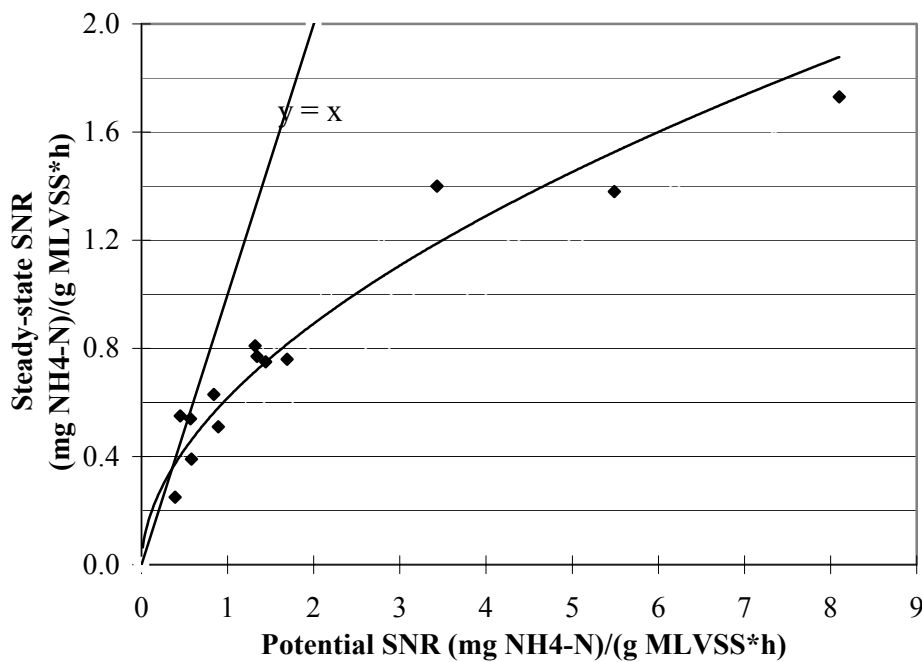
| Series No. | Reactor | S_{NH}^o (mg/L) | A_N (mg/liter feed) | Intercept (mg/L) | X (mg/L) | α (mg/L h ⁻¹) | β (mg/L h ⁻²) | m (h ⁻¹) | Potential SNR (k_N) (mg NH ₄ -N)/(g MLVSS) h ⁻¹ | Steady-state SNR (mg NH ₄ -N)/(g MLVSS) h ⁻¹ |
|------------|---------|----------------------|--------------------------|---------------------|---------------|-------------------------------------|------------------------------------|---------------------------|------------------------------------------------------------------------------|-----------------------------------------------------------------------|
| 1 | A* | 0.4 | 19.6 | NA | 1864 | NA | NA | NA | NA | 2.00 |
| | B* | 8.0 | 6.10 | 3.32 | 2692 | 0.75 | 0 | 0.167 | 0.39 | 0.25 |
| | C* | 2.9 | 14.4 | -1.45 | 2949 | 1.45 | 0 | 0.167 | 0.57 | 0.54 |
| 2 | A | 9.9 | 10.9 | 20.0 | 1992 | -1.42 | 0 | 0.857 | 1.06 | 1.04 |
| | B | 6.1 | 13.4 | 7.77 | 2686 | 0.75 | 0 | 0.167 | 0.45 | 0.55 |
| | C | 7.2 | 12.0 | 1.51 | 2623 | 0.61 | 0 | 0.167 | 0.89 | 0.51 |
| 3 | A | 0.2 | 20.4 | -20.7 | 2247 | 12.4 | -2.05 | 0.857 | 8.10 | 1.73 |
| | B | 7.7 | 9.80 | 3.76 | 2767 | 0.70 | 0 | 0.167 | 0.58 | 0.39 |
| | C | 0.5 | 18.8 | -12.8 | 2757 | 0.69 | 0 | 0.167 | 1.69 | 0.76 |
| 4 | A | 0.1 | 18.4 | -15.1 | 2533 | 10.1 | -2.03 | 0.857 | 5.49 | 1.38 |
| | B | 0.3 | 17.6 | -11.6 | 2541 | 1.53 | 0 | 0.167 | 1.34 | 0.77 |
| | C | 0.1 | 18.1 | -12.4 | 2667 | 1.28 | 0 | 0.167 | 1.44 | 0.75 |
| 5 | A | 0.0 | 19.4 | -75.3 | 2643 | 8.01 | -1.43 | 0.286 | 3.43 | 1.40 |
| | B | 1.8 | 17.5 | -0.53 | 3089 | 0.73 | 0 | 0.167 | 0.84 | 0.63 |
| | C | 0.1 | 19.7 | 5.87 | 2717 | 0.70 | 0 | 0.167 | 1.32 | 0.81 |

*A, B, and C represent the aerobic zone of the three-stage process and the two IACM tanks, respectively.

The potential *SNRs*, in the two IACM tanks, were generally in a range of 0.4-1.7 mgNH₄-N/gMLVSS h⁻¹; as expected, these rates were significantly lower than those in the aerobic zone of the three-stage process (3.4-8.1 mgNH₄-N/gMLVSS h⁻¹), at a DO concentration of 3 mg/L. As suggested by the steady-state evaluation, both autotrophic nitrification and heterotrophic nitrification could occur in the IACM tank (Zhao, 1998; Zhao et al., 1999). Therefore, the lower rates in the IACM tank could be caused by an inhibition of autotrophic nitrification, by low DO conditions, or by the lower intrinsic heterotrophic nitrification rate (compared to the autotrophic nitrification rate).

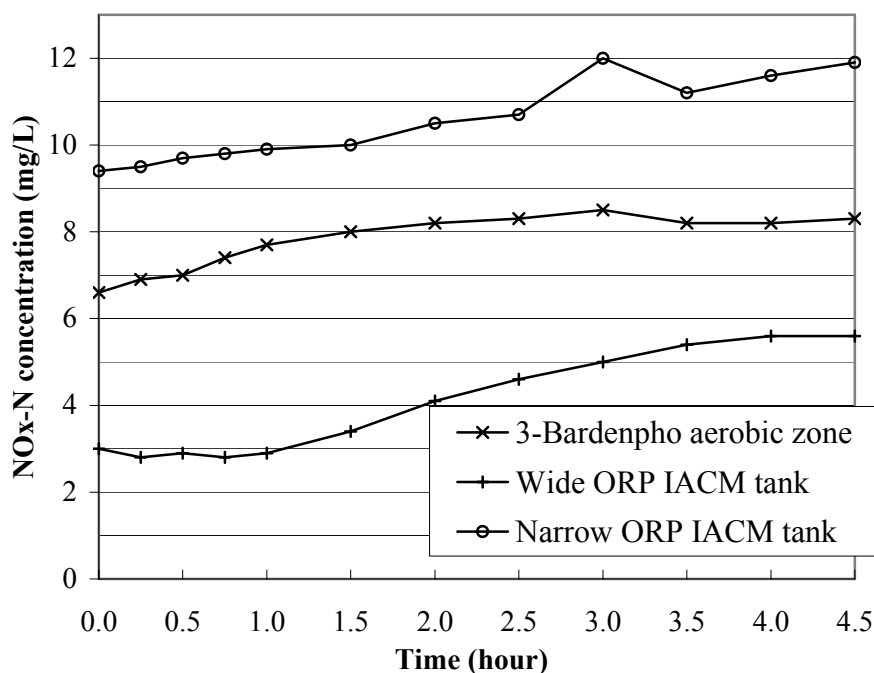
Figure 6 presents the comparisons between the steady-state and potential *SNRs*. As noted, the potential rate agrees with the steady-state rate in the low value range and is significantly higher than the steady-state rate in the high value range. The discrepancy between the two rates in the high value range is believed to result from the ammonia-N shock loading. Since ammonia-N limiting conditions were usually experienced during the steady-state phase at high nitrification rates, the shock loading eliminated that condition, thus, resulting in a higher potential *SNR*.

Figure 6 Comparison of the potential *SNRs* with the corresponding steady-state *SNRs*.



This explanation can be indirectly proven by the results shown in Figure 7. During the steady-state phase, the low ammonia-N concentrations (0.1, 0.3 and 0.1 mg/L) suggested that ammonia-N limiting conditions were experienced in all three tanks. The ammonia-N shock loading would accelerate the nitrification rate, by increasing the ammonia-N levels in these tanks. Therefore, in response to the shock loading, a gradual increase in NO_x-N concentration was observed in the three aeration tanks.

Figure 7 Measured $\text{NO}_x\text{-N}$ Profiles In The Aeration Tanks In Response To The Ammonium Shock Loading.



Specific Denitrification Rate (SDNR)

The potential, and steady-state, *SDNRs* are summarized in Table 5. The potential *SDNR* in the anoxic zone of the three-stage process, was $2.57 \text{ mgNO}_x\text{-N/gMLVSS h}^{-1}$ at an external acetate dosage of 100 mg COD/L . This rate is considerably lower than the corresponding rates obtained by Ekama et al. (1984) in batch tests and Carucci et al. (1996) in a lab-scale, semi-batch system. The discrepancy was expected, since the added acetate was directly available for the denitrification in their batch and semi-batch systems, but not available in the anoxic zone of the three-stage process, as indicated by zero VFA concentrations in the preceding anaerobic zones (Zhao, 1998; Zhao et al., 1999). In contrast, the value of $2.57 \text{ mgNO}_x\text{-N/gMLVSS h}^{-1}$ falls into the ranges of 1.25 to $6.25 \text{ mgNO}_x\text{-N/gMLVSS h}^{-1}$ (U.S. EPA, 1975) and 1.6 - $3.3 \text{ mgNO}_x\text{-N/gMLVSS h}^{-1}$ (Stensel, 1981; Burdick et al., 1982) reported for both pilot-scale and full-scale BNR plants.

The comparison between the two types of *SDNRs* are presented in Figure 8. It should be noted that the potential rates obtained from the cases with the two linear phases were not included in the comparison, since the potential rates of any phases do not represent the average, as do the steady-state rates. As shown in Figure 8, similar results to the *SNRs* were also observed for the *SDNRs*; that is, the potential *SDNRs* appear to agree with the steady-state *SDNRs* in the low value range and are significantly higher than the steady-state rates in the high value range. The nitrate-N shock loading (by eliminating the $\text{NO}_x\text{-N}$ limiting conditions) is believed to be the cause of the discrepancy between the two rates in the high value range.

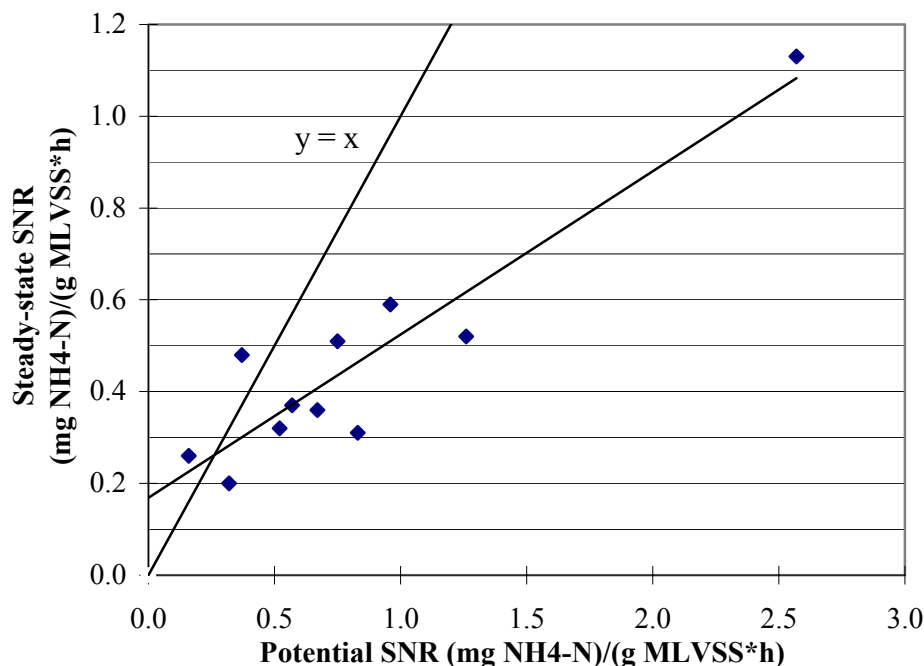
Table 5 Summary of the potential and steady-state SDNRs and the calculation procedure.

| Series No. | Reactor | S^o_{NO} (mg/L) | A_{DN} (mg per liter feed) | <i>Intercept</i> (mg/L) | X (mg/L) | α (mg/L h ⁻¹) | β (mg/L h ⁻²) | m (h ⁻¹) | <i>Potential SDNR (k_D)</i> (mg NO _x -N)/(g MLVSS) h ⁻¹ | <i>steady-state SDNR</i> (mg NO _x -N)/(g MLVSS) h ⁻¹ |
|------------|-----------|----------------------|---------------------------------|----------------------------|---------------|-------------------------------------|------------------------------------|---------------------------|-----------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| 1 | <i>A*</i> | 2.9 | 5.40 | NA | 1864 | NA | NA | NA | NA | 0.77 |
| | <i>B*</i> | 0.1 | 7.40 | -5.7 | 2692 | 0 | 0 | 0.167 | 0.83 | 0.31 |
| | <i>C*</i> | 0.7 | 13.7 | -7.8 | 2949 | 0 | 0 | 0.167 | 1.26 | 0.52 |
| 2 | <i>A</i> | 0.3 | 3.50 | NA | 1992 | NA | NA | 1.20 | NA | 0.47 |
| | <i>B</i> | 0.2 | 12.3 | 0.5 | 2686 | 0 | 0 | 0.167 | 0.75 | 0.51 |
| | <i>C</i> | 0.2 | 11.3 | 5.7 | 2623 | 0 | 0 | 0.167 | 0.37 | 0.48 |
| 3 | <i>A</i> | 2.7 | 9.20 | -48.1/7.6 | 2247 | 0 | 0 | 0.40 | 10.7/0.77** | 1.1 |
| | <i>B</i> | 0.2 | 8.90 | -2.03 | 2767 | 0 | 0 | 0.167 | 0.67 | 0.36 |
| | <i>C</i> | 10.7 | 6.50 | 14.5 | 2757 | 0 | 0 | 0.167 | 0.16 | 0.26 |
| 4 | <i>A</i> | 4.7 | 6.90 | -41.1/5.7 | 2533 | 0 | 0 | 0.857 | 8.3/0.93** | 0.73 |
| | <i>B</i> | 4.4 | 13.6 | 3.5 | 2541 | 0 | 0 | 0.167 | 0.96 | 0.59 |
| | <i>C</i> | 10.4 | 4.80 | 10.0 | 2667 | 0 | 0 | 0.167 | 0.32 | 0.20 |
| 5 | <i>A</i> | 0.3 | 11.2 | -5.5 | 2643 | 0 | 0 | 0.40 | 2.57 | 1.13 |
| | <i>B</i> | 6.9 | 10.3 | 6.7 | 3089 | 0 | 0 | 0.167 | 0.57 | 0.37 |
| | <i>C</i> | 9.8 | 7.80 | 9.1 | 2717 | 0 | 0 | 0.167 | 0.52 | 0.32 |

*A, B, and C represent the anoxic zone of the three-stage process and the two IACM tanks, respectively.

** values represent the first and second linear rates, respectively.

Figure 8 Comparison Of The Potential SDNR With The Corresponding Steady-state SDNR.



SUMMARY AND CONCLUSIONS

This paper introduced a technique to determine reaction rates using reactor's transient responses to shock loading; two examples, one for nitrification and the other for denitrification, were given to demonstrate the procedures.

The proposed technique allows process kinetics (*e.g.*, reaction order and potential rate) to be assessed in continuous processes in one steady-state run. An excellent agreement between predicted and experimental data was obtained in developing the mathematical approach. Although the integral method put forth by the authors can be applied only to reactions with zero-order kinetics, it does not mean that there is a limitation in the application of the experimental technique to other reactions, since a differential method can be used for reactions with non-zero-order kinetics.

A reasonable agreement, between the rates obtained by the proposed technique and those reported in the literature, proved that the rates obtained represent continuous processes. The experimental results also proved:

- Nitrification and denitrification occurred simultaneously in the two IACM tanks;
- Nitrification and denitrification reactions follow zero-order kinetics at substrate (ammonia and nitrate, respectively) concentration ranges of 10-30 mg/L; and
- The potential SNRs and SDNRs in the IACM tank were lower than the corresponding rates in the aerobic and anoxic zones of the three-stage process.

ACKNOWLEDGMENTS

This research was supported by grants from the Natural Sciences and Engineering Research Council of Canada (NSERC), in the form of a scholarship to the first author and operating research grants to the second and third authors. The excellent technical assistance provided by the staff of the Environmental Engineering Lab at the University of B.C. is acknowledged.

REFERENCES

- Batchelor B., (1982). Kinetic Analysis of Alternative Configurations for Single-Sludge Nitrification/Denitrification, *J. Water Pollut. Control Fed.*, **54**, 1493-1504.
- Bishop D. F.; Heidman J. A.; and Stamberg J. B. (1976). Single-Stage Nitrification and Denitrification, *J. Water Pollut. Control Fed.*, **48**, 520-532.
- Brink W. P.; Edwards S. J.; and Schwinn D. E. (1993). Full-Scale Complete-Mix Nitrification Denitrification Using Cyclinal Aeration at Westport WPCF, In: *Liquid Treatment Processes, Proc., 66th Annual Conf., Water Environ. Fed.*, **3**, 337-346.
- Burdick C. R.; Reffling D. R.; and Stensel H. D. (1982). Advanced Biological Treatment to Achieve Nutrient Removal, *J. Wat. Pollut. Control Fed.*, **54**, 1078-1086.
- Carucci A.; Ramadori R.; Rossetti S.; and Tomei M. C. (1996). Kinetics of Denitrification Reactions in Single Sludge Systems, *Water Res.*, **30**, 51-56.
- Ekama G. A.; Marais G. v. R.; Siebritz I. P.; and et al. (1984). *Theory, Design and Operation of Nutrient Removal Activated Sludge Processes*, A collaborative information document prepared for the Water Research Commission by the University of Cape Town, City Council of Johannesburg and the National Institute for Water Research of the CSIR.
- Halling-S rensen B.; and J rgensen S. E. (1993). *The Removal of Nitrogen Compounds From Wastewater*, Studies in Environmental Science 54, Elsevier Science Publishers B. V, Amsterdam, The Netherlands.
- Huang J. (1993). *Process Evaluation and Mathematical Modeling of the Completely Mixed Alternating Aerobic-Anoxic Activated Sludge Process*, Ph.D. Dissertation, Univ. Of Maryland, Maryland, USA.
- Ip S. Y.; Bridger J. S.; and Mills N. F. (1987). Effect of Alternating Aerobic and Anaerobic Conditions on the Economics of The Activated Sludge System, *Water Sci. Technol.*, **19**, 911-918.
- Kleiner D. (1995). Bacterial Ammonium Transport, *FEMS Microbiology Review*, **32**, 87-100.

Kshirsagar M.; Gupta A. B.; and Gupta S. K. (1995). Aerobic Denitrification Studies on Activated Sludge Mixed With *Thiosphaera pantotropha*, *Environ. Technol. Lett.*, **16**, 35-43.

Kugelman I. J.; Spector M.; Harvilla A.; and Parees D. (1991). Aerobic Denitrification in Activated Sludge, In: *Proc. of the 1991 Environ. Eng. Special Conf., Amer. Soc. Civ. Eng.*, Reno, Nev., 312-318.

Moore S. F.; and Schroeder E. D. (1970). An Investigation of the Effects of Residence Time of Anaerobic Bacterial Denitrification, *Wat. Res.*, **4**, 685-694.

Murphy K. L.; and Dawson D. (1972). The Temperature Dependency of Biological Denitrification, *Wat. Res.*, **6**, 71-83.

Randall C. W.; Barnard J. L.; and Stensel H. D. (1992). *Design and retrofit of wastewater treatment plants for biological nutrient removal*, Water Quality Management Library - Volume 5. Technomic Publishing Company, Inc. Lancaster, PA.

Stensel H. D. (1981). Biological Nitrogen Removal System Design, In: *Water-1980*, AIChE Sympo. Ser., **77**, 327-338.

Stensel H. D.; Loehr; and Lawrence (1973). Biological Kinetics of Suspended Growth Denitrification, *J. Wat. Pollu. Control Fed.*, **45**, 399-410.

U.S. Environmental Protection Agency (1975). *Process Design Manual for Nitrogen Control*, Office of Technology Transfer, Cincinnati, Ohio.

U.S. Environmental Protection Agency (1987). *Technology Transfer Design Manual—Phosphorus Removal*, USEPA/625/1-87/001 CERI Cinn., OH 45268.

Zhao H. W.; Mavinic D. S.; Oldham W. K.; and Koch, F. A. (1999). Controlling Factors for Simultaneous Nitrification and Denitrification in a Two-Stage Intermittent Aeration Process Treating Domestic Sewage, *Water Research*, **33**, 961-970.

Zhao H. W. (1998). *Oxidation-Reduction Potential and Organic Carbon Sources as Two Control Parameters for Simultaneous Nitrification and Denitrification in Biological Nutrient Removal Process*, Ph.D. Thesis, University of British Columbia. Vancouver, B.C.