Pergamon

Wat. Sci. Tech. Vol. 37, No. 12, pp. 103–110, 1998.
IAWQ

0273–1223/98 $19·00 + 0·00

PII: S0273-1223(98)00342-4

A TITRATION TECHNIQUE FOR ON-LINE NITRIFICATION MONITORING IN ACTIVATED SLUDGE

Krist Gernaey*, Herwig Bogaert*, Peter Vanrolleghem**, Alessandro Massone***, Alberto Rozzi*** and Willy Verstraete*

* *Laboratory for Microbial Ecology, University of Gent, Coupure Links. 653, B-9000 Gent, Belgium*
** *Department of Applied Mathematics, Biometrics and Process Control (BIOMATH), University of Gent, Coupure Links 653, B-9000 Gent, Belgium*
*** *Politecnico di Milano, DIIAR Sez, Ambientale, Piazza Leonardo da Vinci 32, 20133 Milano, Italy*

ABSTRACT

A titrimetric method to monitor nitrification was applied on a pilot activated sludge plant for biological N removal. Mixed liquor was sampled from the aerobic compartment of the treatment plant and a titration in-sensor experiment was performed. Interpretation of the cumulative base addition curves resulting from each titration in-sensor experiment was done using both a simple slope extrapolation method and a model-based non-linear parameter estimation method. The NH_4^+-N concentrations obtained with both methods correlated well with the NH_4^+-N concentrations measured on the effluent of the pilot plant using an on-line NH_4^+-N analyser. Contrary to most physical/chemical NH_4^+-N analysers, no sample pretreatment of the mixed liquor is needed for the measurements. It is shown in detail that interpretation of the titration curves yields information about the nitrification kinetics too, which can be an important advantage for process control purposes. © 1998 Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Activated sludge; ammonium concentration; in-sensor experiment; kinetics; nitrification; sample pretreatment; titration.

INTRODUCTION

Biological nitrogen removal is a rather complicated process consisting of two steps: nitrification and denitrification. Nitrification is normally the rate limiting reaction step. The increasing importance of biological nitrogen removal in wastewater treatment has resulted in the development of on-line instrumentation (e.g. on-line NH_4^+ and NO_2^- + NO_3^- analysers, respirometers, toxicity detection monitors,...) that allow a better monitoring and control of the ongoing activated sludge processes (Harremoes *et al.*, 1993; Gernaey *et al.*, in press). However, the majority of existing on-line sensor equipment for NH_4^+ concentration measurements in mixed liquor is expensive, rather complicated, consuming considerable amounts of expensive and polluting chemicals and requiring intensive maintenance. Moreover, sample pretreatment is often necessary when measuring in the mixed liquor, the best sampling place when NH_4^+-N concentration values have to be used for control of the treatment plant. Sample

pretreatment usually consists of an ultrafiltration step. Finally, the chemical analysis based NH_4^+-N analysers have the disadvantage that they only yield NH_4^+-N concentration values and no information about the nitrification rate of the sludge, except when they are installed on alternating systems that induce important concentration dynamics that can be interpreted in so-called software sensors (Lynggaard-Jensen *et al.*, 1996).

Traditionally, respirometric in-sensor experiments have been used to characterize the nitrifying biomass in activated sludge samples (Drtil *et al.*, 1993, Vanrolleghem and Verstraete, 1993; Kong *et al.*, 1996; Surmacz-Gorska *et al.*, 1996). Use of respirometric methods is favoured by the high oxygen consumption for nitrification (Eq. 1).

$$NH_4^+ + 2\,O_2 \rightarrow NO_3^- + H_2O + 2\,H^+ \quad (1)$$

The main problem to be solved before nitrification activities can be determined in a respirometer is to separate the nitrification oxygen uptake from the oxygen uptake for carbon substrate oxidation and endogenous metabolism. In practice, measuring the oxygen uptake for nitrification is done by adding NH_4^+-N to a sample of activated sludge in the endogenous state (Drtil *et al.*, 1993), or by designing a suitable COD/NH_4^+-N substrate mixture which allows the simultaneous characterization of heterotrophic and autotrophic bacteria in a sludge sample (Vanrolleghem and Verstraete, 1993; Kong *et al.*, 1996). Alternatively, selective nitrification inhibitors can be used to obtain the separation between oxygen uptake for nitrification and endogenous metabolism (Surmacz-Gorska *et al.*, 1996).

Besides its DO consumption, nitrification also has a pH effect, as 2 protons are formed for each NH_4^+-ion that is oxidized (Eq. 1). This pH effect has already been used for the control of nitrogen removal processes in alternating activated sludge systems (Al-Ghusain *et al.*, 1994; Hao and Huang,1996). It also has led to the construction of titrimetric biosensors for nitrification monitoring in activated sludge (Ramadori *et al.*, 1980; Aivasidis *et al.*, 1992; Massone *et al.*, 1995, 1996; Gernaey *et al.*, in press). Contrary to respirometry however, a titration experiment can also yield information about the anoxic denitrification process (Vanderhasselt, 1995; Bogaert *et al.*, in press).

In this paper, results of titration in-sensor experiments on a pilot-scale activated sludge plant with a recently developed titrimetric biosensor are described. Aim of the tests was to show that the titration method is a valid alternative to existing nitrification monitoring methods.

MATERIALS AND METHODS

Titration in-sensor experiments were done on a pilot activated sludge plant for biological N removal (Figure 1). The pilot plant (V=150 l) is a predenitrification system with an anoxic zone of 30 l. The aerobic zone is subdivided into two compartments of 30 l each and a final compartment of 60 l. The plant was fed with a synthetic substrate. The daily load to the plant corresponded to a sine wave, varying between 453 and 1058 mg N/h. This corresponded to an average volumetric N loading of 6.3 mg N/l.h (calculated on the volume of the aerobic compartment). A lab-scale titration unit with an aerated reactor vessel (V=3.4 l; Qair=70 l/h) was modified for on-line use, and installed on the pilot plant. A more detailed description of the layout of the titration system was given by Massone *et al.* (1995). An on-line NH_{4+}-N analyser with a gas-sensitive NH3 electrode (Minworth Systems Ltd., Sutton Coldfield, U.K.) was operated on the effluent on the pilot plant.

During a period of 2.5 weeks, sludge was sampled from the last aerobic compartment of the pilot plant once every 2 hours. The reactor vessel of the titration unit can be filled gravitationally, by opening the electromagnetic pinch valve situated between the pilot plant and the titration unit for a fixed duration. Dosing always exactly the same volume of sludge is done by activating pump 1 (see Figure 1), connected to a tube installed at a fixed height in the titration unit, for 60 seconds to remove the excess mixed liquor which was initially sampled. A titration in-sensor experiment with a fixed duration of about 2 hours is started immediately after sampling. A standard addition of 1.33±0.05 mg NH_4^+-N/l was dosed to the sludge sample at the beginning of a titration experiment, to allow the measurement of the nitrification rate of the sludge

sample even when the mixed liquor in the pilot plant did not contain any NH_4^+-N. A precise description of the titration procedure can be found elsewhere (Massone *et al.*, 1995, 1996; Gernaey *et al.*, in press). At the end of a titration experiment, pump 2 was activated and the mixed liquor sample was recycled into the anoxic zone of the pilot plant.

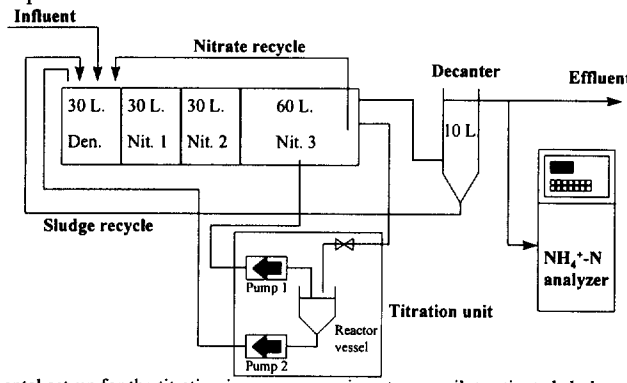

Figure 1. Experimental set-up for the titration in-sensor experiments on a pilot activated sludge plant for biological N removal. Volumes of the different reactor compartments are indicated.

RESULTS AND DISCUSSION

Titration data

A typical cumulative base addition curve and a pH profile collected during one of the titration experiments is shown in Figure 2. In a first phase, the pH of a nitrifying activated sludge sample is increased to the pH setpoint, and base is added at the maximum rate. This phase took about 2 minutes for the example of Figure 2. For the experiments described here, a pH setpoint ± ΔpH interval value of 8.2±0.03 was used. In a second phase, the sludge is actively nitrifying and the pH of the sludge is varying around the pH setpoint. Every time the pH of the sludge sample becomes lower than 8.17 (=pH setpoint minus ΔpH interval), base is added to the sludge. Base addition to the sludge is done by opening an electromagnetic pinch valve for 1.5 s (=1 base pulse). Dosage of base is repeated until the pH has returned within the pH setpoint ± ΔpH interval range. Results are stored every 10 seconds as the actual pH in the reactor vessel of the titrator and the cumulative number of base pulses dosed to the sludge sample.

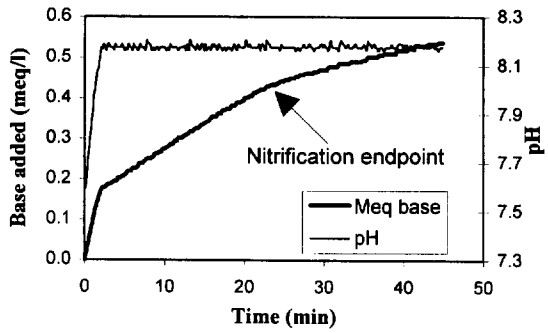

Figure 2. Typical cumulative base addition curve (expressed as amount of base dosed per litre of activated sludge sample) and pH profile obtained during an on-line titration experiment with a mixed liquor sample. For this example, the nitrification phase is finished after about 25 minutes.

Every two days, a calibration of the system was done by measuring the volume of base dosed during 50 base pulses. The calibration is needed to be able to convert the cumulative base addition curves from cumulative

number of base pulses added to the sludge sample into meq/l units. Obviously, the slope of the cumulative base addition curve is considerably lower during the nitrification phase compared to the first phase. When all substrate (NH_4^+-N) is consumed (after about 25 minutes in Figure 2), the slope of the cumulative hase addition curve decreases further to a baseline level.

Data interpretation

In a first phase, a simple data analysis procedure was developed to calculate the nitrification rate and the NH_4^+-N concentration in the activated sludge sample based on a cumulative base addition curve (Massone *et al.*, 1995). The data analysis procedure is mainly based on the detection of the two slope changes in the cumulative base addition curve, followed by an extrapolation of the different slopes to the Y-axis (Figure 3). The NH_4^+-N concentration S_{NH} (mg N/l) and the nitrification rate r (mg N/l.h) were calculated according to equations 2 and 3. B1 and B2 are expressed in meq/l units. The factor 0.143 meq/mg N was derived from equation 1. S1 and S2 are expressed in meq/l.min units.

$$S_{NH} = \frac{(B2 - B1)}{0.143} \tag{2}$$

$$r = \frac{(S1 - S2)}{0.143} * 60 \tag{3}$$

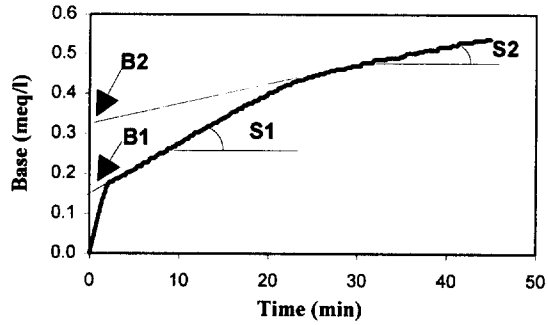

Figure 3. Principle of the slope extrapolation data analysis method. The slopes S1 and S2 are extrapolated to the Y-axis, resulting in B1 and B2.

In a second phase, it was tried to describe the titration curves by fitting the model described in equations 4 and 5 to the titration data using a non-linear parameter estimation algorithm (Brent, 1973). Minimization of the sum of squared errors (SSE) was used as the fit criterion. The estimation procedure was performed automatically with MOSIFIT (MOdel SImulator and FITter, available on request), a software package that has already shown its usefulness to estimate kinetic parameters based on respirometric data (Vanrolleghem and Verstraete, 1993; Spanjers and Vanrolleghem, 1995; Kong *et al.*, 1996).

$$\frac{dH^+}{dt} = \frac{2 + Y_A * i_{XB}}{14 * Y_A} * \mu_A * \frac{S_{NH}}{K_{NH} + S_{NH}} * X_{BA} + BPPR \tag{4}$$

$$\frac{dNH_4}{dt} = -(\frac{1}{Y_A} + i_{XB}) * \mu_A * X_{BA} * \frac{S_{NH}}{K_{NH} + S_{NH}} \tag{5}$$

When estimating parameters for a single Monod model from respirometric data, 3 parameter combinations are structurally identifiable (Vanrolleghem *et al.*, 1995): $[(1-Y_i)*\mu_{maxi}*X/Y_i]$, $[(1-Y_i)*K_i]$ and $[(1-Y_i)*S_i(0)]$. The identifiability problem for parameter estimations from titration data is comparable. Based on titration data, the following 3 combinations of parameters are identifiable from perfect data:

$$\frac{2+Y_A*i_{XB}}{14}*\frac{\mu_A*X_{BA}}{Y_A}\ ;\ \frac{2+Y_A*i_{XB}}{14}*K_{NH}\ ;\ \frac{2+Y_A*i_{XB}}{14}*S_{NH}(0)$$

Calculation of $(\mu_A*X_{BA})/Y_A$, K_{NH} and $S_{NH}(O)$ was done assuming Y_A=0.24 and i_{XB}=0.086 (Henze *et al.*, 1987).

Ammonium nitrogen concentrations

Ammonium N concentration values obtained from titration in-sensor experiments with mixed liquor sampled from the last aerobic compartment of the pilot plant were compared to NH_4^+-N concentrations measured in the effluent of the pilot plant (Figure 4). The NH_4^+-N concentration values obtained by interpreting titration data using the slope extrapolation method were normally close to (standard added) 1.33 mg NH_4^+-N/l during the periods that the effluent of the pilot plant contained no NH_4^+-N. Based on the titration data, a concentration of 1.32±0.185 mg NH_4^+-N/l was found for the experiments carried out between day 2 and day 10, a one week period during which the effluent contained no NH_4^+-N. This means that it was possible to accurately calculate the amount of NH_4^+-N added to the sludge sample at the beginning of each titration experiment based on the titration data and the slope extrapolation data analysis procedure (see Figure 3). Moreover, an increase of the effluent NH_4^+-N concentration was always detected by both the titration method and the on-line NH_4^+-N analyser. This shows that the titration method is a reliable method to determine NH_4^+-N concentrations in mixed liquor samples. The diurnal effluent NH4+-N peak observed at the end of the experimental period is due to the diurnal loading pattern to the plant.

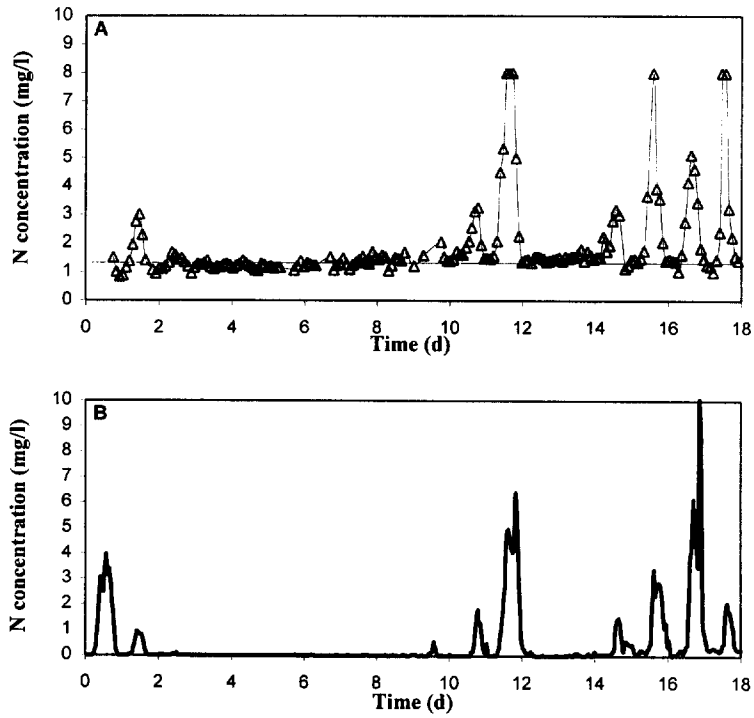

Figure 4. Comparison between the NH_4^+-N concentration values obtained by interpreting the recorded cumulative base addition curves using the slope extrapolation method (A), and NH_4^+-N concentrations measured in the effluent of the pilot plant using an on-line NH_4^+-N analyser (B). The solid line (A) indicates the NH_4^+-N concentration dosed to the sludge at the beginning of each titration experiment (1.33 mg N/l).

Interpretation of the cumulative base addition curves using a non-linear parameter estimation method generates $S_{NH}(O)$ concentrations that are comparable to the $S_{NH}(O)$ concentrations obtained with the slope extrapolation method, as confirmed by the high correlation found between both NH_4^+-N concentration data sets (Figure 5). This shows that both the slope extrapolation method and the model-based non-linear parameter estimation technique yield useful information about nitrification in activated sludge.

The titration procedure has advantages compared to chemical NH_4^+-N analysers, because no sample preparation step is needed, nitrification rates can be measured too, no expensive and polluting chemicals are used. Even more important from a control point of view is that the titration method could possibly be applied for the measurement of the overall influent N load. Contrary to chemical NH_4^+-N analysers, the titration procedure will not only measure NH_4^+-N but also organic N, just like respirometric measurements do (Spanjers and Vanrolleghem, 1995), because the activated sludge will hydrolyse most organic N compounds during the in-sensor experiment itself and allow them to be nitrified, and, thus, be measured.

A negative point maybe is the response time of the titration method, which is dependent on both the NH_4^+-N concentration and the nitrification rate of the sludge sample. However, effluent NH_4^+-N concentrations should be low for a well-operated treatment plant. For mixed liquor NH_4^+-N concentrations in the range of 1 to 2 mg N/l the titration can be finished within 20 to 30 minutes. Moreover, an increase of the response time of the titration procedure can already form a strong indication for malfunctioning of the treatment plant, even without fully completing the titration experiment. Full-scale validation experiments of control loops involving this sensor will be the final step in the development, because such experiments are the only way to prove that data obtained from titration in-sensor experiments can be used as input to biological N removal control strategies in activated sludge wastewater treatment plants.

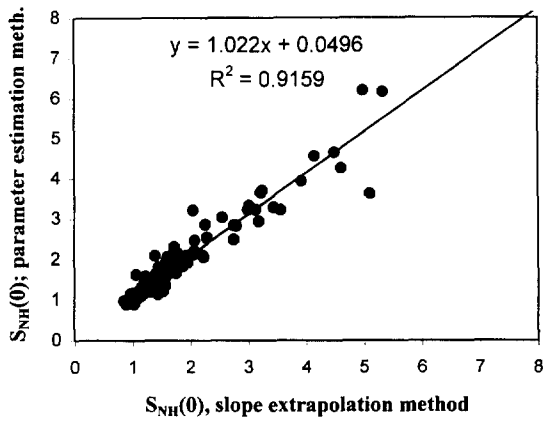

Figure 5. Comparison between $S_{NH}(O)$ values obtained for on-line in-sensor titration experiments using slope extrapolation and model-based non-linear parameter estimation data interpretation methods.

Nitrification rate

Nitrification rates of the sludge can also be derived from the cumulative base addition curves. Two phases could be distinguished in the experimental period. During the first phase, the nitrification rates were varying between about 3 and 5 mg N/l.h. For the data recorded between day 1 and day 14, the average nitrification rate of the sludge equaled 3.84±0.59 mg N/l.h. On day 15, the measured nitrification rate decreased. For the data recorded between day 15 and day 18, an average nitrification rate of 2.76±0.54 mg N/l.h was obtained. The decrease in the nitrification rate of the sludge coincided with an increase of the effluent NH_4^+-N concentration (Figure 4). The maximum nitrification capacity values resulting from the non-linear parameter estimation procedure showed a similar pattern (Figure 6). For the titration experiments carried out between day 1 and day 14, an average maximum nitrification capacity of 4.58±0.84 mg N/l.h was obtained, while for

the second period (day 15 to day 18) an average maximum nitrification capacity of 3.10±0.75 mg N/l.h was calculated.

The availability of information about the nitrification kinetics certainly is an advantage compared to physical/chemical NH_4^+-N analysers. Whenever an NH_4^+-N concentration peak is detected in the mixed liquor, one can distinguish between a normal N overloading and a reduction of the nitrifying activity in the activated sludge (e.g. due to toxicants), because the latter will be detected by a decrease in the nitrification rate.

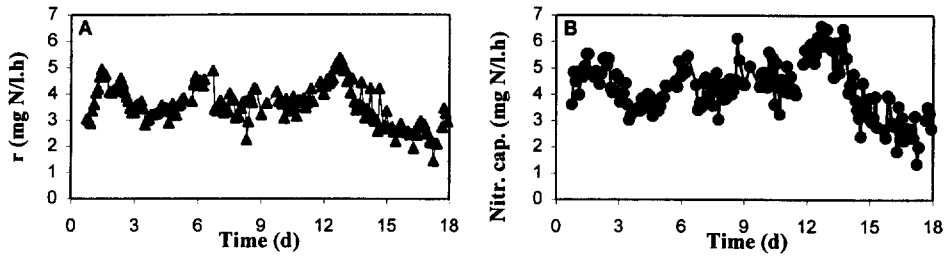

Figure 6. Results of on-line titration in-sensor experiments: comparison between nitrification rate values (r) obtained using the slope extrapolation method (A) and maximum nitrification capacity values resulting from a non-linear parameter estimation procedure (B).

CONCLUSIONS

Experiments on a pilot activated sludge plant for biological nitrogen removal show that titration in-sensor experiments are a valid alternative to existing nitrification monitoring methods. A big advantage of the proposed method is that NH_4^+-N concentrations in mixed liquor samples can be obtained without any need for a sample pretreatment system. Moreover, interpretation of the cumulative base addition curves also yields information about the nitrification kinetics.

ACKNOWLEDGEMENT

This research has been funded by a scholarship from the Flemish Institute for the Improvement of Scientific-Technological Research in the Industry (IWT). Financial support was partly provided also through a research grant (G.0286.96) by the Belgian National Fund for Scientific Research (N.F.W.O.).

NOMENCLATURE

B1:	Amount of base needed to increase the pH of the sludge to the pH setpoint (meq/l)
B2:	Sum of B1 and the amount of base added to neutralize the protons formed during nitrification (meq/l)
BPPR:	Background proton production rate (meq/l.min)
dH^+/dt:	Proton production rate (meq/l.min)
dNH_4/dt:	Ammonium removal rate (mg N/l.min)
i_{XB}:	Fraction of N in biomass (g N/g COD)
K_{NH}:	Monod half-saturation coefficient for NH_4^+-N (mg N/l)
r:	Nitrification rate (mg N/l.h)
S_{NH}:	Ammonium concentration (mg N/l)
$S_{NH}(0)$:	Initial substrate concentration (mg N/l)
X_{BA}:	Autotrophic biomass concentration (mg COD/l)
Y_A:	Yield coefficient for autotrophic biomass (g COD/g N nitrified)
μ_A:	Maximum specific growth rate for autotrophic biomass (1/min)
$(\mu_A * X_{BA})/Y_A$:	Nitrification capacity of the mixed liquor sample (mg N/l.h)

REFERENCES

Aivasidis, A., Hochscherf, H., Rottman, G., Hagen, T., Mertens, M. T., Reiners, G. and Wandrey, C. (1992). Neuere Konzepte zur Prozessüberwachung und -regelung bei der biologischen Stickstoffelimination. *Abwassertechnik*, **42**(5), 48-55.

Al-Ghusain, I. A., Huang, J., Hao, O. J. and Lim, B. S. (1994). Using pH as a real-time control parameter for wastewater treatment and sludge digestion processes. *Wat. Sci. Tech.*, **30**(4), 159-168.

Bogaert, H., Vanderhasselt, A., Gernaey, K., Yuan, Z., Thoeye, C. and Verstraete, W. (1997). A new sensor based on the pH-effect of the denitrification process. *J. Environ. Eng.*, (in press).

Brent, R. P. (1973). *Algorithm for minimization without derivatives*. Prentice-Hall. Englewood Cliffs. N.J.

Drtil, M., Nemeth, P. and Bodik, I (1993). Kinetic constants of nitrification. *Wat. Res.*, **27**, 35-39.

Gernaey, K., Bogaert, H., Vanrolleghem, P., Van Vooren, L. and Verstraete, W. (1996). Sensors for nitrogen removal monitoring in wastewater treatment. In: J.M. Lynch and A. Wiseman (Eds.), *Proceedings EB 96: Environmental biomonitoring: the ecotoxicology-biotechnology interface*. Surrey (UK), June 6-7 1996. (in press).

Hao, O. J. and Huang, J. (1996). Alternating aerobic-anoxic process for nitrogen removal: process evaluation. *Wat. Environ. Res.*, **68**, 83-93.

Harremoës, P., Capodaglio, A. G., Hellström, B. G., Henze, M., Jensen, K. N., Lynggaard-Jensen, A., Otterpohl, R. and Soeberg, H. (1993). Wastewater treatment plants under transient loading - performance, modelling and control. *Wat. Sci. Tech.*, **27**(12), 71-115.

Henze, M., Grady, C. P. L. Jr., Gujer, W., Marais, G. v. R. and Matsuo, T. (1987). *Activated sludge model No. 1*. Scientific and technical Report No. 1, IAWQ, London.

Kong, Z., Vanrolleghem, P. A., Willems, P. and Verstraete, W. (1996). Simultaneous determination of inhibition kinetics of carbon oxidation and nitrification with a respirometer. *Wat. Res.*, **30**, 825-836.

Lynggaard-Jensen, A., Eisum, N. H., Rasmussen, I., Svankjaer Jacobsen, H. and Stenstrom, T. (1996). Description and test of a new generation of nutrient sensors. *Wat. Sci. Tech.*, **33**(1), 25-35.

Massone, A., Gernaey, K., Bogaert, H., Vanderhasselt, A., Rozzi, A. and Verstraete, W. (1996). Biosensors for nitrogen control in wastewaters. *Wat. Sci. Tech.*, **34**(1-2), 213-220.

Massone, A., Gernaey, K., Rozzi, A., Willems, P. and Verstraete, W. (1995). Ammonium concentration measurements using a titrometric biosensor. *Med. Fac. Landbouww. Univ. Gent*, **60**, 2361-2368.

Ramadori, R., Rozzi, A. and Tandoi, V. (1980). An automated system for monitoring the kinetics of biological oxidation of ammonia. *Wat. Res.*, **14**, 1555-1557.

Spanjers, H. and Vanrolleghem, P. (1995). Respirometry as a tool for rapid characterization of wastewater and activated sludge. *Wat. Sci. Tech.*, **31**(2), 105-114.

Surmacz-Gorska, J., Gernaey, K., Demuynck, C., Vanrolleghem, P. and Verstraete, W. (1996). Nitrification monitoring in activated sludge by oxygen uptake rate (OUR) measurements. *Wat. Res.*, **30**, 1228-1236.

Vanderhasselt, A. (1995). *Ontwikkeling van een on-line denitrifikatie sensor*. Engineers thesis. Fac. Agricultural and Applied Biological Sciences. University Gent, Belgium. pp. 90. (in Dutch).

Vanrolleghem, P. A., Van Daele, M. and Dochain, D. (1995). Practical identifiability of a biokinetic model of activated sludge respiration. *Wat. Res.*, **29**, 2561-2570.

Vanrolleghem, P. and Verstraete, W. (1993). Simultaneous biokinetic characterization of heterotrophic and nitrifying populations of activated sludge with an on-line respirographic biosensor. *Wat. Sci. Tech.*, **28**(11-12), 377-387.