TITRIMETRIC BIOSENSING OF BIOLOGICAL WASTEWATER TREATMENT PLANTS

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ABSTRACT

The development of titrimetric sensor applications to monitor biological wastewater treatment processes is shortly described, and the measurement principle (based on a pH controller) is illustrated. 3 applications that were developed during the past years are used to illustrate the capabilities of titrimetric sensors. The ammonium and the nitrate concentration can be measured to monitor the nitrification and the denitrification process respectively. Ammonium concentration measurements obtained via the titrimetric method gave similar results as an on-line ammonium analyser. Titrimetric nitrate measurements compared reasonably well with chemical nitrate measurements. Nitrification process rates could be measured via the titrimetric sensor too. For the denitrification process the titrimetric nitrate measurement was used as an input to control the carbon source dosage in the anoxic zone of a predenitrification plant. Finally, a simultaneous respirometric-titrimetric experiment was applied to measure the nitrifiable nitrogen concentration in synthetic wastewater samples.

KEYWORDS

Ammonium, Control, Denitrification, Nitrate, Nitrification, Sensors, Titration

INTRODUCTION

For a bioreactor, the pH effects observed in the liquid medium can be related to the biological process rates and kinetics. However, a difficulty related to the observation of pH changes is the variable buffer capacity of the liquid medium due to the presence of several acid-base buffer systems with pH depending buffer capacity (Stumm and Morgan, 1981). The pH variation of the liquid medium during biological reactions is thus difficult to convert into a precise number of protons that are released or consumed. The data interpretation problems caused by the pH depending buffer capacity of the liquid medium can be avoided by controlling the pH of a liquid medium at a constant pH setpoint through addition of acid and/or base. Monitoring the acid and/or base consumption rate, needed to keep the pH constant, provides the rate of proton formation or consumption due to biological reactions.

The principle of the pH-STAT was already described in 1957, as a device that could quantify the amount of protons consumed or produced during biochemical reactions (Jacobsen *et al.*, 1957). The measuring principle of the pH-STAT relies on a continuous pH measurement in a reactor vessel, while a pH controller is used to keep the pH of the reactor vessel contents at a constant pH setpoint through addition of small amounts of acid and/or base. The apparatus generates data that consist of the cumulative amount of acid and/or base that was dosed as a function of time. Acid and/or base dosage can be related to the reactions taking place in the reactor vessel, and can thus provide information about the kinetics of the process that is studied.

It should be clear that a pH-STAT only allows to monitor processes or biological reactions that will result in a proton production or consumption. Biological reactions that do not produce or consume protons cannot be monitored. Jacobsen *et al.* (1957) described applications of the pH-STAT for processes such as enzymatic splitting of peptide bonds. In later years, the pH-STAT principle was developed further and applied for

fermentation monitoring (San and Stephanopoulos, 1984; Siano, 1995), and wastewater treatment plant monitoring (as discussed below).

The growing importance of wastewater treatment also resulted in the development of titrimetric sensor applications in this field. Titrimetric biosensor principles were soon developed for the nitrification process (Beccari *et al.*, 1980; Ramadori *et al.*, 1980; Aivasidis *et al.*, 1992), as an alternative to respirometry (measurement of the oxygen uptake rate). In the titrimetric sensor, the stoichiometric conversion of NH_4^+ to produce 2 H^+ ($NH_4^+ + 2\ O_2 \rightarrow NO_3^- + H_2O + 2\ H^+$) is used to obtain information about the nitrification process. A good correlation was obtained between the amount of ammonium added to activated sludge and the amount of ammonium measured with the titrimetric sensor, where the latter was obtained by applying the stoichiometric conversion factor to the measured amount of protons produced during nitrification of the ammonium (Massone *et al.*, 1995, 1998). This measuring principle has thus been developed and applied further to the on-line measurement of the nitrification rate in activated sludge (Gernaey *et al.*, 1997), the on-line measurement of the ammonium concentration in activated sludge (Gernaey *et al.*, 1997), the estimation of biokinetic parameters for the nitrification process, (Gernaey *et al.*, 1998, 2001; Ficara *et al.*, 2000; Petersen *et al.*, 2000, 2001), and the detection of toxic effects of wastewater and chemical compounds (Aivasidis *et al.*, 1992; Gernaey *et al.*, 1999; Rozzi *et al.*, 1999).

However, contrary to dissolved oxygen measurements and respirometry, a pH measurement can also be used to monitor the anoxic denitrification process. Denitrification usually results in proton consumption, and this characteristic of the denitrification process is applied in titrimetric sensors. The applications include determination of volatile fatty acid concentrations (Massone *et al.*, 1996), nitrate concentration measurement (Bogaert *et al.*, 1997), measurement of the amount of carbon source needed to obtain full denitrification (Bogaert *et al.*, 1997), and addition of carbon source based on measurement results provided by a titrimetric sensor (Bogaert *et al.*, 1997; Yuan *et al.*, 1997).

MEASUREMENT PRINCIPLE

Several authors have presented a titrimetric biosensor. In principle most titrimetric biosensors consist of some basic units: a reactor vessel, equipment to mix the contents of the reactor vessel, a pH electrode, an acid and base dosage system, and a PC to collect and process experimental data. For titrimetric experiments under aerobic conditions (nitrification process), the reactor vessel is equipped with an aeration system. For titrimetric experiments under anoxic conditions (denitrification process), N_2 gas can be supplied to the reactor vessel to assure anoxic conditions.

As an illustration, an example of a titration unit is given in Fig. 1. For on-line applications, the basic sensor shown in Fig. 1 is equipped further with a sampling system to take fresh activated sludge and/or wastewater from the activated sludge wastewater treatment plant into the reactor vessel, an overflow and a drain valve to empty the reactor vessel each time a titrimetric experiment is completed.

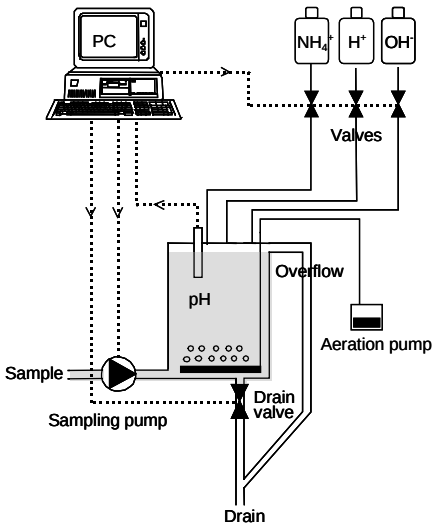

Figure 1. Scheme of a titrimetric biosensor

APPLICATIONS

On-line measurement of ammonium concentration and nitrification rate in activated sludge (Gernaey *et al.*, 1997)

A titrimetric method to monitor nitrification was applied on a pilot activated sludge plant for biological N removal. 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. An on-line NH_4^+-N analyzer with a gas-sensitive NH_3 electrode was operated on the effluent on the pilot plant, to provide reference effluent NH_4^+-N concentrations that could be compared with the results of the titrimetric experiments. Mixed liquor was sampled from the aerobic compartment of the treatment plant and a titrimetric experiment was performed. At the beginning of a titrimetric experiment 1.33 ± 0.05 mg NH_4^+-N/l were dosed to the sludge sample

Interpretation of the cumulative base addition curves resulting from each titrimetric experiment was done using a simple slope extrapolation method (Fig. 2), assuming that 14 mg N will produce 2 meq protons when completely nitrified. The NH_4^+-N concentration S_{NH} (mg N/l) and the nitrification rate r (mg N/l.h) were calculated according to Eq. 2 and 3. B1 and B2 are expressed in meq/l units. S1 and S2 are expressed in meq/l.min units.

$$S_{NH} = \frac{2}{14} \cdot (B2 - B1) \qquad (1)$$

$$r = \frac{2}{14} \cdot (S1 - S2) \cdot 60 \qquad (2)$$

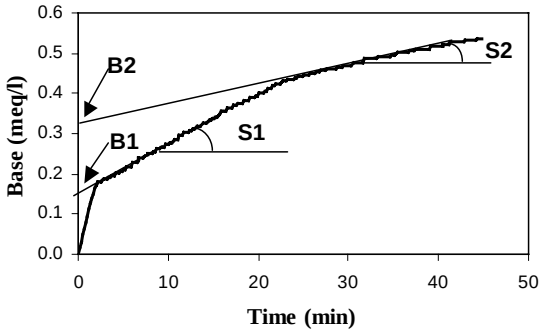

Figure 2. Principle of the slope extrapolation method. S1 and S2 are extrapolated to the Y axis, resulting in B1 and B2

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 (Fig. 3). The NH_4^+-N concentration values obtained by interpreting titrimetric 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 titrimetric data, a concentration of 1.32 ± 0.19 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 titrimetric experiment based on the titrimetric data and the slope extrapolation data analysis procedure (see Fig. 2). Moreover, increased effluent NH_4^+-N concentrations were always detected by both methods (titration and on-line NH_4^+-N analyzer), indicating that the titrimetric procedure is a reliable method to determine NH_4^+-N concentrations in mixed liquor samples. The diurnal effluent NH_4^+-N peak observed at the end of the experimental period is due to the diurnal loading pattern to the plant.

Nitrification rates of the sludge can be derived from the cumulative base addition curves. Two phases could be distinguished in the experimental period (Fig. 4). During the first phase, the nitrification rates varied 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 (Fig. 3 and 4).

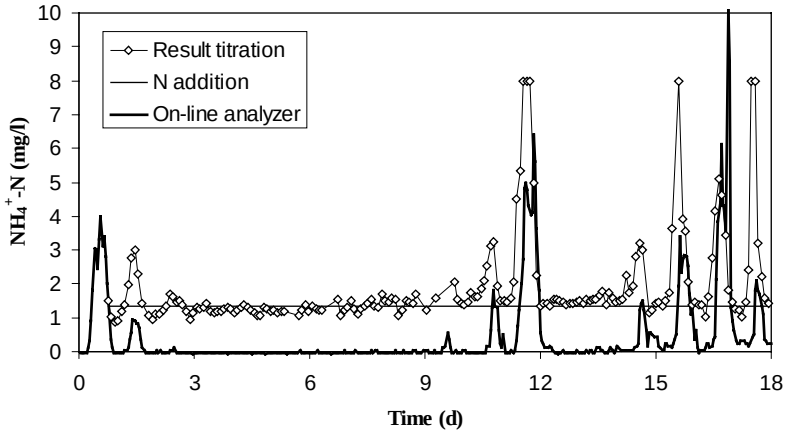

Figure 3. Comparison between the NH_4^+-N concentration values obtained using the developed titration procedure with a mixed liquor sample and the NH_4^+-N concentrations measured in the effluent of the pilot plant using an on-line analyzer. The solid line indicates the NH_4^+-N concentration that was dosed to the sludge at the beginning of each titration experiment (1.33 mg N/l)

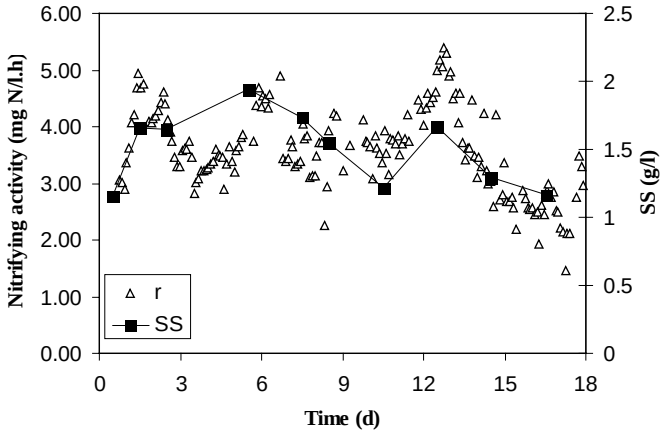

Figure 4. Nitrification activities (r) calculated based on the difference between the slopes S1 and S2 and suspended solids (SS) concentrations of the sludge measured during the experimental period

On-line measurement of nitrate concentration in activated sludge + control of carbon source addition for denitrification (Bogaert *et al.*, 1997; Yuan *et al.*, 1997)

The titrimetric sensor used in this application is operated under anoxic conditions, and measures the proton stoichiometry of the denitrification reaction. During the measurement, the pH of the mixed liquor is kept at a setpoint and the denitrification reaction endpoint is detected based on the proton consumption measurement (which is obtained from the acid and base addition rate of the pH controller). A biodegradable carbon source is added to a nitrate containing mixed liquor sample in such a way that the added amount of carbon source exactly matches the amount needed to denitrify the nitrate present in the mixed liquor sample. From the volume of carbon source added, one can calculate the following:

- The nitrate concentration in the sample, if a carbon source of known composition is used and the denitrification COD/N stoichiometry for that carbon source has been established.
- The volume of a carbon source of unknown composition that is needed per volume unit mixed liquor to completely remove the nitrate present can be obtained, without knowledge of the exact composition and concentration of the carbon source.
- The denitrification rate, expressed as mass units nitrogen per volume unit mixed liquor per time unit.

A comparison between nitrate measurements of the titrimetric sensor and nitrate concentrations measured via a chemical analysis is given in Fig. 5.

A prototype of the sensor was set up at the wastewater treatment plant of Zwalm. This plant (30,000 inhabitant equivalents) treats domestic wastewater plus the wastewater of a small slaughterhouse. The COD/N ratio in the influent is low, and therefore acetic acid was dosed as an external carbon source to support the denitrification. The acetic acid addition was done based on nitrate concentration measurements obtained with the titrimetric sensor.

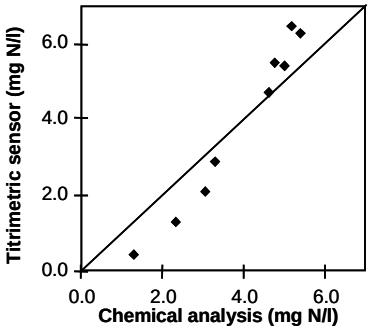

Figure 5. Comparison between nitrate concentrations measured with a titrimetric sensor and results of a chemical nitrate determination

Period without automatic control

This period started on September 15, 1995, ended on September 27, 1995. The nitrate concentration in the anoxic zone measured by the titrimetric sensor is shown in Fig. 6 (measurement noise was smoothened out with a moving average regression over a period of two hours). In the first three days, no external carbon was dosed. The high nitrate concentration in the anoxic zone was striking, indicating a lack of biodegradable carbon source for denitrification. From 18 September on, the external carbon was dosed with a constant rate of 185 kg COD/d. The average nitrate level was reduced, but still reached peak levels up to 10 mg N/l. The large variation of the nitrate concentration demonstrated the need for automatic control of the carbon dosage.

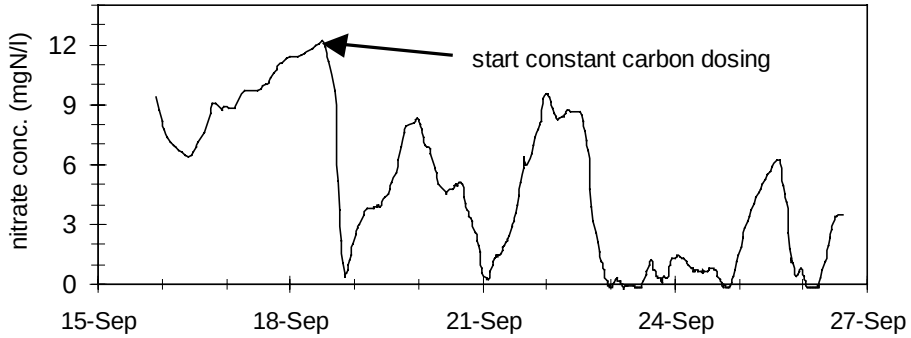

Figure 6. Anoxic zone nitrate concentration during the period without automatic carbon dosage control

Period with automatic carbon dosage control

The results of the dosing experiment are shown in Fig. 7 (measurement noise smoothened out). The large peaks in the nitrate concentration are due to power failures. The power to the plant was interrupted a few times for a very short instance. However, the nitrate recirculation pump of the plant did not start automatically after these interruptions. During the other periods, the nitrate concentration in the anoxic zone was successfully controlled at a low level.

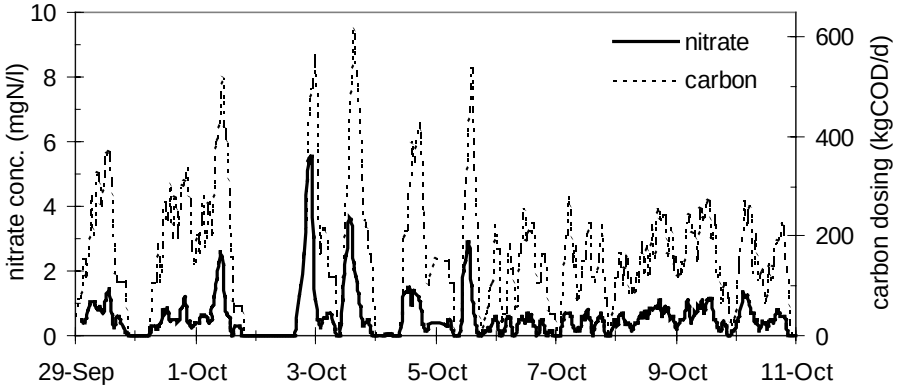

Figure 7. Nitrate concentration in anoxic zone and carbon dosing rate during the period with automatic carbon dosage control. The few large peaks in the nitrate concentration were caused by power failures at the treatment plant

The full-scale experiments ran from 15 September until 11 October 1995 during a period of about 1 month. A diurnal pattern can be distinguished in the carbon dosage rate in Fig. 7. The variations from 19-23

September (Fig. 6) are not diurnal because of the heavy rainfall during that period. The impact of the higher influent COD/N ratio during the weekends of 23-24 September and 30-31 September, when the slaughterhouse did not discharge, is visible in Fig. 6 and 7.

Measuring nitrifiable nitrogen concentration with a titrimetric respirometer (Yuan and Bogaert, 2001)

A titrimetric sensor is not readily applicable to the measurement of nitrifiable nitrogen contained in wastewater. Fig. 8 shows the titration curve resulting from adding 40 ml synthetic wastewater (milk powder + ammonium chloride) containing 194 mg COD, 14.3 mg ammonia N and 6.1 mg organic nitrogen to 4.22 liters nitrifying sludge. The readily biodegradable COD (RBCOD) present in the wastewater pulse caused the following problems:

- The change in pH induced by CO_2 production from COD oxidation resulted in an extra bending point on the titration curve. Depending on wastewater composition, the extra bending point(s) may or may not occur and may appear at different places, which complicates identification of the nitrification endpoint.
- Heterotrophic biomass growth in the presence of COD leads to the assimilation of significant amounts of ammonia into new biomass. This nitrogen fraction is not measured with a titrimetric sensor. As will be shown later, the cell-assimilated nitrogen in the experiment reported in Fig. 8 represents 25 % of the total amount of nitrogen that was added.

It was proposed to solve these problems by measuring the dissolved oxygen concentration, in parallel to measuring and controlling the pH, resulting in a titrimetric respirometer.

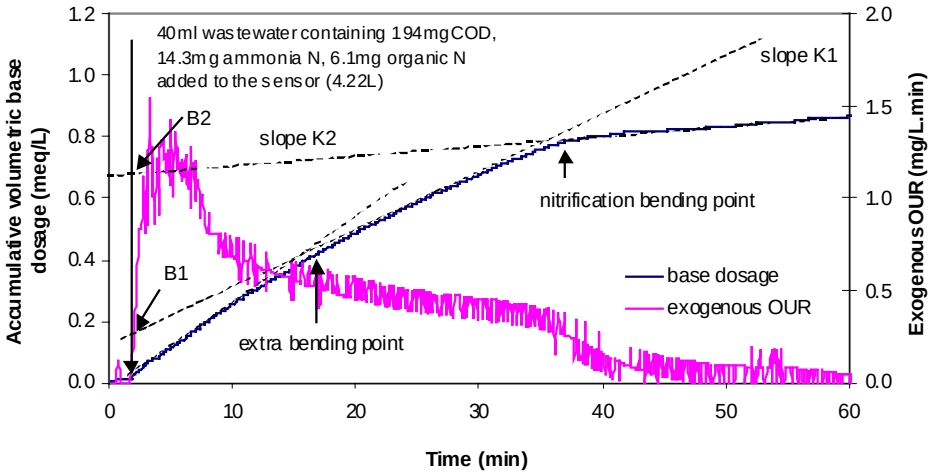

Figure 8. The base titration curve and the exogenous OUR profile obtained in an experiment using the titrimetric respirometer to measure a synthetic wastewater (composition shown in the figure)

The oxygen uptake rate (r_O) profile derived from the dissolved oxygen signal helps to identify the nitrification endpoint as the bending point on the base titration curve appears shortly before the exogenous r_O approaches zero (see Fig. 8). Secondly, the exogenous r_O profile together with the base titration curve allows calculation of the short-term BOD (stBOD) and thus the amount of cell-assimilated nitrogen. Below, the procedure is illustrated to calculate the nitrifiable nitrogen concentration from the data shown in Fig. 8.

- Step 1: Calculation of the nitrified nitrogen concentration (denoted as $S_{N,Nitrified}$) and the nitrification activity ($r_{nitrif,max}$) with Eq. 1 and 2, taking the slope just before the nitrification endpoint in Fig. 8 as S1. $S_{N,nitrified}$ = (0.69-0.17)*7 = 3.64 mg N/l. $r_{nitrif,max}$ = (0.0187-0.0033)*7 = 0.108 mg N/l.min
- Step 2: Calculation of the Total Biological Oxygen Consumption (TBOC) by integrating the exogenous r_O. stBOD is then derived by subtracting the nitrogen oxygen demand from the TBOC (Eq. 3)

$$stBOD = TBOC - \gamma_{N,O} \cdot S_{N,Nitrified} \quad (3)$$

$\gamma_{N,O}$ is the oxygen consumption per unit mass nitrogen nitrified. The theoretical value of $\gamma_{N,O}$ is 4.57-Y_A, with Y_A (expressed as g biomass COD/g N) being the nitrifying biomass yield (Henze *et al.*, 1987). The amount of nitrogen assimilated into biomass per unit volume of sludge (denoted as $S_{N,cell}$) is thus calculated (Eq. 4),

$$S_{N,cell} = \gamma_{cellN,stBOD} \cdot stBOD \quad (4)$$

$\gamma_{cellN,stBOD}$ is the ratio between the amount of nitrogen assimilated into new biomass and the short-term BOD. Theoretically, $\gamma_{cellN,stBOD}$ can be calculated using the following equation,

$$\gamma_{cellN,stBOD} = Y_H i_{XB} / (1 - Y_H) \quad (5)$$

Y_H is the short-term yield of the heterotrophic biomass (g biomass COD/g COD) and i_{XB} is the fraction of nitrogen in a biomass cell (g N/g biomass COD) (Henze *et al.*, 1987). Given the fact that both Y_H and i_{XB} are dependent on the sludge used and the wastewater measured, and should therefore be calibrated, the direct calibration of the parameter $\gamma_{cellN,stBOD}$ using the following equation is recommended.

$$\gamma_{cellN,stBOD} = \frac{(S_{N,ini} - S_{N,Nitrified})}{stBOD} \quad (6)$$

$S_{N,ini}$ is the known initial nitrogen concentration, which is obtained by measuring the amount of nitrogen initially added using a chemical analysis, $S_{N,Nitrified}$ is the nitrified nitrogen concentration calculated in Step 1, and stBOD is the short-term BOD calculated in Step 2. To improve the accuracy, multiple experiments should be used for the calibration. A value for $\gamma_{cellN,stBOD}$ can be obtained using a least squares algorithm.

For the data of Fig. 8, following results were obtained: TBOC = 23.1 mg O_2/l. $\gamma_{N,O}$ = 3.78 mg O_2/mg N (calibrated with an independent experiment). stBOD = 23.1-3.78*3.64 = 9.34 mg O_2/l. $\gamma_{cellN,stBOD}$ = 0.126 mg N/mg O_2 (calibrated with experiments not involving this one). $S_{N,cell}$ = 0.126*9.34 = 1.18 mg N/l.

- Step 3: The total nitrogen is thus,

$$S_N = S_{N,Nitrified} + S_{N,cell} \quad (7)$$

For the example given in Fig. 8, S_N = 3.64 + 1.18 = 4.82 mg N/l. The total amount of nitrogen added is thus measured as 4.82 mg N/l*4.22 l (volume of the sludge sample) = 20.3 mg N. The amount of nitrifiable nitrogen calculated by applying the above procedure to the OUR and titration data shown in Fig. 8 (20.3 mg N) is thus very close to the amount measured analytically (20.4 mg N = 14.3 mg ammonia nitrogen + 6.1 mg organic nitrogen).

A synthetic wastewater, obtained by mixing milk powder with ammonium chloride, was used for a series of experiments. The wastewater contained 4.85 g COD/l and 510 mg total Kjeldahl N/l. About 30 % of the nitrogen was organic. The test consisted of 12 batch experiments with wastewater pulses of various sizes (ranging from 10 to 50 ml) being added to the sludge samples (around 4 l). Results are shown in Fig. 9.

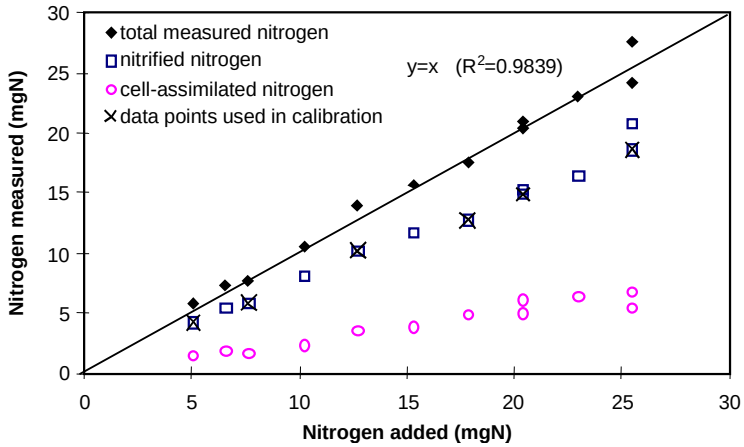

Figure 9. Results of experiments with a synthetic wastewater (milk powder + ammonium chloride, C/N ratio 9.5) and activated sludge: nitrogen measurement. Data points with crosses on were used in calibrating parameter $\gamma_{cellN,stBOD}$. The correlation coefficient was calculated from the nitrifiable nitrogen data not involved in the calibration of $\gamma_{cellN,stBOD}$.

CONCLUSIONS

For wastewater treatment plants, titrimetric sensor applications were developed specifically for biological nitrogen removal processes. The applicability of these sensors was illustrated in this paper. For the nitrification process, the ammonium concentration and the nitrification rate of activated sludge samples can be measured. Ammonium concentration measurements obtained via the titrimetric method gave similar results as an on-line ammonium analyzer. For the denitrification process, a titrimetric sensor was used to

measure nitrate nitrogen concentrations in the anoxic zone of the treatment plant. Based on titrimetric nitrate measurements the carbon source dosage in the anoxic zone of a predenitrification plant was controlled successfully. A simultaneous respirometric-titrimetric experiment was applied to measure the nitrifiable nitrogen concentration in synthetic wastewater samples.

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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, **5**, 48 – 55. (In German)

Beccari M., Passino R., Ramadori R. and Tandoi V. (1980) Inhibitory effects on nitrification by typical compounds in coke plant wastewaters Inhibitory effects on nitrification by typical compounds in coke plant wastewaters Environ. Technol. Lett., **1**, 245 – 252.

Bogaert, H., Vanderhasselt, A., Gernaey, K., Yuan, Z., Thoeye, C. and Verstraete, W. (1997) A new sensor based on pH-effect of the denitrification process, J. Environ. Eng., **123**, 884 – 891.

Ficara E., Musumeci A. and Rozzi A. (2000) Comparision and combination of titrimetric and respirometric techniques to estimate nitrification kinetics parameters. Water SA, **26**, 217 – 224.

Gernaey K., Bogaert H., Massone A., Vanrolleghem P. and Verstraete W. (1997) On-line nitrification monitoring in activated sludge with a titrimetric sensor. Environ. Sci. Technol., **31**, 2350 – 2355.

Gernaey K., Vanrolleghem P. and Verstraete W. (1998) On-line estimation of Nitrosomonas kinetic parameters in activated sludge samples using titration in-sensor-experiments. Water Res., **32**, 71 – 80.

Gernaey K., Maffei D. Vanrolleghem P. and Verstraete W. (1999) A new pH-based procedure to model toxic effects on nitrifiers in activated sludge. J. Chem. Technol. Biotechnol., **74**, 679 – 687.

Gernaey K., Petersen B., Ottoy J.P. and Vanrolleghem P. (2001) Activated sludge monitoring with combined respirometric – titrimetric measurements. Water Res., 35, 1280-1294.

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

Jacobsen C.F., Léonis J., Linderstrøm-Lang and Ottesen M. (1957) The pH-STAT and its use in biochemistry. Meth. Biochem. Anal., **4**, 171 – 210.

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

Massone A., Antonelli M. and Rozzi A. (1996) The denicon: a novel biosensor to control denitrification in biological wastewater treatment plants. Med. Fac. Landbouww. Univ. Gent, **61**, 1709 - 1714.

Massone A., Gernaey K., Rozzi A. and Verstraete W. (1998) Measurement of ammonium concentration and nitrification rate by a new titrometric biosensor. Water Environ. Res., **70**, 343 – 350.

Petersen B., Gernaey K. and Vanrolleghem P.A. (2000) Improved theoretical identifiability of model parameters by combined respirometric-titrimetric measurements. A generalisation of results. In: Proceedings IMACS 3rd Symposium on Mathematical Modelling, February 2-4, 2000, Vienna University of Technology, Austria. Vol.2, 639-642.

Petersen B., Gernaey K. and Vanrolleghem P. (2001) Practical identifiability of model parameters by combined respirometric-titrimetric measurements. Wat. Sci. Tech. (in Press).

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

Rozzi A., Ficara E., Cellamare C.M. and Bortone G. (1999) Characterization of textile wastewater and other industrial wastewaters by respirometric and titration biosensors. Water Sci. Technol., **40**(1), 161 – 168.

San K.Y. and Stephanopoulos G. (1984) Studies on on-line bioreactor identification. IV. Utilization of pH measurements for product estimation. Biotechnol. Bioeng., **26**, 1209 – 1218.

Siano S. (1995) On the use of pH control reagent addition rate for fermentation monitoring. Biotechnol. Bioeng., **47**, 651 – 665.

Stumm W. and Morgan J.J. (1981) Aquatic Chemistry, An introduction emphasizing chemical equilibria in natural waters. John Wiley & Sons, New York, 780 p.

Yuan Z., Bogaert H., Vanrolleghem P.A., Thoeye C., Vansteenkiste G.C. and Verstraete W. (1997) Control of external carbon addition to predenitrifying systems. J. Environ. Eng., **123**, 1080 – 1086.

Yuan Z. and Bogaert H. (2001) Titrimetric respirometer measuring the nitrifiable nitrogen in wastewater using in-sensor-experiment. Water Res., 35, 143-150.