On-Line Nitrification Monitoring in Activated Sludge with a Titrimetric Sensor

KRIST GERNAEY,† HERWIG BOGAERT,† ALEX MASSONE,§ PETER VANROLLEGHEM,‡ AND WILLY VERSTRAETE*,†

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

Nitrification is an important part of activated sludge wastewater treatment processes in view of the severe effluent discharge standards for nitrogen (N) that are nowadays imposed by legislation. Several on-line analyzers have been developed to achieve better monitoring and control of biological N removal processes. In this paper, the results of on-line experiments on a pilot-scale activated sludge plant with a recently developed titrimetric sensor are described. Based on a titration of an activated sludge sample, it was possible to estimate the ammonium N (NH_4^+-N) concentration in the activated sludge, without the need for any sample pretreatment. The NH_4^+-N concentrations obtained with the titration method were consistent with the NH_4^+-N concentrations measured with an on-line analyzer, which was operated on the effluent of the pilot plant. Contrary to chemical on-line NH_4^+-N analyzers, the titration method provides data about the nitrification rate of the activated sludge.

Introduction

Activated sludge wastewater treatment plants are confronted with severe effluent discharge standards for nitrogen (N). As a consequence, there is a growing interest for biological N removal, because this is in most cases the cheapest alternative to meet the required effluent standards as compared to physical/chemical approaches (*1*). Biological N removal is a rather complicated process consisting of two steps: nitrification and denitrification. Nitrification is normally the slowest step of the biological N removal process (*2*).

The increasing importance of biological N removal in wastewater treatment has resulted in the development of on-line instrumentation (e.g., on-line NH_4^+ analyzers, respirometers, etc.) to achieve a better monitoring and control of the on-going biological processes (*3*, *4*). Most on-line NH_4^+-N analyzers use an ion-selective electrode or colorimetric measurements (*3*−*5*). However, most on-line sensors for NH_4^+-N concentration measurements are expensive, rather complicated, consume large amounts of expensive and polluting chemicals, and require intensive maintenance (*4*, *5*). Moreover, sample pretreatment is often needed when measuring in mixed liquor, the best place for sampling when NH_4^+-N concentration values have to be used for control of the treatment plant (*3*, *4*). Sample pretreatment usually consists of an ultrafiltration step. Recently, a new generation of on-line NH_4^+-N sensors with a very low chemical consumption was presented (*6*). No sample pretreatment is necessary because the analyzer is immediately placed in the aeration tank. However, no long-term experience with this type of sensors is available for the moment.

In addition to the measurement of NH_4^+-N concentrations, methods have been developed to measure the nitrifying activity of activated sludge. Most existing methods consist of a batch experiment with activated sludge. Regular sampling and chemical analysis of NH_4^+-N or (NO_2^- + NO_3^-)-N is necessary for the calculation of the nitrifying activity of the sludge (*7*, *8*). Alternatively, respirometric methods have been used to measure the nitrifying activity of a sludge sample (*9*−*13*). Use of respirometric methods is favored by the high oxygen consumption for nitrification (eq 1).

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

Besides its DO consumption, nitrification also has a pH effect because two protons are produced for each NH_4^+ ion that is oxidized (eq 1). Recent experiences have shown that a pH measurement can be a valid alternative for monitoring and control of N removal processes in activated sludge (*4*, *14*−*17*). Contrary to DO measurements, a pH measurement can also be used to monitor the anoxic denitrification process (*4*, *14*, *15*, *17*).

In this paper, results of on-line experiments with a titrimetric sensor to measure the NH_4^+-N concentration and the nitrification rate in activated sludge samples are described. The aim of the tests was to show that a titration is a valid alternative to existing nitrification monitoring methods.

Methods

Pilot Activated Sludge Plant. The pilot plant (V = 150 L) was a pre-denitrification system with an anoxic zone of 30 L. The aerobic nitrification zone (V = 120 L) was divided into three parts to create a kind of a plug-flow system. The first two compartments had a volume of 30 L each, and the final compartment (the one immediately before the decanter) had a volume of 60 L. To simulate a diurnal loading pattern, the influent flow to the pilot plant corresponded to a sine wave with an average flow of 8 L/h and a variation between 6.2 and 9.8 L/h (hydraulic retention time varying between 15 and 24 h). The pilot plant was fed with a synthetic wastewater. The influent N (NH_4^+-N + organic N) concentration varied between 73 and 108 mg of N/L, with an average of 91 mg of N/L. The variation of the N concentration was in phase with the flow variation, resulting in a load variation between 453 and 1058 mg of N/h, with an average of 756 mg of N/h. This corresponded to an average volumetric N loading of 6.3 of mg N/L·h (calculated on the volume of the aerobic compartment). With a substrate chemical oxygen demand (COD)/N ratio of about 10/1, an average COD load of 7.4 g/h was fed to the pilot plant. At regular time intervals, sludge from the pilot plant was sampled and analyzed for its suspended solids (SS) content according to standard methods (*18*).

An on-line NH_4^+-N analyzer (Minworth Systems Ltd., Sutton Coldfield, U.K.) was used to measure the NH_4^+-N concentration in the effluent of the pilot plant. The analyzer was operated on the effluent of the pilot plant to avoid the need for an expensive ultrafiltration unit that would be necessary for sample pretreatment when operating the

* Author to whom all correspondence should be addressed; telephone: +32 9 264 59 76; fax: +32 9 264 62 48; e-mail address: Willy.Verstraete@rug.ac.be.

† Laboratory for Microbial Ecology.

§ DIAAR—Sezione Ambientale.

‡ Department of Applied Mathematics, Biometrics and Process Control.

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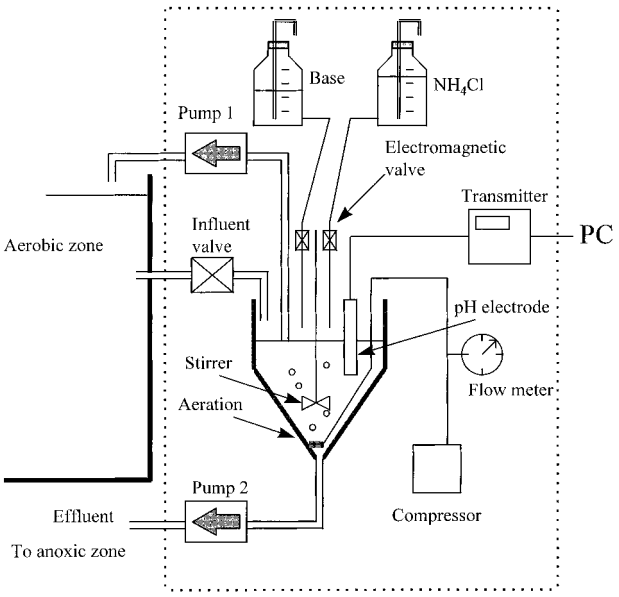

FIGURE 1. Schematic overview of the on-line titration unit installed on the pilot activated sludge plant.

analyzer immediately on the mixed liquor. The effluent NH_4^+-N concentration values obtained from the on-line analyzer were hourly averages of the continuously measured NH_4^+-N concentration in the effluent of the pilot plant. Results of the effluent measurements were used to check the reliability of the NH_4^+-N concentration values obtained by the titration experiments.

Titration Unit. The titration unit (Figure 1) consisted of a reactor vessel (V = 3.4 L) that was continuously aerated with a small compressor (Q_{air} = 70 L/h) and mixed with a submersible pump (Q_{pump} = 1000 L/h). Two mariotte bottles containing an NH_4Cl solution (1 g of N/L) and a 0.1 N NaOH solution, respectively, were placed above the reactor vessel. The bottles were connected to the open air by a capillary tube. At the end of this capillary tube (nearly at the bottom of the flasks), the pressure was always equal to the air pressure. This allowed us to dose a liquid by gravity but under constant hydraulic head, as long as the liquid level in the bottles was not below the capillary tubes. Addition of NH_4^+-N or base was done by opening the respective electromagnetic pinch valves that were normally keeping the NH_4Cl and base supply closed. The titration unit further consisted of a third electromagnetic pinch valve necessary for sampling of the mixed liquor, two peristaltic pumps (pump 1 and pump 2; see Figure 1) and a pH electrode connected to a transmitter generating a 4−20-mA signal to the computer. Pumps and valves were all controlled by the same computer.

Sampling Procedure. About every 2 h, an activated sludge sample was gravitationally taken from the last aerobic compartment of the activated sludge plant. Sampling was done by opening the influent valve (Figure 1) for a fixed time. After closing the influent valve, pump 1 (Figure 1), connected to a tube fixed at a constant height in the reactor vessel, was activated for 60 s to recycle the excess mixed liquor to the last aerobic compartment of the pilot plant. By using this sampling procedure, it was possible to always dose 3.4 L of sludge without installing a complicated level detection system.

Immediately after finishing the sampling procedure, the valve connected to the mariotte bottle containing the NH_4Cl stock solution was opened for 40 s to dose some NH_4^+-N in the mixed liquor sample. The flow of the NH_4Cl solution was measured once every 2 days. On the average, 1.33 ± 0.05 mg of NH_4^+-N/L reactor was dosed to the mixed liquor sample. The addition of NH_4^+-N enabled us to measure the nitrification rate of an activated sludge sample even when no NH_4^+-N was initially present in the sludge sample.

Each titration experiment was continued for a fixed duration of 2 h. When a titration experiment was finished, pump 2 was activated and the mixed liquor sample was recycled into the anoxic zone of the pilot plant (Figure 1).

Principle of the Measurement

Theoretical Background. Recording pH profiles is suited for the detection of nitrification and denitrification end points, which can be important for process control in alternating processes (*14*, *15*). However, pH profiles can not be used for the calculation of stoichiometry-based nitrification rates since a pH decrease can not be related to the number of protons that are formed, because the buffer capacity of the mixed liquor is not constant as a function of pH, due to the presence of different acid/base buffer systems (*19*).

A pH controller was used to keep the pH of the mixed liquor sample at a fixed pH set point. Every time the pH tended to decrease, e.g., due to the nitrifying activity of the sludge sample, base was added to the sludge to keep its pH at the pH set point value. By using this measuring principle, the protons produced due to nitrification are continuously neutralized by the addition of NaOH.

The choice of a pH set point for the controller is important. As nitrification is an aerobic reaction, continuous aeration of the reactor vessel of the titration unit is necessary to replace the oxygen consumed to oxidize NH_4^+-N. Under such conditions, the equilibrium pH of a system is determined by its alkalinity and its CO_2 content (*19*). Several processes determine the equilibrium pH of the sludge: CO_2 production by the respiration activity of the heterotrophic biomass, CO_2 stripping by the aeration system, proton production due to nitrification, etc. For pH values of 7−8, a decrease of the CO_2 content normally results in a pH increase and vice versa (*19*). Aeration of the reactor vessel of the titration unit was done by blowing ambient air through the sludge sample at a constant rate (Q_{air} = 70 L/h). A pH set point ± ΔpH interval value of 8.20 ± 0.03 was used for the titration experiments, because this pH value was always higher than the equilibrium pH obtained by just aerating the sludge in the reactor vessel of the titration unit.

Titration Procedure. The operation of the pH controller was started immediately after sampling. In a first phase, the pH of the mixed liquor sample was increased to the pH set point. Once the pH set point was reached, base was only dosed to the mixed liquor when the pH became lower than the pH set point minus the ΔpH interval. Base addition was done by opening for 1.5 s (= 1 base pulse) the pinch valve that was normally closing the mariotte bottle with the NaOH stock solution. This procedure was repeated until the actual pH in the titration vessel was in the pH set point ± ΔpH interval. Every 10 s, a computer stored the actual pH in the reactor vessel and the total number of base pulses dosed to the sludge during a titration experiment. The flow per base pulse was checked once every 2 days. On the average, a flow of 6.40 ± 0.27 mL per 50 base pulses was measured.

Normally, three phases can be distinguished during each titration (Figure 2). In a first phase, the sludge is already actively nitrifying and the pH of the sample is increased to the pH set point (8.20 ± 0.03). During this phase, which took about 3 min for the titration shown in Figure 2, the base is dosed at the maximum rate. In Figure 2 about 70 base pulses were needed to increase the pH of the sludge sample to the pH set point. In a second phase, the base is dosed at a constant rate, which is considerably lower than the maximum base addition rate. Finally, when all NH_4^+-N is oxidized, the base addition rate decreases further. In Figure 2 this nitrification end point can be observed after about 35 min. At this point, about 190 base pulses had been dosed to the sludge sample.

Data Analysis Procedure. A data analysis procedure was developed that could be used for on-line data processing.

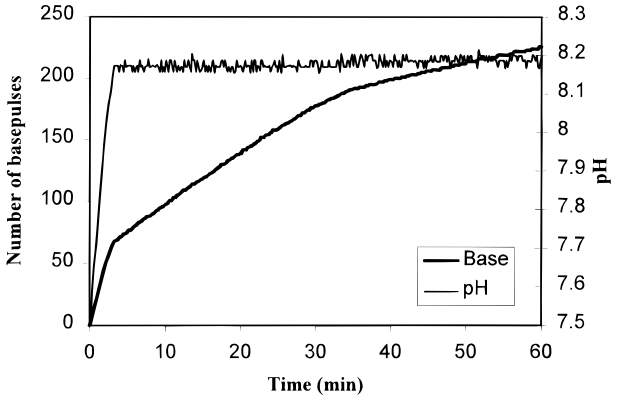

FIGURE 2. Example of a titration curve and pH profile obtained during an on-line titration experiment with a mixed liquor sample.

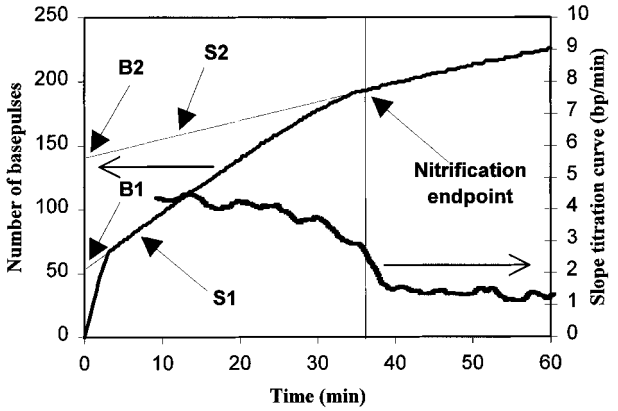

FIGURE 3. Data analysis method. A titration curve is shown, with the extrapolation of the slopes S1 (4.40 bp/min) and S2 (1.45 bp/min) to the *Y*-axis, resulting in the values B1 (54 bp) and B2 (141 bp), respectively. The slope values calculated using the moving window regression method are also shown. For this example, the second slope change is detected after about 36 min, when the result of the (S1, moving window slope) calculation becomes higher than 1.8 bp/min.

The procedure is based on the detection of the two slope changes of the titration curve (Figure 3). The first slope change of the titration curve can be detected easily, because it is situated at the point where the pH set point ± ΔpH interval is reached for the first time, as can be observed from Figure 2. Once this point is detected, the slope of the titration curve is calculated using data points collected during the first 500 s following the moment of its detection. This slope (S1) is extrapolated to the *Y*-axis, and a first number of base pulses (B1) is obtained, corresponding to the amount of base necessary to increase the pH of the sludge sample to the pH set point.

Due to the pH controller, the pH of the mixed liquor is always fluctuating around the pH set point after the first slope change of the titration curve. The second slope change of the titration curve—the nitrification end point—is therefore not related to any characteristic pH value that could be used for its detection. This is a similar problem as the detection of a NO_3^- knee, the slope change of an oxidation−reduction potential (ORP) curve indicating the disappearance of NO_3^- during the denitrification phase in alternating activated sludge systems (*20*−*22*). For each titration curve, a window (window size = 5 min; $n = 30$) is moving over the data. With the data points in the window, the slope of the titration curve is calculated, and the window is moved one data point further. This procedure is repeated for all the available data of the titration curve. Figure 3 shows a titration curve and the results of such a moving window slope calculation. The calculated slope of the titration curve decreases when the nitrification phase is finished (after about 36 min in Figure 3). The slope values calculated with the moving window procedure are subtracted from S1. When the difference between S1 and the moving window slope becomes higher than 1.8 base pulses/min (bp/min) (a value determined using the first 10 titration curves, which showed a reliable and fast end point detection), nitrification is considered to be finished, as shown in Figure 3.

The detection of the nitrification end point is followed by the calculation of a second slope (S2), using the data points collected during the first 500 s following the detection of the nitrification end point. This second slope is extrapolated to the *Y*-axis and a number of base pulses B2 is obtained (Figure 3), corresponding to the sum of the amount of base necessary to compensate for the protons produced due to nitrification and the amount of base needed to increase the pH of the mixed liquor to the pH set point.

Calculation of Ammonium Concentrations. Taking into account the stoichiometric relation between the amount of nitrified NH_4^+-N and the protons produced (eq 1), NH_4^+-N concentration values can be calculated based on the difference between B2 and B1, according to eqs 2 and 3

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

$$k = \frac{Q_{base} N \times 7}{V_{reactor}} \tag{3}$$

where S_{NH} is the initial NH_4^+-N concentration in the reactor vessel of the titration unit (mg of N/L); B1 is the number of base pulses needed to increase the pH of the sludge to the pH set point (bp); B2 is the sum of B1 and the number of base pulses necessary to compensate for the protons produced during nitrification (bp); k is the calibration constant, typical for the titration unit ((mg of N/L)/bp); Q_{base} is the volume of base dosed per base pulse (mL/bp); N is the base normality (mequiv/mL); $V_{reactor}$ is the volume of sludge in the reactor vessel of the titrator (L); and 7 is the conversion factor (mg of N/mequiv).

Calculation of the Nitrification Rate. The nitrification rate of the mixed liquor (mg of N/L·h) was obtained based on the difference between the slopes S1 and S2, according to eq 4:

$$r = (S1 - S2)k \times 60 \tag{4}$$

where r is the nitrification rate of the mixed liquor sample (mg of N/L·h); S1 is slope 1, recorded following the detection of the first slope change of the titration curve (bp/min); S2 is slope 2, recorded following the detection of the nitrification end point (bp/min); and 60 is the conversion factor (min/h).

Results

Ammonium Concentration Measurements. Ammonium N concentrations calculated using titration data are shown in Figure 4, together with the results of the on-line NH_4^+-N measurements on the effluent of the pilot plant. The solid line in Figure 4 represents the NH_4^+-N concentration that was added to the activated sludge sample in the sensor at the beginning of each titration experiment. When the effluent of the pilot plant contained no NH_4^+-N, results of the titration experiments should theoretically be equal to the amount of NH_4^+-N added at the beginning of the titration experiment. Based on the titration data, a concentration of 1.32 ± 0.185 mg of NH_4^+-N/L was found for the experiments carried out between day 2 and day 10, a 1-week period during which the effluent contained no NH_4^+-N. This average value corresponded well with the concentration of 1.33 ± 0.05 mg of NH_4^+-N/L initially dosed to the sludge sample.

On the first day of the titration experiments, the effluent of the activated sludge pilot plant contained some NH_4^+-N.

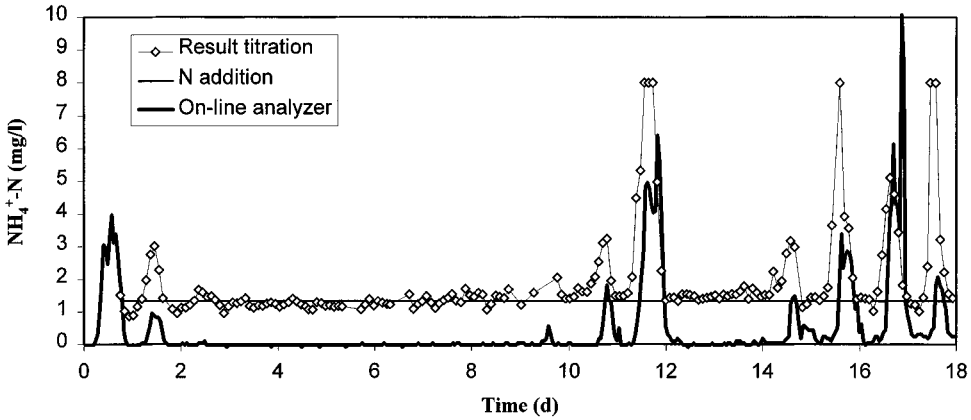

FIGURE 4. Comparison between the NH_4^+-N concentration values obtained using the developed titration procedure with a mixed liquor sample and the NH_4^+-N concentrations measured in the effluent of the pilot plant using an on-line analyzer. The solid line indicates the NH_4^+-N concentration, which was dosed to the sludge at the beginning of each titration experiment (1.33 mg of N/L).

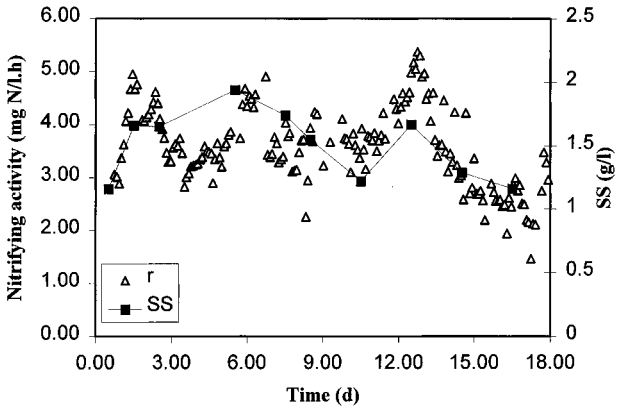

FIGURE 5. Nitrification activities (*r*) calculated based on the difference between the slopes S1 and S2 and suspended solids (SS) concentrations of the sludge measured during the experimental period.

The results show that the temporary increase in the effluent NH_4^+-N concentration was detected by both the titration method and the on-line NH_4^+-N analyzer. During the second half of the period with titration experiments, the effluent regularly contained some NH_4^+-N. Again, the titration experiments and the on-line NH_4^+-N measurements showed a similar response. For some experiments (e.g., 3 times on day 12), the NH_4^+-N content of the activated sludge sample was too high and the nitrification end point could not be detected within the fixed duration of the titration experiment. For such measurements, a default concentration of 8 mg of NH_4^+-N/L was given in Figure 4. Also, the on-line effluent NH_4^+-N measurement once showed a short peak (on day 17) that was not detected by the titration experiments.

Nitrification Rate of the Mixed Liquor. Figure 5 shows nitrification rates calculated based on the titration data. Two periods can be distinguished. During a first period, the nitrification rate varied between about 3 and 5 mg of N/L·h. For the data recorded between day 1 and day 14, the average nitrification rate of the sludge equals 3.84 ± 0.59 mg of N/L·h. The nitrification rate decreased at the end of day 14. For the data recorded between day 15 and day 18, an average nitrification rate of 2.76 ± 0.54 mg of 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).

Discussion

Titration Procedure. A typical titration curve presented in Figure 3 shows that some base was still added to the sludge when the nitrification phase was already finished (baseline of the titration curve). The baseline slope (S2) of the titration curve is due to the continuous aeration in the reactor vessel. When constantly aerating the sample, the pH of the sludge sample will tend to an equilibrium pH. However, the pH set point of the pH controller (8.20 ± 0.03) is higher than this equilibrium pH, which explains why some base addition is necessary to keep the pH of the sludge at the pH set point. If no base was dosed to the sludge, the sludge would after some time reach the equilibrium pH.

The calculation of the results could theoretically be simplified by choosing the pH set point always exactly the same as the equilibrium pH. The baseline slope S2 should always be equal to zero for such a titration experiment. In practice, this situation is not achievable, because the equilibrium pH of the mixed liquor in the pilot plant is continuously changing, e.g., due to changes in the alkalinity of the mixed liquor caused by the diurnal loading pattern to the pilot plant. Another approach to simplify the choice of the pH set point would be to aerate the sludge sample with a mixture of air enriched with some CO_2. The % CO_2 in the gas mixture would then determine the equilibrium pH of the sludge sample. A certain pH set point could be reached by just changing the CO_2 content of the gas mixture. However, using a specific gas mixture would make the titration system more complicated and more expensive to operate.

Theoretically, the initial pH of the sludge sample in the pilot plant could become higher than the pH set point. Therefore, experiments with a variable pH set point were performed too. During these experiments the pH set point was obtained as the sum of the initial pH of the sludge sample and a constant factor of 0.5 pH unit. Results similar to the data presented in this paper were obtained (data not shown).

pH is a factor that influences the nitrification rate of activated sludge. A change in the pH of the sludge sample, as happens when increasing the pH of the sludge sample to the pH set point, could influence the nitrification rate of the sludge sample. However, according to literature data (*1*, *23*), pH has only a minor influence on the nitrification rate for the pH range of the titration experiments described here (pH 7.4−8.2). Moreover, lab activity tests carried out with sludge sampled from three different full-scale activated sludge systems confirmed the literature data (*24*).

Pilot Plant Results: Ammonium Concentration Measurements. A simple data analysis procedure was developed based on the recorded titration curves. By implementing this data analysis procedure in the software of the titration unit, an on-line sensor is obtained that immediately yields the combined information about the actual mixed liquor NH_4^+-N concentration and the nitrification rate of the activated sludge. Automation of the data analysis procedure implies that the response time of the measurement

would decrease significantly, because each measurement could be finished immediately after the calculation of S2 (see Figure 3).

In the experiments described here, the length of each titration experiment was fixed to 2 h. For some experiments, 2 h was not enough to nitrify the NH_4^+-N in the sludge. The maximum NH_4^+-N concentration that could be determined is dependent on the nitrification rate of the sludge. An automated nitrification end point detection could avoid problems with a too high NH_4^+-N concentration in the mixed liquor (see Figure 4), because the measurement could be continued until NH_4^+-N is completely oxidized, even when this takes, for example, 3 h. The question rises if it is useful to continue the measurement for such a long period. Applying a maximum duration (e.g., 2 h) for the measurements may be a better strategy. In case the sludge sample still contains NH_4^+-N after 2 h, no nitrification end point will be detected during the titration experiment. This is a strong indication that something goes wrong with the nitrification process in the sampled plant. In this case, the sensor exerts a warning function for malfunctioning of the full-scale plant, even without exactly knowing the NH_4^+-N concentration in the plant.

Effluent NH_4^+-N concentrations measured with the on-line analyzer compared well with the results of the titration experiments (Figure 4). An increase of the effluent NH_4^+-N concentration was each time detected by both methods. This indicates that the titration experiments give valuable information about the effluent NH_4^+-N concentration.

For periods during which the effluent of the pilot plant contained NH_4^+-N, both methods indicate similar trends, but the difference between the concentration values obtained with both methods is not always exactly equal to 1.33 mg of NH_4^+-N/L. There are several reasons to explain the observed differences. First of all, a titration experiment yields an NH_4^+-N concentration corresponding to the actual situation in the last aerobic compartment of the pilot plant at the moment of sludge sampling, while the curve representing the measurement results of the on-line NH_4^+-N analyzer presented in Figure 4 is composed of hourly averages of the on-line measurements. Second, a difference existed between the location of the sampling points of the titration unit (last aerobic compartment) and the on-line NH_4^+-N analyzer (effluent). When the mixed liquor of the last aerobic compartment still contained NH_4^+-N, some NH_4^+-N could probably be nitrified in the decanter ($V = 10$ L) situated between the two sampling points. In addition, the diurnal hydraulic loading pattern of the pilot plant caused a variable time shift between both measurements, with a hydraulic retention time varying between 15 and 24 h.

The observed diurnal effluent NH_4^+-N peak can be explained by the diurnal loading pattern to the plant. In periods with a high N load to the plant, all organic N is converted to NH_4^+-N, but the nitrification capacity of the sludge is not sufficient to nitrify the NH_4^+-N completely, and an effluent NH_4^+-N peak appears.

Pilot Plant Results: Nitrification Rates. For the first period (day 1−14), an average nitrification rate of 3.84 ± 0.59 mg of N/L·h was found, while for the second period (day 15−18) this value decreased to 2.76 ± 0.54 mg of N/L·h (Figure 5). The difference between the activities obtained during the first and the second period can be explained by a decrease of the sludge concentration, due to a temporary failure of the decanter. Figure 5 shows how the SS concentration in the pilot plant decreased on day 14 due to this mechanical interruption. This explanation is confirmed by the fact that the effluent contained more NH_4^+-N during the second period, although the loading pattern to the plant did not change as compared to the first period.

During the first period, the average nitrification rate was considerably lower than the loading rate (6.3 mg of N/L·h), and still the effluent did not contain any NH_4^+-N for most of the time. The explanation for this phenomenon is that only part of the influent N load has to be nitrified, because some N is needed for the formation of new biomass.

Comparison with Existing Methods. Compared to existing chemical on-line NH_4^+-N analyzers, no sample preparation step is needed for the titration procedure. Most of the chemical on-line NH_4^+-N analyzers need an expensive and maintenance-intensive pretreatment of the mixed liquor sample to avoid clogging of the analyzer (*3*, *5*). Moreover, the titration procedure does not use expensive and environmentally unfriendly chemicals (e.g., EDTA) as most of the on-line NH_4^+-N analyzers do (*3*, *5*). A disadvantage of the titration method is its variable response time, which is dependent on both the NH_4^+-N concentration in the sludge sample and the nitrification rate of the sludge. However, the effluent NH_4^+-N concentration should be close to 0 mg/L for a properly operated treatment plant. In that case, a titration experiment can be finished within about 0.5 h as compared to a response time of 3−20 min for the chemical on-line NH_4^+-N analyzers (*4*, *5*). Especially colorimetric NH_4^+-N analyzers suffer from a too long response time. For analyzers with an ion-selective NH_3 electrode, the response time is normally lower than 10 min (*4*). An extra delay of 3−9 min should be added to the response time of the chemical analyzers, corresponding with the time needed to put the sample through the ultrafiltration unit placed between measuring point and analyzer (*4*). This makes the titration procedure an attractive alternative for existing chemical on-line NH_4^+-N analyzers.

Contrary to chemical on-line NH_4^+-N analyzers, the developed titration method provides useful data about the nitrification rate of the sludge. The titration method is automated, which makes it better applicable and more user-friendly than traditional batch experiments with intensive sampling followed by chemical lab analyses of the samples (*7*, *8*). Of course, on-line NH_4^+-N analyzers too can be used for the determination of the nitrification rate of activated sludge, especially on activated sludge systems that are operated discontinuously as for example, sequencing batch reactors or alternating activated sludge systems. For completely mixed systems however, the quantification of the nitrifying activity of the sludge with an on-line NH_4^+-N analyzer would be more complicated. A batch experiment with a sludge sample would be necessary to obtain information about the activity of the nitrifying bacteria in the aeration tank. During the batch experiment the analyzer would of course not be available for the normal analysis of the mixed liquor NH_4^+-N concentrations, while the response time of the sample preparation system and the analyzer could disturb interpretation of the data obtained from such a batch experiment.

The proposed titration procedure can be compared more or less to the respirometric measurements that were developed earlier for the quantification of the nitrifying activity of activated sludge. This means that in fact the sum of NH_4^+-N and nitrifiable organic N is measured with the titration method, just like respirometric measurements do (*25*). When operated on the influent of a plant, the titrimetric sensor could measure the concentration of nitrifiable influent N. However, this particular application of the titrimetric method could generate erroneous data in case the N-containing organics are only slowly biodegradable, because the amount of base consumed during the titration would then underestimate the nitrifiable N concentration. Chemical NH_4^+-N analyzers will only measure the NH_4^+-N content of the wastewater and thus underestimate the total N load (NH_4^+-N + organic N) to the plant. Respirometric measurements, however, are always confronted with the problem of how to separate the oxygen uptake for nitrification from the oxygen uptake for the oxidation of the biodegradable organics.

Contrary to some respirometric procedures (*9*, *13*), no nitrification inhibitors are necessary for the titration procedure, which makes the method suited not only for full-scale but also for lab-scale activated sludge plants because the sampled sludge can be recycled to the plant when a measurement is finished. Compared to other respirometric techniques (*11*, *12*, *22*), no specific experimental conditions have to be designed for the titration experiments.

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