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Sensors to monitor biological nitrogen removal and activated sludge settling

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Abstract

A brief overview of methods and sensors to characterize activated sludge is presented, summarizing techniques related to two important activated sludge processes: biological nitrogen removal (nitrification and denitrification) and sludge settling. Traditional off-line methods, typically applied in a laboratory environment to determine nitrifying/denitrifying sludge activities and sludge settling properties are briefly described. The main part of the paper covers a more detailed description of on-line sensors which were recently developed to continuously provide information about important activated sludge properties in a full-scale plant. The most important future work in this research field is the development of control strategies based on the data provided by these sensors. © 1998 Elsevier Science B.V.

Keywords: Activated sludge; Denitrification; Nitrification; Respirometry; Sludge settling; Titration experiment

1. Introduction

The activated sludge process is one of the most widespread wastewater purification technologies. In this process, wastewater is mixed with a concentrated biomass suspension (the activated sludge) responsible for the degradation of the pollutants. When microbial degradation processes have come to an end, the sludge flocs are separated again from the purified wastewater through sedimentation in a decanter. The purified water is discharged into surface waters while the concentrated sludge suspension is continuously withdrawn at the bottom of the decanter. The majority of the concentrated sludge suspension is recycled and mixed again with wastewater entering the treatment plant. Excess sludge produced due to bacterial growth during degradation processes is normally discarded as a fraction of the concentrated sludge flow withdrawn at the bottom of the decanter, and treated separately in the sludge treatment facilities of the activated sludge plant.

Originally, activated sludge system design was only concerned with the removal of organic carbon substances from the wastewater. During the last two decades however, more stringent effluent standards for nutrients (nitrogen (N) and phosphorus (P)) imposed by legislation have in many countries led to the development of more complicated activated sludge process configurations specifically designed to achieve biological nutrient removal. A general characteristic of all systems is that mixed liquor is cycling through aerobic, anoxic and anaerobic conditions to obtain nitrification, denitrification and biological P removal (Randall, 1992).

In view of the variety of biological processes

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taking place in a biological nutrient removal activated sludge plant, researchers, control engineers and treatment plant operators experienced a need to develop simple and elegant methods to identify the conversion rates of different activated sludge processes separately by performing a short experiment. The simple design of some of the experiments resulted in the construction of sensors which automatically carry out these experiments. In this research field, the concept 'in-sensor-experiment' covers a group of experimental devices consisting of a down-scaled reactor in which a simple and robust sensor element [DO (dissolved oxygen), pH, ORP (oxidation reduction potential), turbidity, etc.] is used to monitor the response of the biomass to a well-known disturbance, e.g. on a substrate addition (Vanrolleghem and Coen, 1995). A common feature of the sensors designed according to this concept is that information about the biomass characteristics can be obtained without operating a sample pretreatment system on the mixed liquor.

Efficient removal of organic carbon substances can be achieved without any problem in most activated sludge plants, and numerous respirometric techniques have been developed for detailed monitoring of organic carbon removal in activated sludge (Vernimmen et al., 1967; Blok, 1974; Ros et al., 1988; Vanrolleghem et al., 1994; Vanrolleghem and Spanjers, 1994; Spanjers and Vanrolleghem, 1995; Spanjers et al., 1996). However, research is now concentrating on optimizing biological nitrogen (N) removal and sludge settling processes. As a consequence, several methods and sensors were developed recently to collect detailed information about these processes. In view of this evolution, the scope of this paper will be limited to methods to measure nitrification and denitrification rates of activated sludge. In addition, sensors for on-line characterization of sludge settling properties will be discussed briefly.

2. Monitoring nitrification and denitrification in activated sludge

Biological N removal requires three reaction steps. In a first phase, ammonium N (NH_4^+-N) is released by hydrolysis and degradation of N-containing organic compounds. In a second aerobic step, nitrification or the biological oxidation of NH_4^+ to nitrite (NO_2^-) and nitrate (NO_3^-) takes place, by NH_4^+ and NO_2^- oxidizing bacteria respectively (stoichiometric Eq. (1)) (EPA, 1993). The measurement of the nitrification rate is based on stoichiometric Eq. (1). During nitrification, the substrate consumption or product formation rate can be monitored by regular sampling followed by chemical analysis of the samples. Alternatively, the oxygen consumption or proton formation rate can be used as a measure for the nitrification rate. The CO_2 consumed for the formation of new nitrifying biomass is too low to be used to quantify the nitrification rate accurately. The same goes for the amounts of biomass ($C_5H_7O_2N$) and H_2O formed during nitrification.

$$NH_4^+ + 1.890\ O_2 + 0.081\ CO_2 \rightarrow 0.016\ C_5H_7O_2N + 0.950\ H_2O + 0.980\ NO_3^- + 1.980\ H^+ \quad (1)$$

In a third anoxic step, denitrification occurs. Oxidized N species serve as electron acceptors and are converted into nitrogen gas (N_2) that escapes from the mixed liquor. Contrary to nitrification, alkalinity is produced. The denitrification reaction with methanol as electron donor is shown in stoichiometric Eq. (2) (EPA, 1993). The denitrification process can be monitored using chemical (NO_3^- consumption rate) or titrimetric methods. Again, the amounts of biomass and H_2O produced are too low to be of practical use to measure the denitrification rate of a sludge sample. A N_2 measurement in the gas phase is not useful in practice, because N_2 is released in the atmosphere which already consists for a large part of N_2 gas. Finally, measurements of the decrease of the carbon source concentration could be performed to monitor denitrification processes. However, it is difficult to convert carbon source consumption data into denitrification process rates, due to the variable Chemical Oxygen Demand (COD)/NO_3^--N ratio which is observed in practice for denitrification processes (EPA, 1993).

$$NO_3^- + 1.080\ CH_3OH + 0.240\ H_2CO_3 \rightarrow 0.056\ C_5H_7O_2N + 0.470\ N_2 + 1.680\ H_2O + HCO_3^- \quad (2)$$

2.1. Chemical methods

Monitoring NH_4^+ consumption or NO_2^- and NO_3^- production rates in a batch experiment with activated sludge is one of the most popular ways to measure the nitrification rate of activated sludge samples (Benmoussa et al., 1986; Kristensen et al., 1992; Arvin et al., 1994; Eilersen et al., 1994). Regular sampling and chemical analysis of the samples for NH_4^+-N or NO_x^--N ($=NO_3^- + NO_2^-$) is necessary, which makes this method expensive and rather time consuming. Alternatively, monitoring NO_2^- production or consumption rates in the presence of a selective inhibitor for NO_2^-- or NH_4^+-oxidizing bacteria respectively, was proposed as a valid method to measure the activity of NH_4^+- and NO_2^--oxidizing bacteria separately (Völsch et al., 1990).

For denitrification processes, similar experiments are performed by monitoring the NO_3^- uptake rate of activated sludge, which is again a rather labor-intensive job (Kristensen et al., 1992; Harremoës and Sinkjaer, 1995). Installation of a flow injection analysis (FIA) system allows automated monitoring of the concentration of inorganic N species during N removal processes in batch experiments (Isaacs and Temmink, 1996). For activated sludge systems with highly varying process conditions, such as for instance in sequencing batch reactors or alternating activated sludge plants, on-line estimation of in-situ nitrification and denitrification rates is possible based on the data provided by on-line NH_4^+ and NO_3^- analyzers (Lynggaard-Jensen et al., 1996). For continuous flow activated sludge systems, however, batch experiments are needed to obtain similar information on the sludge characteristics because continuous input of influent results in data with very little dynamics so that no clear interpretation can be made (Vanrolleghem and Coen, 1995).

2.2. Respirometry

2.2.1. Measuring principles

The in-sensor-experiment concept was originally developed for respirometric experiments with activated sludge sampled from a full-scale plant (Vanrolleghem and Coen, 1995). Respirometry is the measurement and interpretation of the respiration rate of activated sludge. The respiration rate is the amount of oxygen per unit of volume and time that is consumed by organisms. Respirometric methods have been used to characterize heterotrophic and nitrifying biomass in activated sludge samples because oxygen uptake is a key activity in both carbon oxidation and nitrification. Respirometry is preferred over substrate specific monitoring methods because respirometry is generally applicable, easy to automate and sensitive even for rather small substrate concentrations.

Eight different types of respirometers can be distinguished according to two criteria (Spanjers et al., 1996): (1) the phase where the oxygen concentration is measured (liquid or gas), and (2) whether or not there is input and output of liquid and gas (flowing or static). Respirometric methods included in this review will be limited to respirometers where oxygen is measured in the liquid phase using a dissolved oxygen (DO) electrode. However, the proposed respirometric measurement concepts can be extrapolated to other types of respirometers. Two main respirometric principles will be distinguished: static gas and flowing gas respirometers (Vanrolleghem and Spanjers, 1994; Spanjers et al., 1996; Spanjers, 1993). Static gas respirometers can be operated with a static or a flowing-liquid phase. The static gas-static liquid respirometer is operated by withdrawing a sample of activated sludge from a plant, transferring it into a small reactor vessel and then monitoring the decline of DO concentration with time following a short aerated phase. Use of static gas–static liquid respirometers is restricted because of the danger for oxygen limitation. This type of respirometer is nevertheless very popular because of its simple construction and measurement principle (Vernimmen et al., 1967; Chudoba et al., 1985; Kroiss et al., 1992; Drtil et al., 1993; Surmacz-Gorska et al., 1996; Gernaey et al., 1997a).

Flowing gas–static liquid respirometers on the contrary are continuously aerated and have the advantage that higher sludge concentrations can be used, because there is a continuous input of oxygen and oxygen limitation is unlikely (Blok, 1974; Ros et al., 1988; Vanrolleghem et al., 1994). In this case, the oxygen transfer coefficient and the saturation DO concentration have to be known in order to calculate the respiration rate. Static-liquid respirometers can be automated to operate in a semicontinuous way,

i.e. the respirometer carries out a repeated batch experiment.

Static gas–flowing liquid respirometers measure the DO concentration at both the inlet and the outlet of a closed respiration chamber (Vanrolleghem and Spanjers, 1994; Spanjers, 1993). Aerated sludge is pumped continuously through the respiration chamber. The oxygen uptake rate (OUR) is calculated by making an oxygen mass balance over the respiration chamber using the input and output DO concentration and the residence time in the vessel.

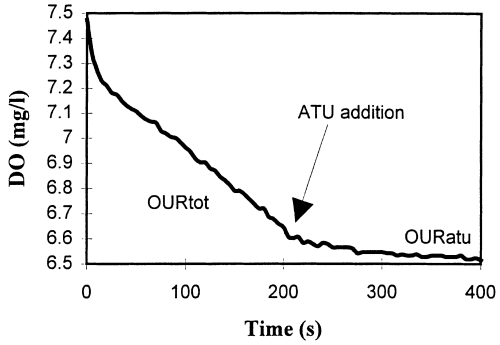

Fig. 1. Example of a typical NITROX (nitrification toxicity tester) measuring cycle (Gernaey et al., 1997a). OUR_{tot} = total oxygen uptake rate; OUR_{atu} = oxygen uptake rate recorded after ATU dosage (nitrification inhibited).

2.2.2. Typical applications

For nitrogen removal systems, respirometric measurements are useful for monitoring purposes. Among others, respirometry can be applied successfully to measure the nitrifying sludge activity, due to the high oxygen consumption for nitrification. The main problem to be solved before the nitrifying activity can be determined is to separate the nitrification oxygen uptake from the oxygen uptake for carbon substrate oxidation and endogenous metabolism. Different methods are applied in practice to obtain this separation, as will be illustrated with some examples.

Normally, batch experiments using a sludge sample in endogenous state are performed to determine the nitrifying activity of the activated sludge. A limited amount of NH_4^+ is injected during the experiment. In static gas–static liquid respirometers for example, the increase of the OUR due to nitrification can be observed clearly after the NH_4^+ addition (Chudoba et al., 1985; Drtil et al., 1993; Nowak and Svardal, 1993). Respirometric methods consisting of pulse substrate additions to activated sludge in endogenous state cannot be used to estimate the actual nitrification rate in a treatment plant, because wastewater entering the plant is continuously providing fresh substrate for both carbon oxidation and nitrification. If one wants to focus on the nitrification process in such circumstances, selective nitrification inhibitors may be helpful, as illustrated in Fig. 1. In fact, a double experiment is performed and a differential analysis made. First the total OUR of the sludge is measured, and then a nitrification inhibitor (allylthio urea or ATU) is added to the sludge sample and a second OUR is measured. By subtraction of both respiration rates, the actual nitrification rate of the sludge can be determined.

Respirometry is frequently used for on-line influent toxicity detection on wastewater treatment plants. Specific applications in this field using nitrifying bacteria as indicator organisms for toxicity are studied intensively (Benmoussa et al., 1986; Arvin et al., 1994; Kroiss et al., 1992; Gernaey et al., 1997a; Nowak and Svardal, 1993; Stensel et al., 1976; Blum and Speece, 1991; Aivasidis et al., 1992; Arbuckle and Alleman, 1992; Kong et al., 1996). Here too, specific nitrification inhibitors are used in many cases to distinguish nitrification oxygen uptake from heterotrophic oxygen uptake. An indication about the toxicity of wastewater towards nitrifying bacteria can also be obtained with bacteria of a specific nitrifying enrichment culture containing little or no heterotrophic bacteria (Gernaey et al., 1997a; Aivasidis et al., 1992; Arbuckle and Alleman, 1992). In this case, the OUR measured in the presence of a wastewater sample is mainly due to nitrification and the use of specific nitrification inhibitors is unnecessary. The interest for nitrifying bacteria as indicator organisms for toxicity detection can be explained by the higher sensitivity of nitrifiers for toxic compounds, compared to heterotrophs (Blum and Speece, 1991).

2.2.3. NITROX

The NITROX (NITRification tOXicity tester) (available from Kelma BVBA, Niel, Belgium) was developed as a respirometric on-line toxicity de-

tection system combining a high sensitivity with a short response time (Gernaey et al., 1997a). The measuring principle is that of a static gas–static liquid respirometer. The actual operation of the NITROX biosensor consists of the measurement of the nitrifying activity of a sludge after mixing it with a potentially toxic wastewater sample. The operating procedure consists of two main phases: a contact phase and a measuring phase. During the contact phase, an amount of sludge is mixed with a fixed volume of wastewater. Excess NH_4^+-N (5 to 10 mg NH_4^+-N/l) is added to the mixture, to ensure zero-order nitrification kinetics, however without causing substrate inhibition effects. The mixture is aerated for a few minutes. Then, aeration is stopped, and the suspension is mixed only while the OUR of the sludge is determined before and after addition of allylthiourea (ATU), a selective nitrification inhibitor (Kroiss et al., 1992; Surmacz-Gorska et al., 1996; Stensel et al., 1976; Sato et al., 1990). The OUR representing the nitrifying activity of the mixture (OUR_N) is obtained as the difference between the total activity (OUR_{tot}) of a mixed culture (nitrifiers and heterotrophs) and the activity of the heterotrophs after inhibiting the nitrification by the addition of ATU (OUR_{atu}). One measuring cycle is presented in Fig. 1.

The toxicity of a sample is determined by comparing the nitrifying activity obtained from a wastewater sample with unknown toxicity ($OUR_{N,sample}$) with that obtained from a reference cycle ($OUR_{N,ref}$), as shown in Eq. (3). Tap water is used as nontoxic reference solution. A reference cycle is normally performed once every two or three hours.

$$\%\text{inhibition} = \frac{OUR_{N,ref} - OUR_{N,sample}}{OUR_{N,ref}} * 100 \qquad (3)$$

Nitrification is a two-step reaction. Only recently, a more sophisticated respirometer was developed which allows the quantification of the activity of both nitrification steps separately (Surmacz-Gorska et al., 1996). The method also provides information about the oxygen uptake for carbon oxidation or endogenous metabolism of the biomass. The measurement is based on the sequential addition of $NaClO_3$ and ATU, specific inhibitors for the NO_2^- and NH_4^+ oxidizing bacteria respectively, to an activated sludge sample. The separate activities can be calculated by subtracting the different OUR values, as illustrated in Fig. 2. Dosing both $NaClO_3$ and ATU gives extra value to respirometric methods. When applied to a nitrifying activated sludge system, the method should for instance allow the detection of the presence of NO_2^--N in the mixed liquor. This data could be used to optimize the activated sludge process in such a way that NO_2^--N is converted completely to NO_3^--N, or inversely, to perform nitrogen removal via the cost-effective NO_2^- route.

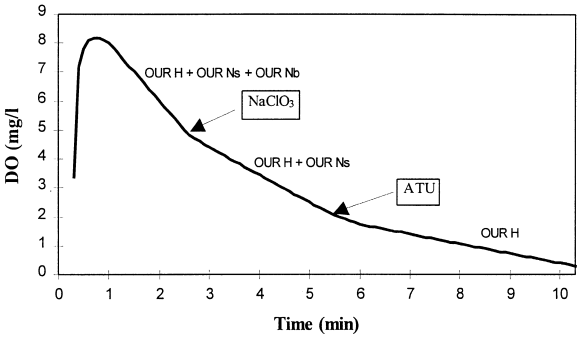

Fig. 2. Schematic representation of a respirometric experiment including the addition of 2 selective nitrification inhibitors to a sludge sample (Surmacz-Gorska et al., 1996). In a first phase, the total OUR is measured. After addition of $NaClO_3$, nitrification step 2 (OUR Nb) is inhibited. Addition of ATU inhibits nitrification step 1 (OUR Ns). The remaining OUR H is the heterotrophic and endogenous OUR.

2.2.4. RODTOX

A flowing gas–static liquid respirometer, the RODTOX (Rapid Oxygen Demand and Toxicity tester) (available from Kelma BVBA, Niel, Belgium) was developed in the eighties (Vandebroek, 1986). Its operating principle has been discussed in detail (Vanrolleghem et al., 1994). Oxidation reactions can completely come to an end in such continuously aerated respirometers, even for a rather high substrate concentration, and a respirogram will be obtained. This respirogram allows the estimation of kinetic nitrification parameters (μ_A or the maximum specific growth rate of the nitrifying bacteria and K_{NH}, the Monod half-saturation coefficient for ammonium) based on a single substrate depletion experiment (Spanjers and Vanrolleghem, 1995; Kong et al., 1996; Vanrolleghem and Verstraete, 1993;

Brouwer and Klapwijk, 1995). For static gas–static liquid respirometers, several experiments may be needed to obtain similar information about the nitrification kinetics (Chudoba et al., 1985; Drtil et al., 1993; Nowak and Svardal, 1993).

A procedure for the simultaneous characterization of carbon oxidation and nitrification was proposed using an appropriate mixture of a readily biodegradable carbon source and NH_4^+ which is added to a nitrifying activated sludge sample in the reactor vessel of the RODTOX sensor (Kong et al., 1996; Vanrolleghem and Verstraete, 1993). An example of raw OUR data obtained from such an experiment is shown in Fig. 3, using acetate as a carbon source. During the first minutes (data not shown), a transient phenomenon occurs that provides no reliable data on the biokinetics (Coen and Vanrolleghem, 1997). The high OUR measured during the first 15 min represents the activity of both the nitrification and carbon oxidation. After about 15 min, the OUR is only due to nitrification of the remaining NH_4^+-N. By fitting an appropriate model describing both the oxygen uptake for organic carbon substrate oxidation and nitrification to the available data, nitrification and carbon substrate oxidation kinetic parameters can be estimated. This procedure was applied for the simultaneous estimation of the effect of toxic compounds (e.g. cyanide) on carbon oxidation and nitrification (Fig. 4). In the first 'shouldered' peak of this figure, the oxygen uptake for nitrification and carbon substrate oxidation in the absence of cyanide can be clearly distinguished. Injection of increasing cyanide concentrations inhibits both the nitrification and the carbon substrate oxidation: the OUR for carbon substrate oxidation and nitrification decreases with increasing toxicant concentrations. The OUR data show that nitrification (the 'shoulder' in the respirogram) is more sensitive to cyanide intoxication; e.g. nitrification is already completely inhibited at 0.788 mg cyanide/l while the OUR for carbon substrate oxidation is still measurable, even for a concentration of 1.588 mg cyanide/l. The % inhibition of both reactions can be calculated using a similar equation as Eq. (3), by comparing the reaction rates measured in the presence of the toxic compound with the reaction rates measured during the reference experiment (the first peak in Fig. 4).

Respirometric applications for nitrogen removal processes are not limited to the estimation of nitrification rates only. Model based interpretation of respirograms recorded after adding a wastewater sample to activated sludge in the endogenous state, was recently used to determine the concentration of nitrifiable nitrogen present in the influent of an activated sludge plant (Spanjers and Vanrolleghem, 1995; Brouwer and Klapwijk, 1995). Initial substrate concentrations can be calculated by interpreting the area under the respirogram. An example of a respirogram is given in Fig. 3.

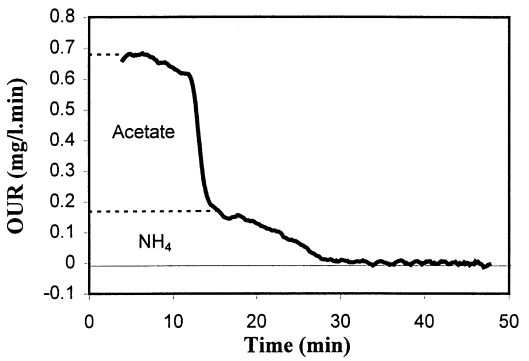

Fig. 3. Raw OUR data obtained after an injection of a mixture of acetate (16 mg COD/l) and NH_4^+-N (1.0 mg/l) into the RODTOX respirometer (Vanrolleghem and Verstraete, 1993). After about 15 min, all acetate is degraded and the OUR is only due to nitrification of the remaining NH_4^+-N.

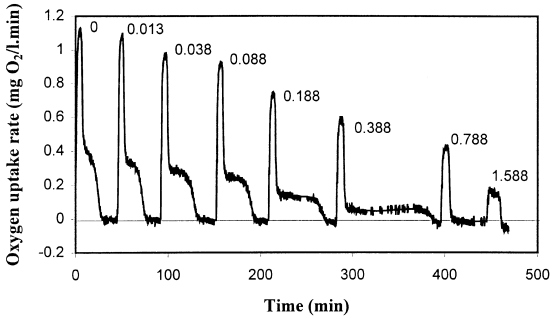

Fig. 4. OUR data obtained after the injection of a mixture of acetate (20 mg COD/l) and NH_4^+-N (2 mg/l) in the RODTOX respirometer for increasing CN^- concentrations (Kong et al., 1996). The figures indicate the CN^- concentrations (mg/l) in the mixed liquor sample.

2.2.5. Titrimetric sensors

Respirometric methods fail completely under anoxic conditions. Regular manual sampling and chemical analysis of the samples allows the determination of the nitrifying or denitrifying activity of a sludge sample, but this approach is labour intensive. Alternatively, the pH effect of the nitrification and denitrification reactions (stoichiometric Eqs. (1) and (2)) can be used to quantify the nitrifying or denitrifying activity of activated sludge. Such measurements are normally performed using a pH controller which keeps an activated sludge sample at a constant pH setpoint (Aivasidis et al., 1992; Ramadori et al., 1980; Massone et al., 1995; Vanderhasselt, 1995; Bogaert et al., 1997; Gernaey et al., 1997a). A pH controller is preferred over monitoring pH profiles. Monitoring pH profiles is suited to detect nitrification and denitrification endpoints, which can be used for process control in alternating processes (Al-Ghusain et al., 1994). However, pH profiles cannot be used to calculate nitrification rates, since a pH decrease cannot be related to a number of protons which are formed. 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, and this disturbs interpretation of the pH profiles.

Several titrimetric sensors were developed to monitor nitrification in activated sludge. The operating principle of the sensors is based on the stoichiometric conversion of NH_4^+ to nearly 2 H^+ (Eq. (1)). Interpretation of the titration data yields information about the nitrification rate and, depending on the design of the sensor, also the NH_4^+-N concentration in the mixed liquor samples (Aivasidis et al., 1992; Ramadori et al., 1980; Massone et al., 1995; Gernaey et al., 1997b). One titrimetric sensor was specifically developed to detect an increase of the toxicity of wastewater (Aivasidis et al., 1992). In this sensor, the nitrifying biomass was immobilized in a flow-through reactor and the wastewater suspected to contain toxicity was supplied continuously. The nitrification rate was calculated based on the base addition rate necessary to keep the pH in the flow-through reactor vessel at a constant level. Most titrimetric sensors, however, perform a simple batch experiment. For each measurement, activated sludge taken from a nitrifying wastewater treatment plant is transferred to the reactor vessel of a titrator and a batch in-sensor-experiment is performed and continued until nitrification is completed. During the measurement, the total amount of base (meq) added to the sludge sample in the reactor vessel, is recorded. In one of the sensors, the nitrification rate is measured during batch experiments, using a pH controller which also included an aeration system with pure oxygen controlled by an additional oxygen probe (Ramadori et al., 1980). Aeration with pure oxygen was preferred to minimize CO_2-stripping effects due to aeration, which could disturb the titration experiments. In other sensors carrying out batch in-sensor-experiments, reactor design was simplified, as the reactor vessel was aerated with ambient air (Massone et al., 1995; Gernaey et al., 1997b). Thus far, lab tests and on-line experiments with different sludge samples using this approach were very satisfying, and did not justify the need to install an aeration system with pure oxygen (Massone et al., 1995; Gernaey et al., 1997b).

2.2.6. BRAM

A typical cumulative base addition curve obtained during such a batch titration experiment with the Biological Residual Ammonium Monitor (BRAM) (available from AppliTek NV, Deinze, Belgium) is presented in Fig. 5. Ammonium (1.3 mg NH_4^+-N/l) was added at $t=0$. It can be seen that base was added at the maximum rate during the first 2.5 min

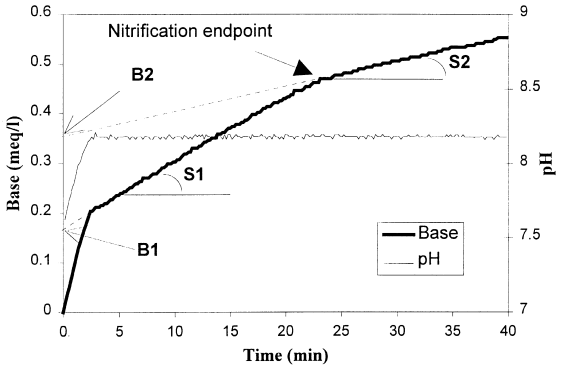

Fig. 5. Typical cumulative base addition curve obtained with activated sludge in endogenous state to which NH_4^+-N (1.3 mg N/l) was added at $t=0$ before the pH of the sludge was increased to the pH setpoint (Massone et al., 1995; Gernaey et al., 1997b). For an explanation of *B*1, *B*2, *S*1 and *S*2: see Section 2.2.6.

of the experiment, to increase the pH of the sludge sample to the pH setpoint (8.2). The nitrifying bacteria were already actively nitrifying during this first phase. In a second phase, base was added to compensate for the protons formed during nitrification. Nitrification was finished after about 23 min. During a third phase of the experiment, some base was still added to keep the pH of the sludge sample at the pH setpoint. In the sequel, this third slope will be called the background proton production rate (BPPR).

Interpretation of such cumulative base addition curves is done by correcting the cumulative base addition curves for both the BPPR and for the amount of base needed to increase the pH of the sludge to the pH setpoint. The data interpretation procedure is illustrated in Fig. 5. The slopes $S1$ and $S2$ (=BPPR) of the cumulative base addition curve were extrapolated to $t=0$, resulting in $B1$ and $B2$. $B1$ represents the amount of base added to increase the pH of the sludge to the pH setpoint, whereas $B2$ equals the sum of $B1$ and the amount of base needed to compensate for the protons formed due to nitrification of the NH_4^+-N substrate. The initial substrate concentration present in the sludge sample ($S(0)$) is obtained based on the difference between $B2$ and $B1$. The nitrification rate of the sludge is calculated based on the difference between $S2$ and $S1$.

2.2.7. DECADOS

The DECADOS sensor (DEnitrification CArbon source DOsage System; patent pending) (Vanderhasselt, 1995; Bogaert et al., 1997) is a biosensor for denitrification monitoring in activated sludge plants. It is based on two simple and 'robust' probes (pH and ORP). The sensor provides relevant information concerning the kinetics and stoichiometry of the denitrification process and, under some conditions of the in-sensor-experiments, the concentration of nitrate.

The concept is that of a 'titration' of the nitrate with a biodegradable substrate as carbon source: Carbon source is added until all nitrate has been respired. The use of pH for monitoring the denitrification process was already suggested (Al-Ghusain et al., 1994), and can be supported by Eq. (2) describing a typical denitrification process. The DECADOS sensor consists of a reactor vessel equipped with a pH electrode. A pump provides for the mixing in the reactor. Two computer-controlled dosing pumps add acid and base for the pH control. A third one is used for the carbon source addition.

A mixed liquor sample is pumped into the vessel and the titration with carbon source is started. The ORP and pH profiles of a typical run are plotted in Fig. 6, referring to an experiment with an initial nitrate concentration of 20 mg N/l. The carbon source is added discontinuously as discrete aliquots. Each arrow indicates a COD addition (COD concentration=20 mg/l after each addition). The first aliquot of carbon results in a sharp response of the pH controller. The acid addition rate drops to zero after a few minutes. This indicates that all carbon is consumed and the denitrification rate has fallen back to the endogenous level. Adding a new pulse again results in a controller response. The pH controller does not respond upon a sixth COD addition, indicating that all nitrate has been converted. This is confirmed by the ORP knee occurring at the end of the consumption of the fifth substrate pulse. One observes that the subsequent addition of small COD aliquots disturbs an adequate ORP knee detection, and hence, one mainly relies on the pH controller data. As a result of the titration, the amount of COD needed to obtain complete denitrification is known. In addition, the NO_3^- concentration and the denitrification rate of the sludge can be calculated from the titration data. Data provided by the DECADOS sensor allow to control the COD addition rate in the denitrification zone of a full-scale activated sludge plant (Bogaert et al., 1997).

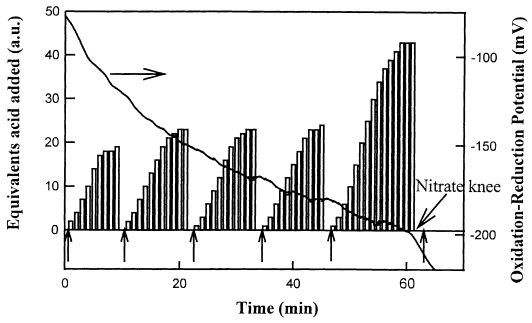

Fig. 6. Equivalents of acid added (□) and ORP (—) during a titration with the DECADOS biosensor (Vanderhasselt, 1995). The arrows indicate COD additions.

3. On-line sensors measuring sludge settleability

The sedimentation phase is the final step of activated sludge wastewater treatment processes. Increasing attention goes to final clarification as one of the processes which is critical to overall treatment plant performance, because decanter malfunctioning will result in an effluent high in suspended solids (SS) which will neutralise a large part of the efforts previously done to purify the wastewater. Indeed, SS contain considerable amounts of COD, N and P. Separation of the sludge flocs from the purified wastewater is dependent on the concentration and the physical properties of the activated sludge flocs, and the hydraulic conditions in the decanter. However, as sludge sedimentation characteristics continuously change in time, there is a need for an on-line measurement that keeps track of sludge settling properties (Vanrolleghem et al., 1996).

In the past, sludge settling characteristics were often quantified manually by the sludge volume index (SVI), resulting from a 30-min batch settling test (Catunda and van Haandel, 1992). However, this is time consuming and the measuring frequency is too low (typically once per day) to detect short time changes in sludge settleability. Moreover, it was proved that the SVI is strongly influenced by the sludge concentration (Dick and Vesilind, 1969). Alternative manual methods for the determination of the diluted sludge volume index (DSVI) or measurement of the initial settling velocity are quite laborious as well. Recent technological progress has resulted in the development of sensors to measure sludge settling characteristics. The main feature of the sensors is often a central glass cylinder allowing the monitoring of the settling characteristics of a mixed liquor sample in a batch sedimentation experiment. All sensors described below are equipped also with an automated sampling device, to allow sludge sample renewal in case of on-line operation of the sensor.

Sekine et al. (1989) were most probably the first to develop such a sensor. At the beginning of an experiment, a glass cylinder is filled with activated sludge. After mixing with air, the sludge is allowed to settle for 30 min. A moving light source/light receiver couple is used to keep track of the height of the sludge blanket. A mixed liquor suspended solids (MLSS) meter is installed at the bottom of the cylinder. The sensor thus provides data about the SVI of the activated sludge sample, the compression point, and the initial settling velocity. A similar sensor was constructed which included a stirrer mechanism in the settling cylinder (Reid and Nason, 1993). The evolution of the sludge blanket was monitored by a fixed vertical series of light emitting diodes and photodiodes. The concentration of suspended solids was measured by an infrared solids monitor. The output of the sensor consisted of a settling curve and the stirred sludge volume index (SSVI).

Vanrolleghem et al. (1996) also described a sensor with a stirrer mechanism in the settling cylinder. Sludge is pumped in a glass cylinder, mixed with air and then allowed to settle. In this settlometer (available from AppliTek NV, Deinze, Belgium), the evolution of the sludge blanket height is recorded with a moving optical detection system. In addition, a sludge concentration measurement can be installed in the sensor. The output of the sensor consists of a settling curve, the initial settling velocity and the sludge volume index. The settlometer allows to record both stirred and nonstirred settling curves. Moreover, an automated dilution of the sample can be performed if necessary. The nature of the recorded sludge index thus depends on the conditions imposed by the operator: the stirrer can be activated or not (SSVI or SVI), or a dilution step can be included (DSVI). A typical settling curve recorded with the settlometer is illustrated in Fig. 7. A single

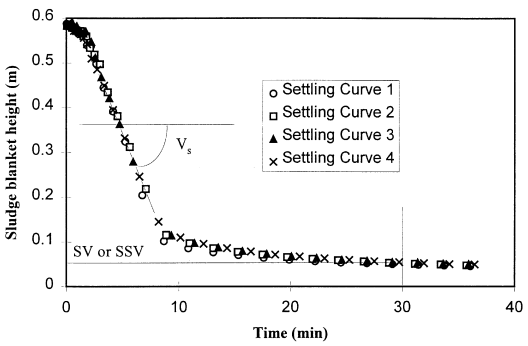

Fig. 7. Repeatability test of the settlometer: 4 settling curves recorded with the same sludge sample. V_s = sludge settling velocity, (S)SV = (stirred) sludge volume.

sample of sludge was 4 times rehomogenized and a settling curve was recorded each time. One observes the good agreement between consecutive experiments. The zone settling velocity, V_s (Fig. 7), is defined as the maximal slope of the settling curve, or the highest velocity of the sludge blanket along its descendence. The maximal slope is found at the inflection point of the settling curve. The slopes are readily available from a moving window regression on the settling curve data. The sludge volume (SV) or stirred sludge volume (SSV) is the volume fraction occupied by thickened sludge after 30 min of settling. It is obtained by interpolation between sludge blanket detections before and after 30 min duration of the settling experiment (Fig. 7). Division by the sludge concentration produces SVI and SSVI results.

A new approach was recently proposed (Rasmussen and Larsen, 1996). In this case a vertical settling column (height = 1.2 m, diameter = 0.3 m) was used. Sludge was continuously pumped through the column at a constant rate. The sludge concentration was measured in the middle and at the inlet of the settling column. The sludge flux at the inlet is the product of the sludge concentration and the bulk liquid flow velocity. The sludge velocity in the middle of the column is composed out of two components: the downward flow velocity of the bulk liquid and the settling velocity of the sludge. Consequently, the sludge flux in the middle of the column is equal to the product of the sludge concentration and the sum of the bulk liquid velocity and the settling velocity of the sludge. The sludge concentration is normally lower in the middle of the column compared to the inlet. Assuming steady-state conditions, and with the bulk liquid velocity and the sludge concentrations known, the settling velocity of the sludge can be calculated.

4. Future perspectives

When facing the daily, weekly and seasonal influent load variations to the treatment plant, it was a tradition for many years to design oversized wastewater treatment plants, to guarantee a good effluent quality without much process adjustment. Nowadays, treatment plant capacity is often insufficient, partly due to increased loads at many existing treatment plants, but mostly because of the more stringent effluent discharge standards which have to be met. Improved understanding of the actual treatment processes (e.g. biological N removal) by increased monitoring allows treatment plant operators to attain advanced treatment objectives by implementing better control of the treatment plant. The latter is also based on the on-line monitoring of relevant process parameters as e.g. NH_4^+-N or NO_3^--N concentrations in the mixed liquor. Such sensor based 'real-time control' of the treatment plant is in many cases more advantageous in terms of required efforts than extending the existing treatment plant capacity by constructing additional reactor volume (Brouwer and Klapwijk, 1995; Thomsen and Nielsen, 1992; Thornberg et al., 1993; Nyberg et al., 1996).

Most of the proposed control strategies for wastewater treatment plants are based on data provided by physical/chemical sensors (DO, pH, NH_4^+-N, NO_3^--N, etc.). However, information related to sludge activity or sludge settling properties can in many cases not be extracted from the data provided by these sensors. Therefore, a number of new on-line sensors is currently under development, aiming at monitoring biological N removal and sludge settling properties according to the 'in-sensor-experiment' concept. Examples resulting from this research were shown in the text. A common characteristic of all sensors is the simple measurement principle, the (in comparison with other sensors) low amount of chemicals which is used during the experiments, the absence of a sample pretreatment unit, and the fact that more detailed information about important activated sludge processes becomes available. Biosensors are also developed to monitor other wastewater treatment processes, as e.g. anaerobic digestion (Grijspeerdt et al., 1995), but a more detailed description of such sensors is not within the scope of this paper.

The second step in this research area will be to further develop control strategies for wastewater treatment plants which are based on the data provided by the new sensors. Such control strategies will help the treatment plant operator to take appropriate measures, e.g. when a toxic influent load or an influent shock load is detected (Müller et al., 1995), or when sludge settling problems occur. Performing

influent toxicity measurements using nitrifying bacteria as indicator organisms is probably one of the best known examples where the measurement of biological activities is a necessity. Nowadays, several biosensors were developed which are able to detect an increased acute toxicity of wastewater caused by toxic shock loads. However, a lot of work still has to be done. Just a few examples to illustrate this: Researchers should try to find reliable detection methods for chronic toxic effects and, closely related with this, how to remediate in the case of nitrification problems. Some options that should be studied thoroughly are the benefits of (1) the addition of quenching agents as e.g. powdered activated carbon or biosupplements (Vansever et al., 1997), and (2) storage and use of surplus sludge to reduce the impact of toxic compounds on nitrification in case a toxic shock load is detected.

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