Pergamon

0273-1223(95)00188-3

Wat. Sci. Tech. Vol. 31, No. 2, pp. 149–160, 1995.

0273–1223/95 $9·50 + 0·00

OPTIMAL DESIGN OF IN-SENSOR-EXPERIMENTS FOR ON-LINE MODELLING OF NITROGEN REMOVAL PROCESSES

P. Vanrolleghem and F. Coen

Centre of Environmental Sanitation, University of Gent, Coupure Links 653, B-9000 Gent, Belgium

ABSTRACT

In-Sensor-Experiments are proposed as a means of providing highly informative data concerning the bioprocesses occurring in N-removal systems. It is highlighted that the changing nature of both wastewater and activated sludge enforces the continuous adjustment of the proposed In-Sensor-Experiments to maintain the quality of the sensor's outputs. Central to the automated design of the experiments performed in these adaptive sensors is a mathematical representation of the processes occurring in the device. This model is continuously updated on the basis of previously acquired data. It is illustrated how different design criteria (objective functions), such as most reliable model selection capability or minimal parameter variance, influence the experimental designs. The concepts are illustrated with real-life data from two types of In-Sensor-Experiments. First, short-term (fed-)batch respirometric experiments are used to estimate the biokinetics of the nitrifying population. Second, a new device is presented in which a sensing element is placed at the end of a plug-flow reactor, hence the term "Plug-Flow-Sensor". The optimally designed and continuously updated variation of the flow rate through the plug flow reactor results in a retention time distribution. This allows us to monitor a variable as function of the reaction time and this within a narrow (user-specified) window of reaction times, increasing the measuring frequency and accuracy compared to equivalent batch experiments. As a first example, ORP is applied as measured variable. By using ORP "nitrate knees" can be detected after a certain reaction time. This information is an indicator of the denitrifying capacity of the sludge.

KEYWORDS

Biosensors, mathematical modelling, model selection, nitrogen removal, optimal experimental design, ORP, oxygen uptake rate, parameter estimation, wastewater treatment.

INTRODUCTION

Model-based control of wastewater treatment systems must ask for on-line modelling of these processes to accommodate on the one hand for the changing nature of the wastewater to be treated and on the other hand for the – often desired – adaptation of the biocatalysts to new process conditions. To accomplish this tedious task, lots of on-line information is required in nitrogen removal systems concerning (1) state variables such as NH_4^+ and NO_3^- concentrations, (2) biokinetic characteristics such as maximum nitrification and denitrification rates and affinities for NH_4^+ and NO_3^- and (3) stoichiometric values such as the yield for autotrophic growth or the readily biodegradable carbon requirements for nitrate reduction.

Traditionally these values are obtained from laboratory analyses but they require considerable efforts and are often not available in due time to allow on-line updating of the process model of the controller.

More possibilities are offered by on-line measuring systems that have become available in recent years and have proven to be sufficiently reliable and maintenance free (Harremoes *et al.*, 1993; Vanrolleghem & Verstraete, 1993a). These high-tech sensors for NH_4^+ and NO_3^- are however quite expensive and need a sensitive ultrafiltration unit to protect the measuring unit. Moreover, in order to deduce stoichiometric and biokinetic characteristics of the nitrogen removal processes two requirements need to be fulfilled. First, a model identification algorithm has to be implemented on site since this is not included with the measuring device. More important, the data produced from the process must contain sufficient information to feed the algorithm. With the exception of a few types of treatment plant, such as sequencing batch reactors (Demuynck *et al.*, 1994) or alternating plants (Isaacs *et al.*, 1994), insufficient excitation of the states is available to allow on-line modelling of the nitrogen removal processes.

A recently proposed alternative (Vanrolleghem, 1994) is to use robust, simple probes such as those for dissolved oxygen or oxidation-reduction potential, in measuring systems that are specially designed to use so-called In-Sensor-Experiments. Such devices typically consist of a down-scaled bioreactor in which the full-scale process is simulated in hardware, and on which specific manipulations such as substrate additions are performed to observe the dynamic response of the biological process. Since no limitations exist to the excitations implemented, high quality information can be gathered from such experiments. Moreover, it is possible to identify the models needed for adequate description of for instance nitrogen removal and this model can be regarded as an additional (high-quality) output of such measuring a device.

ADAPTIVE SENSORS: ON-LINE OPTIMIZATION OF IN-SENSOR-EXPERIMENTS

The experimental conditions for which an In-Sensor-Experiment provides the most interesting data may vary as the conditions in the full-scale process change. It is therefore an essential feature of measuring systems operating according to the In-Sensor-Experiment principle to be capable to automatically adjust the experimental conditions. Only in this way can the quality of the sensor's outputs be maintained. This automated adaptation leads to the concept of the adaptive sensor which is schematized in Fig. 1 (Vanrolleghem, 1994).

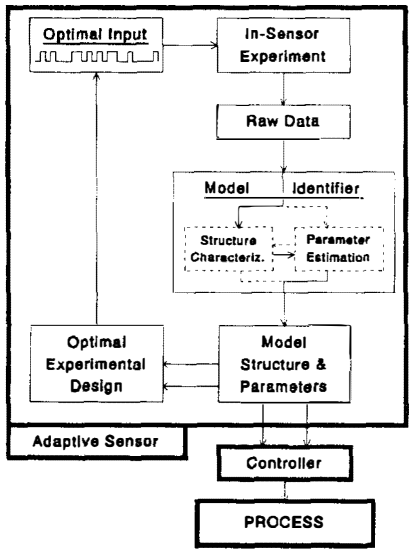

Fig. 1. The adaptive sensor concept (Vanrolleghem, 1994).

The main element of an adaptive sensor is the In-Sensor-Experiment that produces the raw data to be used for model identification, resulting in a process model and associated variables (sensor output).

Adjustment of the experimental conditions imposed on the In-Sensor-Experiment is performed by an optimal experimental design algorithm that uses the model deduced on the basis of the previously acquired data. Essentially, this algorithm "plays around" with the model to find the most appropriate experimental conditions to maximize a user-specified objective. Different design criteria can be used depending on the data desired from the sensor. When the (new) optimal experimental conditions are calculated on the basis of the model describing the behaviour in the measuring device, these are imposed to the device giving rise to a new In-Sensor-Experiment and the cycle is restarted.

In the paper examples will be presented in which model selection, parameter estimation reliability, and detection of a specific process feature are the measurement goals.

EXAMPLE 1: DO PROBE AS SENSING ELEMENT: RESPIROMETRY

Oxygen uptake or respiration is a key activity in both carbon oxidation and nitrification. With dissolved oxygen probes different devices have been developed to monitor the respiration rate of activated sludge (Vanrolleghem *et al.*, 1994). These respirometers can either be used for in situ assessment of the current respiration rate or can be applied as sidestream sensors to characterize the wastewater in terms of its load and/or toxicity. Another application which will be presented here is to use these devices to perform In-Sensor-Experiments to biokinetically characterize the activated sludge and its interaction with the wastewater. In the example developed below, attention is focused on the estimation of the maximum growth rates and affinity constants for autotrophic (and heterotrophic) populations of the sludge. More specifically, examples of optimal experimental designs in which the model selection and biokinetic parameter estimation are the pursued goals will be presented briefly.

Measuring Principle

The respirometer used in the study is a RODTOX device (Kelma bvba, Niel, Belgium), a biosensor developed to characterize the interaction between wastewater and activated sludge (Vanrolleghem *et al.*, 1994). The central part of the apparatus is a constantly aerated, completely mixed reactor containing 10 l of activated sludge taken from the treatment plant at which the sensor is installed. The In-Sensor-Experiments consist of pulse injections of wastewater or calibration samples to this bioreactor. The dissolved oxygen data, obtained from a Conducta 905S DO probe are collected on a personal computer where the transformation into an oxygen uptake rate (OUR) dataset (a respirogram) is performed according to Vanrolleghem (1994). These OUR-data reflect the impulse response of the bioprocess to the sample addition and can be used to biokinetically characterize this interaction. Previous work (Vanrolleghem & Verstraete, 1993b) has shown that it is possible to obtain estimates of the biokinetic parameters of the nitrifying population of activated sludge using pulse additions of NH_4^+-containing samples and identification of a mathematical model in which the nitrification process is incorporated. In the sequel the results of work devoted to the optimal design of experiments to perform such characterization is presented.

Optimal Experimental Design for Model Structure Characterization (OED/SC)

Model structure characterization or the selection of the most appropriate model among a restricted set of candidate models is an often overlooked, but important aspect of any modelling exercise. In Vanrolleghem & Verstraete (1993b) an experimental design was proposed by which it was possible to simultaneously characterize the biokinetic properties of both carbon oxidation and nitrification. This In-Sensor-Experiment is based on the injection of a mixture of acetic acid and NH_4Cl. It was indicated to be essential to have a good ratio between the carbon and nitrogen source in order to be able to differentiate between the oxygen uptake due to heterotrophic and autotrophic activity respectively. The problem stated in Vanrolleghem and Verstraete (1993b) is a model selection problem, as illustrated in Fig. 2 and explained below.

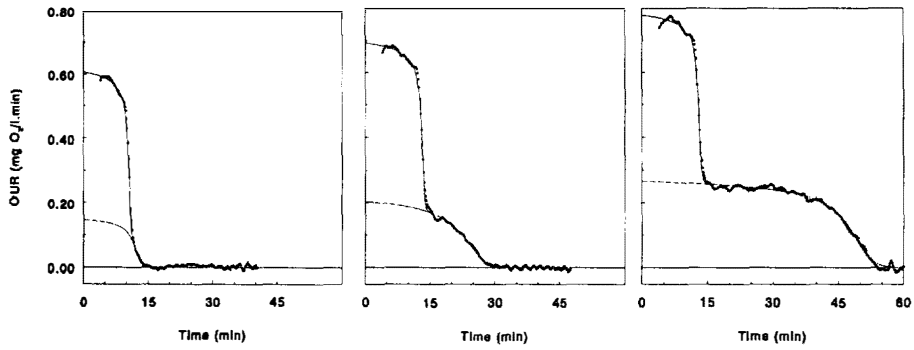

Fig. 2. Respirograms obtained with injections of different mixtures of NH_4Cl and acetate. From left to right the COD/N ratio decreases from 42 (a) to 14 (b) to 7 (c).

In Fig. 2b respirometric results of an experimental design that allows reliable identification of an autotroph/heterotroph (Double Monod) model are shown. Intuitively this can be ascertained by checking whether a "peak-with-shoulder" respirogram is obtained after injection of the carbon/nitrogen mixture. However, although both populations are active in the sludge this cannot be deduced from the data shown in Fig. 2a. On the contrary, these data can be interpreted as originating from a one-population (Single Monod) model and will do so if standard model selection criteria would be applied to this respirogram (Vanrolleghem & Van Daele, 1994). The selection method applied in this work determines the number of inflection points in the OUR-profile to decide on the most appropriate model. In Fig. 2a and 2b one and three inflection points can be observed respectively. The optimal experimental design procedure developed in Vanrolleghem & Van Daele (1994) tries to maximize the reliability with which these inflection points can be determined, taking into account that the noise on the data is amplified considerably by the numeric derivation of the raw data, required for the determination of the inflection points.

It was shown that good experimental designs can be calculated in real-time using this approach. However, one should remark that the reliability of inflection point determination is not the only guideline in the design procedure for structure characterization. Since the goal of the In-Sensor-Experiments is to assess the biokinetic constants of the aerobic populations in the activated sludge in an on-line way, a real-time constraint is also imposed on the experiment. For instance, although the experimental design leading to the respirogram of Fig. 2c results in slightly more reliable structure characterization, it is not in compliance with the second objective of this design procedure.

Vanrolleghem and Van Daele (1994) also showed that changing properties of the activated sludge demand for a change in the experimental conditions to ensure reliable structure characterization. For instance an increase of the nitrification capacity may lead to a gradual degeneration of a "peak-with-shoulder" respirogram into a Single Monod dataset. Hence, on-line OED/SC is required.

Optimal Experimental Design for Parameter Estimation (OED/PE)

If an experiment allows us to reliably characterize the model structure, an evident next goal is to maximize the accuracy of the estimation of the parameters in that model, e.g. the maximum oxidation rate or the affinity constant for NH_4^+. The respirometer described above offers sufficient degrees of freedom to allow an experimental design algorithm to improve the conditions so as to maximize the information content for parameter estimation. The degrees of freedom studied are 1) the initial amount of substrates injected in the reactor and 2) the additional injection(s) of sample in the course of a respirometric experiment, leading to a fed-batch type of In-Sensor-Experiment. One should note again that the maximum length of an experiment was fixed.

Different objectives can be pursued giving rise to different experimental designs as shown below. For instance, one may be interested in the minimization of the variance of a particular parameter, e.g. the affinity constant for NH_4^+; the mean variances of all model parameters may be minimized, or the correlation between two parameters could be made as small as possible (a typical problem in case of Monod-type models is exactly the correlation between the maximum growth rate and the affinity constant). Before an algorithm for optimization of the experimental conditions can tackle such problem an objective function must be defined mathematically. Most criteria used for OED/PE are deduced from the so-called Fisher Information Matrix F (Vanrolleghem, 1994). It essentially summarizes the information content of an experiment and is also the inverse of the parameter estimation error covariance matrix.

The optimal experimental design criteria deduced from this information matrix focus on one or other of the goals mentioned above. The A- and D-criteria are the arithmetic and geometric mean of the identification errors respectively and are calculated as the trace of F^{-1} and the determinant of F respectively. The E-criterion is the largest parameter estimation error and corresponds with the smallest eigenvalue of F. Two modifications of these criteria have also been applied. First, the modified A-criterion is defined as the trace of F^{-1} and the modified E-criterion is the ratio between the largest and the smallest eigenvalue of F. The latter criterion gives a good indication of the correlation between the parameter estimates and the potential numerical difficulties of the estimation problem. Experimental designs may aim at minimizing the A- or modified E-criteria, or at maximizing one of the others.

TABLE 1. Dependence of the Parameter Variances on the Experimental Design

	S_0=23 mg/l no pulse	S_0=60 mg/l no pulse	S_0=23 mg/l pulse at 18.2'	S_0=50 mg/l pulse at 36'	S_0=23 mg/l 6 pulses
Var(μ_{max})	1.00	0.18	0.82	0.20	0.64
Var(K_m)	1.00	0.65	0.43	1.15	0.25
Covar(μ_{max},K_m)	1.00	0.34	0.47	0.38	0.30

In Fig. 3 the (simulated) substrate and corresponding OUR trajectories are shown of experiments in which an additional substrate pulse is given at a time designed according to each of the design criteria. The different criteria clearly result in different designs. One should note that the D- and E-criteria aim at allowing the substrate concentration to evolve some more time closer to the affinity constant concentration so as to maximize the reliability of its estimation. The A- and modified A-criteria on the other hand aim at gathering some more information on the maximum degradation rate while the modified E-criterion based design is a compromise between the two extremes. Figure 4 shows the results of a validation experiment. The top figure shows the reference batch experiment, while the bottom results are obtained from a fed-batch experiment with an additional pulse of substrate given after 14.1 min. The variance and covariance of the Monod parameters was halved with this small extension of the experiment.

The results summarized in Table 1 indicate the potential of optimizing the experimental conditions for parameter estimation and their dependence on the degrees of freedom given to the design algorithm. All results are compared to the batch reference experiment. One observes that the initial substrate concentration is maximized if allowed to, resulting in respirograms that finish just at the maximum allowed length. Such experiments mainly affect the estimation accuracy of the maximum nitrification rate. If a pulse is the additional degree of freedom, the variance of the affinity constant and its covariance with the maximum nitrification rate is decreased. A higher number of pulse additions further improves the estimation accuracy but the benefit become marginal as the experiment complexity increases. In Table 1 the results for six additional pulses are given. More details on this study can be found elsewhere (Vanrolleghem, 1994).

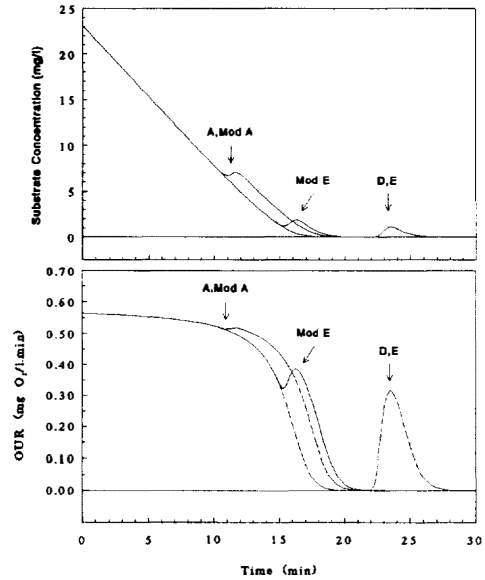

Fig. 3. Dependence of optimal time of pulse addition with respect to the optimal experimental design criterion. Top: substrate profiles, bottom: respirograms.

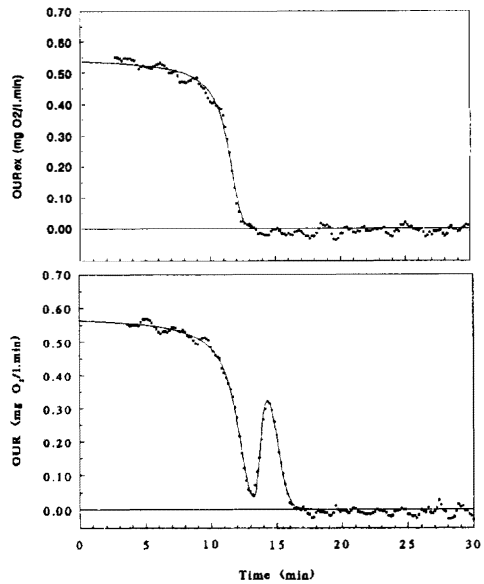

Fig. 4. Validation of the experimental design procedure. Top: reference batch experiment, bottom: fed-batch experiment with pulse at t=14.1 min.

EXAMPLE 2: ORP PROBE AS SENSING ELEMENT: THE PLUG-FLOW-SENSOR

Measuring Principle

Oxidation-Reduction Potential

The oxidation-reduction potential (ORP) is a measure of the activity of electrons involved in oxidation-reduction reactions in an aqueous environment. It can be compared to pH which reflects the activity of protons in acid/base reactions. However, in contrast to pH measurements, the assumption that the reactions taking place are in equilibrium does not hold for ORP. Therefore the observed ORP should be interpreted as a measure of the general oxidative status of the system (Koch & Oldham, 1985). Moreover, it has been shown that the ORP electrode surface itself is not in equilibrium with the dissolved reactants, adding to the problems in interpretation of ORP readings (Heduit & Thevenot, 1992).

Because of this and despite serious efforts (e.g. Londong, 1992) it is as yet not possible to deduce concentrations of redox buffers from the absolute ORP values. However, empirical results have indicated that ORP is an attractive variable for use in nutrient removal processes. Indeed, in contrast to DO data, ORP values also provide information on the bioprocesses occurring under anaerobic and anoxic conditions. In addition, their measurement is based on hardware whose characteristics are comparable to pH probes and, from a technical point of view ORP measurement can be considered accurate and unproblematic (Harremoes *et al.*, 1993).

The way ORP measurements have been interpreted so far is based on the occurrence of breakpoints in ORP profiles, also termed 'knees' (Koch & Oldham, 1985; Charpentier *et al.*, 1988; de la Menardiere *et al.*, 1991; Sasaki *et al.*, 1993; Wareham *et al.*, 1993, Wouters-Wasiak *et al.*, 1993). These knees are indicative of the appearance or disappearance of a redox buffer, comparable to the equivalence points in acid/base titrations. Figure 5b illustrates a typical 'knee' in a simulated ORP profile. The model used to generate these ORP data exploits the equivalence between acid/base and redox titrations and allows to obtain reasonable simulations of ORP profiles in batch experiments with initial presence of oxygen and nitrate.

Essentially the model incorporates three redox buffers corresponding with oxygen, nitrate and a highly reduced redox buffer system that could correspond for instance with sulphate. BOD acts as the reductant in the redox titration which is "catalyzed" by different organisms (aerobic heterotrophs, denitrifiers, fermenting organisms, ...). In the titration curve given in Fig. 5a it is seen that first BOD is being used to reduce the oxygen, after which nitrate is being denitrified. ORP is calculated with the redox buffer equations where "standard potentials" for the oxygen, nitrate and "sulphate" redox reactions are given as 75 mV, -100 mV and -400 mV resp. Also, one has to supply the initial amounts of oxygen, nitrate and "sulphate", in this example: 15.5, 23.75 and 200 mg/l as O_2-equivalents.

To obtain the ORP vs. time profile, the substrate biodegradation as given in Fig. 5b has to be related to the ORP values calculated with the titration model (Fig. 5a). Compared to Fig. 5a one observes a change in ORP profile which is due to the different rates of substrate degradation under aerobic, anoxic and anaerobic conditions (Clayton *et al.*, 1991).

For alternating processes such as SBRs or intermittently aerated continuous flow systems control strategies have been developed that use the detection of these breakpoints to initiate aeration after an anoxic phase (Charpentier *et al.*, 1989; Sasaki *et al.*, 1993; Wareham *et al.*, 1993; Wouters-Wasiak *et al.*, 1993; Demuynck *et al.*, 1994). In this way anaerobiosis can be prevented since this might lead to secondary phosphate release in P-removing systems. On the other hand, one can also use this information to determine whether anaerobic conditions are being reached in the phase intended for P-release. If not, reducing equivalents in the form of readily biodegradable COD can be added to promote P-release (Koch & Oldham, 1985; Wareham *et al.*, 1993; Demuynck *et al.*, 1994).

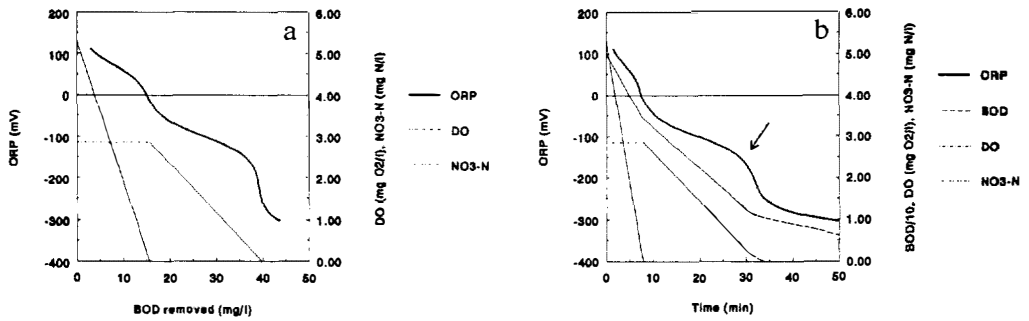

Fig. 5. Simulated ORP profile using a model describing a redox titration with BOD as reductan. Left: titration curve, right: corresponding time evolution of ORP.

For non-alternating continuous flow reactors some authors have suggested using absolute values of ORP to control nitrogen removal (de la Menardiere *et al.*, 1991; Wouters-Wasiak *et al.*, 1993). However, most often it is essential to regularly adjust the limit values on which the control is based to accommodate for the interferences due to changing concentrations of other redox buffers in the system, temperature effects and slow changes on the electrode surface (Heduit & Thevenot, 1992; Wouters-Wasiak *et al.*, 1993). This probably also explains the problems Londong (1992) experienced when estimating nitrate concentrations in a denitrifying reactor on the basis of absolute ORP data.

Thus, the *in situ* use of ORP probes in non-alternating processes is not very attractive. However, one can apply the approach of a sidestream sensor in which batch experiments are performed (with alternating conditions) to assess the state of a denitrifying reactor. This is proposed below.

Batch In-Sensor-Experiments for On-line Monitoring of Denitrifying Capacity

The principle of a batch-wise operating sensor for monitoring a denitrifying reactor is the following. Activated sludge is withdrawn from the denitrification zone, eventually mixed with a nitrate or BOD containing sample, and ORP is monitored until the nitrate knee is detected. The output of such a sensor is the reaction time required to remove all nitrate (and potentially some oxygen) from the mixed liquor. In other words, the actual denitrification capacity or the remaining denitrification time is assessed.

Knee Detection Method

A key ingredient of algorithms that use the ORP signal to monitor denitrification is a reliable nitrate knee detection method. Several methods for knee detection have been evaluated for use in the denitrification sensor mentioned above. Essentially one needs to find the time instant at which the negative slope of the ORP-curve reaches a maximum, i.e. the knee. In Fig. 6a a sequence of 3 complete aerobic(rising ORP)/anoxic(declining ORP) cycles is shown. The nitrate knees correspond with the local maximum in the slope profile (thin line). Sasaki *et al.* (1993) and Wareham *et al.* (1993) use different methods to perform this knee detection as reliably as possible taking into account that differentiation – to obtain the slope – is amplifying any noise on the measurement signal. Both approaches use a "moving window" regression for noise rejection and slope calculation. Another similarity is that two slopes taken at different time instants (at time T and at time T–DT) are compared to decide whether a local maximum is attained. The method of comparison, however, is the main difference between both methods: Sasaki *et al.* (1993) take the ratio of both slopes and compare it to a threshold ratio which should be exceeded before knee detection is reported by the method; Wareham *et al.* (1993) take the difference between both slopes as the decision variable for knee detection. In Fig. 6b and 6c the slope based decision variables of the two methods are given for the same three aerobic/anoxic sequences. One observes that both methods clearly point to the occurrence of a knee.

A number of parameters of the method can be tuned for optimal knee detection. First, the number of data points used in the window regression must be specified. Using an ORP sampling period of 1 minute, optimal noise rejection was found for a window size of 10 measurements. A second tuning parameter concerns the value of DT, i.e. the difference between the time instants at which the two slopes are determined. In Fig. 6 it is shown that a DT of 2 minutes gives a somewhat earlier but less sharp knee detection compared with a 4 minute interval. Finally, the threshold level for the decision variable can be set to minimize false knee detections. For the Sasaki method, a threshold ratio of 1.25 was found adequate, while for the Wareham method the critical slope difference was 5 mV/min. A closer look at the knee detection results shows that the Sasaki method (Fig. 6b) is able to indicate the knee 2 to 4 minutes after occurrence of the local maximum in the slopes (Fig. 6a). The Wareham method lags somewhat behind, requiring 8 to 10 minutes. However, inspection of Fig. 6c reveals that the Wareham decision variable is more smooth and will therefore result in a more confident knee detection.

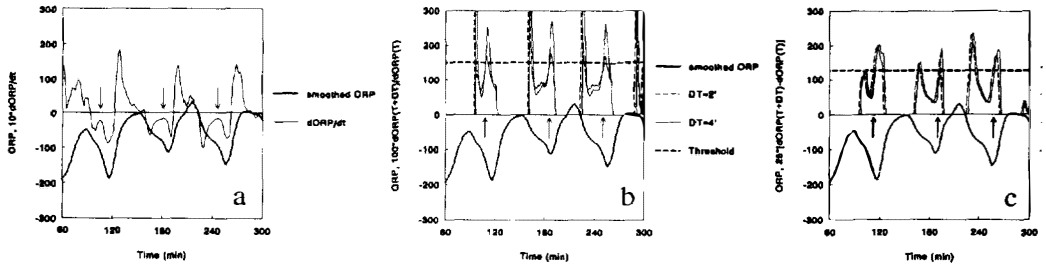

Fig. 6. Evaluation of nitrate knee (indicated by arrows) detection algorithms. ORP profiles (thick line) obtained from 3 consecutive aerobic/anoxic cycles. (a) slope; (b) Sasaki ration of slopes; (c) Wareham difference in slopes.

Plug-Flow-Sensor

While normally one tries to mimic plug-flow behaviour by batch experiments to gather more information with less effort (Clayton *et al.*, 1993), the other way round is performed here, i.e. by proper application of plug-flow behaviour, the progress of a typical batch process is monitored after specific reaction times where particularly interesting phenomena occur, e.g. the appearance of nitrate knees.

The main idea is introduced by an example of what can be achieved in such plug flow devices. Elementary liquid volumes that enter a plug flow reactor with volume V that is operated at constant flow Q will leave the reactor after a reaction time V/Q. A sensor installed at the end of this reactor will therefore only provide information on the progress of the reaction after this particular reaction time. However, if one looks at elementary volumes present along the reactor, then each of them has an associated current reaction (or retention) time $RT(z)$. Therefore, if one wants to monitor the progress of the reaction, more sensors should be installed along the reactor, or a single sensor should be moved up and downstream. However, another approach can be taken. Suppose one is able to temporarily increase the flow through the reactor to infinity. Then all fluid elements present in the reactor will be propelled through the reactor and will pass a sensor installed at the end. It would mean that one can obtain information on the process after all reaction times associated with the fluid elements present in the plug flow reactor before the flow rate was increased. In this extreme – and irrealistic – case, one can therefore monitor the progress of a batch process in an infinitely short period of time, provided an infinitely fast sensor is available.

To bring this concept to a practical implementation, one must apply a more moderate variation. The following – implicit – model allows us to calculate the retention time $RT(t)$ in a plug flow reactor with volume V under varying inflow $Q(t)$:

$$\int_{t-RT(t)}^{t} Q(\tau)\, d\tau = V$$

Essentially this equation says that a fluid element is "pushed out" of the plug flow reactor if the integral of the flow rate over the retention time equals the reactor volume. Except for some special time functions of $Q(t)$, no explicit solution for the retention time can be obtained and a numerical search routine is required. In Fig. 7b the retention times corresponding to the flow regimes specified in Fig. 7a are presented. A number of conclusions can be drawn from this simple example. First, it is clear that the applied flow regimes give rise to a restricted interval of retention times around the mean retention time V/Q. Second, although the only difference in the flow regime is its mean value, one observes a major shift in retention time interval and its distribution (RTD) as Q is changed: for Q=50, a rather uniform RTD is obtained, while for the other mean flows the RTD is skewed.

With this in mind, it is good to introduce the concept of the Plug-Flow-Sensor using the nitrate knee detection example. Suppose that the conditions in a denitrifying reactor are such that a reaction time of 20 minutes is needed to find the nitrate knee. Using a 1 l plug flow reactor operated with the flow regime as in Fig. 7a and Qmean=50 ml/min, then the corresponding retention times are in the range between 16 and 24 minutes. Hence, if one installs an ORP-probe at the end of the plug-flow reactor, ORP values are obtained for reaction times between 16 and 24 minutes. Using the t-RT(t) relationship of Fig. 7b these ORP data can be plotted in function of the reaction time. This plot will show the nitrate knee and allow its detection. Consequently, identical information is obtained as in the batch-wise operating sensor introduced above, but only the interesting part of the ORP profile is monitored, making more efficient use of the single probe. Moreover, continuous flow operation is possible, eliminating the need for fill-and-draw cycles as in the batch sensor.

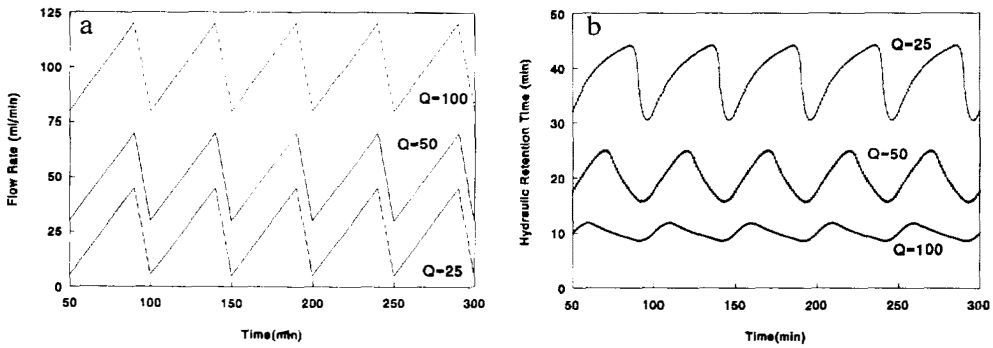

Fig. 7. Flow regime (left) and corresponding retention times in a plug-flow-sensor.

Optimal Experimental Design

The flow regime through Plug-Flow-Sensors is an operational variable that can be adjusted by an optimal experimental design algorithm to increase the information content of the raw data. A number of flow regime parameters can be considered. First, the frequency of the oscillation imposed by the flow regime will determine the frequency at which complete ORP profiles are generated (twice per oscillation: one when going up in retention time and one when coming down). Second, by proper choice of the type of function describing the flow regime, the RTD can be altered and therefore the number of data at critical reaction times can be increased, e.g. in the neighbourhood of the nitrate knee. Third, the dependence of this RTD on the mean flow as exemplified in Fig. 7 imposes another need for adjustment of the flow regime. An example may clarify this point. Suppose the denitrification capacity of the sludge decreases or the loading with nitrate is increased, resulting in a longer reaction time before nitrate knee occurrence. Evidently, the mean flow rate should be reduced accordingly to make sure that the nitrate knee remains observable by the Plug-Flow-Sensor. As these changes in required reaction time may change rather rapidly, the optimal experimental design algorithm must be performed in real-time. However, as shown above, not only the mean flow must be

adjusted. If one wants to maintain a certain RTD, e.g. a uniform distribution, then one should also adjust the functional form of the flow regime accordingly.

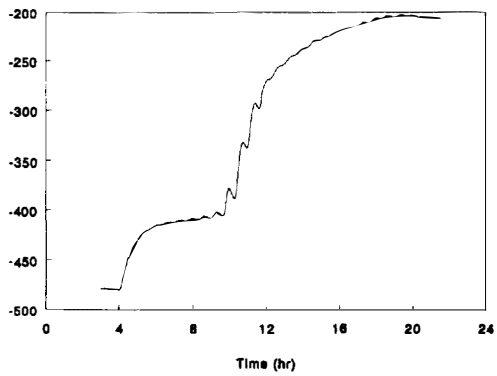

Fig. 8. ORP profile generated in a plug-flow-sensor in which no adjustment of the mean flow is made (V=1.2l; Qmean=60ml/min;RT between 18 and 22 min).

In Fig. 8 experimental results are shown of a 1 day trial of a prototype Plug-Flow-Sensor. No adjustment of the mean flow rate was made and a narrow retention time range of 4 minutes was applied. Two observations can be made. The observed gradual increase in ORP values is caused by the decreasing sludge concentration in the pilot denitrification zone to which the Plug-Flow-Sensor was connected. This result illustrates the need for on-line adjustment of the mean flow rate. Second, oscillations in ORP are only easy to observe for a limited period of time. This is caused by the retention time range that was chosen being too small. Note however that the oscillations are sufficiently large when big changes in ORP occur, which would be the case at a nitrate knee.

CONCLUSIONS

Optimal design procedures were developed for In-Sensor-Experiments devoted to the gathering of on-line information on nitrification and denitrification processes. Nitrification was monitored in a batch-wise operating respirometer. Experimental designs were presented for optimal model selection and parameter estimation. It was shown that a considerable increase in the reliability of the modelling exercise could be obtained by proper experimental design. Denitrification capacity was assessed in a new type of measuring device presented in this paper. The Plug- Flow-Sensor as it was termed because of the plug flow reactor incorporated in the apparatus allows to monitor specific features during a batch process. Using an optimally designed flow regime a desired retention time distribution can be obtained over a restricted retention time range where this process feature occurs. In the case of such sensor geared to monitor denitrification, an ORP probe is installed at the end of the plug flow reactor. This allows us to detect knees occurring in the ORP profile as the result of nitrate depletion of the mixed liquor. The reaction time needed before nitrate knee occurrence is an indication of the denitrification capacity of the denitrifying reactor the Plug-Flow-Sensor is connected to.

ACKNOWLEDGEMENTS

The authors first want to express their gratitude to Herwig Bogaert for his contributions to this paper. The authors also wish to thank Kelma bvba, Niel, Belgium and Biotim NV, Antwerp, Belgium for their financial support and interest. This research was partly financed by the VLIM program (Flemish Impuls Program for Environmental Technology), initiated by the Flemish Minister responsible for the environment.

REFERENCES

Charpentier J., Godart H., Martin G. and Mogno Y. (1989) Oxidation-reduction potential (ORP) regulation as a way to optimize aeration and C, N and P removal: experimental basis and various full-scale examples. *Wat. Sci. Tech., 21*(10/11), 1209-1223.

Clayton J.A., Ekama G.A., Wentzel M.C. and Marais G.V.R. (1991) Denitrification kinetics in biological nitrogen and phosphorus removal activated sludge systems treating municipal waste waters. *Wat. Sci. Tech., 23*(4-6), 1025-1035.

de la Menardiere M., Charpentier J., Vachon A. and Martin G. (1991) ORP as a control parameter in a single sludge biological nitrogen and phosphorus removal activated sludge system. *Water SA, 17*, 122-132.

Demuynck C., Vanrolleghem P., Mingneau C., Liessens J. and Verstraete W. (1994) NDBEPR process optimization in SBRs: Reduction of external carbon source and oxygen supply. *Wat. Sci. Tech., 30*(4), 169-179.

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

Heduit A. and Thevenot D.R. (1992) Elements in the interpretation of platinum electrode potentials in biological treatment. *Wat. Sci. Tech., 26(5-6)*, 1335-1344.

Isaacs S.H., Henze M., Soeberg H. and Kummel M. (1994) External carbon source addition as a means to control an activated sludge nutrient removal process. *Wat. Res., 28*, 511-520.

Koch F.A. and Oldham W.K. (1985) Oxidation-reduction potential - a tool for monitoring control and optimisation of biological nutrient removal systems. *Wat. Sci. Tech., 17*(11/12), 259-281.

Londong J. (1992) Strategies for optimized nitrate reduction with primary denitrification. *Wat. Sci. Tech., 26(5-6)*, 1087-1096.

Sasaki K., Yamamoto Y., Tsumura K., Hatsumata S. and Tatewaki M. (1993) Simultaneous removal of nitrogen and phosphorus in intermittently aerated 2-tank activated sludge process using DO and ORP-bending-point control. *Wat. Sci. Tech., 28(11-12)*, 513-521.

Vanrolleghem P.A. (1994) *On-line Modelling of Activated Sludge Processes: Development of an Adaptive Sensor.* PhD. Thesis. Faculty of Agricultural and Applied Biological Sciences, University of Gent, Belgium. pp. 201.

Vanrolleghem P.A. and Van Daele M. (1994) Optimal experimental design for structure characterization of biodegradation models: On-line in a respirographic biosensor. *Wat. Sci. Tech., 30*(4), 243-253.

Vanrolleghem P.A. and Verstraete W. (1993a) On-line monitoring equipment for wastewater treatment processes: State of the art. In: *TI-KVIV Studiedag Optimalisatie van Waterzuiveringsinstallaties door Proceskontrole en -sturing.* Gent, Belgium, 1-20.

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

Vanrolleghem P.A., Kong Z., Rombouts G. and Verstraete W. (1994) An on-line respirographic biosensor for the characterization of load and toxicity of wastewaters. *J. Chem. Technol. Biotechnol., 59*, 321-333.

Wareham D.G., Hall K.J. and Mavinic D.S. (1993) Real-time control of wastewater treatment systems using ORP. *Wat. Sci. Tech., 28(11-12)*, 273-282.

Wouters-Wasiak K., Heduit A., Audic J.M. and Lefèvre F. (1993) Oxydation reduction potential (ORP)-control of the aeration in a wastewater treatment plant: Nitrogen removal efficiency. A case study: The Benfeld activated sludge plant. In: *Proceedings Workshop on Monitoring, Modelling and Control of Wastewater Treatment Processes. Med. Fac. Landbouww. Univ. Gent, 58*, 2107-2112.