Development of hardware sensors for the on-line monitoring of SBR used for the treatment of industrial wastewaters

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Abstract The main challenge in the management of a sequencing batch reactor, for the biological treatment of urban and industrial wastewaters, is to ensure a stable treatment efficiency under highly variable influent quality and quantity. To cope with this challenge, on-line instrumentation is fundamental, since it allows to characterize both influent variability and process efficiency. The more the on-line data are closely correlated with influent quality and SBRs treatment capacity, the more straightforward is to implement control strategies based on these data. In this paper, two monitoring techniques are described which allow to obtain influent-related and process-related data: set-point titration and UV-spectrophotometry. Despites the very different measuring principles both techniques were successfully applied to SBRs monitoring and control leading to comparable results.

Introduction

During the first experimental phase of the EOLI project, data obtained from process experiments indicate that basic information on the biological behavior of the SBR biomass can be obtained from analytical data and from on-line signals (DO, pH and ORP), although they are more qualitative then quantitative. However, a simple monitoring does not allow plant operators to prevent unwanted events to happen (e.g. nitrification inhibition), but only to realize that they are happening. The need for on-line systems allowing plant operators to have early-warning information on the quality of the influent to be treated, allowing for effective plant operation, would greatly improve process efficiency. To this purpose two techniques were selected, set-point titration and UV-spectrophotometry, for their wide range of possible applications within processes taking care in COD and N removing SBRs.

Set-point titration

Principle of operation

The activity of a microorganism in a batch-fed reactor may be evaluated by monitoring and maintaining constant, by controlled addition (titration) of an appropriate titrant, the concentration of one among the chemical species which is either consumed (substrate) or produced (product) by the assayed biomass [1]. This principle of operation is applicable to those bioreactions which involve, at least, one reagent/product which is allowable to be measured and controlled at a constant (*static*) concentration, i.e. by set-point titration. To clarify how this technique operates, let's consider a general bioreaction taking place in a fed batch reactor and converting substrates S_i into products P_j according to the stoichiometric coefficients s_i and p_j:

$$\Sigma_i(s_i S_i) \xrightarrow{r} \Sigma_j(p_j P_j) \qquad (1)$$

If S_n can be measured continuously, a control system can be set up which actuates the dosage of a S_n-containing concentrated solution to maintain constant its in-reactor concentration (Figure 1). This means that the rate of consumption of S_n by reaction (1) equals the rate of S_n addition, which is indicated as titration rate (r_t in Figure 1). The titration experiment normally continuous until reaction (1) stops because a limiting substrate (S_L) is fully consumed. At this point, the titration rates declines markedly and the titration curve, i.e. the cumulative amount of titrant added during the course of the titration test, reaches a sub-horizontal asymptote

(Figure 1). From the titration curve a number of reaction-related information can be derived. First, the titration rate is proportional to the reaction rate (r) via stoichiometric coefficients:

$$r = \frac{1}{p_j}\frac{dP_j}{dt} = -\frac{1}{s_i}\frac{dS_i}{dt} = -\frac{1}{s_n}\frac{dS_n}{dt} = \frac{1}{s_n} r_t \qquad (2)$$

Secondly, the total amount of titrant added (V_T) is stoichiometrically related to the amount/concentration of S_L present at the beginning and converted during the course of the titration test ($[S_L]_0$):

$$V_T = \frac{s_n}{s_l}[S_L]_0 \qquad (3)$$

Moreover, the concentration of S_L at time t is calculated from the volume of titrant added at time t (V(t)), which is proportional to the fraction of S_L converted, as:

$$[S_L]_t = [S_L]_0 - V(t)\cdot s_l/s_n \qquad (4)$$

Finally, by relating the concentration of S_L to the reaction rate r, indications on the reaction kinetics can be drawn. Typically, bioreactions in biological processes for wastewater treatment are described by a Michaelis-Menten model:

$$r(t) = \hat{r}\frac{[S_L]}{[S_L] + K_{S_L}}, \qquad (5)$$

where, as usual:

$\hat{r}$ is the maximum reaction rate,

K_{S_L} is the semi-saturation constant for the limiting substrate S_L.

These two parameters can be assessed by fitting the $S_l(t)$ data obtained during a titration experiment.

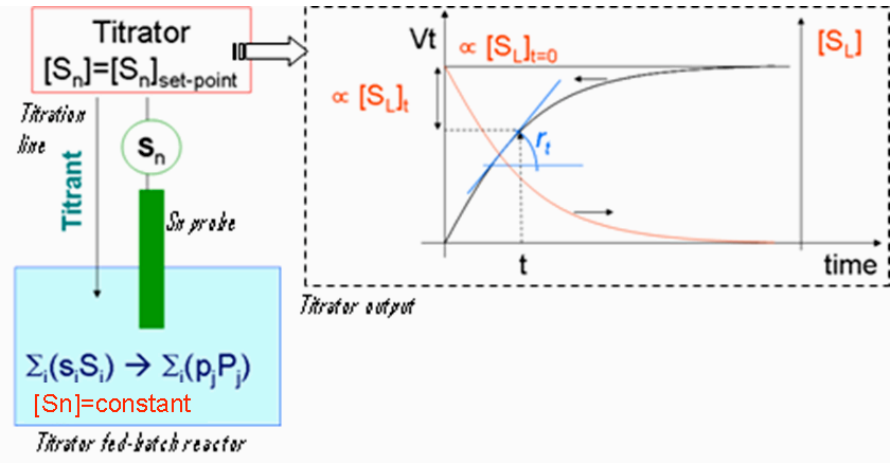


Figure 1: Set-point titration experiment: titrator lay-out and experimental output.

So far, this technique has been applied to reactions producing acidity or alkalinity and to reactions consuming dissolved oxygen. In the first case, protons concentration is measured by a pH probe and maintained constant by addition of an acidic or alkaline solution (pH-stat titration). In the second case, dissolved oxygen (DO) is measured by a DO-probe and maintained constant by addition of an oxygen-enriched solution (DO-stat titration).
Main experimental results of pH-stat and DO-stat titration applied to biological processes involved in wastewater treatment by SBRs are hereafter briefly presented.

Applications of set-point titration to bioprocesses involved in wastewater treatment

The first bioreaction to which the principle of set-point titration was successfully applied is nitrification. This process is commonly considered as the bottleneck phase in the aerobic biological treatment, therefore a great effort had been devoted to the development of reliable monitoring techniques. The applicability of pH-stat titration was proposed [2] due to the simple stoichiometric relation between ammonium oxidation and protons production ($NH_4^+ + 1.5O_2 \rightarrow 2H^+ + NO_2^- + H_2O$). This idea was then extensively developed and results on the

estimation of nitrification rate and to ammonia concentration can be found in the literature [3]. Later, DO-stat titration was also applied and coupled with pH-stat titration [4] to the monitoring of the whole nitrification process which includes a second oxygen consuming step, i.e. the oxidation of nitrites to nitrates. Titration curves of such a combined titration test are reported in Figure 2. Initially, titration curves are almost superposed since the oxidation of ammonium to nitrates involves an equi-molar consumption of oxygen and production of acidity. As soon as ammonium is oxidised (t_{F1}), a further addition of oxygen is evidenced corresponding to the oxidation of the nitrites which are still present at time t_{F1}. The end of nitrites oxidation is evidenced by the second bending point on the DO-stat titration curve (t_{F2}). Later, further titrants are requested for the endogenous microbial respiration (involving oxygen consumption and carbonic acid production). The right side graph in Figure 2 depicts the back-calculation of the ammonium concentration during the course of the titration test. With a further simple calculation, nitrites concentration can also be obtained (not shown). In summary, as far as the nitrification process is concerned, set-point titration allows to assess:

- the potentially nitrifiable ammoniacal-nitrogen content of a wastewater;
- the relevance of nitrites accumulation during nitrification ;
- the process rate;
- the potential toxicity of a wastewater to the nitrifying organisms by comparing their activity before and after exposure to the wastewater under study.

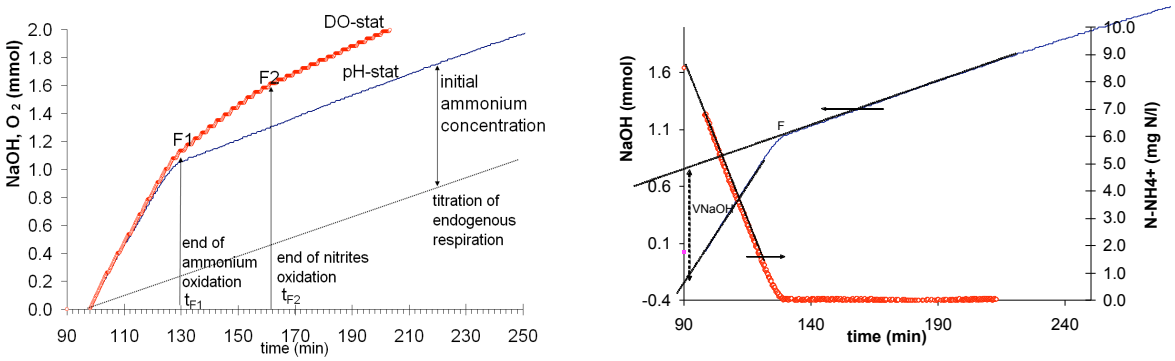


Figure 2 : pH/DO-stat titration curve on a nitrifying activated sludge sample.

Besides nitrification, denitrification can be also monitored by pH-stat titration since this is also a pH-affecting process [5-7]. The assessment of the ratio between nitrate consumption and proton production (*N*/*H*) from is not straightforward, as it is for nitrification, since it depends on the carbon source, on the sludge characteristics and on the set-point pH. However, set-point titration resulted to be a very promising process to assess nitrate concentration and maximum denitrification rates once a calibration step is adopted to evaluate N/H [8].

Application to SBRs monitoring

As mentioned above, set point titration allows the assessment of two kind of information of great interest in the monitoring of SBRs:

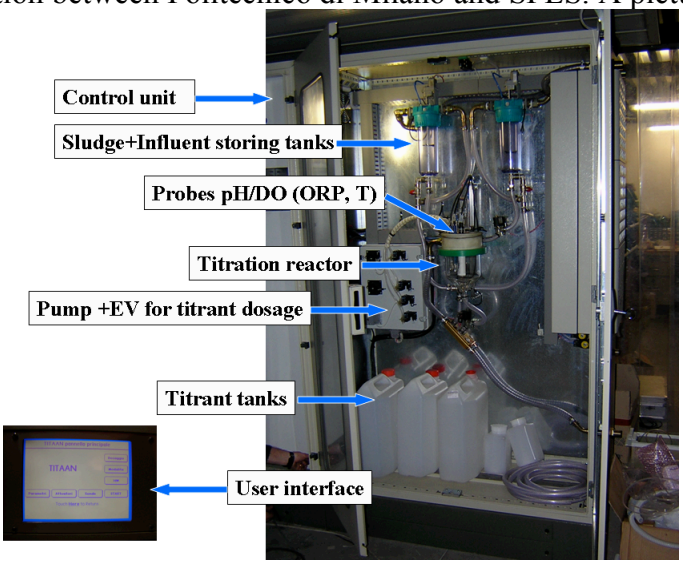
- influent treatability, in terms of sewage toxicity to the biomass and pollution load;
- treatment capacity, in terms of biomass process rate.

The following procedures have been developed and experimented:

1) detection of influent acute toxicity to nitrifying biomass;
2) estimation of the influent nitrifiable nitrogen content;
3) measurement of the nitrification capacity of the SBR, assessed in terms of maximum rates of oxidation of ammonium to nitrite and of nitrite to nitrate, allowing to predict nitrite build up;
4) monitoring of ammonium oxidation process during the aerobic react phase of the SBR reactor;
5) estimation of nitrate concentration.

A description of each of the above listed procedures can be found in [9]. All procedures were validated on a lab-scale SBR and results can be found in [10]. Then, these procedures were

implemented by an at-line automated titrator named (TITrimetric Automated Analyser) developed in cooperation between Politecnico di Milano and SPES. A picture of the first field prototype is shown in Figure . The instrument allows the sampling of sludge and influent by dedicated sampling lines and their storage into mixed/aerated tanks, located inside the titrator case. In the titration vessel, loaded with the appropriate influent to sludge ratio, pH/DO-stat tests are performed. At the end of the titration test, the titration vessel is emptied and rinsed to be ready for a new determination [11].



During the EOLI project, the TITAAN worked at two pilot-scale installations. The first one was located in Bologna (I) and consisted in a 500 l SBR working according to 4 cycles per day and fed on municipal wastewater. This first field test lasted approximately 8 months and was mainly dedicated to instrument fine tuning and software debugging. However, several process information could be retrieved such as the occasional presence of influent toxicity and the nitrifying activity trend during the winter season. The second field test was conducted on a pilot-scale SBR located at the INRA laboratory (F) treating a dairy effluent (COD=3000÷5000 mg/L, COD/N = 10÷20 gCOD/gN) according to one cycle per day with 2÷5 feeding phases per cycle (step-feeding). The TITAAN was used according to procedure number 1, which was aimed at the evaluation of the influent toxicity. No relevant acute toxicity events could be detected. However, by performing regular nitrification activity tests, the nitrifying capacity of the system could be traced with time (Figure). After the plant was re-started (on the 10th of August), the rate of ammonium oxidation remained quite stable for almost twenty days according to both titration (pH-stat and DO-stat) techniques. Then, from the beginning of September, a relevant improvement in the nitrification process was detected. Most likely, the increase of the ammonia oxidation rate was the result of the process modification operated on September the 5th, consisting in the increase from 2 to 5 of daily feeding phases, together with an increase in the anoxic/aerobic time ratio from 0.1 to 0.125. As for nitrite oxidation, it was generally slower than ammonium oxidation, suggesting that nitrites are produced from ammonium faster than they are oxidised to nitrate. Thus, nitrites may accumulate during the aerobic reaction phase of the SBR although they are fully oxidised before the end of this phase.

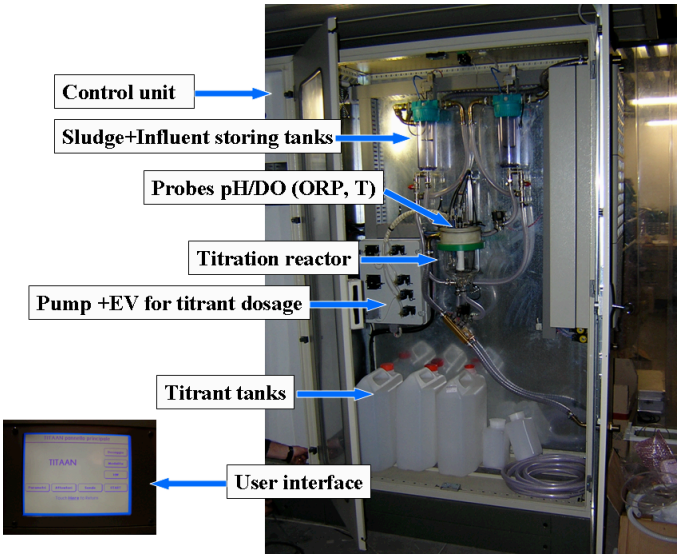


Figure 4: Field prototype on the at-line titrator TITAAN.

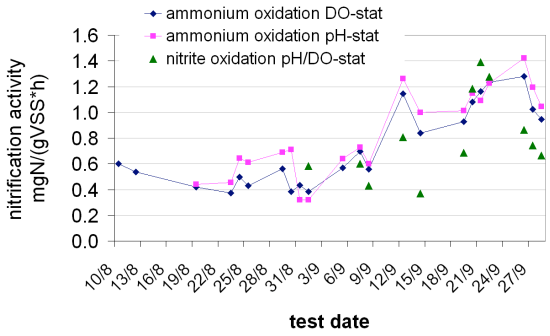


Figure 5 : Nitrification (ammonium and nitrite oxidation) rate in the INRA-SBR, as automatically measured by the TITAAN instrument.

UV-Spectrophotometry

Principle of operation

The UV spectra are linked to the absorbance of non-binding electrons in molecules, and to the diffusion of light by suspended solids and colloid in the liquid solution. The absorbance is proportional to compound concentrations, but the UV spectrum shapes are quite wide, and their specificities are often low due to the number of close absorbance rays.

Therefore, UV spectra are often used as it to handle the qualitative evolution of an effluent, with a special focus to one or more specific wavelengths. Spectra are understood as fingerprints of specific wastewaters, whose variations by time are essentially considered [13]. Several off-line or on-line commercial UV-spectrophotometers are available for the monitoring of nitrate, COD or other components (Awa-instruments, PAI, Secomam, TriOS, ABB…). However the interferences with other present molecules, as well as the variation of the process and therefore of the treated wastewater, largely affect the accuracy of the content estimation by UV-spectra. The calibration of the device must be carefully achieved and repeated for each process variation.

It is however possible to be ahead of the qualitative aspects using decomposition techniques. The UV-spectra are there considered as sum of UV-spectra of single components [14, 15]. With a sufficient number of experimental spectra and the corresponding actual experimental values, specific models can be built to decompose the crude UV-spectra and to estimate the components concentration. The models are obviously specific to the treated wastewater. Those decomposition techniques were applied efficiently to some industrial processes.

In SBRs the nitrate, nitrite and carbon contents greatly vary during the cycle. If nitrate or nitrite alone are easily estimated by UV-spectrophotometry, the estimation of a mixture is quite difficult, due to the too similar UV-spectra (maximum peak at 205 and 211 nm respectively). In the EOLI project, we aimed however to estimate on-line those components. To achieve this objective, we designed a specific spectrophotometer, called STAC, by modification of an existing device developed by the SECOMAM company.

The STAC spectrophotometer is composed of three connected modules, a rinsing / dilution module, an electronic module, and an optic module (Figure 6). The UV range is 190-360 nm with a 0.5 nm resolution. The UV cell is filled and rinsed automatically, each 5 to 30 minutes. This device can analysed nitrate and nitrite from 1 to 50 mg/L and the carbon material expressed as 5 to 350 mg/L of soluble COD.

The electronic module contains an embedded Windows XP, and an adapted version of the UV-Pro software (SECOMAM) for the decomposition step.

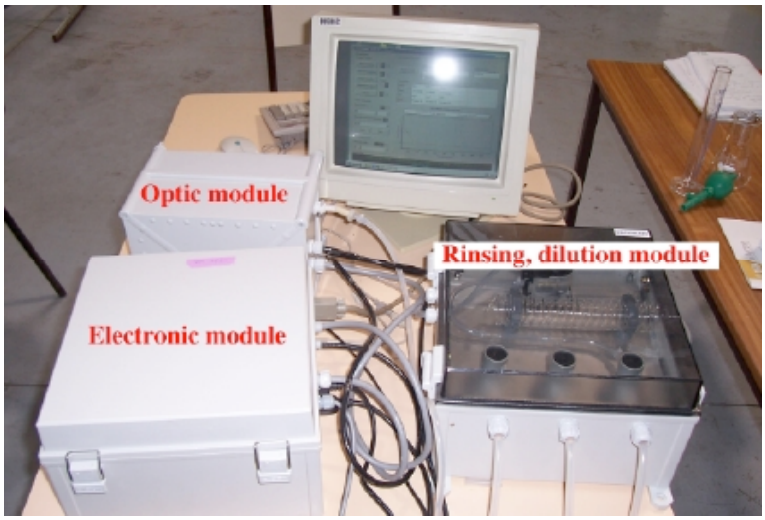
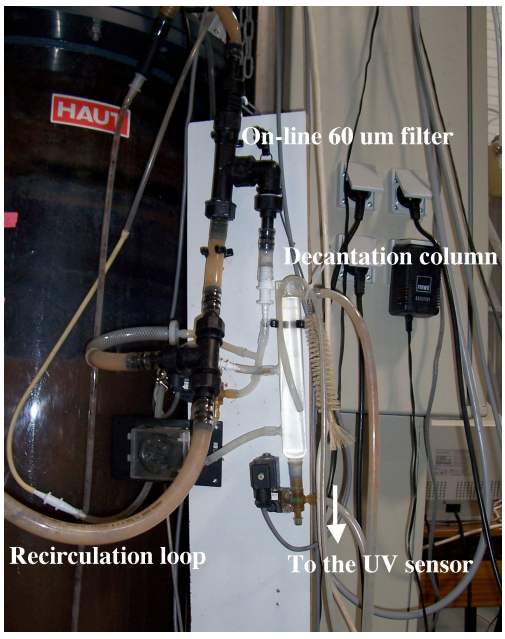


Figure 6 : global view of the STAC spectrophotometer.

Three decomposition techniques were tested, two PLS regressions and the one contained in the UV-Pro software.

Calibration of the STAC spectrophotometer

The STAC device was installed at the pilot-scale SBR located at the INRA laboratory (F), side-by-side the TITAAN as explained before. An on-line 60 µm filter was installed before the STAC on a recirculation loop, as shown in Figure 7.



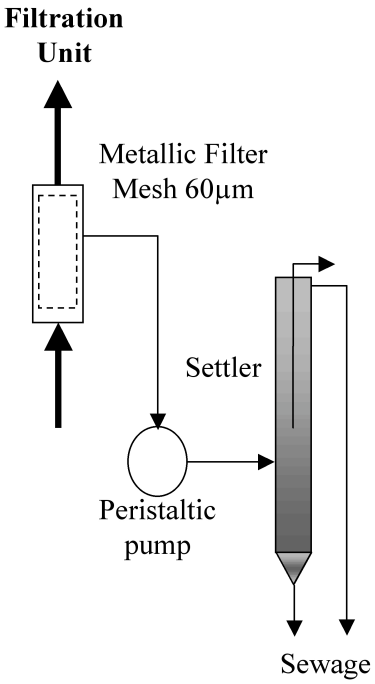


Figure 7: Installation of the STAC on the recirculation loop.

18 samples, representative of all steps during the cycles, were analysed by reference methods. With these values and the corresponding UV-spectra, three decomposition models were created, one with the UV-Pro software and two with Matlab, simple PLS and mild-centrum PLS (Partial Least Square Regression). For all the models the actual values perfectly fitted with the estimated values (data not shown). It is thus possible to estimate the nitrite, nitrate, and the carbon contents in a mixture by UV-technique.

20 other samples, representative of all running steps of the cycles, were used to validate the three obtained models. It can be seen in the Table 1 below that, if the nitrate and nitrite were correctly estimated by all decomposition techniques, UV-Pro never provides aberrant results,

conversely to PLS methods. For soluble COD, again UV-Pro gave better results. It can also be noticed that some analytical results are suspects, indicating the analytical limits.

Table1 : Comparison between the experimental and the estimated values

Yellow, orange and red colours respectively refer to suspect experimental values, to suspect estimated values, and to aberrant values.

Lab	UVPRO	PLS none	PLS mc
23.6	24.5	24.4	23.8
0	0.7	2.3	2.4
15.2	15.4	15.4	15.4
25.9	27.2	27.1	27.1
26	24.6	25.9	25.4
5	0	1.4	1.1
0	0	-0.1	0.3
0	0	1.5	1.6
0	0	-0.7	-0.6
0	0	-1.9	-1.9
0	0	-1.9	-2
2	3.2	2.5	2.4
10.5	8.3	8.4	8.4
18.5	17.7	17.7	17.9
33.6	24	23.2	23.9
34.2	30	27.7	28.8
45	36.9	43.9	45.5
0	0	-2.6	-2.4
20	20.3	19.9	19.8
36	37.2	27.2	28.6

Nitrate

Lab	UVPRO	PLS none	PLS mc
0.0	0.1	-0.1	0.4
0.0	0.7	0.6	0.4
11.1	11.4	11.6	11.6
10.6	11.8	11.9	11.8
0.0	0.2	-0.1	0.4
0.0	0.0	-0.6	-0.1
0.0	0.0	0.2	-0.3
0.0	0.0	-0.8	-1.0
0.0	0.0	-0.3	-0.6
0.0	0.0	0.4	0.3
0.0	0.0	0.8	0.9
5.0	4.6	5.2	5.2
9.0	10.5	10.8	10.7
11.6	14.2	14.4	14.1
16.7	19.5	21.4	20.5
16.8	23.7	26.6	25.3
0.0	15.8	15.3	12.9
0.0	0.0	0.6	0.2
11.0	13.1	13.4	13.5
15.0	16.9	28.7	26.9

Nitrite

Lab	UVPRO	PLS none	PLS mc
19.0	78.0	77.3	45.7
34.0	172.0	65.2	77.1
14.0	62.0	60.2	57.2
12.0	24.0	34.3	42.8
50.0	80.0	74.8	45.1
395.0	366.0	394.9	360.3
340.0	353.0	338.6	365.6
328.0	317.0	294.9	311.6
162.0	178.0	183.1	204.6
109.0	95.0	111.6	124.5
109.0	92.0	103.7	102.7
80.0	95.0	87.9	87.9
60.0	106.0	76.6	84.6
60.0	64.0	61.0	81.6
50.0	83.0	-11.6	48.5
50.0	36.0	-60.1	26.2
11.0	35.8	-457.8	-289.3
90.0	150.0	149.8	171.4
50.0	81.0	76.5	74.1
13.0	205.0	-153.0	-31.3

Soluble COD

The UV-Pro software was finally selected for the SBR on-line monitoring.

Application to SBRs monitoring

Since August 2005, the STAC works at the INRA pilot-scale installation. The Figures 8 below shows the estimated nitrate and nitrite contents, compared to the actual values; the same for soluble COD in Figure 9.

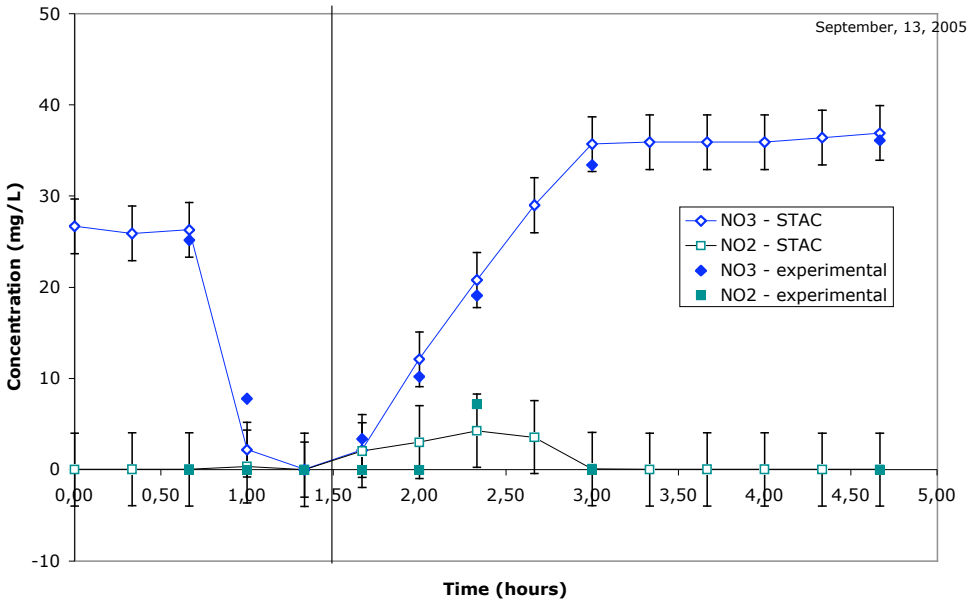


Figure 8 Nitrate and nitrite contents during a cycle, September 13th 2005.

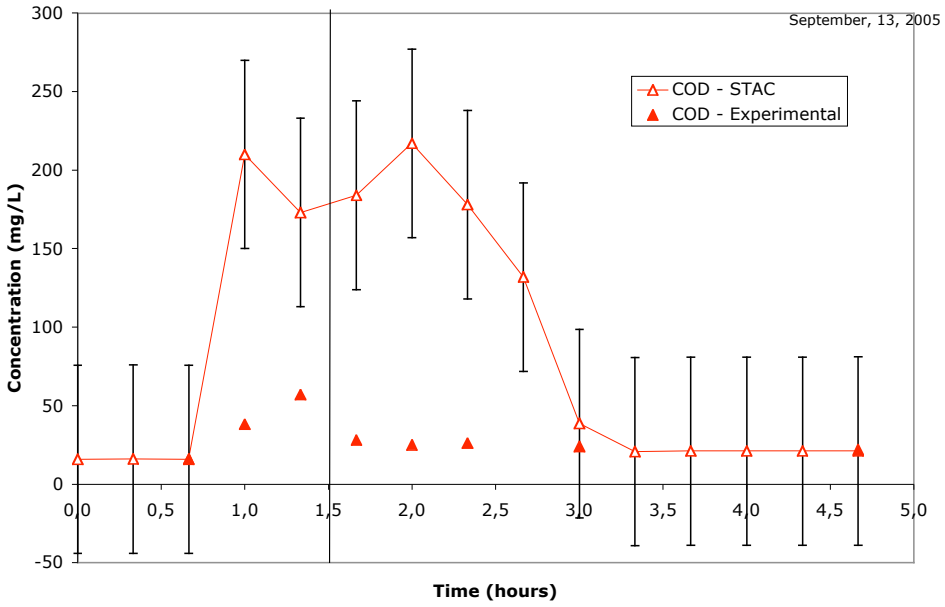


Figure 9 Soluble COD during a cycle, September 13th 2005.

The results obtained since August indicate that nitrate and nitrite can be accurately estimated by UV decomposition, which is less true for soluble COD, even if the sCOD time evolution estimated by UV technique is analog to the experimental shape.
The Figure 8 also shows that the nitrite variation was better given by UV estimation, due to the lower limit of the experimental technique.

Cross validation of set-point titration and UV-spectrophotometry

To validate data obtained on the INRA-SBR from the two hardware sensors developed within the EOLI project, the titrimetric TITAAN and the UV-spectrophotometer STAC, they were combined and compared. To this purpose, nitrification activity data at 20°C ($act(20^0C)_{TITAAN}$, both from pH-stat and DO-stat titration), were used to estimate the amount of nitrate formed during the SBR nitrification phase ($\Delta NO^-_{3,TITAAN}$), by the following calculation:

$\Delta NO^-_{3,TITAAN} = act(20^0C)_{TITAAN} \cdot 1.08^{T-20} \cdot X \cdot d_{nit}$, where: X is the biomass concentration in the SBR, T is the SBR working temperature (°C) and d_{NIT} is the time during which nitrification was supposed to occur under non limiting conditions (DO > 2 mg/L and N-NH_4 > 1 mg/L as deduced by the DO trend in the SBR).
These data were compared to the nitrate produced as assessed by the UV on-line sensor ($\Delta NO^-_{3,UV}$). This comparison is shown in Figure10, which can be considered to be indeed satisfactory.

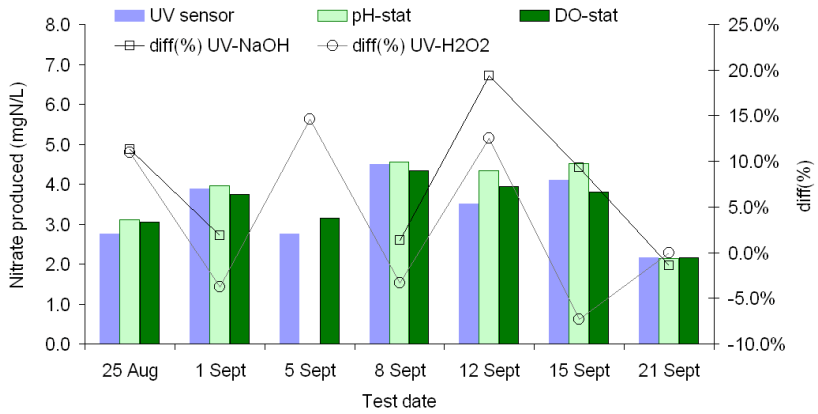


Figure 10: Comparison between nitrate production as estimated by TITAAN-Mode 1 (according to both pH-stat and DO-stat titration data) and by the UV-sensor. Percentage differences are reported on the right y-axis.

Conclusions

Two monitoring techniques were developed in this project, they allow obtaining influent-related and process-related data: set-point titration and UV-spectrophotometry.

The set-point titration technique can be applied to SBR for nitrification and denitrification monitoring without classical analytical determination. This technique allows the assessment of two kind of information of great interest in the monitoring of SBRs:

- influent treatability, in terms of sewage toxicity to the biomass and pollution load;
- treatment capacity, in terms of biomass process rate.

An at-line automated titrator named TITAAN (TITrimetric Automated Analyser) was developed in cooperation between Politecnico di Milano and SPES

The UV-spectrophotometry can be applied to estimate the chemical contents of an bioreactor medium. An on-line spectrophotometer named STAC was developed in cooperation with the SECOMAM company. After calibration and validation of some specific decomposition models it was possible to estimate efficiently the nitrate, nitrite and carbon contents of the SBRs during the whole cycle. As for continuous processes, SBRs can be monitored with UV spectrophotometry.

Both monitoring devices were installed at the INRA pilot plant, and, despites the very different measuring principles, both techniques were successfully applied to SBRs monitoring and control leading to comparable results.

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Companies selling off-line and on-line spectrophotometers :

Awa instruments, 38240 Meylan, France. http://www.awa-instruments.com

PAI Process Analysers, 27432Hipstedt, Germany. http://www.p-a-i.de/e/main.htm

Secomam company, 95335 Domont Cedex, France. http://www.secomam.com

TriOS Optical sensors, 26135 Oldenburg, Germany. http://www.trios.de

ABB, 8050 Zurich, Switzerland. http://www.abb.com/