On-line monitoring of nitrification efficiency by set-point titration

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Abstract
The applicability of set-point titration for monitoring biological processes has been widely demonstrated in the literature. Based on published and on-going experiences, some operating procedures have been specifically developed to be applied to biological nitrogen removal, so that real-time information about the process and/or the effects of the influent on nitrifying biomass can be obtained. This, in turn, would allow plant operators to select the most appropriate actions properly and timely, especially in the case of Sequencing Batch Reactor plants. Operating modes are described for the monitoring of influent toxicity to nitrifying biomass, and the nitrification capacity: first results gathered by means of the on-line titrator TITAAN (TITrimetric Automated ANalyser) which is in operation on a pilot scale SBR.

Keywords
Toxicity; nitrification; on-line monitoring; pH/DO-stat titration; SBR.

INTRODUCTION

The main challenge in the management of an activated sludge plant, for biological nitrogen removal from urban and industrial wastewaters, is to ensure a stable treatment efficiency under highly variable influent quality and quantity. To help the plant operators 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 plant's treatment capacity, the more straightforward is to implement control strategies based on these data.

As it is widely demonstrated in the literature of the past decade, pH/DO-stat titration allows the assessment of two kind of information of great interest in the monitoring of WWTP for N-removal:

- tractability of the influent, in terms of sewage toxicity to the biomass and pollution load (e.g.: Massone et al., 1998; Ficara and Rozzi, 2001; Yuan et al., 2001; Rozzi et al., 2004; Ficara and Rozzi, 2004);
- the biomass treatment capacity, in terms of process rate (see e.g. Ramadori et al., 1980; Massone et al., 1996; Bogaert et al., 1997; Massone et al., 1998; Gernaey et al., 1998; Ficara et al., 2000; Petersen et al., 2002; Foxon et al., 2002).

Under aerobic conditions, pH/DO-stat titration operates as other respirometric techniques, but, differently from respirometry, pH-stat titration is applicable under anoxic conditions as well. Therefore, set-point titration was considered as a suitable technique to be applied to the monitoring of N-removing WWTPs.

The following procedures, or modes, have been developed, based on the above listed literature, and experimented in our laboratories by means of the lab scale titration unit MARTINA (Multiple Analysis Reprogrammable TItration Analyser):

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 activated sludge, 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 an SBR reactor;
5) estimation of nitrate concentration in an SBR tank.

Measuring procedures and main outputs, as they are implemented by an on-line automated titrator that equips a pilot scale SBR (TITAAN, TITrimetric Automated ANalyser), have been recently presented at the Conference ICA-IWA 2005 (Fiocchi et al., 2005). This titrator is the result of a cooperation between SPES s.c.p.a. (Fabriano, I) and the Technical University of Milan (Politecnico di Milano, I) and it's the evolution of the pre-existing lab-scale instrument MARTINA. Main components of this instrument are outlined in Fig. 1.

Experimental titration curves, reported in the following paragraphs, were obtained during an on-going experimentation on the monitoring of a 500 L pilot-scale SBR fed on urban wastewater, located at the WWTP of Trebbo di Reno (Bologna, Italy). Here below are described the modality of operation of the titrator for the on-line detection of influent toxicity to nitrifying biomass (mode 1) and the on-line monitoring of the maximum nitrification rate (mode 3): first results are presented.

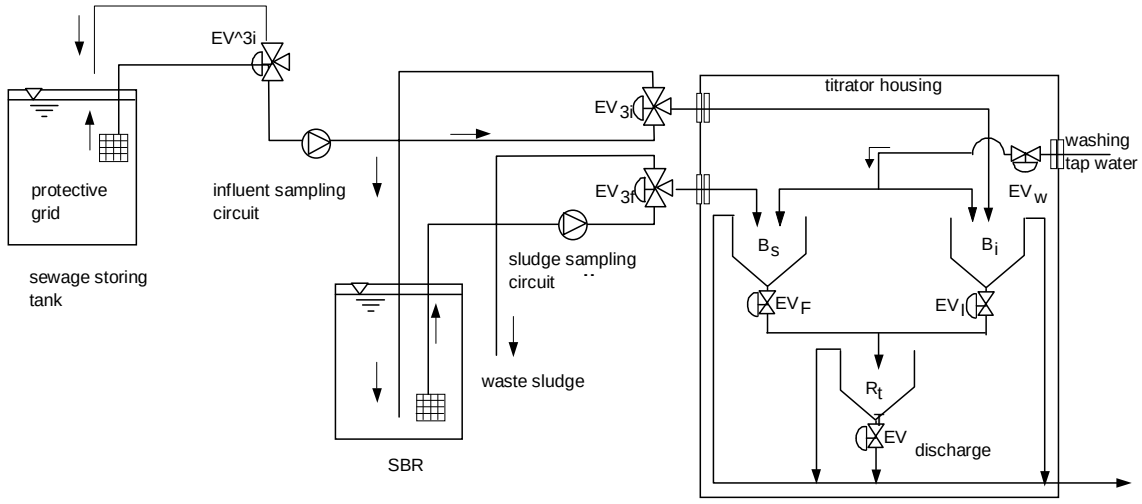

Figure 1 : Main components of the on-line titrator (TITAAN). Bs: sludge storing beaker; Bi: influent storing beaker; Rt: measuring and titration beaker; EV_3: actuated 3-way solenoid valves; EV: actuated solenoid valves.

MODES OF OPERATION

Mode 1: Detection of influent acute toxicity to nitrifying biomass

It consists in performing a pH/DO-stat titration on a sludge sample, to which a selected amount of influent is dosed, to assess the activity of ammonium oxidizing bacteria (AOB) and nitrite oxidising bacteria (NOB). Influent acute toxicity is detected when biomass activities are found to be significantly lower than historical values.

Simplified titration curves obtained according to the following procedure are reported in Fig. 2a, typical experimental data are reported in Fig. 2b.

The titration reactor *Rt* is partially filled with the influent sample on which the toxicity test has to be performed. Then, activated sludge is withdrawn from the SBR tank (normally at the end of the aerobic phase) and loaded in *Rt* (test time t = 0). A known amount of NH_4Cl is dosed in order to ensure a non-limiting ammonium concentration during the whole nitrification test. The aerator is switched on for a short time (1–5 minutes) and titrants, NaOH and H_2O_2, are dosed until set-point values are reached, for both pH and DO. pH/DOstat titration starts when pH and DO set-points have been reached ($t = t_{sp}$). Starting from t_{sp}, titrant volumes are recorded and the corresponding cumulated curves can be drawn (Fig. 2a). Looking at these curves, three or four phases with different titration rates can be observed.

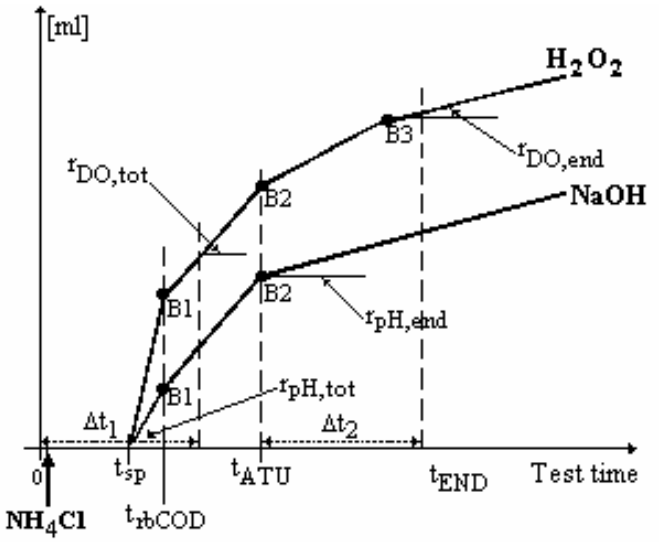

Figure 2a : Scheme of titration curves in MODE 1.

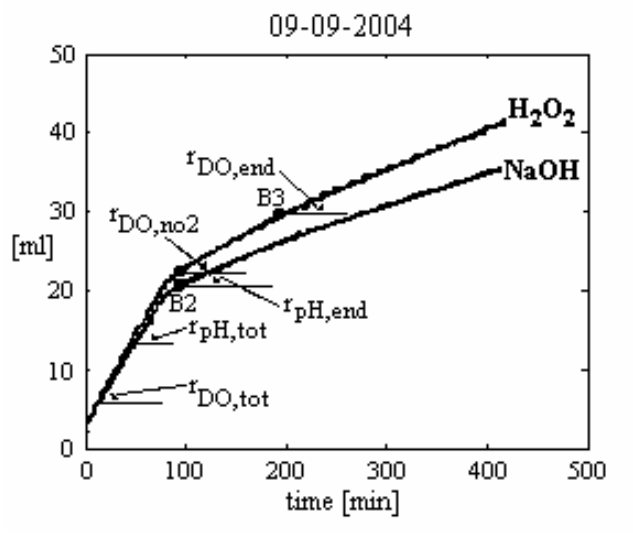

Figure 2b : Actual titration curves : B2 and B3 are automatically detected.

The titration rate is highest initially (at $t<t_{rbCOD}$), because all of the following processes occur simultaneously:

a) O_2 consumption/CO_2 production by heterotrophic oxidation of the rbCOD;
b) O_2 consumption/protons production by autotrophic ammonium oxidation;
c) O_2 consumption by autotrophic nitrite oxidation;
d) O_2 consumption/CO_2 production by heterotrophic oxidation of slowly biodegradable COD (sbCOD);
e) O_2 consumption/CO_2 production by heterotrophic endogenous respiration.

The value of t_{rbCOD} depends on the rbCOD content of the wastewater. If it is very low, it can happen that $t_{rbCOD}<t_{sp}$, and the first bending point (B_1) cannot be observed, as it is the case shown in Fig. 2b. For this reason, a fixed time interval Δt_1 is defined, according to the result of calibration tests, within which the rbCOD is, normally, fully oxidised.

In the following phase ($t>\Delta t_1$), titration rates are due to processes b) to e). The system can identify both slopes ($r_{DO,TOT}$ and $r_{pH,TOT}$) automatically and in real time at a given accuracy.

Once these slopes have been calculated, a peristaltic pump doses allylthiourea in the titration reactor ($t=t_{ATU}$), in order to inhibit ammonium oxidizing bacteria (AOB). A second bending point (B_2) is observed in both titration curves. Later on, only processes c) to e) are active and, therefore, can be titrated. The value of $r_{pH,end}$ is now assessed, which includes endogenous heterotrophic respiration and sbCOD oxidation.

A third bending point on the hydrogen peroxide titration curve (B_3) could be detected, due to the complete oxidation of nitrites. An algorithm tries to identify the bending point B_3. Actually, if ammonium oxidation is slower than nitrite oxidation, no nitrite build-up occurs in the titration reactor. In this case, B_2 and B_3 take place almost simultaneously, making the detection of B_3 impossible. Therefore, a fixed time interval Δt_2 (e.g. $\Delta t_2 = 0.5 t_{ATU}$) is established, after which the system calculates the value of $r_{DO,end}$, even if B_3 has not been detected.

By taking into account the stoichiometry of the two nitrification reactions and from the two slopes "r_i" [$mL_{titrant}$/min] of each titration curve, activities (ACT, [$mgN_{oxidized}\ L_{sludge}^{-1}\ h^{-1}$]) of both ammonium and nitrite oxidizing bacteria are calculated as follows:

$$ACT(AOB) = \frac{(r_{pH,tot} - r_{pH,end}) \cdot M_{NaOH} \cdot f_{stNaOH} \cdot 60 min/h}{\theta^{(T-20)} \cdot V_{sludge}} \quad (1)$$

$$ACT(NOB) = \left[\frac{(r_{DO,tot} - r_{DO,end}) \cdot 32\, mgO_2/mmol \cdot M_{O2} \cdot 60\, min/h}{\theta^{(T-20)} \cdot V_{sludge}} - ACT(AOB) \cdot f1_{stO2} \right] \cdot \frac{1}{f2_{stO2}} \quad (2)$$

where:

f_{stNaOH} = 7 mgN/mmolNaOH : stoichiometric factor (oxidation of ammonium to nitrite);
$f1_{stO2}$ = 3,42 $mgO_2/mgN\text{-}NH_4^+$: stoichiometric factor (oxidation of ammonium to nitrite);
$f2_{stO2}$ = 1,14 $mgO_2/mgN\text{-}NO_2^-$: stoichiometric factor (oxidation of nitrite to nitrate);

T : test temperature in degrees Celsius;
θ=1,08 : temperature compensation coefficient for nitrifying bacteria (activity normalized at 20°C);
M_{NaOH} : molarity of the NaOH titrant;
M_{O2} : molarity of the H_2O_2 titrant (in $mmolO_2/mL$);
V_{sludge} : volume of sludge used for the test [L];
$r_{pH,tot}$, $r_{DO,tot}$: slope of the cumulated NaOH/H_2O_2 curve when rbCOD has been consumed;
$r_{pH,end}$: slope of the cumulated NaOH curve when AOB activity has been inhibited;
$r_{DO,end}$: slope of the cumulated H_2O_2 curve when heterotrophic respiration is the only active process.

Toxicity, which is the output of this procedure, is evaluated by comparing actual AOB and NOB activities with their mean values, calculated in a number "*n*" of previous tests and by taking into account the variability of these mean values, expressed as coefficient of variation (CV, % ratio between the standard deviation and the mean).

$$TOX\,(\%) = \left[\frac{ACT_{mean} - ACT_{measured}}{ACT_{mean}} \right] \cdot 100 \qquad (3)$$

If TOX (%) > 1.2 CV(%), influent acute toxicity is diagnosed and an alarm is generated on the instrument's control panel.

Mode 3: Measurement of the nitrification capacity of the SBR, assessed in terms of oxidation rates of both ammonium to nitrite and of nitrite to nitrate

Mode 3 is a pH/DO-stat test for the measurement of maximum activities of AOB and NOB which characterize the nitrification capacity of the activated sludge. In the case of an SBR plant this type of test can be performed at the end of the idle phase of the SBR reactor, on sludge samples under endogenous conditions. In the case of a continuous flow system, the instrument can perform a pre-aeration procedure of the sludge sample in order to ensure endogenous conditions. A simplified titration curve according to mode 3 is reported in Fig. 3.

The sludge sample is loaded into *Rt*. At the beginning, the control routine brings pH and DO to their set-point values. Then, at time t_{sp}, a known amount of NH_4Cl is dosed by a peristaltic pump to trigger the nitrification process. Titration rates are then measured on-line ($r_{pH,tot}$, $r_{DO,tot}$, $r_{pH,end}$ and $r_{DO,end}$, in Fig. 3). Nitrification activities are calculated as in mode 1.

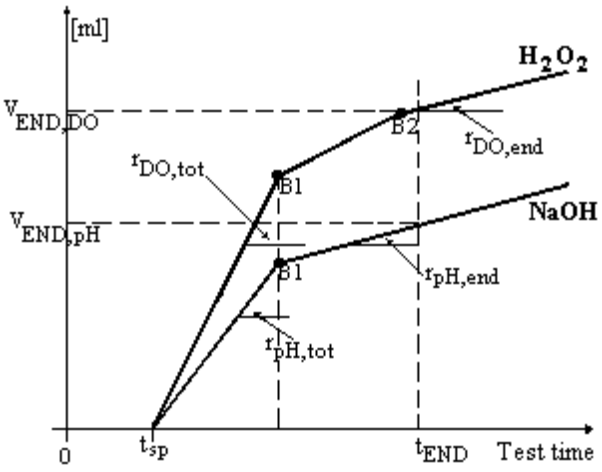

Figure 3 - Scheme of a pH/DO-stat titration test in mode 3.

RESULTS AND DISCUSSIONS

Mode 1: First experimental results achieved on a real sewage pilot SBR

Mode 1 is a pH/DOstat test that allows to detect the presence of toxic/inhibitory substances having acute effects on autotrophic biomasses, both nitrite and ammonium oxidizing.
In Fig 4 we reported titration curves obtained with a pH/DOstat test in mode 1 performed on the SBR pilot plant sludge with real sewage on the 3rd May, we elaborated data with a software dedicated application.
Figure 4 is particularly interesting because of the presence of NOB knee (in H_2O_2 curve at 50 minutes) which is not possible to detect in the majority of the experiments.

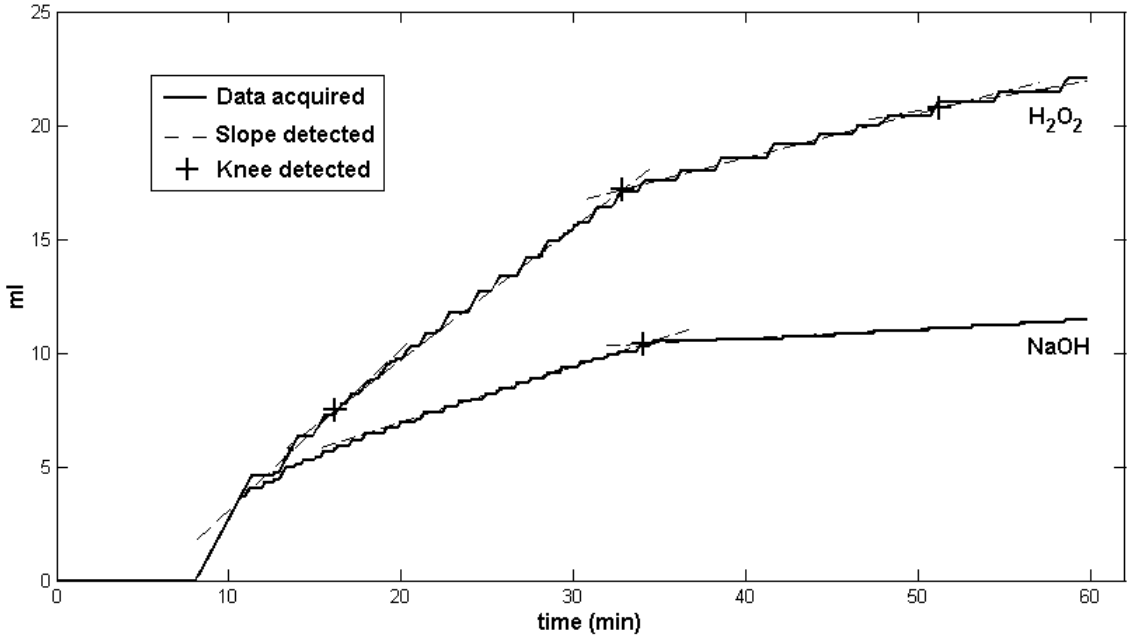

Figure 4 - Titration curves from mode 1 pH/DOstat test on the 3rd May'05

From the middle of April '05 the TITAAN prototype showed a sufficient robustness in the execution of test in mode 1. Therefore we started a periodic monitoring of the SBR plant in terms of toxicity assessment. From 19th to 22nd April a series of mode 1 tests were performed on the SBR sludge. The first AOB activity specific rates were measured with TITAAN and they are reported in Table 1: the values are the average from pHstat and DOstat titration tests performed on the same sludge and influent sample. To compare results obtained from tests performed at different temperatures, the activity rates are normalized at the temperature of 20° C in accordance to Eq. 1, while SBR's temperature fluctuated between 14° and 17° C.
We reported some problems with the TITAAN's temperature control device in the existing configuration. At present the titrator is equipped with two air heaters and an air cooler that can keep the temperature inside the instrument at the value set by the operator. We experienced that if the temperature of the solution of sewage and sludge was sensitively lower (about 2° C or more) than the temperature in the titrator, the solution's temperature rose very slowly to the upper value. In these cases, we couldn't deduce a reliable AOB activity value from titration data because of the strong relationship existing between bacterial activity and temperature. Hence in Table 1 are reported only activity values obtained with tests in which the temperature in the titration reactor was almost constant during the bioassay (± 0.5° C). In the near future a system working with a *Peltier cell* will equip the titration reactor, allowing a very quick heating or cooling of the solution of sludge and sewage, therefore avoiding the problem of an important temperature shift during the experiment.

Table 1 – AOB activity measured with TITAAN prototype on real sewage (average from pHstat and DOstat test)

DATE and TIME of test	*Test number*	*AOB activity normalized at 20°C [mgN gVSS^{-1} h^{-1}]*	*NOB activity normalized at 20°C [mgN VSS^{-1} h^{-1}]*	*Average sludge temperature during the test [°C]*
19 / 04 / 05 10 : 45	1	3.30	X	16.6
19 / 04 / 05 12 : 09	2	3.03	X	16.3
20 / 04 / 05 11 : 30	3	1.92	X	18.9
21 / 04 / 05 10 : 44	4	1.80	X	16.8
22 / 04 / 05 11 : 57	5	2.19	2.34	17.8
03 / 05 / 05 15 : 56	6	1.89	2.84	19.7

First of all we observed that reported values were in accordance to lab-scale titration test activity measures that we performed by means of a MARTINA titrator unit in the days immediately before the performance of the above reported bioassay series with TITAAN: actually the average value that we reported was of 2.9 mgN gVSS^{-1} h^{-1}.
An important reduction of the nitrifying activity was reported during the 4 days of monitoring that we performed. We can assume that the decrease of the activity is due to the occasional presence of compounds toxicant for autotrophs in the sewage. Anyhow, the trend of the activity in Fig. 5 suggests that a gradual inhibitory effect was reported.
Actually the SBR we use to test the titrator is fed with real municipal sewage: this is adducted to the pilot reactor by means of the same hydraulic system that equips the municipal WWTP. In the morning of the 19th April, the operators of the municipal WWTP diverged an important flow from a sludge thickening basin to the inlet of the municipal plant, and as a consequence, to the inlet of the pilot SBR too. It was not feasible to estimate the amount of this flow because the workers managed the operation manually, without any measuring device.
It is possible that the return flow from the sludge thickening basin, typically marked by high nitrogen loaded and high concentration of slowly biodegradable compounds, had a detrimental effect on the sludge nitrifying activity. On the basis of activity data reported in Tab. 1, we can suppose that the partial inhibition of the autotrophic biomass lasted for at least three days after the adduction of the return flow.

Mode 3: First experimental results achieved on a real sewage pilot SBR for monitoring maximum nitrification activity

pH-DO-stat tests have been performed with TITAAN prototype, following the above reported procedure named mode 3, to evaluate the maximum nitrification rate of the sludge and to understand the evolution of the SBR autotrophic biomass activity (only for AOB at first). All experiments were performed under non-limiting oxygen concentrations (DOstat = 8 mgO_2/L), pH = 8.3 and at the controlled temperature of 20.5°C. Data are reported in Fig. 6 in terms of maximum specific nitrification activity (AOB), calculated as average values from a pH-DO-stat test. Figure 6 shows that nitrification was very poor in December ’04 (2.6 mgN-NH4 gVSS^{-1}h^{-1}), after that the plant operated continuously since August 2004 with nitrification efficiencies in the range of 96-99% in terms of removal of the influent’s TKN. In the first days of 2005 we emptied the reactor and we performed a new inoculum of sludge from the municipal WWTP with the aim to restore a good nitrification process.
Few days after the restart with new sludge, the pH-DO-stat test was repeated and the specific activity was at its lowest value, most probably because of the cold temperature (about 8°C) in the aeration basin of the full-scale plant since November ‘04.
Tests were repeated periodically and allowed us to detect the improvement of the nitrification process in time. The comparison with on-line and analytical data confirmed that nitrification efficiency slowly increased with time, according to the data reported below.

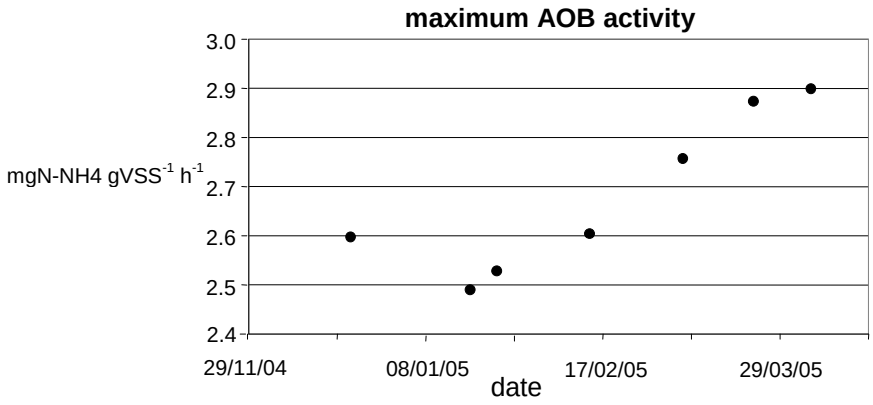

Figure 6 - Maximum specific nitrification activity (AOB) for SBR sludge, estimated with on-line pH-DO-stat tests at 20.5°C

CONCLUSIONS

Process monitoring of a WWTP is strongly suggested to ensure proper operation, especially if biological nitrogen removal is to be achieved. An automated titrator (TITAAN: TITrimetric Automated ANalyzer) has been developed, capable to perform several on-line tests aimed to assess both the activated sludge maximum nitrifying activity and the influent toxicant effects on autotrophic biomass.

Then, five set-point titration procedures (called modes) were defined for the monitoring of an SBR: in the present paper two of the procedures that can be applied to any activated sludge WWTP are presented in the details and the first experimental results are shown. The periodic on-line estimate of the maximum nitrifying activity (mode 3) allowed us to monitor efficiently the evolution of the autotrophic activity in a pilot scale SBR fed with real municipal sewage, pointing out the process malfunction and, subsequently, its recovery.
We performed a series of determinations of the nitrifying activity of the sludge in the presence of an influent that contained slowly degradable matter and characterized by extremely low redox potential (procedure mode 1): the tests allowed to detect a decrease of the activity due to the presence of compounds toxicant for autotrophs in the sewage.
The automatic titrator allows to estimate both AOB and NOB activity rates (see Eq. 1 and 2), but for the first field experiments reported above (both in mode 1 and 3) we achieved reliable estimations only for AOB. Tests are currently continuing and reliable data on NOB activity rates will be soon available.

Data collected during the titration tests are automatically elaborated by the master computer linked with TITAAN and results are stored in a permanent memory. It has to be stressed that TITAAN is a powerful tool in order to prevent faults in biological processes and to implement correct operational strategies as follows:

- mode 1 gives toxicity early warning that allows the operator to divert part of the influent flow to a storage tank and/or to operate other countermeasures (e.g.: addition of powdered activated carbon).
- modes 3 allows checking whether both autotrophic populations (AOB and NOB) are working at their optimal rates. By looking at historical data, the operator can check whether nitrite oxidation rate trend is decreasing, leading to possible nitrite build-up, and consequently can take adequate early countermeasures to restore optimal conditions (i.e.: increasing the duration of the aeration phase in batch systems and/or inoculate fresh fully nitrifying sludge).

A series of toxicity tests with typical toxicants (as ATU and chlorophenol) has been planned to collect more data on mode 1. The development on the field of the other titration modalities is nowadays on the run.

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