APPLICABILITY OF pH/DO-STAT TITRATION TO MONITOR SEQUENCING BATCH REACTORS

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ABSTRACT

A new titration system developed by Politecnico di Milano was applied to monitor biological nitrification by means of pH/DO-stat technique in a lab-scale SBR treating synthetic sewage. During the aerobic phase of the SBR it was possible to measure the maximum and the real activity for both ammonium and nitrite oxidizers and to assess the end of the nitrification process with a satisfactory accuracy. Further tests were performed to detect the nitrogen content in the SBR influent and the presence of a toxicant in the feed: in both cases the titration unit allowed to get reliable information on influent composition. The instrument could be used for on-line monitoring of the nitrification process aimed at optimizing the duration of the aeration phase and at saving energy.
Moreover, a strategy for a feed forward control can be implemented by performing a rapid test on the influent before of the SBR fill phase: in this way, filling of a toxic influent in the SBR could be avoided. Finally, it could be possible to adapt the duration of the react phases on the basis of the influent nitrogen content.

KEYWORDS

nitrification; titrimetric techniques; respirometry; pH/DOstat; process monitoring; SBR; ammonium; nitrite.

INTRODUCTION

Automatic monitoring may increase greatly the applicability of the SBR technology, which is very sensitive to loading variations, like those which usually occur in wastewater treatment. This experimentation is aimed to assess the feasibility of monitoring a discontinuous process, typically taking place in an SBR, by the pH/DO-stat respirometric technique. This technique allows measuring the activity of those biological processes which affect pH or dissolved oxygen concentration (DO).

The pH-stat titration is a technique developed mainly during the nineties to monitor the activity of any bacterial consortium which converts a neutral substrate into an acidic or alkaline product or an acidic or alkaline substrate into a neutral product, thus affecting the pH of the suspension (Ficara et al., 2003). It consists in the controlled addition of dilute acidic or alkaline solutions to maintain a constant pH in systems where the pH affecting reaction is taking place. The titration rate is then proportional to the reaction rate. The DO-stat titration is a technique developed more recently, compared to the pH-stat, which makes it possible to monitor aerobic reactions. It consists in the controlled addition of gaseous O_2 or of an oxygen-rich solution to maintain a constant DO concentration in systems where the DO

affecting reaction is taking place. Ficara et al. (2000) designed a DO-stat instrument where the dissolved oxygen concentration is maintained constant with addition of hydrogen peroxide.

In wastewater treatment, pH-stat titration was proposed to monitor nitrification activity (e.g. Massone et al., 1998) and inhibition (Ficara and Rozzi, 2001), denitrification (e.g. Massone et al., 1996) and oxidation of organic substrates (Ficara and Rozzi, 2002), while DO-stat titration was applied to measure Oxygen Uptake Rate (OUR) of nitrifiers (Ficara et al., 2000) and of heterotrophic bacteria (Rozzi et al., 2003). The instrument used in this experimentation may operate all these tests and has been called MARTINA (Multiple Analysis Reprogrammable TItratioN Analyser).

MATERIAL AND METHODS

The lab-scale SBR

The SBR used in this experimentation (Fig. 1) had a 20 L working volume (V_{MAX}) and was equipped with: three peristaltic pumps for feeding, effluent and waste sludge discharging, an aeration system (3 air compressors + multiple pipe diffusers), a variable speed mechanical mixing system, a controlled heating system to maintain sludge temperature at 25 ^{o}C and 4 timers for activation/deactivation of pumps, mixer and aeration system.
This SBR operated according to 4 cycles per day. Each cycle lasted 6 hours and included the following phases: ANOXIC FILL (10 min); ANOXIC REACT (150 min); AEROBIC REACT (AER) (150 min); SETTLE (37 min); DRAW (23 min).
The SBR was fed with a synthetic influent (modified from *OECD Guidelines for testing of chemicals*. 1993 - 209 'Activated sludge inhibition Test', OECD Paris) with the following composition: peptone (0.343 g/L), meat extract (0.236 g/L), NaCl (0.015 g/L), $CaCl_2 \cdot 2H_2O$ (0.012 g/L), $MgSO_4 \cdot 7H_2O$ (0.005 g/L), K_2HPO_4 (0.06 g/L). According to analytical analyses, this influent was characterised by a COD of 600 mg/L and an N content of 75 mg N_{tot}/L (COD/N=8).
At the beginning of each cycle, 4 L of the influent described above were loaded (ΔV). Therefore, the resulting volumetric exchange ratio (VER=ΔV / V_{MAX}) was 0.2 and the hydraulic retention time was 30 h. Biomass concentration was kept at 2.4 gVSS/L (3.0 gTSS/L) by periodic sludge discharge, resulting in an average SRT of 22-23 d.

Periodically, the SBR feed was modified to simulate loading variations, both by changing the COD/N or F/M ratios. The SBR performance was then monitored by NH_4^+, NO_2^- NO_3^-, COD, TOC analyses (12 samples distributed during the REACT phase, see Fig. 2), by following DO, pH and ORP values and by performing pH/DO-stat titration tests on sludge sampled at the beginning of the aeration phase.

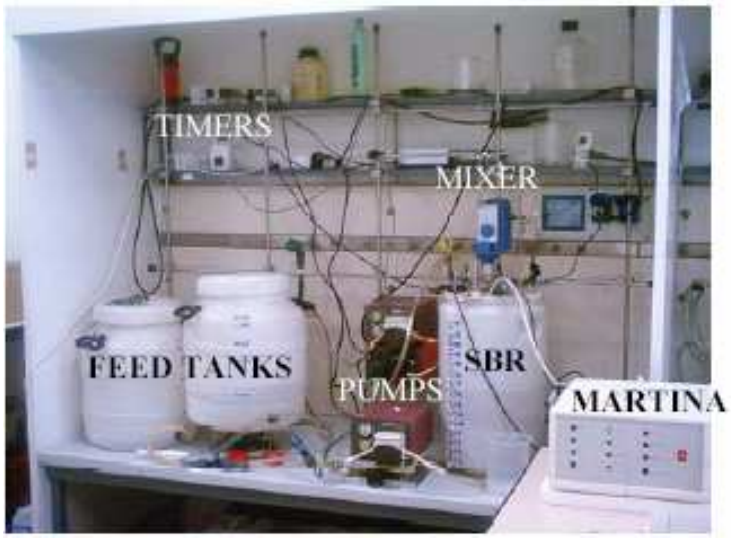

Figure 1. The laboratory experimental equipment for on-line monitoring of SBR biological processes.

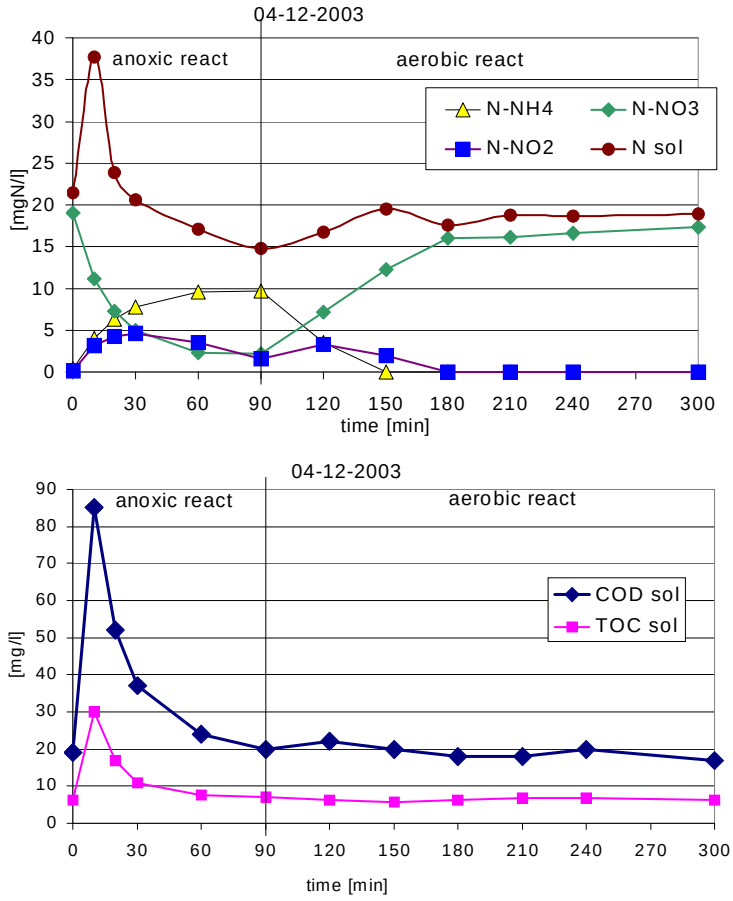

Figure 2. Monitoring of an SBR cycle by analytical determinations.

Titration tests

Titration tests on SBR sludge samples (0.8 l volume) were performed with a MARTINA unit. MARTINA is a new titration system developed by Politecnico di Milano in cooperation with an industrial partner (SPES scrl, Fabriano, AN, Italy), characterised by an improved software flexibility and by a new signals acquisition board developed to increase hardware reliability and to reduce components cost. The main advantage of this new device is the possibility of coupling pH and DO set-point titrations.

In the experiments described in the present paper, NaOH (0.05 N) was dosed to balance the acidity produced by ammonium oxidation or CO_2 produced by heterotrophic respiration, while H_2O_2 (0.06-0.12 N) was provided to the biomass to balance the oxygen consumption due to ammonium and nitrite oxidation and heterotrophic respiration. Set point values were 8.3 for pH and 6-8 mgO_2/l for DO.

RESULTS AND DISCUSSION

Evaluation of the inhibiting effect of the influent to nitrifiers (Mode 1)

The feasibility of assessing the inhibitory effect of the influent wastewater to nitrifiers was experimented by adding a specific inhibitor of ammonium oxidisers (allylthiourea - ATU) to the SBR standard influent and by monitoring the actual ammonium oxidation rate during the AER phase by pH/DO-stat titration. In order to select the appropriate ATU concentration, a preliminary inhibition test was performed on a 0.8 L sludge sample, drawn from the main SBR reactor. The test was performed according to the procedure described in Ficara and Rozzi (2001). An EC_{50} of 0.17 mg/l was estimated, while a concentration

corresponding to the EC_{30} (0.11 mg/l) was selected for the full scale test. In Figure 3, the ammonium oxidation profile estimated by pH-stat titration, during the latter test, is compared with NH_4^+ analytical determinations, and an excellent agreement can be observed. By comparing the actual nitrification rate, determined at the beginning of the AER phase, with that one measured during a previous cycle in the absence of the inhibitory substance, an actual inhibition of 56% was calculated. The observed discrepancy in the inhibition response may be due to the different dosing procedure in the two tests (shot addition in the SBR, cumulative additions in the small-scale preliminary test).

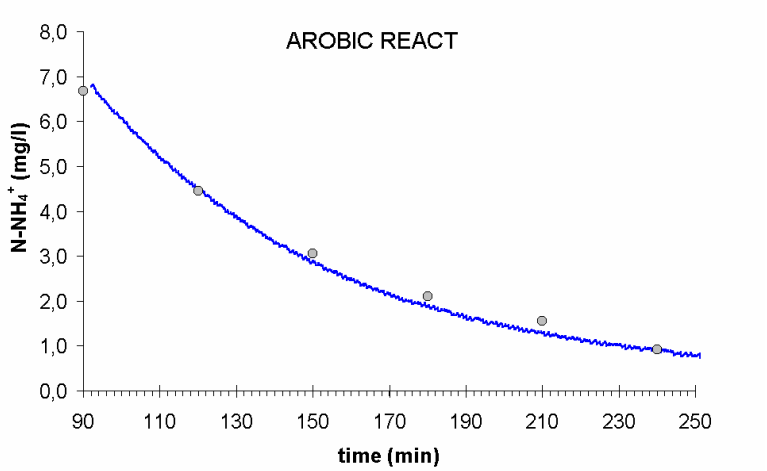

Figure 3. Comparison between the NH_4^+ oxidation profile estimated by pH-stat titration (continuous line) and by analytical determinations (circles) during an SBR cycle in the presence of ATU.

Evaluation of nitrifiable nitrogen in the influent stream (Mode 2)

For this purpose, pH-stat titration was performed on sludge samples drawn at the beginning of the AER phase. A typical titration curve obtained in such tests is reported in Figure 4, together with the corresponding calculated ammonium profile. In the first part of the titration curve, two acidifying processes are taking place: ammonium oxidation and heterotrophic CO_2 production. The flex point, F, identifies the end of the oxidation of ammonium, after which, the rate of CO_2 production can be estimated and subtracted from the total titration rate so that pH-stat titration of the sole ammonium oxidation can be evidenced. The initial N-NH_4^+ content is obtained from the volume of NaOH dosed by taking into account the stoichiometry of ammonium oxidation (2 mol NaOH = 1 mol NH_4^+ oxidised; see Massone et al., 1998).

During 10 SBR cycles, the estimation of the nitrified nitrogen was obtained both by balancing NOx species at the beginning (in) and at the end (out) of the AER phase ($N_{analyses}$ = (N-NO2- + N-NO3-)$_{in}$ – (N-NO2- + N-NO3-)$_{out}$) and by pH-stat titration ($N_{titration}$). In Figure 5, N values are reported together with the soluble N in the SBR feed. A very good correlation can be noticed between the N content in the feed and the nitrified nitrogen. An average difference of 1.8 mgN/l was found between estimates of $N_{analyses}$ and $N_{titration}$. This difference can be explained by taking into account the ammonification process, which takes place during the whole AER phase, as indicated by the constant increase of nitrates concentration observed after complete oxidation of ammonium (Figure 2). The average value for ammonification (calculated as: $N_{ammonified} = N_{analyses}$ - (N-NH_4^+)$_{in}$ + (N-NH_4^+)$_{out}$) was found to be 3.4 mgN/l. As a matter of fact, in pH-stat titration tests, point F, which corresponds to the complete oxidation of ammonium, is used to identify the end of the nitrification process. Therefore, this estimate does not account for nitrification of ammonium ammonified later on.

As supported by the encouraging results presented above, a sufficiently accurate estimate of the nitrifiable content could be obtained by pH-stat titration. In view of the application to process control, a primary-treated sewage sample could be added to a concentrated sludge sample (e.g. sludge sampled at

the end of the sedimentation phase) in order to accelerate the nitrification process and make results available in advance for process feed-forward control strategies.

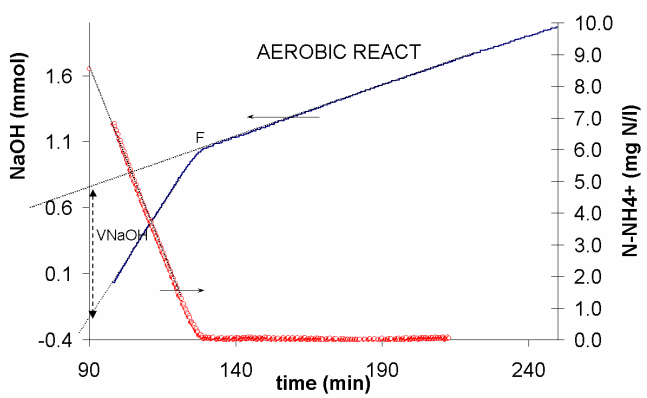

Figure 4. pH-stat titration for the assessment of the N-content.

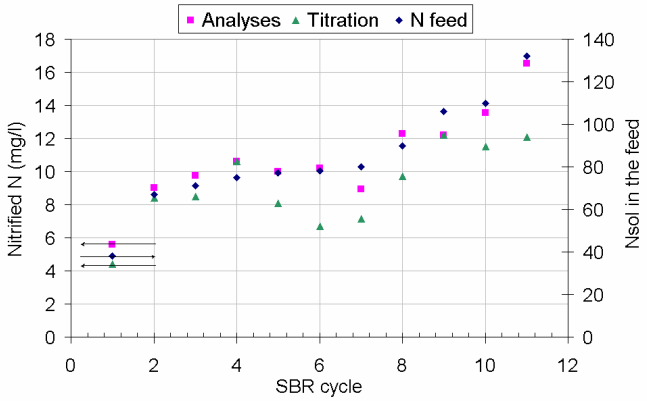

Figure 5. N_{sol} in the feed compared with N nitrified according to NO_x balance (Analyses) and to pH-stat titration (Titration).

Evaluation of the maximum and actual nitrification rate (Mode 3)

Set point titration can be used to assess the actual ammonium and nitrite oxidation rates during the AER phase or the maximum nitrification capacity in presence of non limiting substrate concentration. Actual rates are obtained from the slope of pH/DO-stat titration curves, such as those reported in the following Figure 7. Ammonium oxidation rate is assessed both by pH-stat and DO-stat titration curves by subtracting the rate measured between t_{F1} and t_{F2} from the maximum titration rate. Nitrite oxidation rate can be assessed by coupling pH-stat and DO-stat data. In fact, while DO-stat titration allows determining the oxygen consumption due to both ammonium and nitrite oxidisers, the latter can be evaluated by subtracting the former, estimated by pH-stat titration (Ficara et al., 2000). Results of these evaluations are reported in Table 1 and were found to be coherent with the SBR N-removal capacity. Also, a satisfactory agreement between estimates of actual ammonium oxidation rate by pH-stat and DO-stat titration was obtained.

This methodology allows assessing the actual nitrification rate only at the end of the aeration phase, once titration rates reach the endogenous value, which may be too late for control purposes. However, in order to have a timely evaluation of the nitrification rate, two alternatives can be envisaged. The same titration procedure could be performed on sludge samples taken at the beginning of the anoxic phase, making results available 1-2 hours in advance. A second possibility is to make use of selective inhibitors of ammonium oxidisers (e.g. ATU) to assess the endogenous titration rate before the end of the nitrification reaction. An example of such a test is shown in Figure 6. In this case, ammonium was added at the beginning of the test in order to evaluate the maximum nitrification rate at non-limiting substrate

concentrations. The latter is calculated from the difference between the titration rate (i.e. the slope of the titration curve) measured before and after ATU addition. By anticipating ATU addition, nitrification rate assessment can be completed within 30-60 min.

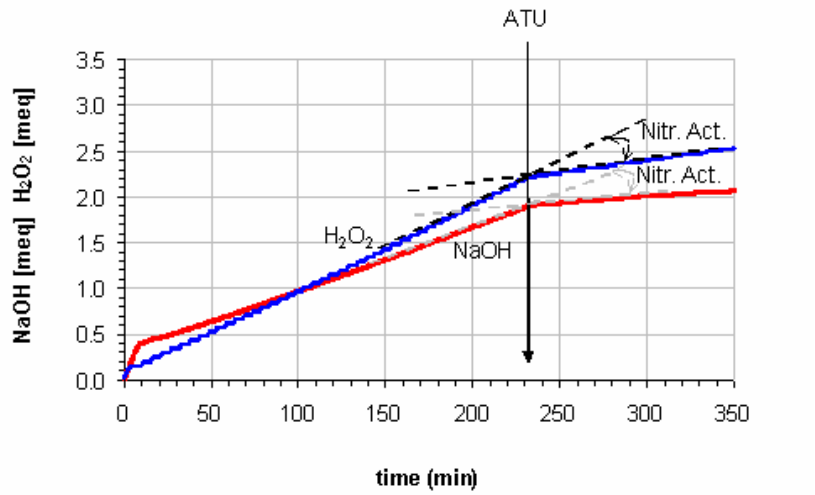

Figure 6. Assessment of the maximum nitrification rate by using an ammonium oxididation specific inhibitor (ATU, 10 mg/l).

Table 1 – Actual ammonium oxidation rate (r_{AOB}) and nitrite oxidation rate (r_{NOB}) assessed during the AER phase by pH/DO-stat titration ($mgN \cdot gSSV^{-1} \cdot h^{-1}$).

Date	r_{AOB} pH-stat	r_{AOB} DO-stat	r_{NOB} DO-stat
04/07/03	3.1		
09/07/03	4.1		
14/07/03	3.1		
22/07/03	3.2	3.8	3.9
11/11/03	5.4	4.5	1.6
20/11/03	5.0	5.3	6.0
26/11/03	5.0	5.0	4.9
04/12/03	6.6	5.4	2.1
10/12/03	6.4	6.4	6.3
18/12/03	2.2	3.4	7.0
27/01/04	5.6	5.5	5.2
29/01/04	3.6	3.9	4.8
04/02/04	5.9	5.8	5.9

Evaluation of the end of the nitrification reaction during the aeration phase (Mode 4)

pH/DO-stat titration tests were performed as described in Mode 2. A typical result is reported in Figure 7. Flex points in both titration curves can be used to identify the end of ammonium oxidation (t_{F1}) and of nitrite oxidation (t_{F2}). It may happen that the DO-stat titration curve does not evidence the F2 flex, indicating either that nitrites oxidation is not completed within the AER phase or that nitrites and ammonium oxidation end almost simultaneously. In these cases, the end point of nitrites oxidation can not be identified by this method. The end points t_{F1} and t_{F2} were compared with those which could be identified from analytical determinations of ammonium and nitrites concentration and with notable points in the trends of DO and pH profiles measured within the SBR reactor (Figure 8). An excellent correlation was observed in all SBR tests (Table 2).

Results demonstrate the feasibility of applying pH/DO-stat titration to assess the end-points of the nitrification reactions. Being the latter the slowest processes, their duration can be used to control the duration of the AER phase, avoiding either incomplete nitrification or excess costs due to unnecessary aeration.

Table 2. End-points of ammonium and nitrite oxidation assessed by titration, N-forms profiles and by notable points of DO and pH trends

Cycle Date	End-point ammonium oxidation (min)			End-point nitrites oxidation (min)		
	DO/pH trend	$[NH_4^+]$	pH/DO-stat	DO trend	DO-stat	$[NO_2^-]$
01/10/03	71	60-90	66	nd	nd	>150
11/11/03	37	30-60	33	69	59	60
20/11/03	55	30-60	59	81	95	60-90
26/11/03	25	<30	15	32	38	<30
04/12/03	48	30-60	43	78	77	60-90
10/12/03	42	30-60	39	77	67	60-90
27/01/04	40	30-60	33	nd	50	30-60
29/01/04	67	60	59	nd	70	60
04/02/04	40	30-60	37	67	62	60

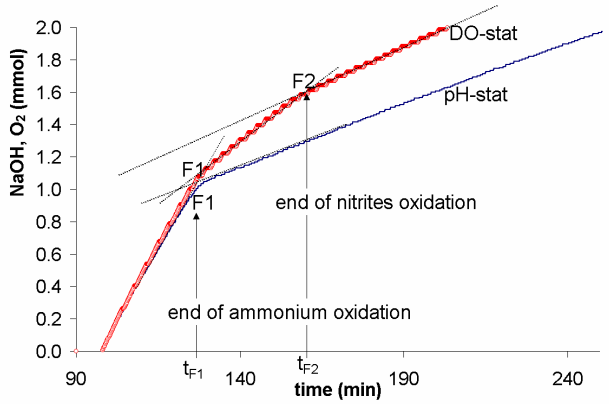

Figure 7. Using pH/DO-stat titration curves to identify the end-point of ammonium oxidation (t_{F1}) and nitrite oxidation (t_{F2})

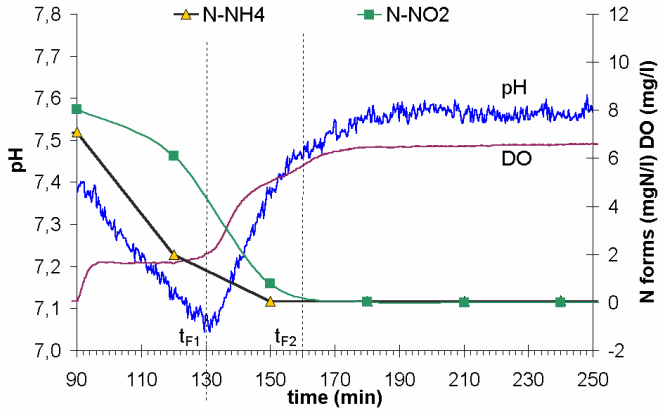

Figure 8. Comparison between t_{F1} e t_{F2} and end-points of ammonium and nitrites oxidation estimated by analytical determination of N forms and by notable points in DO and pH trends

CONCLUSIONS

In conclusion, results of this experimentation on a lab-scale SBR indicate that the pH/DO-stat titration technique can be a useful tool for SBRs monitoring and control. Hence, an on-line titration performed during the aerobic phase could allow to monitor the autotrophic biomass activity and, consequently, ammonium disappearance. Experiments performed on synthetic sewage proved that the end of the nitrification reaction can be detected with reliability by the pH/DO-stat technique.

The determination of the nitrogen load and/or toxicity of the influent could be achieved by performing a titration test on the influent with a concentrated sludge sample to make data available for control purposes before SBR filling. On the basis of these data, a feed-forward strategy for management of nitrogen overload can be developed. Moreover, the detection of strong toxicants in the feed can be used to activate a dedicated control strategy (e.g.: multiple feedings to avoid excessive initial toxicant concentration, or distribution of the feed in several SBR tanks).

Furthermore, periodic titration activity tests on the reactor biomass can be useful to reveal the occurrence of a suffering condition for the autotrophic biomass.

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