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Monitoring denitrification by means of pH and ORP in continuous-flow conventional activated sludge processes

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ABSTRACT

Indirect signal analysis (pH, ORP and DO) are often used in monitoring and control of SBRs (Sequencing Batch Reactors), where operating conditions can be clearly identified during the various cyclic phases. Only few studies applied this methodology to control continuous flow plants, as it is much more difficult to identify operating conditions because of continually variable inflow characteristics. This work applied indirect signal analysis to control pre-denitrification in continuous-flow activated sludge processes: (i) a laboratory-scale plant, fed with synthetic wastewater, simulating real municipal wastewater and (ii) a pilot-scale plant, fed with real sewage. Three different ranges of ORP values identify three operational conditions of the denitrification process. (1) ORP > 0 mV means that nitrates and/or nitrites are present, possibly due to a low C/N ratio. (2) –50 < ORP < –200 mV is typical of normal operating conditions, that is with a balanced C/N ratio. (3) ORP < –350 mV means that oxidized nitrogen load is too low or that C/N exceeds the stoichiometric ratio. The trend of pH, instead, points out if and how the process is evolving from one to another operating condition. The correlation between pH and ORP signals (as well as their derivatives) allows to restore normal operating conditions by acting on the internal recycle flow-rate. Improved denitrification process ensures lower effluent nitrate concentration, and reduce external carbon dosage to achieve stricter nitrogen limits.

Keywords: Denitrification monitoring; ORP signal; pH signal; pre-denitrification systems

1. Introduction

Wastewater treatment plants (WWTPs) must ensure effluent quality standards under variable influent loading and different operating conditions. In medium to small-size wastewater treatment plants (WWTPs <50,000 PE), operating costs are usually higher than in large plants, mainly because of higher variability of influent flow-rates and loads, less efficient electro-mechanical equipment and simpler monitoring devices and control logics. Indirect signal analysis (pH, ORP and DO) are often used in monitoring and control of sequencing batch reactors (SBRs), where identification of operating conditions of the processes has been extensively studied. Continuous flow plants are simpler than SBRs, but are continually influenced by variable inflow characteristics, which makes it much more difficult to identify operating conditions.

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In large WWTPs, automatic control is based on the direct measurement of process parameters, such as nitrogen compounds (NH_4^+-N, NO_3^--N) and is already well known and applied. However, control logics that are based on low-cost pH and ORP probes in continuous-flow processes are not yet sufficiently investigated.

In effect, quite a number of researchers demonstrated that a relationship between these signals and the biological processes exists. It is well known that SBR systems may be monitored through ORP measurement [1,2]. Cecil [3] proposed a method to detect the bend in the redox curve that occurs when the nitrate concentration is reduced to low levels.

Aguado et al. [4] adopted artificial neural networks (ANN) to develop a methodology able to identify the optimal length of SBR phases, Luccarini et al. [5] used feed-forward ANN in order to detect the characteristic points of SBR cycle, such as nitrate knee, ammonia valley and ammonia breakpoint, visible in pH, ORP and DO profiles.

Recently, some studies have addressed continuous-flow systems. For example, de la Vega et al. [6] studied the application in alternate-cycle reactors. Ruano et al. [7] considered the application of pH- and ORP-based control into the benchmark scheme (i.e., 2 anoxic + 3 aerobic tanks). Serralta Sevilla et al. [8] studied a control strategy in a Sharon process.

The present work has studied the pre-denitrification process in a continuous-flow activated sludge process and aims at implementing a low-cost monitoring system, made of robust and cheap sensors, coupled with a stand-alone data-logger (without computer support) to control continuous-flow activated sludge processes, especially for medium to small-size plants. The methodology is based on the identification of a clear relationship between the time trends of indirect signals (pH and ORP), and process conditions of continuous-flow activated-sludge processes. This will allow controlling energy consumption and nitrogen removal efficiency. Control will act on the internal recirculation flow-rate. This has long been defined as a manipulated variable [9,10] and ought to be controlled on-line in a pre-denitrification plant, as it ensures nitrate supply to the anoxic zone. The methodology used in this work differs from those of Zhang et al. [11] and of Thürlimann et al. [12], as we have analyzed pH and ORP signal trends by correlating their derivatives and by applying an automated statistical correlation within the control strategy described in this paper.

2. Materials and methods

The experimentation has been carried out in a laboratory-scale and in a pilot-scale plant, both based on the Ludzack-Ettinger scheme (Fig. 1).

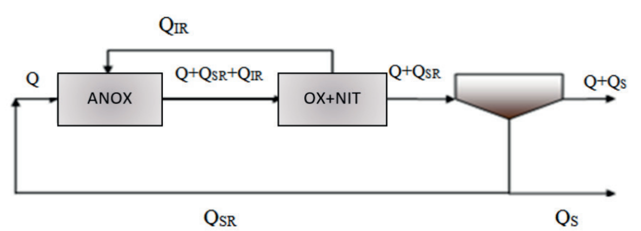

Fig. 1. Flow diagram of the plant.

A summary of the operating conditions for both plants is reported in Table 1.

2.1. *Laboratory*-scale plant

The laboratory-scale plant (Fig. 2) was located in a thermostatic room at a constant temperature of 20°C. The pre-denitrification tank was continuously mixed, while the nitrification one was kept aerobic by aeration provided by an aquarium air pump connected to a porous stone. The DO signal was maintained between 1.5 and 2.5 mgl^{-1} through an on-off controller. The settled sludge was recycled to the anoxic tank. Two peristaltic pumps, both running at variable flow rate provided the internal and external recycle flows. The plant was equipped with pH and ORP probes in the anoxic tank, pH, ORP and DO in the aerobic one. All data were sampled and stored by a data acquisition card (DAQ 6052 by National Instrument) at the rate of 1 sample/min. It has been operated for six months.

Table 1
Operating conditions both for lab scale and pilot plant

	Lab scale plant		Pilot plant	
	Value	U.M.	Value	U.M.
Total volume	5400	ml	360	l
Denitrification tank volume	2000	ml	94.5	l
Nitrification tank volume	2500	ml	2500	l
Settler volume	900	ml	900	l
Inflow, Q_{IN}	5472	ml d^{-1}	460	l d^{-1}
Internal recycle flow, Q_{IR}	16416	ml d^{-1}	760	l d^{-1}
$IR = Q_{IR}/Q_{IN}$	3	–	1.65	–
Sludge recycle flow, Q_{SR}	5554	ml d^{-1}	430	l d^{-1}
$SR = Q_{SR}/Q_{IN}$	1	–	0.93	–
SRT	20	d	20–30	d
HRT	20	h	16	h

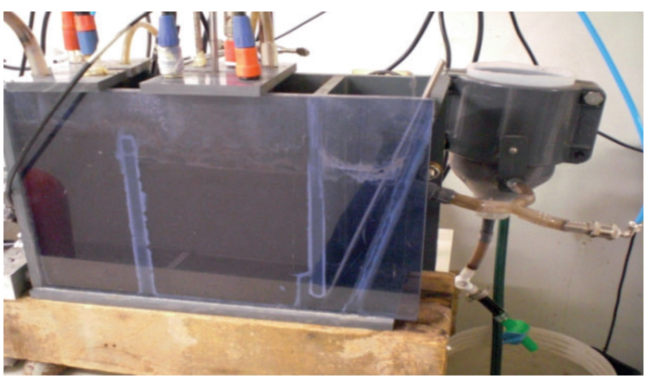

Fig. 2. Lab-scale plant.

2.2. Pilot plant

Fig. 3 shows a front view of the pilot plant, located inside the area of the municipal WWTP in Trebbo di Reno (Bologna). Mechanical equipment includes a stirrer, a variable-flow blower connected to a fine bubble membrane diffuser and three peristaltic pumps, for influent loading, internal and external recycle flows, respectively. The plant was fed with real wastewater, taken downstream of the micro-screen of the full scale plant, and was provided with probes to measure pH, ORP, NH_4^+-N, NO_3^--N in the anoxic tank and pH, ORP, DO, NH_4^+-N, NO_3^--N and TSS in the aeration tank. Data are acquired and stored by a data logger DataTaker DT 80, at a frequency of 1 sample/min.

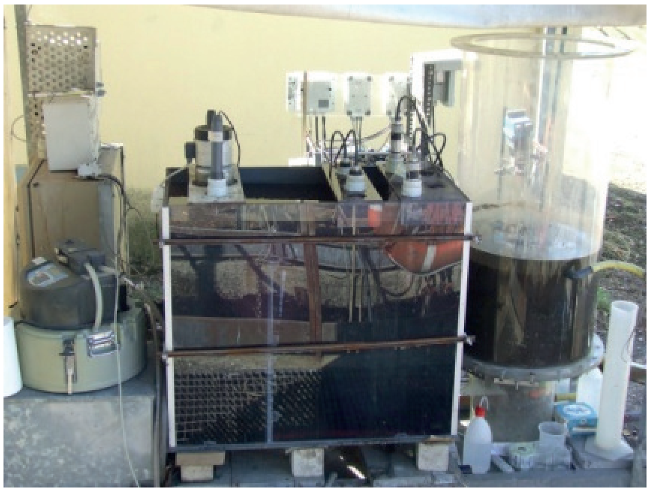

Fig. 3. Pilot-scale plant.

2.3. Influent characteristics

2.3.1. Synthetic wastewater

The lab-scale plant was fed with a synthetic wastewater simulating a real municipal wastewater, modified from the OECD Guidelines for testing of chemicals (OECD Test Guideline No. 209, 2010 [13]), by reducing the C-sources by the factor 100 and by varying the ammonium concentration. Three main COD/N ratios, were tested during the research activity. The pH of the influent has been monitored during all the experimentation and was maintained at 7.5. The feed composition is reported in Table 2.

2.3.2. Real wastewater

Wastewater was sampled at a frequency of 1 sample/h by an automatic sampler, ISCO 6712. Six data sets of 24 h were collected and the daily variability has been expressed as means and 95% confidence interval (CI). Figs. 4 and 5 show NH_4^+-N and COD_{tot} profiles respectively. The high concentration variability in the real wastewater is typical of small municipal wastewater treatment plants.

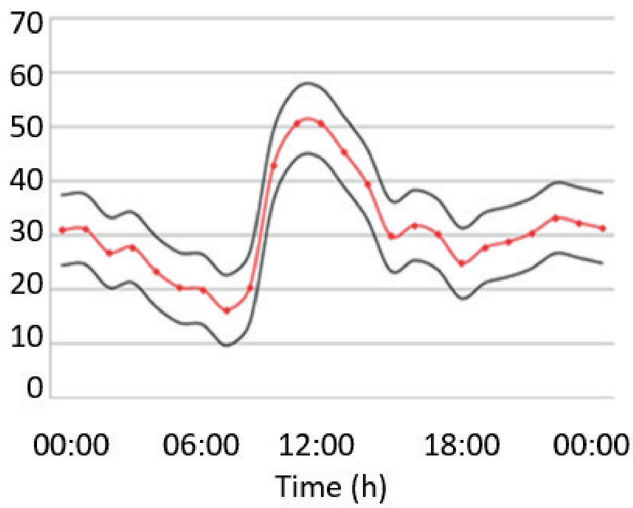

Fig. 4. Influent NH_4^+-N profile.

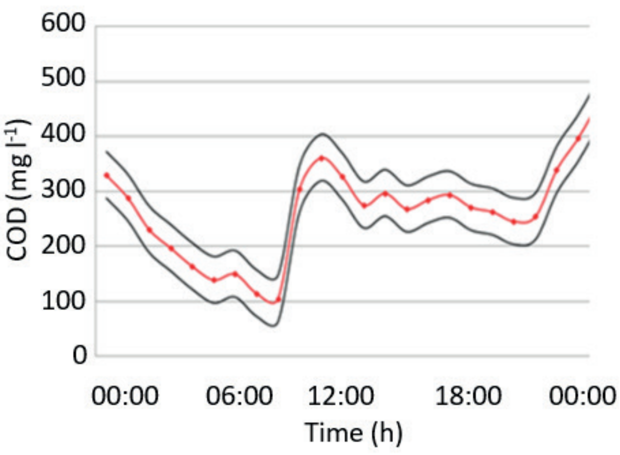

Fig. 5. Influent total COD profile.

3. Results and discussion

Indirect signals (pH and ORP) were analysed in the lab-scale plant, fed with known and constant influent. In particular, their trend in the pre-denitrification tank has been studied in the lab-scale plant. The obtained results found a correspondence with the acquired signal in the pilot-scale plant. Three different operational conditions of the denitrification process have been defined according to the following ranges of the ORP values: (i) ORP > 0 mV, (ii) ORP < –350 mV and (iii) –200 mV < ORP < –50 mV. In particular, two relate to abnormal functioning and are referred to as (i) oxidizing and (ii) reducing (or anaerobic) conditions, while the (iii) is the expected condition and it

Table 2
Synthetic feed composition

COD/TKN	COD (mg l^{-1})	TKN (mg l^{-1})
6.6	633	96
5.8	558.1	96
6	633	105.5

has been referred to anoxic conditions. While ORP signal is useful in defining operating conditions, pH trends allow detecting transitions between them.

3.1. Oxidizing conditions

This case occurs when ORP in the anoxic tank is steadily above 0 mV. Once these conditions have established in the anoxic tank of the lab-scale plant, an experiment has been started to bring the system back to normal anoxic conditions. Table 3 shows the initial operating conditions, while Table 4 shows the evolution of the experimental conditions, where IR is the manipulated variable and pH and ORP the controlled variables. NH_4-N, NO_3-N, NO_2-N, are also presented.

Trends of pH and ORP are shown in Figs. 6 and 7, respectively. At the beginning, the ORP signal is around 100 mV, with a low positive first derivative of the signal (0.2 mV/min), corresponding to oxidizing conditions. Analyses of nitrates (3.31 mgl^{-1}) and nitrites concentration (1.7 mgl^{-1}) showed that the denitrification process was not complete. The assumption was made that the oxidized nitrogen that was carried back to the anoxic tank by the internal recycle flux exceeded the available biodegradable carbon. Therefore, the internal recycle flow-rate has been decreased, passing from a ratio of 3 to 2.5 times the influent flow-rate (label "A" in both Table 4 and Figs. 6 and 7). The pH signal suddenly started increasing and performed a detectable positive evolution with a first derivative around 10^{-3} pH units/min, passing from 7.6 to almost 7.8 after 2 h (12:40). As the ORP value was still positive (60 mV), despite its first derivative was around –2.5 mV/min, IR ratio was decreased further from 2.5 to 2 (label "B" in Table 5 and Figs. 6 and 7). As a result, pH further increased, while ORP maintained its negative trend. At point "C", pH signal reached a new maximum point, ORP signal decreased below –150 mV, its trend slowed down and its first derivative tended to zero. Analyses have shown that at point "C", nitrogen compounds reduced approximately to zero (NO_3-N = 0.7 mgl^{-1}; NO_2-N = 0.2 mgl^{-1}).

It is noticeable that the absolute maximum of pH values corresponds to a nearly zero value of dORP/dt, at

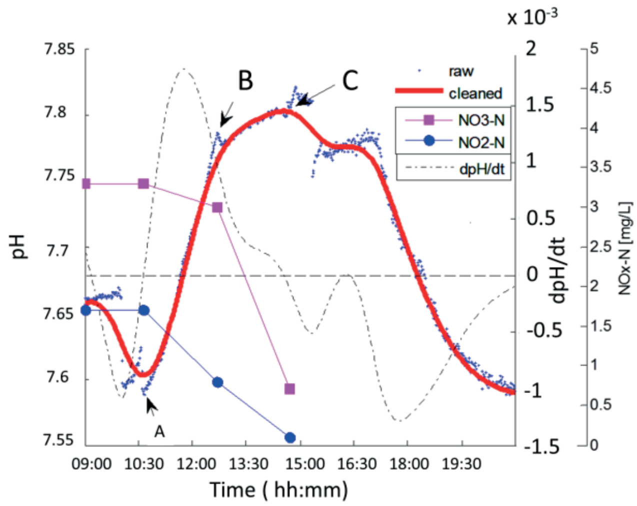

Fig. 6. pH, dpH/dt and NOx-N profiles in the anoxic tank.

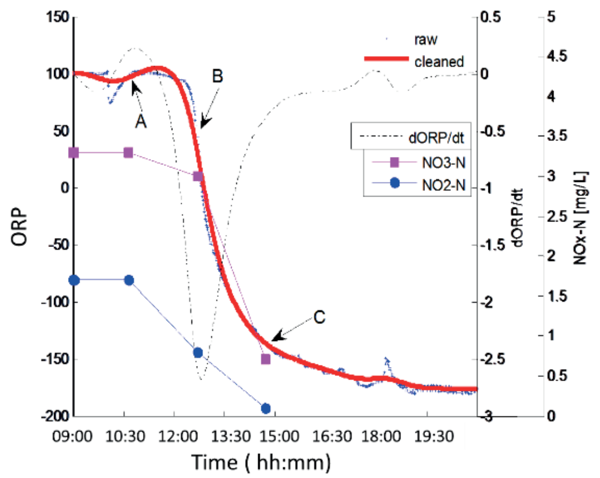

Fig. 7. ORP, dORP/dt and NOx-N profiles in the anoxic tank.

Table 3
Initial operating conditions

Q_{In} = 0.3 l/h	Q_{IR} = 0.9 l/h	Q_{SR} = 0.3 l/h	IR = 3	SR = 1	SRT = 20 d	HRT = 20 h	COD:TKN = 6
NH_4–N	NO_3–N	NO_2–N	pH	dpH/dt		ORP	dORP/dt
8.0 mgl^{-1}	3.3 mg l^{-1}	1.7 mg l^{-1}	7.6	10^{-5} pH/min		100 mV	0.2 mV/min

Table 4
Operating conditions during the experiment

Time (hh:mm)	Label	IR	NH_4–N (mgl^{-1})	NO_3–N (mgl^{-1})	NO_2–N (mgl^{-1})	pH	dpH/dt (pH/min)	ORP (mV)	dORP/dt (mV/min)
10:40	A	2.5	8.0	3.3	1.7	7.59	10^{-5}	100	0.2
12:40	B	2	9.0	3.0	0.8	7.78	10^{-3}	60	–3.0
14:45	C	2	11	0.7	0.1	7.85	10^{-4}	–150	–0.3

ORP around –150 mV, corresponding to anoxic conditions. These conditions correspond to a stable and complete denitrification.

3.2. Reducing (or anaerobic) conditions

In this case ORP values in the anoxic tank were steadily below –350 mV, corresponding to strongly reducing conditions. Initial operating conditions of the system are indicated in Table 5, with a highly negative stable value of the ORP signal (–375 mV and dORP/dt = 0); analyses of the soluble compounds in the anoxic tank showed that oxidized nitrogen was nearly zero but also showed that there was a considerable soluble COD residual (29 mgl^{-1}). Therefore, some denitrification capacity was still available, and more nitrates could be removed by increasing the internal recycle.

Table 6 shows the operating conditions during the experiment. The internal recycle ratio IR was gradually increased from 1.5 (initial condition) to 3 (final condition). In Figs. 8 and 9 arrows labeled with A, B, C, D, E and F correspond to the same labels reported in Table 6 and mark the instant when the internal recycle ratio IR has been changed. In particular, these points correspond to a relative maximum of the pH signal, indicating that denitrification temporarily stopped under those conditions.

Table 6 reports the effects of varying the manipulated variable IR on pH and ORP signals. In additions the values of the controlled variables NH_4-N, NO_3-N, NO_2-N, COD_{sol}, are presented. Fig. 8 shows the profiles of pH and dpH/dt, while Fig. 9 shows ORP and dORP/dt profiles. Both Figs. 8 and 9 show the measured values of COD_{sol}, NH_4-N, and NOx-N. During the experiment, the ORP signals kept stable around –350 mV, indicating that the denitrification potential was not exhausted. This was confirmed by measured analytical data, as soluble COD was significantly high and NO_x-N was always zero during all the period. These observations confirmed that the denitrification

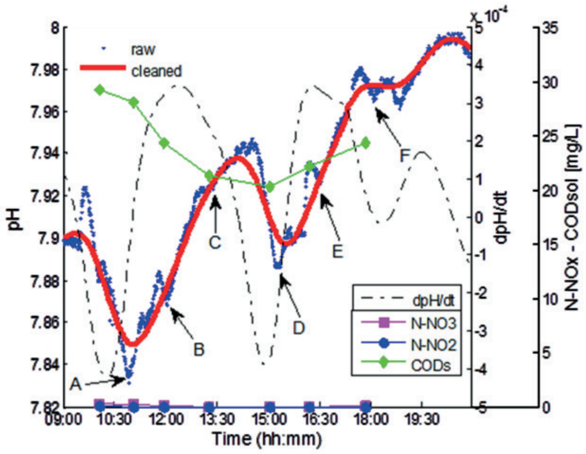

Fig. 8. pH, dpH/dt and NOx-N profiles in the anoxic tank.

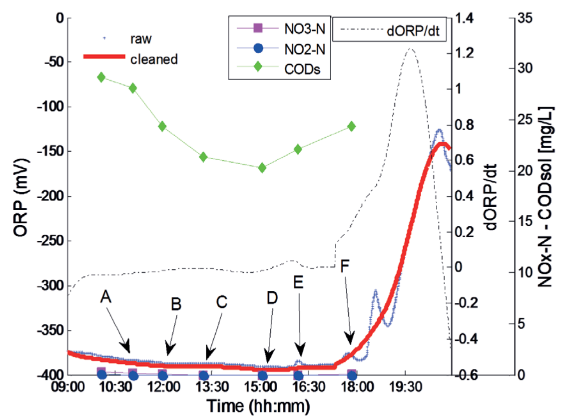

Fig. 9. ORP, dORP/dt and NOx-N profiles in the anoxic tank.

Table 5
Initial operating conditions

Q_{In} = 0.3 l/h	Q_{IR} = 0.45 l/h	Q_{SR} = 0.3 l/h	IR = 1.5	SR = 1	SRT = 20 d	HRT = 20 h	COD:TKN = 6
COD_{sol}	NO_3–N	NO_2–N	pH	dpH/dt		ORP	dORP/dt
29.2 mg l^{-1}	0.3 mg l^{-1}	0.1 mg l^{-1}	7.88	-3.9×10^{-5} pH/min		–375 mV	0.0 mV/min

Table 6
Operating conditions during the experiment

Time (hh:mm)	Label	IR	COD_{sol} (mgl^{-1})	NH_4–N (mgl^{-1})	NO_3–N (mgl^{-1})	NO_2–N (mgl^{-1})	pH	dpH/dt (pH/min)	ORP (mV)	dORP/dt (mV/min)
10:05	T0	1.5	29.2	20.0	0.3	0.1	7.88	-3.9×10^{-4}	–375	0.0
11:05	A	1.75	28.1	18.7	0.2	0.0	7.83	-4.3×10^{-4}	–380	0.0
12:00	B	2.0	24.0	19.0	0.0	0.0	7.87	3.3×10^{-4}	–380	0.0
13:20	C	2.25	21.3	19.5	0.0	0.0	7.92	2.4×10^{-4}	–380	0.0
15:10	D	2.50	18.5	18.5	0.0	0.0	7.89	-2.5×10^{-4}	–390	0.0
16:20	E	2.75	20.5	18.5	0.1	0.0	7.93	3.5×10^{-4}	–390	0.0
18:00	F	3	24.2				7.96	0.0	–370	0.3

capacity was not yet fully exploited. At point "F" (6 PM), the internal recycle IR was increased to 3 times the influent feed. Then the ORP profile finally increased, reaching the expected value (around –150 mV), indicating that the denitrification capacity was exhausted. Samples for analytical determinations could not be taken, as these conditions happened during the night.

Continuous measurement of pH and ORP allowed an effective monitoring of the denitrification process in CAS processes. In particular, the observation of ORP values during the experiments confirmed the identification of three characteristic operational conditions as assumed above. A summary is reported in Table 7.

3.3. Pilot-scale plant

Following the achievements obtained in the lab-scale plant, a similar methodology has been approached to the pilot plant, fed on real wastewater. Figs. 10 and 11 show pH and ORP trends in the anoxic tank and NO_3^--N and NH_4^+-N in the effluent of the pilot-scale plant, recorded in two consecutive days. In particular, effluent ammonium nitrogen appears to be steadily around zero, while effluent NO_3^--N shows significant fluctuations between 2 and 17 mg l^{-1}. This variability is due to the influent load fluctuations reported in Figs. 4 and 5, where a NH_4^+-N peak occurs during the day and a COD peak occurs during the night.

Figs. 10 and 11 show some ORP and pH patterns that are similar to those already observed in the lab-scale plants. In particular, pH maxima correspond to flexes in the ORP signal (points A1, A2, B, C). These points are a warning of changing conditions, from low ORP to high ORP or vice-versa. During the two monitored days, two "reducing" abnormal conditions were recorded with ORP below –300 mV. This happened during nighttime COD peaks. If the IR ratio would have been increased, according to the criteria defined above, lower effluent NO_3^--N concentration could have been achieved during the night. On the contrary, the high NO_3^--N peak during daytime could not be reduced, as this was the consequence of a high NH_4^+-N peak which did not correspond to a similar COD peak. As ORP and pH in the anoxic tank were indicating that denitrification was operating under normal conditions, an increase of the IR recycle rate would have not improved the overall nitrogen removal.

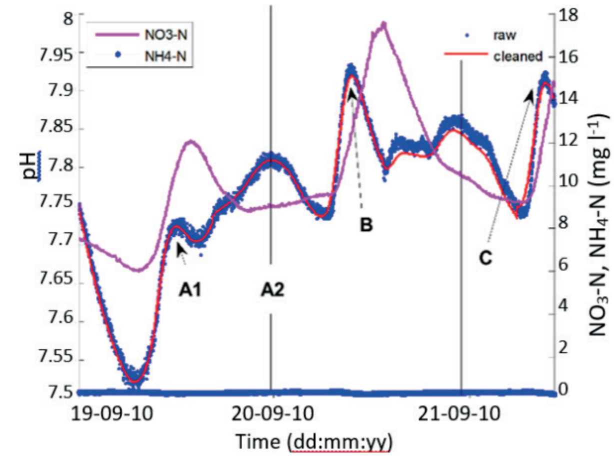

Fig. 10. pH trend along two days; the date is placed at midnight.

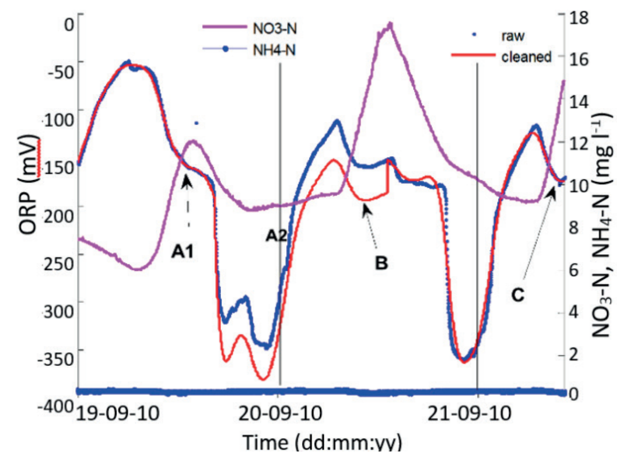

Fig. 11. ORP trend along two days; the date is placed at midnight.

Table 7
Summary of operating conditions in the lab-scale, continuous-flow activated sludge denitrification process

Field of operating conditions	• Range of ORP values • Corresponding NO_x^- - N range of values • Explanation of process conditions
Oxidizing (anomalous)	• ORP >>0 mV (commonly above 50 mV, up to 100 mV) • NO_x^- - N > 0 mgl^{-1} • Lack of biodegradable substrate (bCOD) compared to the nitrogen load; or excess NO_x– - N recycled to the anoxic tank (i.e., too high IR ratio)
Reducing, or anaerobic (anomalous)	• ORP << 0 mV (commonly less than ~ –250 mV till ~ – 400 mV) • NO_x^- - N = ~0 mgl^{-1} • Excess of bCOD compared to nitrogen; or lack of NO_x– - N (i.e., too low IR ratio)
Anoxic (expected)	• ORP < 0 mV (normal operating range between ~ –250 mV till ~ – 50 mV) • NO_x^- - N = ~ 0 mgl^{-1} • bCOD to nitrogen ratio close to stoichiometric requirement

4. Conclusions

The relationship between pH and ORP profiles and biological processes in SBR cyclic phases is well known. However, few studies have investigated this relationship in continuous-flow reactors, and even fewer have used these correlations to control the denitrification process. This study indicates that there is the possibility to achieve important information about the denitrification process by monitoring pH and ORP trends in the anoxic tank. In particular ORP characterizes typical operational conditions (e.g., excess carbon and lack of nitrate, or vice-versa, or a balanced ratio of the two), while pH trend indicates possible transitions between two different conditions (e.g., due to variable influent COD/N ratios). This information may be used to assess the operational condition of the pre-denitrification process in real time and continuously, and it would detect whether operational conditions are changing. The proposed methodology is a promising way to control denitrification. Whenever, a substantial process variation occurs, the most appropriate control strategy may be implemented, such as varying the internal recycle flow rate, or adding external organic carbon if the COD/N ratio is too low.

Acknowledgements

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Symbols

ANN	—	Artificial neural networks
CI	—	Confidence interval
DO	—	Dissolved oxygen concentration
HRT	—	Hydraulic residence time
IR	—	Internal recycle ratio: Q_{IR}/Q_{IN}
ORP	—	Oxidation reduction potential
PE	—	Population equivalent
Q_{IN}	—	Flow at the inlet
Q_{IR}	—	Internal recycle flow
SBR	—	Sequential biological reactor
SR	—	Sludge recycle ratio: Q_{SR}/Q_{IN}
SRT	—	Solids retention time
WWTP	—	Wastewater treatment plant

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