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Nutrient removal performance within the biological treatment of the Marrakech wastewater treatment plant and characterization of the aeration and non-aeration process

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ABSTRACT

The strategy for controlling and monitoring aerobic/anoxia cycles at the level of the 4 biological treatment basins of the wastewater treatment plant of Marrakech is mainly based on the measurements provided by the dissolved oxygen (DO) and redox potential (oxidation–reduction potential) sensors (ORP). In this work, the comparison of the ammonium (NH_4^+) of the 24 h balance with the daily average values of DO and ORP for each basin showed that when the oxygen concentration is low, the NH_4^+ concentration is high. The maximum NH_4^+ value of around 10.3 mg N/L is obtained on the day when the DO concentration is almost zero at the level of one of the 4 basins, which is basin B1. Moreover, knowing that the influent flow is unstable, the punctual monitoring of these parameters at the exit of each basin showed that during the mornings the punctual concentrations of NH_4^+ are generally low in comparison to NO_3^- concentrations which are high and the measurements of DO and ORP which correspond are important. Conversely, the results obtained during afternoons with high values of NH_4^+ correspond to low values of DO, ORP and NO_3^-. This shows that the need for oxygen also fluctuates during the day. In real-time control, the use of key parameters obtained from temporary readings of the DO and ORP profiles provide valuable information on the biological nitrification–denitrification process: The DO breakpoint indicates the disappearance of NH_4^+ during the aerobic phase (end of nitrification), called DO elbow are break points on ORP profiles; the ORP knee on the ORP profile signifies the control point where the nitrate has been effectively reduced during the non-aeration cycle (the nitrate knee), The oxygen-uptake rate which can reflect the activity of microorganisms… In this work, given the large amount of information provided by the system, these key parameters are used to accurately interpret some aeration/non-aeration cycles within the four basins.

Keywords: Marrakech wastewater treatment plant; Dissolved oxygen; Oxidation–reduction potential; Ammonium; Key parameter indicators

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1. Introduction

Today the standards for discharging water into the natural environment have become more and more demandin. To overcome this problem, removing nutrients and organic matter from wastewater is what treatment plants exist for. Removal of nitrogen through biological treatment is the most economical process [1]. In biological reactors, the alternation of aerobic and anoxic phases allows the elimination of nitrogen. The first step, through nitrifying bacteria [2], autotrophic nitrification is carried out by the biological oxidation of ammonium (NH_4^+) into nitrite (NO_2^-), then into nitrate (NO_3^-) [3]. The next step is done by heterotrophic denitrifying bacteria that use organic carbon for their growth and as an electron donor [4]. The majority of these bacteria are facultative anaerobes. They reduce nitrate once again to nitrite (NO_2^-) then to gaseous compounds (N_2) in the absence of oxygen [3,5].

To ensure the reliability and performance of the nitrogen treatment system, real-time process control is a necessary step. It is done in different ways; either by a direct method, to optimize the oxygen requirement by the pollution to be treated, continuous online monitoring of the concentrations of the forms of nitrogen, NH_4^+ and NO_3^- thus allowing lower energy consumption [6]. But this approach neglects the metabolism of the microorganisms involved. In addition, dissolved oxygen (DO) readings less than 0.1–0.2 mg/L are unreliable in anoxic and anaerobic processes [7,8]. Another indirect approach is based on monitoring the values of redox potential, oxidation–reduction potential (ORP). Reactors for biological processes (activated sludge, sequential batch reactors (SBR), biofilm) are characterized by numerous redox reactions that take place at the same time. ORP monitoring can indicate the different phases of water treatment and it reveals the biochemical state of the environment. Nitrification takes place between +100 and +350 mV, on the other hand denitrification takes place between –50 and +50 mV [9]. In addition, supervision by the ORP can save up to 20% of energy consumed [10]. Even continuous monitoring of pH can help reflect the state of the medium, it decreases due to the release of the proton during nitrification which is the transformation of ammonia into nitrite [11].

Besides, the use of respirometric sensors can also generate a lot of interest in process control. While the oxygen-uptake rate (OUR) is directly related to biomass growth and substrate consumption [12]. This approach will make it possible to assess the fluctuations in pollutant loads and the presence of toxicants in water capable of inhibiting the activity of biomass [13–15] as well as the degree degradation of carbon and nitrogen pollution. Online control by the combination of two or more of the indirect parameters is very useful at the level of treatment stations such as activated sludge, given the low maintenance cost and the reliability of its instruments than the other methods. Online monitoring of both OUR and ORP will allow detection of extreme points of aerobic and anoxic reaction phases, respectively [1]. Additionally, researchers have shown that identifying key parameters on ORP, DO and pH profiles can be used to control the aeration/non-aeration cycle. As oxygen rise average slope (ORAS) on the DO profile which represents the slope of the linear approximation of this curve during the aeration cycle and on the ORP profile (nitrate knee), shows a sudden drop in this parameter (nitrate) determining the end denitrification during the anoxic phase [16]. On the other hand, on the pH profile, the end of nitrification during the aerobic phase is called the ammonia valley [17,18], it is a minimum point of the pH corresponding to the complete depletion of ammonia which is closely related to a remarkable increase in the concentration of O_2 in the medium [1].

In general, for a thorough treatment of nitrogen, the regulation of aeration is generally carried out on a clock, on threshold values in oxygen, in redox potential, or by a mixture of the three [6]. In wastewater treatment plants, the control of the nitrification–denitrification process is often carried out by probes measuring the DO and ORP values thanks to proven technology and low acquisition and maintenance costs compared to other types of probes also used in these treatment plants [19].

2. Material and methods

2.1. Study area

The raw effluent from the STEP of the city of Marrakech (1,300,000 inhabitant equivalent) is first physically pretreated, after this step, there is another which is the primary settling in order to eliminate a large part of the undissolved pollution.

Subsequently, the biological treatment (secondary treatment) at the wastewater treatment plant is a treatment of the activated sludge type at low load. It is devoted not only to the removal of organic pollution, but also to the removal of nitrogen. At the level of the distribution chamber, the water coming from the primary treatment is mixed with the recycled sludge coming from the secondary settling tanks. The biological treatment consists of four aeration basins of the carousel type placed in parallel and each basin receives 25% of the mixture. Each basin is equipped with an aeration system (fine bubbles) supplied by high capacity booster pumps; the aeration syncope allows nitrification–denitrification within the same carousel, due to the fact that in the absence of aeration denitrification takes place. After a residence time, the mixed liquor from each carousel will continue its way to the last secondary treatment step which is clarification and where the separation of the purified water and the settled sludge takes place.

The aeration processes are controlled by a strategy based on the information obtained from the ORP and DO profiles. The probes continuously measure the DO (mg/L), ORP (mV), installed (submerged) respectively near the outlet of the aeration basins since they clearly represent what is happening in the rest of the channel, the probes of air flow (Nm^3/h) at the inlet, on the other hand the water flow sensors (m^3/h) are placed at the outlet of each clarifier (Table 1).

The automation of the different phases is carried out using an Industrial Programmable Logic Controller (Schneider CPU Type: Quantum), linked with a SCADA (Supervisory Control and Data Acquisition) supervision system, software (Topkapi Vision 32, Version 5.0 of Areal France), from measurements made by transmitters (SC 100 transmitter works with all Hach probes; reference LXV404.99.00551) of air flow, redox potential (platinum electrodes) and dissolved oxygen, towards on–off valve type actuators and regulating

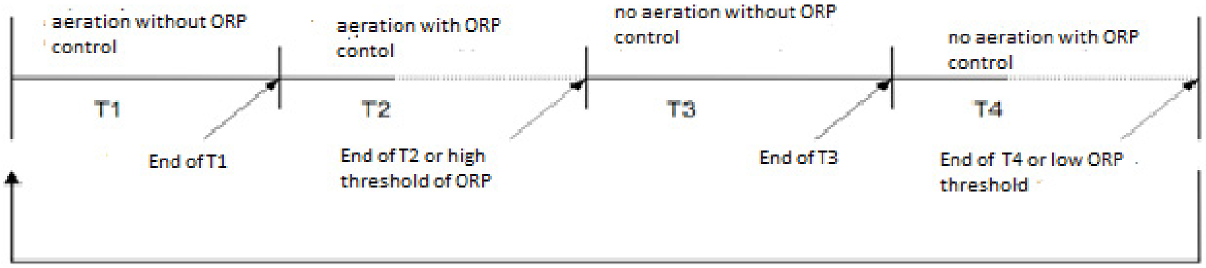
Table 1
The various sensors and flow meters used for the control of aeration and flow rates in biological basins

Sensor	Role	Mark	Reference
Treated water flow meter	Inlet and outlet water flow measurement	Siemens (RS Hydro Located in Harris Business Park, Canalside, Stoke Prior, Bromsgrove B60 4DJ, United Kingdom)	HydroRanger 200
LDO sc In-line dissolved oxygen sensor	Oxygen probe	Hach (HACH LANGE is a world-renowned company in the field of laboratory water analysis. Its location in Morocco is 367 Boulevard Mohamed Zerktouni, Casablanca 20250)	LXV416.99.20001
pHD sc Redox sensor	Redox probe	Hach	DRD1R5.99
Air flow meter	Air flow measurement at the entrance to biological ponds	COMBIMASS® (Binder Group AG Buchbrunnenweg 18, 89081 Ulm, Germany)	C 100472 FIT-2412.5

aeration systems by blowing fine bubbles. The SCADA system records DO and ORP readings every half hour, then reports an average hourly value.

The alternation of aeration phases (T1 and T2) and non-aeration (T3 and T4) allows time for the denitrification to take place in the aeration basins at the end of each cycle, and the concentration of dissolved oxygen is often zero during non-aeration phases.

The aeration–non-aeration cycle includes 4 phases as shown in the diagram below:



- Duration of the first phase T1 (aeration without ORP control), is predetermined, and does not undergo ORP control.
- Second phase T2 (aeration with ORP control), the sequence checks the ORP threshold determined in the aerobic/anoxia basin.
- The non-aeration phase without ORP control (T3) begins with the stopping of the aerators and the end of phase T2. It ignores the control of the ORP value, its duration of this phase is limited to 10 min.
- T4 non-aeration phase is carried out with the verification of the ORP potential. It ends – either at the end of a time delay of the phase duration T4 (40 min) or by the detection of a low ORP measurement threshold (30 mV).

The duration of the ventilation setpoint phases T1 and T2 at the level of each line was set by the operator, and carried out manually according to the results of point analysis of NH_4^+ or the line reading of the DO and ORP curves

2.2. Analytical methods

The various parameters were analyzed according to the standardized rapid methods on reagents purchased from Hach, at the entry and exit of the biological treatment and at the exit of the biological tanks (Table 2).

The results were monitored from December 1 to 31, 2016 and analyzed in the following three sections:

2.2.1. Analyzes on 24-h samples

The so-called 24-h composite average samples are representative samples of sub-samples proportional to the flow rate, taken automatically by refrigerated automatic samplers, placed at the outlet of the primary treatment and at the outlet of the clarifiers. They allow daily balances to be made for the various parameters [chemical oxygen demand (COD), biological oxygen demand (BOD_5), total Kjeldahl nitrogen (TKN), total suspended solids (TSS), NGL and total phosphorus (TP)].

The efficiency of the treatment process was calculated by comparing input and output pollution concentrations. It was obtained from:

$$R = \frac{C_{si} - C_{so}}{C_{so}} \times 100\% \quad (1)$$

where C_{si} represents the input concentration of a certain parameter and C_{so} its output concentration.

In parallel, the results obtained during the process included readings of DO probes and ORP probes with the other parameters measured in situ (air flow rate supplied, water flow rate treated) are included.

Table 2
Laboratory analysis method

Parameter	Standard	Method	Platform	Measuring range
COD	ISO 6060-1989, DIN 38409-H41-H44	Bichromate	Cuvette test: LCK 514 Cuvette test: LCK 314	[100–2,000 mg/L O_2] [15–150 mg/L O_2]
Total phosphorus (TP)	ISO 6878-1-1986, DIN 38405 D11-4	Phosphomolybdic blue	Cuvette test: LCK 350 Cuvette test: LCK 348	[2–20 mg/L] [0.5–5.0 mg/L]
Total nitrogen (TN)	ISO 7150-1, DIN 38406 E5-1, UNI 11669	Koroleff Digestion (with peroxodisulphate) and photometric detection with 2,6-dimethylphenol	Cuvette test: LCK 338 Cuvette test: LCK 138	[20–100 mg/L TNb] [1–16 mg/L TNb]
Ammonium NH_4–N	ISO 7150-1, DIN 38406 E5-1, UNI 11669:2017	Indophenol blue	Cuvette test: LCK305	[1.3–15 mg/L NH_4]
Nitrate NO_3–N	ISO 7890-1-2-1986, DIN 38405 D9-2	2,6-dimethylphenol	Cuvette test: LCK 339	[0.23–13.5 mg/L NO_3–N]

2.2.2. Analyzes on grab samples

- On–off samples are taken by immersing a bottle at the outlet of each basin. The analysis was associated with the DO and ORP readings that correspond to each sample. They were carried out on one liter samples as follows:
- Mornings (around 10 a.m.) to assess NH_4^+ concentrations, TSS, Mohlman index, mass load and sludge age, throughout the month of December. – afternoons (around 4 p.m.) for 10 d in December for NH_4^+;
- NO_3^-, mornings from the 19th to the 31st of the month; afternoons from the 19th to the 26th of the month (depending on the availability of kits).

2.2.3. Monitoring of data recordings from the two ORP (mV) and DO (mg/L) probes

The sequencing of the aeration allows the alternation of aerobic and anoxic conditions (aeration/non-aeration cycle) and therefore the nitrification–denitrification phases. The evaluation of the temporary profiles of DO and ORP allowed us to obtain other parameters which help to identify and characterize the process state of the nitrogen treatment. In this section of the results some parameters will be identified from temporary monitoring of the DO and ORP profiles of some aeration/non-aeration cycles within the 4 basins.

3. Results and discussions

The loads of COD, BOD_5, TSS, TNK, and TP for the biologic treatment tributary during this study were as follows (Table 3).

Table 3
Characteristics of settled water at the entrance to secondary treatment during the study period

Contents	Minimum	Maximum	Average	Time (d)
Settled water flow (m^3/d)	97,687.34	153,896.82	113,773.9	31
Load in COD (kg/d)	63,649.13	104,834.68	80,504.85	30
Load in BOD_5 (kg/d)	19,416.87	64,666.42	48,305.63	30
Load in TSS (kg/d)	16,888.26	37,319.79	23,727.45	30
Load in TNK (kg/d)	7,784.77	12,736.73	9,980.86	30
Load in TP (kg/d)	710.63	1,907.13	1,308.95	30

3.1. Average balance of 24 h

The 24-h report enables the quality of the water discharges to be checked and compliance with regulatory obligations. The percentages of elimination and the concentrations of the various parameters detected at the end of the biological treatment are judged by the minimum thresholds and defined by:

- Moroccan Regulations according to decree n° 2942-13 of 1st hija1434 (BO n° 6202 of November 7, 2013) sets the general limit values for discharge into surface or ground [20].
- According to Order No. 2943-13 of 1st hija1434 (October 7, 2013) sets the yields of wastewater purification devices. For domestic wastewater, the yields to take into account the rate of elimination of oxidizable materials (OM) [21].
- Regulations of the European Union and According to the Directive of the Council of the European Communities (91/271/EEC) of May 21, 1991 [22].

3.1.1. Removal efficiency, discharges and regulatory standards

Fig. 1 provides information on the degree of purification performance of the biological treatment of the water sector within the Marrakech wastewater treatment plant (Fig. 1a) and the concentration of these performance indicators at the end secondary treatment (Fig. 1b). The elimination percentages obtained exceed 90% for the performance indicators COD, TSS, TNK and BOD_5.

These high purification yields correspond to and respect the minimum performance expected and required by Moroccan and European Legislation. The TP removal yields vary between 47% and 95% with an average percentage of about 85%. With the exception of the minimum value, TP removal efficiencies are around the recommended minimum percentage and are set at 80%. This shows that the rate of elimination of pollutants at the wastewater treatment plant is very high and efficient (Fig. 1a).

The monitoring of the evolution of the concentrations of these indicators at the end of the biological treatment of the wastewater treatment plant (WWTP) showed excellent results including the elimination of COD, BOD_5 and suspended solids with an average of approximately 43.76 mgO_2/L, 4.42 mgO_2/L and 7.96 mg/L respectively and which comply with both Moroccan and European Standards. Similarly, the results of TNK (with an average of 6.09 mg N/L) are also much lower and far from the maximum Moroccan concentration set at 40 mg N/L of TNK. On the other hand, just the high value of NGL of the order of 18.90 mg N/L (which corresponds to the maximum value of TNK 13 mg N/L), obtained on the first of the month exceeds the European limit value set at 10 mg N/L of NGL. In addition, with the average value 1.31 mg P/L, the TP concentrations are around the Moroccan limit value set at 2 mg P/L, but they are much greater than or equal to the European limit concentration set at 1 mg/L (Fig 1b).

3.1.2. Daily average of NH_4^+ at the end of the biological treatment and the daily average of DO and ORP at the level of the four basins

Fig. 2 displays the results of the evolution of the daily average concentrations of NH_4^+ measured from the 24-h composite samples taken at the end of the secondary treatment and the daily average of dissolved oxygen at the level of the four biological basins (Fig. 2a). And also the evolution of the daily average values of the redox potential measurements carried out via the redox probes at the level of the four basins (Fig. 2b).

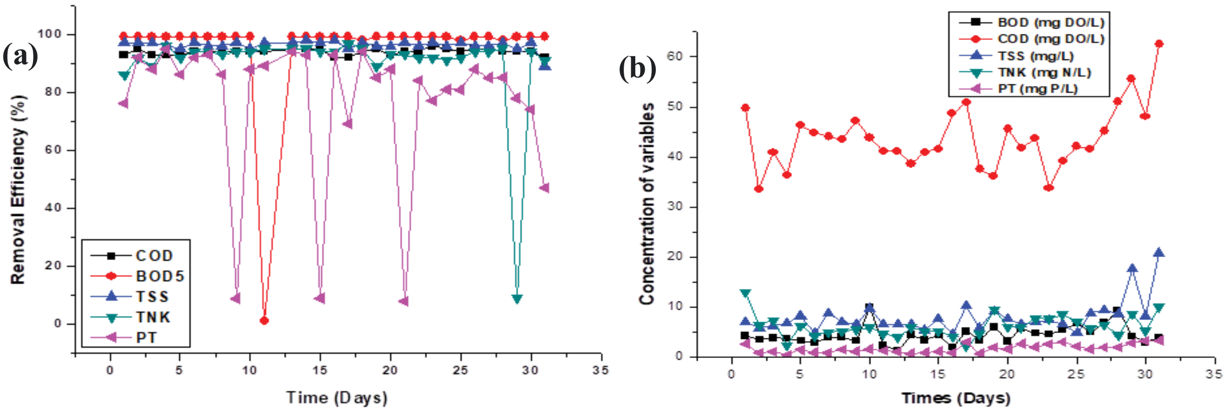


Fig. 1. Evolution of the removal efficiency of the performance indicators of TSS, COD, BOD_5, TP and TNK (a) and their concentrations at the end of the secondary treatment (b).

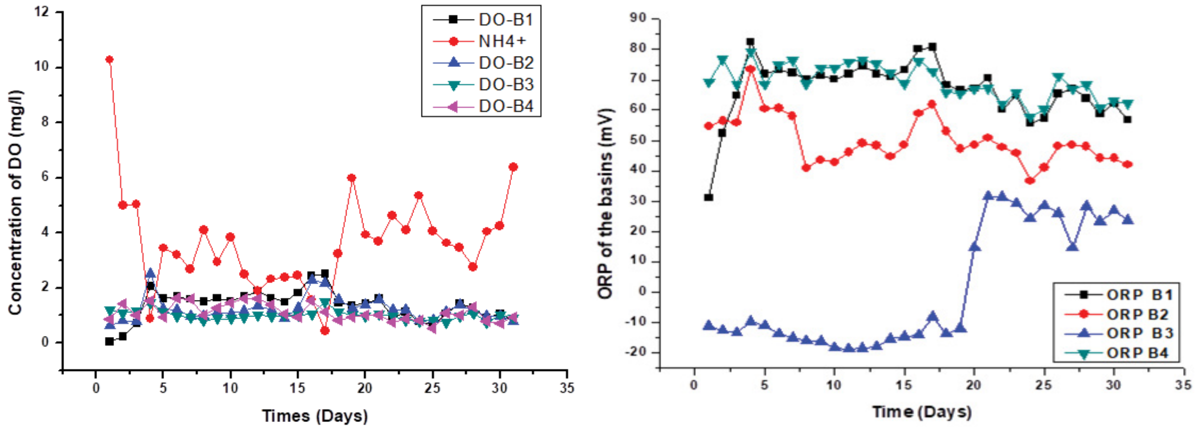


Fig. 2. Evolution of the average daily concentration of DO in its four basins (B1, B2, B3 and B4) and average daily concentration of NH_4^+ mg N/L at the outlet of the biological treatment as a whole, and evolution of daily ORP averages at the level of the four basins B1, B2, B3 and B4.

The detailed analysis of Fig. 2 shows that when the DO concentration is low, the NH_4^+ value is high and vice versa. Apart from the values relating to the discharge levels, we have observed on several occasions that the NH_4^+ values reach and exceed the threshold of 5 mg N/L which is the imperative reference value not to be exceeded in treated water. And for proper operation, ammonium concentrations should be less than or equal to 1–2 mg N/L. this is an optimal value to ensure a sufficient supply of oxygen when needed [23]. The maximum NH_4^+ value of 10.3 mg N/L is obtained on the first of the month corresponding to the maximum values of TNK and NGL (Fig. 1), and where the daily average DO concentration of basin B1 at this minimum point which is of the order of 0.01 mg/L. On the other hand, the minimum daily average concentration of NH_4^+ is 0.44 mg N/L taken on the 17th of the month, corresponding to the daily average DO concentrations of B1, B2, B3 and B4 of approximately 2.22, 2.18, 1.49 and 1.14 mg/L respectively.

In proportion to the daily mean DO concentration, the minimum point of the redox potential of B1 was recorded on the first of the month. Since the average monthly detected redox potential of B1, B2, B3 and B4 is respectively of the order of +57.98, +45.83, +0.96 and +58.46 mV; and which showed that the redox of B1 dominates the first place followed in this by B4, then B2. The daily redox potential is generally positive. In addition, the negative values of B3 which were revealed during the first two thirds of the monitoring month explain the low average monthly value of this pool which occupies the last place in the ranking, unlike the results of the other basins which are positive values. This is most likely due to the issue with the ORP sensor signal transmitter at B3 or an issue with the sensor as the rest of the month was marked with higher ORP values after fixing the issue. Indeed, the predominantly negative values signifying that the reducing conductions are convincing and this is not the case with B3. To understand what is happening in each basin, we have monitored these parameters on an ad hoc basis.

3.1.3. Daily air flow

Fig. 3 shows the evolution of the air flow supplied at the level of the four lines of biological treatment.

The average daily flow value supplied at line 1 of B1 is of the order of 202,260.9 Nm³/d with an interval of 154,638.7 to 225,835.6, this line occupies the first place followed by line 4 of B4 with an average of 183,096.37 Nm³/d and minimum and maximum values of around 150,212.48 and 212,616.38 Nm³, respectively. Coming after line 3 (from B3) with an average air flow of around 142,003.7 Nm³/d. Finally, line 2 of B2 took last place by an average value of 125,501.9 Nm³ and values fluctuate between 11,338.5 and 132,522.5 Nm³. The difference in flow delivered in level of each line is perhaps due to the difference in the duration of the aeration instructions (T1 and T2) set from time to time at the level of each basin.

3.2. Punctual results

3.2.1. Evolution of the punctual NH_4^+ results with the concomitant values of DO and ORP

Fig. 4 shows the evolution of the morning and afternoon punctual results of the DO values (mg/L), ORP (mV) corresponds to the concentrations of NH_4^+ (mg N/L)/L) evaluated at the exit of each basin (B1, B2, B3 and B4) at the end of the biological treatment.

In the presence of oxygen, the redox potential follows a logarithmic function and their values evolve in the same way. Generally, during spot samples in the morning, the two DO and ORP probes display more or less important values for the four basins. The DO values vary between (0–5.69), (0–6.64), (0–5.4) and (0.1–5.3) mg/L respectively for pools B1, B2, B3 and B4. Then, the ORP point values fluctuate between (1.69 and 92 mV) for B1; between (+14.5 and +83.9) for B2; between (–55.6 and +42.9) for B3 and between (+62.4 and +92.4 mV) for B4. On the other hand, the afternoons are characterized by more or less low values compared to those of the mornings. For B1 the ORP varies between (+8.89 and +73.9 mV), (between +15.4 and +55.1 mV) for B2, (between –34.72 and +33.7 mV) for B3 and between (+33.7 to +74.1 mV) for B4 (Fig. 4a_1–d_1). And at the same time the oxygen concentrations are for the most part very low and close to the value 0. During monitoring the ORP values which are negative mean that the medium is in a state of reduction all the time and, therefore it is not the case for B3 because the results of the nitrogen treatment are good (alternation of oxidation and reduction) (Fig. 4c_1 and c_2). These punctual morning recordings often correspond to low NH_4^+ concentrations. Like the example of B1, which generally reflects

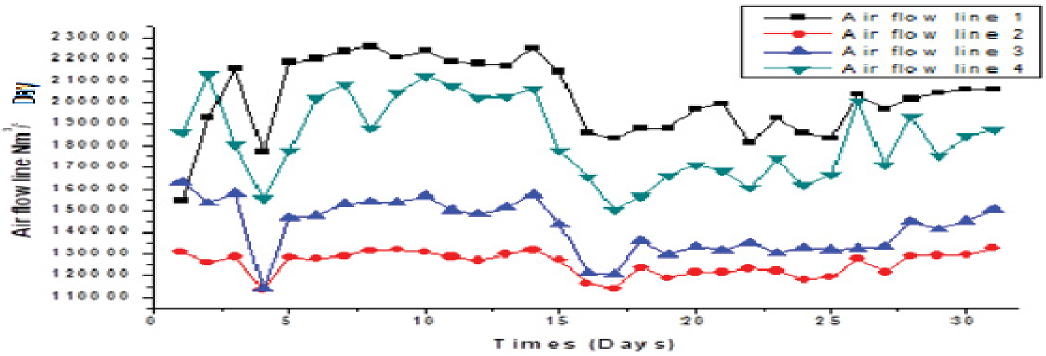


Fig. 3. Evolution of air flow supplied to the four biological treatment basins.

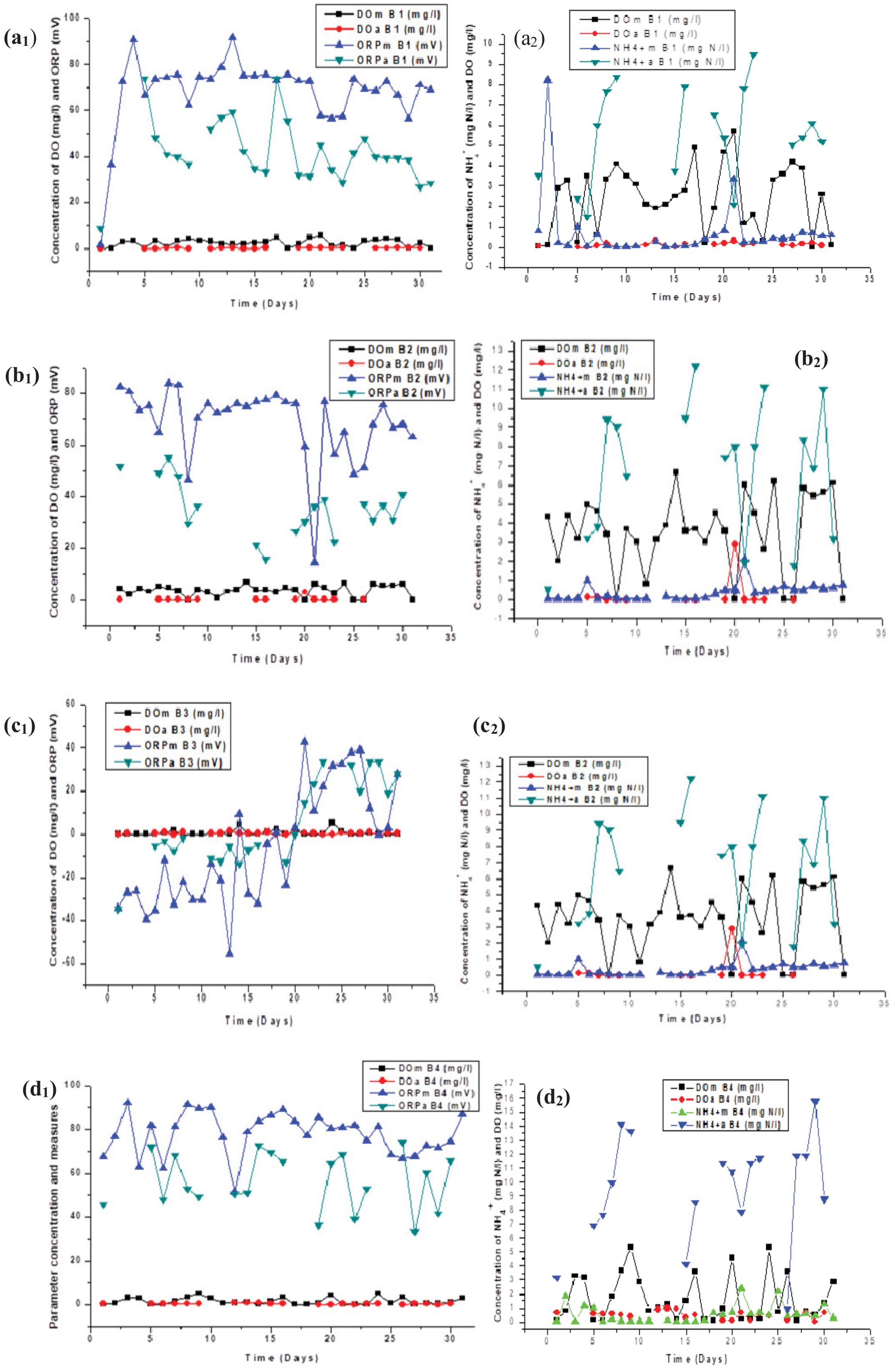


Fig. 4. Evolution of the point values of DO (mg/L) and ORP recorded concomitantly with the morning and afternoon point measurements of NH_4^+ (mg N/L) at the level of the 4 basins B1 (a_1,a_2), B2 (b_1,b_2), B3 (c_1,c_2) and B4 (d_1,d_2) (index (m) means morning and the (a) means the afternoon).

low values of NH_4^+ which drops to 0.03 mg N/L on the 9th of the month, and corresponds to 4.1 mg/L of DO and 62.7 mV of ORP. However, the remarkable values of NH_4^+ like that of the maximum value (8.25 mg N/L) (Fig. 4a$_2$) are little evaluated during the mornings. In particular, this last high value is due to insufficient oxygenation at the level of line 1 which was very low the day before. This subsequently gave an average NH_4^+ concentration (24 h ratio) exceeding the setpoint for good nitrification. On the other hand, the NH_4^+ concentrations in the afternoons are higher in front of lower recorded values of DO and ORP as already mentioned, going up to maximum values of the order of 9.49, 12.2, 12, 9 and 15.8 mg N/L for the four basins B1, B2, B3 and B4 respectively (Figs. 4a$_2$–d$_2$).

In an oxidizing environment, ammonium is transformed into nitrites then into nitrates; which induces oxygen consumption [24]. The period when the ammonium becomes weak or disappears from the environment with aeration, the oxygen level increases and this often happens in the mornings. In addition, in general, the higher the oxidant concentrations, the higher the ORP values and vice versa [7]. Then, when the activated sludge system experiences a high organic load, oxygen is consumed and a reduction in the environment occurs [25], this is precisely what can happen in the afternoon when the flow rates are high until they reach their maximum (peak flow), carrying interesting pollutant loads.

3.2.2. Evolution of the punctual NO_3^-

Fig. 5 illustrates the evolution of the results of occasional samples (morning and afternoon) of NO_3^- carried out concomitantly with that of NH_4^+. Simultaneously with the results of NH_4^+, DO, ORP for the period from the 19th to the 31st of the month, the punctual morning measurement of NO_3^- gave more or less significant concentrations compared to those of NH_4^+. They vary between (0.49 and 8.09 mg N/L); (0.42 and 7.23 mg N/L); (0.31 and 1.69 mg N/L) and (0.66 and 6.31 mg N/L) respectively for basins B1, B2, B3 and B4. The medium being more or less oxidizing in the morning, the denitrification conditions are difficult to achieve (Fig. 5a). However, dissolved oxygen values greater than 0.3 mg/L affect denitrification yields [26]. This may explain the detection of high values of NO_3^- accumulated during the nitrification phase.

In addition, the measurement of NO_3^- from some samples in the afternoon, showed generally low values compared to the concentrations of NH_4^+ detected in the same sample. This result is due to the high availability of rapidly biodegradable carbon provided by the afternoon effluent which makes nitrogen denitrification faster [27] and this quantity can be estimated by the COD. The two parameters DO and ORP are more or less related and in relation to the air flow supplied, which explains the classification of the 4 basins participating in the biological treatment, that is to say that the low average of redox and DO was taken by B3, on the other hand the highest was taken by the first basin (B1). This confirms that on the day of minimum air flow at the level of B1, the mean DO was zero and low for the ORP, which resulted in a significant value of NH_4^+ (10.4 mg N/L) at the end of secondary treatment. Especially since the longest aeration time without redox control has been programmed for the B1. On the other hand, December 17, was marked by a balance value of 24 h minimum NH_4^+ (3.75 mg N/L), due to sufficient air flows in the four basins that day.

3.3. Monitoring of treatment process by DO and ORP probe

The DO and ORP were selected to characterize the state of the continuous activated sludge process and as control variables. In this article we will determine from the DO profiles, the ORAS, to characterize the aeration phases, including oxidation of organic matter and nitrification [16], the time to stop the aeration (t_{off}). ORAS$_{\text{arrow}}$, DO$_{\text{elbow}}$, NH_4^+ slope, over-aeration (OA) slope [28] and OUR are defined as follow:

ORAS represents the slope of the linear approximation to the DO curve during the aeration cycle:

$$\text{ORAS} = \frac{\text{DO}_h - \text{DO}_{\text{on}}}{t_h - t_{\text{on}}} \tag{2}$$

where DO$_h$ represents the highest value DO reaches and DO$_{\text{on}}$ its value when aeration starts. t_h and t_{on} represent the time at those values. The DO curve provides information

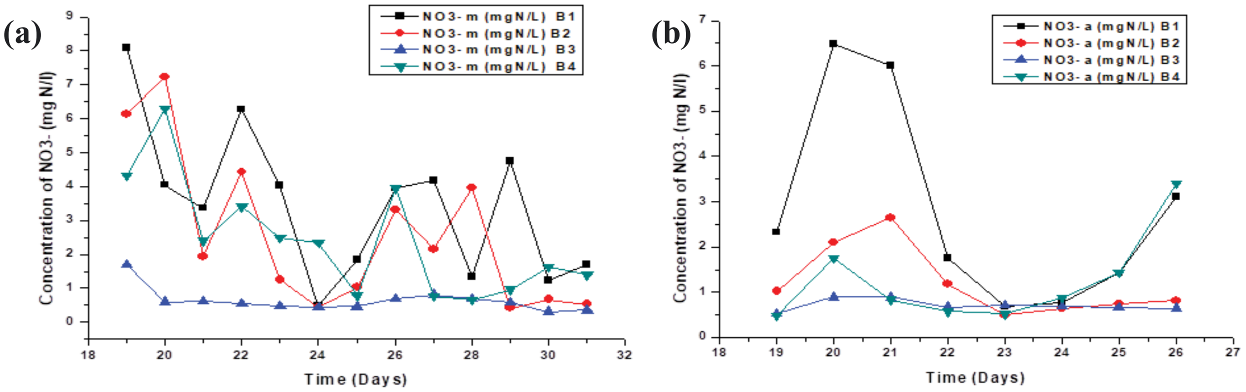


Fig. 5. Morning and afternoon evolution of occasional NO_3^- results at the exit of the four basins B1, B2, B3 and B4. (index (m) means morning and the (a) means the afternoon).

regarding the balance between the rate at which oxygen is transferred to the vessel by blowers and the rate at which bacteria consume it [16].

$\text{ORAS}_{\text{arrow}}$: This parameter measures the maximum distance between the rising DO profile and the linear approximation of the DO profile during the aeration phase [28]:

$$\text{ORAS}_{\text{arrow}}\left(\text{DO}_i, t_i\right) = \frac{\left(t_{\text{off}} - t_{\text{on}}\right)\left(\text{DO}_i - \text{DO}_{\text{on}}\right) + \left(t_i - t_{\text{on}}\right)\left(\text{DO}_{\text{off}} - \text{DO}_{\text{on}}\right)}{2\sqrt{\left(\text{DO}_{\text{off}} - \text{DO}_{\text{on}}\right)^2 + \left(t_{\text{on}} - t_{\text{off}}\right)^2}} \tag{3}$$

where (t_{on}, DO_{on}) defines the start of the aeration phase, (t_{off}, DO_{off}) is the end of the aeration phase, and (t_i, DO_i) is the DO actual value at time t_i.

DO_{elbow} defines the end of nitrification and the start of the over-aeration phase. It is usually calculated as the change in the rise slope of the DO profile. However, in this work, it has been obtained based on $\text{ORAS}_{\text{arrow}}$, in order to guarantee that its value is more accurate and less sensitive to outliers: the DO value, in its rising profile, for which the $\text{ORAS}_{\text{arrow}}$ is a maximum.

$$\text{DO}_{\text{elbow}} = \frac{\text{DO}_i}{\text{ORAS}_{\text{arrow}}} = \max\begin{pmatrix} \text{ORAS}_{\text{arrow}}\left(\text{DO}_i, t_i\right) \\ \vee \text{i} \in \left[\text{DO}_{\text{on}}, \text{DO}_{\text{off}}\right] \end{pmatrix} \tag{4}$$

- NH_4^+ slope measures the DO slope between the start of the aeration phase and DO elbow:

$$\text{NH}_4 + \text{slope} = \frac{\text{DO}_{\text{elbow}} - \text{DO}_{\text{on}}}{t_{\text{elbow}} - t_{\text{on}}} \tag{5}$$

- OA slope measures the DO slope between DO elbow and the maximum DO value: $\text{ORAS}_{\text{arrow}} = \max(\text{ORAS}_{\text{arrow}}(\text{DO}_i, t_i) \ \forall\ \text{DO}_i \in [\text{DO}_{\text{on}}, \text{DO}_{\text{off}}],\ \forall\ t_j \in [t_{\text{on}}, t_{\text{off}}]$.

$$\text{OA}_{\text{slope}} = \frac{\text{DO}_{\text{off}} - \text{DO}_{\text{elbow}}}{t_{\text{off}} - t_{\text{elbow}}} \tag{6}$$

- Oxygen-uptake rate (OUR):

It represents the oxygen consumption rate in the non-aeration cycle. Its value can be obtained from:

$$\text{OUR} = \frac{0.8\text{DO}_h - 0.4\text{DO}_h}{t_{0.4} - t_{0.8}} \tag{7}$$

where DO_h is the highest value reached by DO when aeration is switched off. DO is measured at 80% and 40% of that maximum value DO (with $t_{0.4}$ and $t_{0.8}$ representing their corresponding times) to avoid nonlinearities that appear when its value begins to decrease and when it approaches 0 mg/L, as established in Monod kinetics. OUR represents a very precise approximation to the value of the DO curve slope in that time interval [19].

Then from ORP profiles, the nitrate breakpoint (NBP) is determined, it represents the value of the ORP profile when DO elbow appears [19]. Then during the anoxia phase of the cycle, ORP knee nitrate is determined which is identified as the second inflection point during the aerator off cycle, where the slope of the ORP curve begins to increase after a period of flattening [29]. In the denitrification process, the ORP curve decreases at a slow rate initially, but it falls steeply when the process reaches a bending point, known as 'nitrate knee' α of the ORP profiles [16]. ORP knee is a checkpoint signifying that nitrate has been effectively reduced [18,30]. Another parameter is ORP plateau, this parameter measures the change rate in ORP between the oxidation phase (where oxygen is the electron acceptor) and the anoxic phase (where nitrate is the acceptor). It is defined as the ORP slope between the maximum ORP and the ORP for which DO is lower than 0.1 mg/L [19]:

$$\text{ORP plateau} = \frac{\left(\text{ORP}\middle|\text{DO} = 0.1 - \text{ORP}_{\max}\right)}{\left(t\middle|\text{DO} = 0.1 - t\text{ORP}_{\max}\right)} \tag{8}$$

Plus ORP arrow, the maximum distance between the ORP curve and its linearization [28]. This parameter is related to the inhibition of denitrification process caused by substrate limitations. ORP arrow is obtained from:

$$\text{ORP}_{\text{arrow}}\left(\text{ORP}_i, t_i\right) = \frac{\begin{bmatrix} \left(t_\alpha - t_p\right)\cdot\left(\text{ORP}_p - \text{ORP}_i\right) \\ +\left(t_i - t_p\right)\cdot\left(\text{ORP}_\alpha - \text{ORP}_p\right) \end{bmatrix}}{\sqrt{\left(\text{ORP}_p - \text{ORP}_\alpha\right)^2 + \left(t_\alpha - t_p\right)^2}} \tag{9}$$

where ORP_p is the ORP value when DO is 0 mg/L, ORP_α the value where the ORP knee appears and ORP_i the ORP values between these two limits. t_p, t_α and t_i represent their corresponding time instants.

ORP decrease average slope (ODAS) represents the linearization of the ORP profile while the denitrification process is carried out (during t_{dn}).

In this document, certain cycles will be detailed including bending points that allow us to understand and interpret the nitrification/denitrification process, only on days when the NH_4^+ removal yields reach their maximum and their minimum.

3.3.1. Low removal efficiency of NH_4^+ in the four basins

Fig. 6 shows the number of aeration–non-aeration cycles linked to the evolution of the ORP (mV and DO at the level of each biological treatment basin (B1, B2, B3, B4) on the first of the month. 18 aerobic/anoxia cycles are alternated at the level of the first pelvis (B1), with a maximum DO value of around 0.27 mg/L and throughout the day is less than or around 0.1 mg/L. For the pool (B2) the number of cycles is close to 19, some of which have a maximum ORP of around +83.35 mV, identically for B3 (19 cycles) with DO values varying between 0.001 and 7, 79 mg/L, then the ORP values vary between –41.01 and +18.30 mV. On the

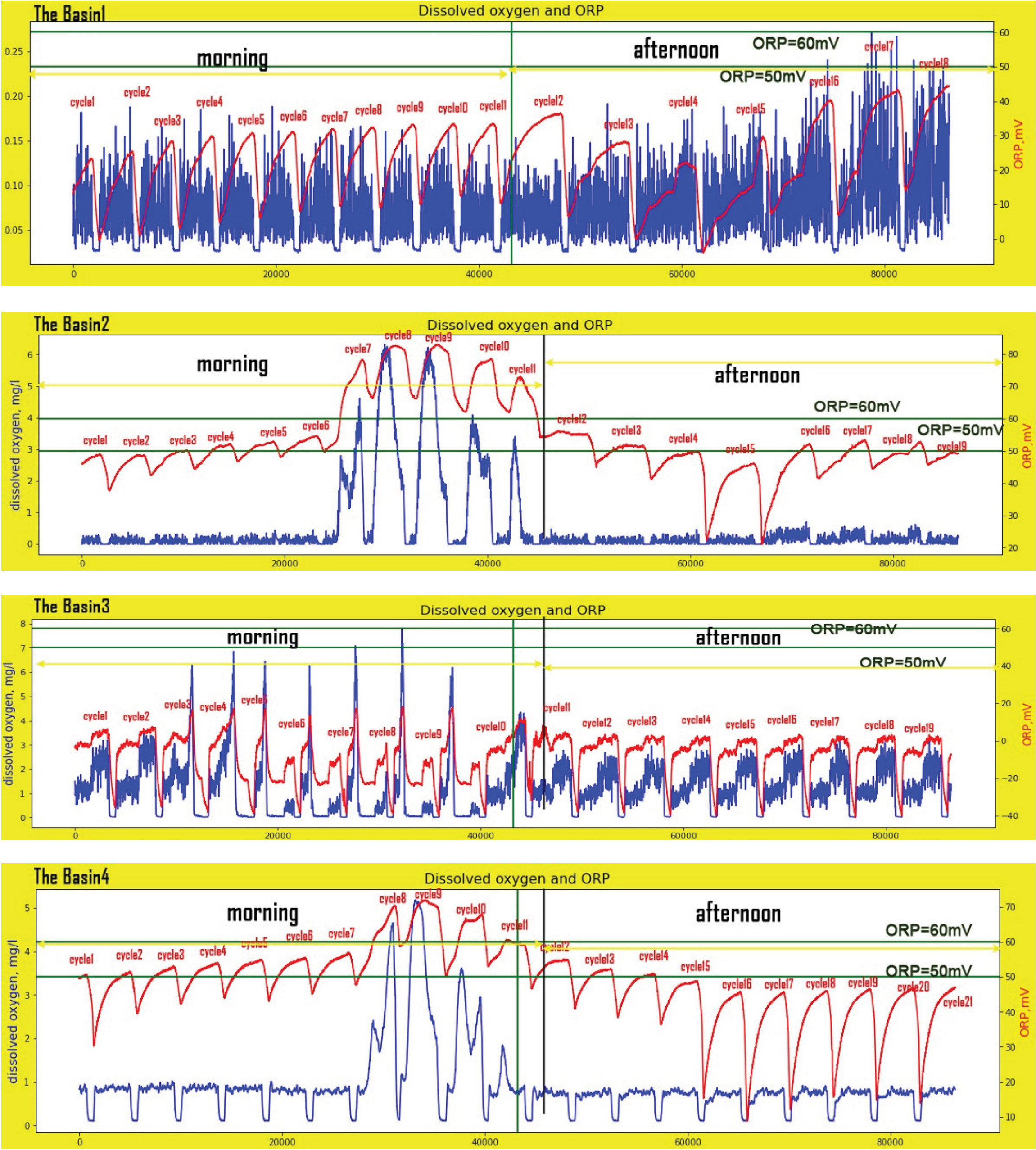


Fig. 6. Illustration of the alternation of aeration–non-aeration cycles and evolution of ORP (in red) and DO (in blue) at the level of pools 1, 2, 3 and 4 during the day when the removal efficiency of NH_4^+ is low.

other hand, the B4 underwent nearly 21 cycles. In the case of reactors B1, B2, B3 and B4, not only the variation of the pollutant load determines the number of aeration/non-aeration cycles per day but also the duration of the setpoints T1 and T2 programmed at the level of each basin (on the other hand, the two setpoints T3 and T4 are identical us for the 4 basins. Ensuring a reduction in the setpoint duration T1 (ventilation without redox control) leads to an increase in the starting frequency of the aerators, it can sometimes reach up to two starts per hour. And therefore either a limitation of the oxygenation of the medium or insufficient time for denitrification, or an overconsumption of energy.

3.3.2. Key points regarding the aeration–non-aeration cycle

3.3.2.1. Cycles 9 and 10 in B2 and the low removal efficiency of NH_4^+

Given the amount of information provided by each biological treatment basin which has a minimum and maximum value and a range of ORP and DO varying from one basin to another, only a few cycles have been chosen and illustrated in order to be understood using the key points. Fig. 7 shows the evolution of the ORP and DO profiles including the key points of two morning cycles 9 and 10 within basin 2; at the beginning of the month.

When the aerators are turned on (t_{on}), an increase in the oxygen concentration is observed at cycle 9 and identically for cycle 10. Determination of the linear approximation of the DO curve during the aeration phase ORAS, then $ORAS_{arrow}$ (the maximum distance between this linear approximation and the DO profile) 12.606 for cycle 9 and 12.092 for cycle 10 allow the calculation of DO_{elbow} 0.487 and 0.4878 mg/L for each cycle respectively. The DO_{elbow} defines the end of nitrification during the over-aeration phase, that is to say the end of nitrifying activity which corresponds to low concentrations of NH_4^+ in the reactor, and is accompanied by a sudden drop in sludge respiration which implies a rapid increase in the dissolved oxygen concentration which reaches almost 6 mg/L at the level of these two cycles. This rapid increase in the dissolved oxygen concentration results in an inflection point on the ORP curve which is the NBP. It corresponds to the disruption of the nitrate production rate because at this point ammonium becomes limiting for the autotrophic population and the reason of nitrification is diminished rapidly as well. The NH_4^+ slope, represents the slope of DO between the start of the aeration phase (t_{on}) and DO_{elbow}. This parameter can be considered as an elimination rate of NH_4^+, which is of the order of 0.000706 mg/L s for cycle 9 and of the order of 0.0005891 mg/L s for the cycle 10. Then, depletion of DO from the environment allows the anoxic phase to take place to denitrify the accumulated NO_3^- from the first phase. Initially, the ORP curve decreases at a slow rate, (ORP plateau), representing the transition phase between the aerobic phase and the anoxia phase. Then the ORP decreases rapidly until the appearance of the alpha point, at time 31,464 s in cycle 9 of B2, and at time 35,604 s in cycle 10 of B2, the detection of the alpha point or the nitrate knee on the ORP curve is a sign of nitrate depletion during the non-aeration phase, complete denitrification.

3.3.2.2. Cycles 8 and 9 in B4 and the low removal efficiency of NH_4^+

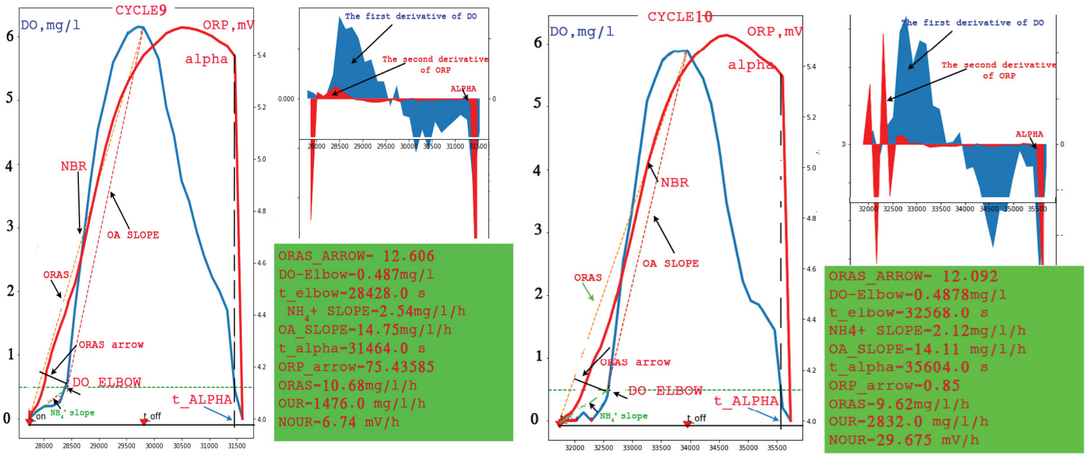
Fig. 8 illustrates the development of the two morning cycles 8 and 9 of B4 with net inflection points recorded at the beginning of the month. DO_{elbow} 1.782 and 1.19 mg/L for cycles 8 and 9 respectively show the end of nitrification for each cycle, plus the NBP point showing the breaking point of NO_3^- production. Then, in the anoxic phase, the appearance of alpha points at the level of the two cycles shows that the denitrification is complete and that the NO_3^- is exhausted from the environment.

Then, according to Martín de la Vega and Jaramillo-Morán [19], the higher values of OUR indicates the presence of easily biodegradable organic matter, which is not consumed during the previous aeration cycle. The OUR in the non-aeration phase is higher in cycle 9 compared to cycle 8 which can show that the quantity of organic matter which is easily biodegradable during cycle 9 is more or less important by report to cycle 8.

Afternoon cycles are characterized by low concentrations of DO and ORP lower than those of the mornings, which implies a weak nitrification and accumulation of NH_4^+ (Fig. 6). Subsequently some inflection points cannot appear. But generally the punctual drop (over a cycle) in nitrification efficiency (in the case of afternoon cycles) is compensated by a spread in the time of elimination of total nitrogen. In fact, there are often periods of polluting under load which will ensure the nitrification of the incoming nitrogen (as in the case of morning cycles).

3.3.2.3. Cycles 3 and 17 in basin 2 and high removal efficiency of NH_4^+

Fig. 9 represents the evolution of the ORP profiles during the aeration and non-aeration phases of the morning cycle number 3 and of the afternoon cycle number 17 in B2. The day the overall ammonium removal performance shows a high value and a low concentration of NH_4^+ at the outlet (17th of the month). When the aerators are switched on (t_{on}), an increase in ORP values is noticed at the level of the two cycles 3 and 10, the appearance of the point of inflection beta, NBP during the aeration phase on the ORP curve of the two cycles, presents the breaking point of the nitrate production rate and the ammonium becomes limiting, therefore



```
ORAS_ARROW= 12.606
DO-Elbow=0.487mg/l
t_elbow=28428.0 s
 NH4+ SLOPE=2.54mg/l/h
OA_SLOPE=14.75mg/l/h
t_alpha=31464.0 s
ORP_arrow=75.43585
ORAS=10.68mg/l/h
OUR=1476.0 mg/l/h
NOUR=6.74 mV/h
```

```
ORAS_ARROW= 12.092
DO-Elbow=0.4878mg/l
t_elbow=32568.0 s
NH4+ SLOPE=2.12mg/l/h
OA_SLOPE=14.11 mg/l/h
t_alpha=35604.0 s
ORP_arrow=0.85
ORAS=9.62mg/l/h
OUR=2832.0 mg/l/h
NOUR=29.675 mV/h
```

Fig. 7. ORP (in red) and DO (in blue) profiles during cycles 9 and 10 in basin 2: ORAS, $ORAS_{arrow}$, DO_{elbow}, beta (NBP), NH_4^+ slope, OA slope, OUR, ORP arrow, and alpha (ORP knee).

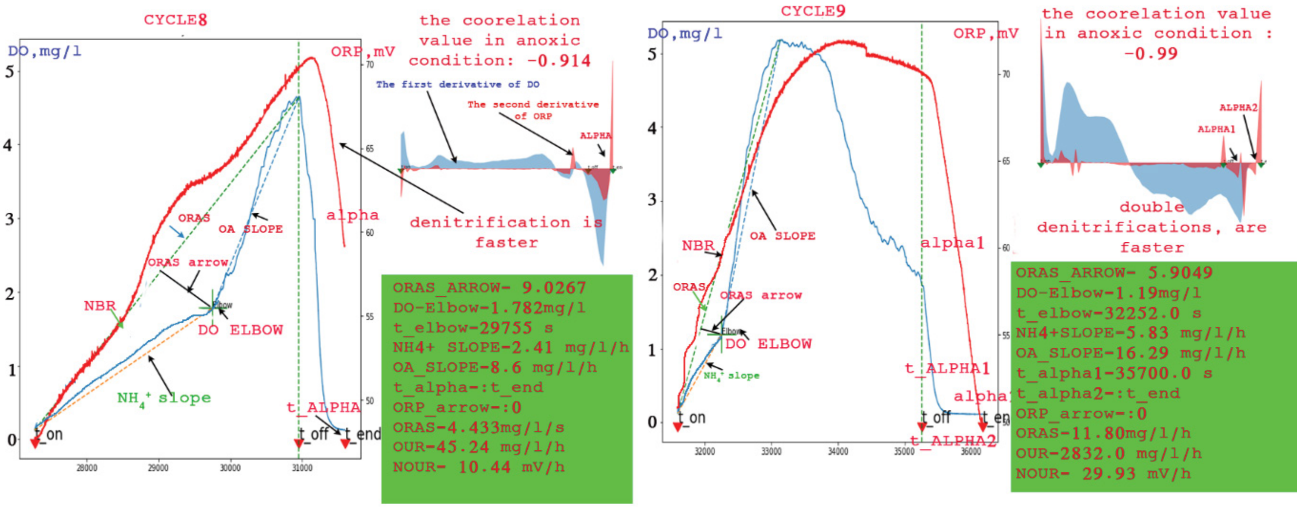


Fig. 8. ORP (in red) and DO (in blue) profiles during cycles 8 and 9 in basin 4: ORAS, ORAS$_{\text{arrow}}$, DO$_{\text{elbow}}$, beta (NBP), NH_4^+ slope, OA slope, OUR, ORP arrow and alpha (ORP knee).

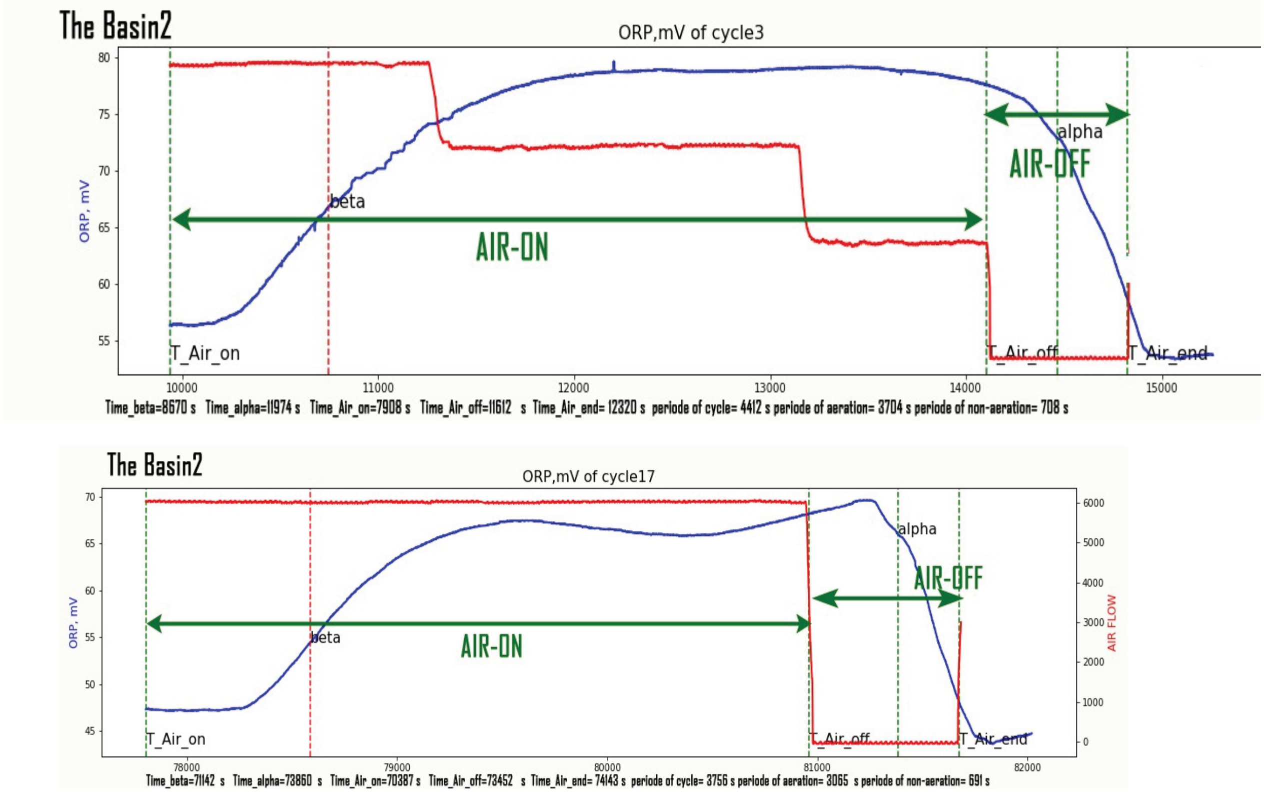


Fig. 9. ORP (in blue) and air flow (in red) profiles during cycles 3 and 17 in basin 2: beta (NBP) in aeration phase and alpha (ORP knee) in non-aeration phase.

the nitrification is complete. In addition, the appearance of the second alpha point (nitrate knee) during the non-aeration phase shows that the denitrification is complete during the two cycles 3 and 17. This explains the performance of the nitrogen elimination treatment during this day.

Knowing that the DO concentration must contain less than 2 mg/L and preferably between 0.5 and 1 mg/L [31]. According to all the above results, on the one hand, the morning cycles mostly exceed this interval and therefore undergo over-aeration which imposes a loss of energy and therefore the ventilation time may have to be shortened. On the other hand, the majority of afternoon cycles will see periods of under aeration inducing the accumulation of NH_4^+, and may need to undergo enlargement. It emerges from all the recorded values of ORP that none reaches +100 mV, (value between which and +350 mV nitrification takes place [9]. It needs to reach +50 mV for the environment to become aerobic and the nitrification takes place. This is the case with the reactors at the Marrakech WWTP.

4. Conclusion

The biological treatment of wastewater at the Marrakech WWTP shows good elimination of organic matter and nitrogen with purification yields that meet national and European discharge standards and elimination rates. Average and point analyzes of the various NH_4^+, DO and ORP parameters have shown that the alternation of aeration/non-aeration cycles by the presence of DO allows nitrification of NH_4^+ then its absence allows denitrification of NO_3^- produced by the first step.

Afternoon cycles are characterized by low concentrations of DO and ORP lower than those of the mornings. But generally the punctual drop in the nitrification yield during a given cycle is often compensated for by the performance of the cycles receiving polluting under loads which will ensure the nitrification of the incoming nitrogen.

The activated sludge system is a continuous system that is difficult and time-consuming to analyze, especially on a real scale, due to the large amount of information received and controlled at the same time. The bending points appearing on the ORP and DO control curves are used to interpret the aeration–non-aeration process in the biological basins of the Marrakech WWTP. It even allows you to set the correct ORP thresholds and timing for adaptive adjustment to the incoming load condition. This is the objective of the next article, which will study possible ways of saving the energy provided by aeration.

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