Solids and hydraulic retention time effect on N_2O emission from moving bed membrane bioreactors

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Abstract

Biological nutrients removal was operated at different solids and hydraulic retention times (SRT and HRT, respectively) in order to assess their influence on nitrous oxide (N_2O) emission from a hybrid moving bed membrane bioreactors. The observed results showed that the N_2O production decreased when the SRT/HRT was decreased. The maximum N_2O gaseous concentration (0.2 mg N_2O-N L^{-1}) was measured in the aerobic reactor at the end of Phase I (SRT/HRT of 56d/30h), and it decreased through Phases II (SRT/HRT of 31d/15h) and III (SRT/HRT of 7d/13h). From mass balances over the reactors of the system, the aerated (aerobic and membrane) reactors were the largest producers of N_2O. This shows that the great part of N_2O was produced during the nitrification process.
Keywords: N_2O; Biological nutrient removal; Integrated fixed film activated sludge Membrane bioreactor; sludge retention time; hydraulic retention time

1. Introduction

Nutrients (phosphorus and nitrogen) as well as organic carbon can have several adverse environmental impacts when released into the environment. Indeed, nutrients favor eutrophication and can be toxic to aquatic organisms [1,2]. Among the various methods for nutrients and carbon removal from wastewater, biological processes are highly effective compared to other methods. Biological nutrient removal (BNR) processes that couple nitrogen and phosphorus removal have been deeply studied during the last decades. BNR processes offer the advantage of avoiding the use of chemicals, thus preventing all the issues related to chemical sludge management/disposal. Biological nitrogen removal is usually realized by aerobic nitrification followed by the heterotrophic denitrification under anoxic conditions. In particular, nitrogen removal processes attracted particular attention in the last years since they can be responsible of nitrous oxide (N_2O) production [3] and emission to the atmosphere. N_2O is a greenhouse gas (GHG) with a high global warming potential (GWP) (298 times higher than carbon dioxide - CO_2), whose anthropogenic emission [4,5] needs to be reduced [6]. The N_2O production in WWTPs occurs mainly during biological nitrogen removal. Indeed,

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N_2O can be produced both during nitrification and denitrification. More precisely, N_2O can be produced by Ammonia Oxidizing Bacteria (AOB) (AOB denitrification or incomplete hydroxylamine oxidation) and by heterotrophic bacteria due to the incomplete denitrification [7–11].

Biological phosphorus removal is achieved by applying an anaerobic-aerobic sequence, exploiting the ability of polyphosphate-accumulating organisms (PAOs) to store large amounts of phosphorus as polyphosphates [12]. Nitrogen and phosphorus removal are inter-related, indeed during the anoxic conditions denitrifying PAOs (dPAOs) can also remove nitrogen and phosphorus simultaneously using nitrate (NO_3^-) or nitrite (NO_2^-) as electron acceptors [13]. Consequently, N_2O formation can also occur during biological phosphorus removal. Indeed, Kampschreur et al. [7] reported that N_2O could accumulate during dPAOs activity removal process due to the competition for electrons between the denitrifying enzymes. With this regard, it was found that with the increase of the influent phosphorus loading rate the N_2O emission were reduced, due to the decrease of N_2O yield by heterotrophic denitrification [14]. Recently, many efforts have been done in order to investigate the role of biological phosphorus removal processes in N_2O emission. With this regard, Ribera-Guardia et al. [15] have found that glycogen accumulating organisms (GAOs), which compete with PAOs for the organic carbon availability without performing phosphorus removal, mainly favor the N_2O accumulation. Consequently, in order to improve phosphorus removal and reduce the N_2O emissions, dPAOs over denitrifying GAOs must be favored. Despite the attempts of the last years, knowledge on the N_2O formation during biological phosphorus removal processes is still limited and need further investigation. This lack of knowledge is even more pronounced when the BNR processes are implemented by adopting innovative and advanced technologies. Indeed, during the last years, researchers have aimed at achieving the stringent effluent limits imposed for nutrients focusing the attention on the use of advanced wastewater treatment [1,16]. For example, advanced wastewater treatment include the use of membrane bioreactors (MBRs) or the moving bed biofilm reactor (MBBR) and their coupling with the moving bed biofilm membrane bioreactor (MB-MBR) or Integrated Fixed Film Activated Sludge (IFAS) [17]. This latter has the advantage of combining suspended and attached biomass inside the same reactor coupled with the membrane for solid liquid separation. However, the role of specific operating parameters affecting the gaseous emissions from these systems has been scarcely investigated. Todt and Dörsch [18] have recently highlighted that most of the literature studies focus on suspended biomass and that poor attention has been paid to biofilms. Therefore, more knowledge is required on the key operating factors affecting both biomass interactions (suspended and attached) and N_2O emissions from biofilm systems. Concerning the role of the solids (SRT) and hydraulic (HRT) retention time on N_2O emissions, as authors are aware, only few studies can be found in the technical literature investigating a two-stage membrane bioreactor treating solid waste leachate at different HRT (5 to 2.5 days) [19]. Nuansawan and co-workers [19] found that with the decrease of the HRT (from 5 to 2.5 days) the N_2O emitted decreased. More precisely, the N_2O emission factor (% of the influent N emitted as N_2O) related to the anaerobic tank reduced from 0.16% to 0.04% from the HRT of 5 to 2.5 days, respectively. Nevertheless, as authors are aware, very little knowledge still exists on the role of SRT and HRT on BNR processes in terms of N_2O emissions.

Bearing in mind these considerations, in this study a University of Cape Town (UCT) Integrated Fixed Film Activated Sludge (IFAS) Membrane BioReactor (MBR) pilot plant has been monitored for 87 days at three different SRT/HRT phases. More specifically, the pilot plant was operated for three phases (each of around 30 days): Phase I SRT/HRT 56d/30h, Phase II SRT/HRT 31d/15h and Phase III SRT/HRT 7d/13h. The SRT and HRT control has been carried out by manipulating the influent and sludge wastage flow rates. The higher influent flow rates resulted in increased organic loading rates, which required higher sludge waste flow rates to keep the suspended solids concentration in the aerobic reactor at about 3 gTSS L^{-1}, which in turn decreased the SRT of the suspended biomass. During each

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phase, the role of SRT/HRT on N_2O production by both suspended biomass and biofilm has been investigated.

2. Material and methods

2.1 The UCT-IFAS-MBR pilot plant

The UCT-IFAS-MBR pilot plant under study was operated according to the schematic layout shown in Figure 1. The pilot plant comprised a sequence of anaerobic (62 L), anoxic (102 L) and aerobic (211 L) reactors according to the UCT scheme [20] (Figure 1). Furthermore, according to the side stream configuration, an ultrafiltration hollow fibre membrane (PURON® 3 bundles, pore size 0.03 μm, membrane area 1.4 m^2) was located inside an aerated 36 L MBR tank for solid-liquid separation. Moreover, according to the IFAS-MBR systems, the anoxic and aerobic compartments were filled with suspended plastic carriers for biofilm growth (Amitech® carriers, density = 0.95 g cm^{-3} and specific surface = 500 m^2 m^{-3}), with a 15 and 40% filling ratio in the anoxic and aerobic reactor, respectively.

The membrane module was operated in a 10 minute cycle; 9 min filtration (permeate pumped from the MBR tank, through the membrane, to the clean in place tank – CIP) and 1 min backwashing (permeate pumped from the CIP back to the membrane). The pilot plant was operated at three different SRT/HRTs phases, from 56d/30h in Phase I to SRT/HRT 7d/13h in Phase III, by increasing the influent wastewater flow rate (Q_{IN}) and consequently increasing the instantaneous permeate flow rates ($Q_{OUT,IST}$). For each Phase the backwashing flow rates (Q_{BW}) was set equal around 1.2 times $Q_{OUT,IST}$. Thus, the net permeate flow rate (Q_{OUT}) followed the influent flow changes.

According to the UCT scheme, a flow rate (Q_{R1}) was continuously recycled from the anoxic to the anaerobic tank, at a Q_{R1}/Q_{IN} (r) ratio of 1.5. Furthermore, a flow rate (Q_{R2}) of mixed liquor was pumped from the aerobic to the MBR tank, with a Q_{R2}/Q_{IN} (s+1) ratio of 5, where s is the sludge return recycle ratio (the internal recycle form the aerobic to the anoxic compartment, for heterotrophic denitrification). Therefore, a flow rate ($Q_{RAS} = sQ_{IN}=Q_{IN}$) was continuously returned from the MBR to the anoxic tank through an Oxygen Depletion Reactor (ODR) (40 L) having the role to reduce the dissolved oxygen (DO) recycled to the anoxic tank (Figure 1). In order to maintain an approximately constant aerobic reactor total suspended solid (TSS) concentration (X_{taer}, gTSS L^{-1}), the waste sludge flow rate (Q_{WAS}) withdrawn from the aerobic reactor was increased with each decrease in HRT. The increase in Q_{WAS} decreased the SRT from 56 d in Phase I to 31 d in Phase II and 7 d in Phase III.

In order to allow the gas sampling all the reactors were equipped with specific covers (Figure 1).

[FIGURE 1]

2.2 Experimental campaign and influent wastewater features

The UCT-IFAS-MBR pilot plant was operated for 87 days, around 30 days for each phase. Table 1 lists the main influent and operational features of the three experimental phases.

The pilot plant was fed with municipal wastewater spiked with a synthetic wastewater containing sodium acetate (CH_3COONa) (30% of COD), glycerol ($C_3H_8O_3$) (70%) and dipotassium hydrogen phosphate (K_2HPO_4); nitrogen was provided by the municipal wastewater. The synthetic wastewater was added in order to maintain an influent C/N concentration ratio of 10 mgCOD/mgTKN-N. Indeed, the real raw wastewater (collected from the sewer system of the University campus) was rich in TKN rather than organic carbon (C/N ratio of the real wastewater close to 2.7). Therefore, it was needed to spike the feeding wastewater with external organic substrates.

An extensive sampling campaign has been performed during the pilot plant operation. More precisely, the influent wastewater, permeate and the mixed liquor (from each tank) samples were

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withdrawn twice per week and the key chemical/physical compounds were analysed. Total and volatile suspended solids (TSS, VSS), total chemical oxygen demand (COD_{TOT}), supernatant COD (COD_{SUP}), ammonium nitrogen (NH_4-N), nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N), total nitrogen (sum of all nitrogen forms) (TN), phosphate (PO_4-P), and total phosphorus (TP), Biochemical Oxygen Demand (BOD), dissolved nitrous oxide (N_2O). All the aforementioned parameters were measured in accordance to standardized procedures [21]. Other operational parameters as pH, dissolved oxygen (DO) concentration and temperature were also measured by adopting a multi-parameter probe. Furthermore, from the anaerobic, anoxic, aerobic and MBR tanks gas samples were withdrawn to measure gaseous N_2O concentration. The biofilm growth on the suspended carriers was evaluated according to the procedure reported by [22]. Briefly, carrier samples were periodically taken from the anoxic and aerobic compartments dried at 105°C and then weighed (W1). After biofilm was removed, the carriers were dried again and then weighed (W2); the amount of the attached biomass was then calculated as W1 - W2.

[TABLE 1]

2.3 Removal performance

Data acquired during experiments enabled evaluation of the removal performances of the pilot plant according to [23], i.e. the biological COD removal efficiency (η_{BIO}) and the total COD removal efficiency (η_{TOT}). The key difference between η_{BIO} and η_{TOT} is that η_{BIO} has been calculated without taking into account the removal effect due to the membrane filtration. Indeed, the difference between η_{TOT} and η_{BIO} represents the removal efficiency due to the membrane filtration ($\eta_{CAKE,FILT}$). Moreover, the nitrification (η_{nit}), denitrification (η_{denit}), nitrogen (ηN_{total}) and ortho-P (OP) (η_{OP}) removal efficiencies were also evaluated according to literature [23].

2.4 Gas sampling

Gas samples were collected from the funnel shaped cover of each tank (anaerobic, anoxic, aerobic and MBR) with syringes and then transferred into glass vials. Gas samples were analysed by adopting a gas chromatograph (GC) (Thermo Scientific™ TRACE GC), equipped with Electron Capture Detector (ECD) to evaluate the N_2O concentration. The air/gas exit velocity was measured with a TMA 21HW Hot Wire anemometer. Data of air/gas exit velocity were used to evaluate the gas flux emitted from each tank.

Mixed liquor samples collected from the anaerobic, anoxic, aerobic, MBR and ODR reactors as well as from the permeate line were treated according to the method proposed by [24] in order to evaluate the dissolved N_2O concentration. Also, the N_2O emission factors were calculated with the procedure proposed by [25].

For further details regarding gas sampling and analysis, the reader is referred to the literature [26,27].

A N_2O-N mass balance over each tank was evaluated in order quantify the flux of produced/consumed N_2O-N according to Equation (1).

$$N_2O-N_{p,c} = N_2O-N_{dissolved,OUT} - N_2O-N_{dissolved,IN} + N_2O-N_{Gas,OUT} \quad (1)$$

where: N_2O-$N_{dissolved,IN}$ [mg N_2O-N h^{-1}] and N_2O-$N_{dissolved,OUT}$ [mg N_2O-N h^{-1}] are the fluxes of the influent and effluent dissolved N_2O-N in each reactor, respectively; N_2O-$N_{Gas,OUT}$ [mg N_2O-N h^{-1}] is the gaseous N_2O-N exiting a reactor; and N_2O-$N_{p,c}$ [mg N_2O-N h^{-1}] is the flux of N_2O-N produced (if positive) or consumed (if negative) in the reactor.

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3. Results and discussion

3.1 Pilot plant performances and membrane fouling

For sake of completeness a brief overview of the UCT-IFAS-MBR performance are reported in this section. Figure 2 shows the trend of η_{BIO}, η_{TOT} and $\eta_{CAKE,FILT}$ (Figure 2a), ηN_{total}, η_{nit} and η_{denit} (Figure 2b), η_{OP} (Figure 2c) throughout experiments. Table 2 summarizes the average values of pollutant removal efficiency for each experimental phase. Although standardized methods have been adopted, data presented here are affected by the uncertainty related to sampling, handling and analytical procedures.

By analyzing data reported in Figure 2a and in Table 2, it is worth noting that the UCT-IFAS-MBR pilot plant showed excellent treatment performance in terms of COD removal. Indeed, the average total COD removal was of 98.6% in Phase I (SRT=56d) and 99% for both Phase II (SRT=31d) and Phase III (SRT 7d) (Figure 2a, Table 2). A slight increase of the η_{BIO} occurred (from 84% to 88.5%) when the HRT was decreased from 30 hours (Phase I) to 15 hours (Phase II) (Figure 2a, Table 2). This result is likely due to the fact that with the increase of the organic loading rate (due to the increase of the influent flow rate) from Phase I to Phase II the heterotrophic activity of both suspended and biofilm have been promoted. Indeed, as deeply discussed by [34], an increase of the heterotrophic growth rate, $\mu_{H,max}$, for both suspended biomass (from 6.82 to 17.73 d^{-1}) and biofilm (from 2.34 to 7.62 d^{-1}) occurred from Phase I to Phase II. A further decrease of the HRT and SRT from Phase II (SRT 31d/HRT15h) to Phase III (SRT 7d/HRT 13h), produced only a slight decrease of η_{BIO} from the average value of 88.5 to 85.7% (Figure 2a, Table 2).

[FIGURE 2]

The SRT/HRT variation also influenced the nitrogen removal (Figure 2b, Table 2). More precisely, the UCT-IFAS-MBR showed excellent nitrification performance (η_{nit}) throughout experiments, with average values of 90.9, 97.2 and 92.5% in Phases 1 to 3 respectively (Figure 2b, Table 2). This result suggested that over the entire experimental period, the growth of biofilm in the aerobic reactor could have enhanced the complete nitrification of the influent ammonia despite the high influent concentration (up to 120 mg NH_4-N L^{-1}) and very short SRT of 7d in Phase III.

Regarding the total nitrogen removal and denitrification performances (ηN_{total} and η_{den}, respectively) data of Figure 2b showed an increasing trend of both ηN_{total} and η_{den} with the decrease of the SRT/HRT, especially between Phase I and Phase II (Table 2). During all phases, a very high nitrification efficiency (90.9% for Phase I, 97.2% for Phase II and 92.5% for Phase III) was obtained despite the decrease of the SRT value. This result is debited to the growth of the attached biofilm biomass inside the aerobic reactor which have a greater capacity of nitrifying than suspended biomass even at low SRT [34].

In terms of phosphorus removal, the results reported in Figure 2c show an increasing trend of the η_{OP} value with the decrease of the SRT/HRT. Indeed, the average η_{PO} value was 87.5, 90.5 and 96.6% in Phases I, II and III respectively. Despite the low SRT during Phase III reduces the PAOs growth, the greater flux of wasted sludge as SRT decreases, increases the amount of P removed from the system [28].

The SRT/HRT variation has strongly influenced the membrane fouling. Since the membrane flux (J) increased from $4.06 \cdot 10^{-6}$ to $6.85 \cdot 10^{-6}$ m^3 m^{-2} s^{-1} (as average value) from Phase I to Phase II, a decrease of membrane fouling in terms of total resistance (R_T) occurred. Specifically, R_T decreased from $10.54 \cdot 10^{12} m^{-1}$ (Phase I) to $3.88 \cdot 10^{12} m^{-1}$. A further slight decrease of R_T occurred from Phase II to Phase III (average R_T equal to $3.69 \cdot 10^{12} m^{-1}$). A detailed discussion of membrane fouling for each phase is reported in [34].

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[TABLE 2]

3.2 Dissolved N_2O-N concentration

N_2O dissolved concentration in the liquid phase for each experimental phase trend is depicted in Figure 3, while Table 4 summarizes the average dissolved N_2O concentrations in the experimental phases.

[Figure 3]

Data reported in Figure 3 and Table 3 show a decrease of the dissolved N_2O concentration with decrease of the HRT and SRT. This result shows that the HRT and SRT decrease reduced the production of nitrifier denitrification (ND) intermediates. Consequently, the occurrence of incomplete nitrification or denitrification or hydroxylamine oxidation decreased leading to the decrease of the N_2O production in the bulk phase.

Indeed, the results reported in Figure 3 and Table 3 are in good agreement with pilot plant biological performances summarized in Figure 2 and Table 2. During Phase I, the lowest biological COD, as well as nitrification and denitrification, removal efficiency occurred. Since N_2O production is a result of incomplete nitrification, denitrification or hydroxylamine oxidation [7], this results suggest that the highest N_2O concentration was observed at the same time as the lowest nitrification and denitrification efficiency. With the SRT/HRT decrease, the process kinetics were enhanced, thus increasing the biological performances during Phases II and III.

[TABLE 3]

3.3 Gaseous N_2O-N concentration and flux

The N_2O-N concentrations measured in the head space of each reactor and N_2O gas exit fluxes (derived by multiplying head space concentration and gas flow) from each reactor are shown in Figures 4a and 4b. Table 4 reports the average values for N_2O-N concentration (both dissolved and gaseous) and exit flux.

[Figure_4]

By analysing the results in Figure 4, the highest N_2O-N concentrations were measured during Phase I, characterized by the longest SRT/HRT (HRT = 30h and SRT =56d). Specifically, the N_2O-N concentration peak (0.2 mg N_2O-N L^{-1}) was achieved during day 30 in the aerobic reactor when the SRT/HRT were changed to the values of Phase II. After reducing the SRT/HRT from Phase I (56d/30h) to Phase II (31d/15h) and then to Phase III (7d/13h) the average gaseous N_2O-N concentrations decreased in the aerobic and MBR tanks, while showing a slight increase in the anaerobic/anoxic compartments (Table 4). This decrease in the aerated compartments is in good agreement with the results achieved by [19] who found a decrease of N_2O emission with the decrease of HRT, in a two stage (anaerobic/aerobic) MBR system treating leachate. Authors attributed this result to a reduction in the diversity of nitrifying bacteria due to the low SRT/HRT [19]. Similar results were found by [29]. Indeed, Boonnorat and co-workers found that the SRT/HRT decrease led to the disappearance of specific bacterial species (during the investigation of a MBR system aimed at removing micro pollutant from leachate by varying C/N and HRT).

In this investigation, the decrease of N_2O production can be also related to the OLR increase that might have improved the heterotrophic denitrification, thus reducing the amount of N_2O produced.

[TABLE 4]

By analysing the results reported in Figure 4b it is possible to observe that also the N_2O fluxes were affected by the SRT/HRT decrease. Moreover, it has to be stressed that due to the absence of aeration, the N_2O fluxes from both anaerobic and anoxic reactors were negligible compared with the

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aerobic and MBR reactors. Even though the air flow rates supplied to aerobic and MBR reactors were almost constant throughout experiments (the gas velocity exiting from the aerobic and MBR reactor was 14.48 ± 3.28 m s^{-1} and 5.80 ± 0.52 m s^{-1}, respectively), a significant decrease of the N_2O fluxes occurred with the decrease of the SRT and HRT (Figure 4 b, Table 4).

3.4 N_2O-N emission factors

The N_2O emission factor, evaluated according to [25], was calculated for each experimental phase as the N_2O emitted as a % of the influent N. The results of the emission factors as well as the average contribution of each reactor to the total N_2O emission are reported in Figure 5.

[FIGURE 5]

The results shown in Figure 5 confirm the above discussed effect exerted by the SRT and HRT decrease on the N_2O production/emission. During Phase I the average N_2O emission from the whole pilot plant was 2.1 ± 3.0% of the inlet nitrogen with a maximum value of 8.9%. During Phase II the average N_2O emission was equal to 0.7 ± 0.8% of the inlet nitrogen, with a maximum percentage of 2.6%. During Phase III the average percentage of N_2O emission was 0.6 ± 0.5% of the influent nitrogen with a maximum of 1.6 %. The measured emission factors are in agreement with data available in the technical literature even though a direct comparison is difficult because emission factors can be evaluated with different expressions [18].

Indeed, the results reported in the technical literature underline a huge variability of emission factors evaluated in hybrid systems, with both suspended and attached biomass. [30] found that the emission factor in a MBBR system varied from 0.7% up to 8.5% of the influent nitrogen transformed by means of biological processes. [31] investigating a MBBR system with intermittent aeration, found an emission factor of 2.7% of the influent nitrogen transformed by means of biological processes. [32] obtained an emission factor of 21% of the influent nitrogen in an IFAS system operated with intermittent aeration.

However, it has to be stressed that none of the previous results were achieved in systems with a membrane as the solid-liquid separation step, meaning that the knowledge of N_2O emissions from IFAS systems combined with MBR is still at its infancy and deserves significant efforts to properly elucidate the main mechanisms. Indeed, the membrane presence might significantly affect the diversity of the activated sludge community inside the reactor, thus influencing the N_2O production. Moreover, data reported in Figure 5 (b, c and d) highlight that although the decrease of SRT/HRT resulted in a decrease N_2O emission, the contribution of each reactor to the total emission factor showed significant fluctuations. In detail, during Phase I the main source of emission was the MBR reactor, with 59.9% of the total emission factor. In contrast, during Phases II and III, the main contribution to the emission factor was given by the aerobic reactor with an average value of 58.4% and 42.8%, respectively. Furthermore, as previously discussed (Figure 4), the contribution of the anaerobic and anoxic reactors increased with the decrease of SRT/HRT. Such results suggest that the decrease in SRT/HRT, established by increasing the influent flow and OLR and the suspended sludge wastage flow, resulted in a modification of the metabolic activity that occurred in the different reactors.

3.5 N_2O-N mass balance over the tanks

In Figure 6 the daily N_2O mass balance in each reactor, according to Equation 2, is shown.

[FIGURE 6]

The results reported in Figure 6, show that no N_2O was produced (or consumed) in the anaerobic reactor indicating, as expected, that no denitrification was taking place there as required for good biological P removal. The main source of N_2O production was the aerobic reactor (Figure 6 c), where

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the nitrification process occurred. This result can be likely due to the incomplete hydroxylamine oxidation. Moreover, in the MBR reactor (Figure 6d) a significant production of N_2O occurred despite the relatively smaller reactor than the aerobic reactor. In contrast, in the anoxic reactor the mass balance mainly shows a consumption of N_2O. This indicates that the anoxic reactor was probably under loaded with nitrate by the aerobic to anoxic (s) recycle (= 4:1) allowing complete nitrate removal down to very low nitrate and nitrite concentrations to take place in the anoxic reactor with negligible denitrification intermediates production. Unfortunately, nitrate and nitrite concentrations in the anoxic reactor were not measured to confirm this – in the N mass balance (see below), they were assumed zero for reasons mentioned above.

The N_2O mass balances related to Phases II and III show that the N_2O production is quite negligible compared with Phase I. This result confirms that the decrease of the HRT and SRT, obtained increasing Q_{IN} and Q_{WAS}, led to an overall improvement of the biological performances and consequently to a reduction of N_2O production/emission.

3.6 Nitrogen mass balance

Figure 7 shows the nitrogen mass balance for each experimental day (Figure 7a) and the average values of each N fraction computed over each experimental phase (Figure 7b –Phase I; Figure 7c – Phase II and Figure 7d–Phase III). Data reported in Figure 7 highlight the N forms (expressed as percentage of the influent N) discharged into the environment (gaseous, dissolved and solid in sludge wastage).

By analysing data reported in Figure 7a it is possible to observe that the SRT/HRT variation influenced the N transformation inside the pilot plant. More precisely, the greatest emission of N_2O both in liquid and gaseous form was achieved during Phase I at SRT/HRT 56d/30h. Indeed, during Phase I 5.5% of the influent N was emitted as N_2O-N (gaseous and dissolved) and NO_2-N. This result can be due to the partial denitrification occurring during this Phase as demonstrated by the low average denitrification efficiency (52%, Table 2). With the decrease of the SRT/HRT, a decrease was observed of the combined emission of N_2O-N (gaseous and dissolved) and NO_2-N, from 5.9% in Phase I to 2.6% in Phase III. In contrast, percentage of assimilated ammonia for growth presented a significant variation through experiments. Indeed, it increased from 13% in Phase I up to 25.5% in Phase III, thus suggesting that the availability of biomass to synthesize new cells changed with the HRT variation. Moreover, it is important to specify that a slight difference in terms of N removed by means of sludge wastage occurred decreasing the SRT from 56d (Phase I) to 7d (Phase III). More precisely, 11 mgN L^{-1} and 28 mgN L^{-1} (average values) were removed due to the sludge wastage from the aerobic reactor.

[FIGURE 7]

4. Conclusions

The N_2O production/emission from a UCT-IFAS-MBR pilot plant was investigated. Three experimental Phases were performed: i. Phase I, SRT/HRT equal to 56d/30h; ii. Phase II, equal to SRT/HRT 31d/15h; iii. Phase III, SRT/HRT equal to 7d/13h.

Results obtained here have demonstrated a substantial reduction of the N_2O production due to the decrease of SRT/HRT. Specifically, 2.1% of the influent total nitrogen was emitted as N_2O during Phase I, 0.7% during Phase II and 0.6% during Phase III.

Aerated reactors (aerobic and MBR) resulted the main contributors of N_2O emission during each phase. The aerobic reactor was the main N_2O contributor (73%, 85% and 71% in Phases I, II and III respectively). While the MBR reactor was the second contributor with 25%, 12% and 14% of the emitted N_2O in Phases I, II and III respectively. Low N_2O was produced during the denitrification process because N_2O was consumed in the anoxic reactor. This result was likely due to (i) under

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loaded anoxic reactor with nitrate by the recycle, allowing complete nitrate removal with little denitrification intermediates production, (ii) increased N removal via sludge wastage at lower SRT resulting in less nitrate removal by denitrification and (iii) higher heterotrophic biomass fraction of the VSS at lower SRT which assisted the heterotrophic denitrification thus reducing the N_2O production/emission (N_2O is also produced during incomplete denitrification). In view of reducing the amount of N_2O produced during the denitrification, results suggested to operate BNR systems with under loaded anoxic reactors. The N_2O emission factors were in good agreement with literature data. However, it has to be stressed that none of the literature data deals with system in which the solid liquid separation is with a membrane bioreactor.

N_2O mass balance showed that N_2O production during Phases II and III was quite negligible compared to that of Phase I. This result suggested that the decrease of the HRT and SRT led to an overall improvement of the biological performances favoured by the biofilm growth and consequently to a reduction of N_2O production/emission.

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Symbols

$N_2O\text{-}N_{Dissolved,OUT}$	[mg N_2O-N h^{-1}]	fluxes of dissolved N_2O-N exiting a reactor
$N_2O\text{-}N_{Dissolved,IN}$	[mg N_2O-N h^{-1}]	fluxe of dissolved N_2O-N entering a reactor
$N_2O\text{-}N_{Gas,OUT}$	[mg N_2O-N h^{-1}]	gaseous N_2O-N exiting a reactor
$N_2O\text{-}N_{p,c}$	[mg N_2O-N h^{-1}]	flux of N_2O-N produced (+) or consumed (-) in the reactor.
Q_{BW}	[$L{\cdot}h^{-1}$]	backwashing flow rate
Q_{IN}	[$L{\cdot}h^{-1}$]	influent wastewater flow rate
Q_{OUT}	[$L{\cdot}h^{-1}$]	net permeate flow rate
$Q_{OUT,IST}$	[$L{\cdot}h^{-1}$]	instantaneous permeate flow rate
Q_{R1}	[$L{\cdot}h^{-1}$]	Recycle flow rate from anoxic to anaerobic reactor
Q_{R2}	[$L{\cdot}h^{-1}$]	Recycle flow rate from aerobic to MBR reactor
Q_{RAS}	[$L{\cdot}h^{-1}$]	Recycle flow rate from MBR to anoxic reactor
Q_{WAS}	[$L{\cdot}h^{-1}$]	waste sludge flow rate
r	[-]	recycle ratio
s	[-]	sludge return recycle ratio
X_{taer}	[$gTSS{\cdot}L^{-1}$]	aerobic reactor total suspended solid concentration

Greek letters

η_{BIO}	COD Removal efficiency
η_{TOT}	Total COD
$\eta_{CAKE,FILT}$	Removal efficiency due to the membrane filtration
η_{nit}	Nitrification efficiency
η_{denit}	Denitrification efficiency
ηN_{total}	Total Nitrogen efficiency
η_{OP}	Ortho-Phosphates removal efficiency

Abbreviations

AOB	Ammonia Oxidizing Bacteria
BNR	Biological Nutrient Removal
BOD	Biochemical Oxygen Demand
CIP	Clean in Place tank
COD	Chemical Oxygen Demand
COD_{SUP}	Supernatant Chemical Oxygen Demand
COD_{TOT}	Total Chemical Oxygen Demand

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DO	Dissolved Oxygen
dPAOs	Denitrifying Polyphosphate-accumulating Organisms
ECD	Electron Capture Detector
GAOs	Glycogen Accumulating Organisms
GC	Gas Chromatograph
GHG	Greenhouse Gas
GWP	Global Warming Potential
HRT	Hydraulic Retention Time
MBBR	Moving Bed Biofilm Reactor
IFAS	Integrated Fixed Film Activated Sludge
MB-MBR	Moving Bed Biofilm Membrane Bioreactor
MBRs	Membrane Bioreactors
NH_4-N	Ammonium Nitrogen
NO_2-N	Nitrite Nitrogen
NO_3-N	Nitrate Nitrogen
ODR	Oxygen Depletion Reactor
OP	Ortho-Phosphates
PAOs	Polyphosphate-accumulating Organisms
SRT	Solids Retention Time
TKN	Total Kjeldahl Nitrogen
TN	Total Nitrogen
TP	Total Phosphorus
TSS	Total Suspended Solids
UCT	University of Cape Town
VSS	Volatile Suspended Solids
W_i	Weight of the carriers
WWTPs	Wastewater Treatment Plants

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Tables with headings

Table 1. Average features of the inlet wastewater, including additives, and operation conditions during each experimental phase; X_{tave} = volume weighted average total suspended solid (TSS) concentration; X_{vave} = volume weighted average volatile suspended solid (VSS) concentration. Values in brackets ( ) are wastewater concentrations before supplementing with organics.

Parameter	Units	PhaseI	Phase II	Phase III
Total COD	[mg L^{-1}]	831 (229)	1049 (290)	971 (274)
Total nitrogen (TN)	[mg L^{-1}]	(86)	(121)	(97)
NH_4-N	[mg L^{-1}]	(80)	(119)	(96)
Phosphate (PO_4-P)	[mg L^{-1}]	7.82 (7.65)	13.72 (8.85)	12.24 (8.43)
Temperature	[°C]	17.2	23.8	27
Permeate Flux	[L m^{-2} h^{-1}]	21	26	29
Q_{IN}	[L h^{-1}]	15	30	35
Q_{OUT}	[L h^{-1}]	14.76	29.56	32.55
Q_{R1}	[L h^{-1}]	15	30	35
Q_{R2}	[L h^{-1}]	75	150	175
Q_{RAS}	[L h^{-1}]	60	120	140
Q_{WAS}	[L h^{-1}]	0.54	0.99	2.54
X_{tave}	[gTSS L^{-1}]	3.5	4.8	3.7
X_{vave}	[gVSS L^{-1}]	3.2	4.4	3.4
TS Biofilm anoxic	[gTS L^{-1}]	0.83	0.52	0.75
TS Biofilm aerobic	[gTS L^{-1}]	3.3	2.40	2.35
HRT	[h]	30	15	13
SRT(1)	[d]	56	31	7
OLR(1)	[kgBOD_5 kgSSV^{-1} d^{-1}]	0.22	0.37	0.40
Duration	[d]	30	28	29

(1) values referred to suspended biomass only

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Table 2. Average values of the pollutants removal efficiencies for each experimental phase

Description	**Phase I**	**Phase II**	**Phase III**
Total COD removal efficiency (η_{TOT}) [%]	98.6	99.0	99.0
Biological COD removal efficiency (η_{BIO}) [%]	84.0	88.5	85.7
Nitrification efficiency (η_{nit}) [%]	90.9	97.2	92.5
Denitrification efficiency (η_{denit}) [%]	60.0	76.1	65.1
Total nitrogen removal efficiency (ηN_{total}) [%]	69.4	81.4	76.7
Phosphorus removal efficiency (η_{OP}) [%]	87.5	90.5	96.6

Table 3. Average N_2O-N dissolved concentration for each reactor and experimental phase.

N_2O-N dissolved concentration [mg N_2O-N L^{-1}]	Phase I	Phase II	Phase III
Anaerobic	0.017	0.014	0.025
Anoxic	0.009	0.012	0.012
Aerobic	0.100	0.087	0.016
MBR	0.325	0.099	0.017
Permeate flux	0.086	0.089	0.037
ODR	0.104	0.021	0.020

Table 4 Average N_2O-N gas concentration (mgN_2O-N L^{-1} headspace volume and average N_2O-N flux in mgN_2O-N per m^2 horizontal cross sectional surface area at the water – headspace interface per h for each reactor and experimental phase).

N_2O-N gas concentration [mg N_2O-N L^{-1}]	Phase I	Phase II	Phase III
Anaerobic	0.008	0.002	0.012
Anoxic	0.015	0.026	0.036
Aerobic	0.070	0.047	0.017
MBR	0.040	0.015	0.014
N_2O-N flux [mg N_2O-N m^{-2} h^{-1}]	Phase I	Phase II	Phase III
Anaerobic	0.424	0.051	0.324
Anoxic	0.119	0.285	0.384
Aerobic	26.56	23.74	11.75
MBR	46.97	17.25	14.47

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Figures and captions

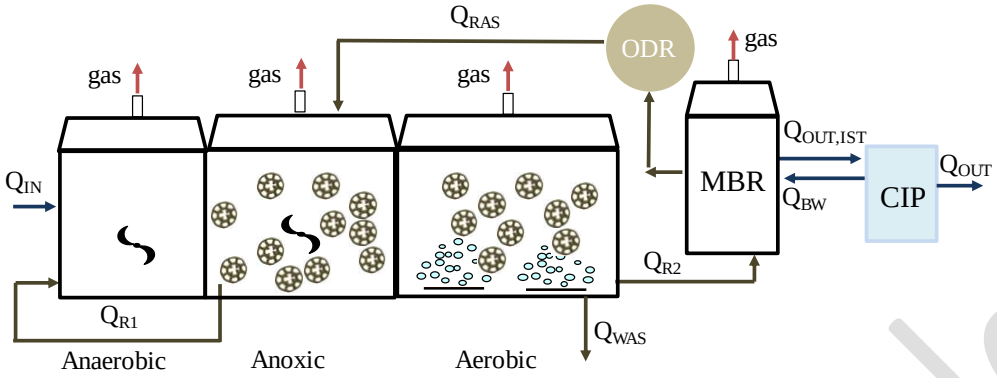

Figure 1. Layout of the UCT-IFAS-MBR pilot plant. Where: Q_{IN} = influent wastewater; Q_{R1} = mixed liquor recycled from the anoxic to the anaerobic tank; Q_{R2} = mixed liquor recycled from the aerobic to the MBR tank; Q_{RAS} = Recycled sludge from the MBR to the anoxic tank; Q_{OUT} = effluent permeate flow rate; ODR = Oxygen Depletion Reactor; $Q_{OUT,IST}$ = instantaneous effluent permeate flow rate during filtration; Q_{WAS} = waste sludge flow rate; Q_{BW}= backwashing flow rate; CIP = Clean In Place

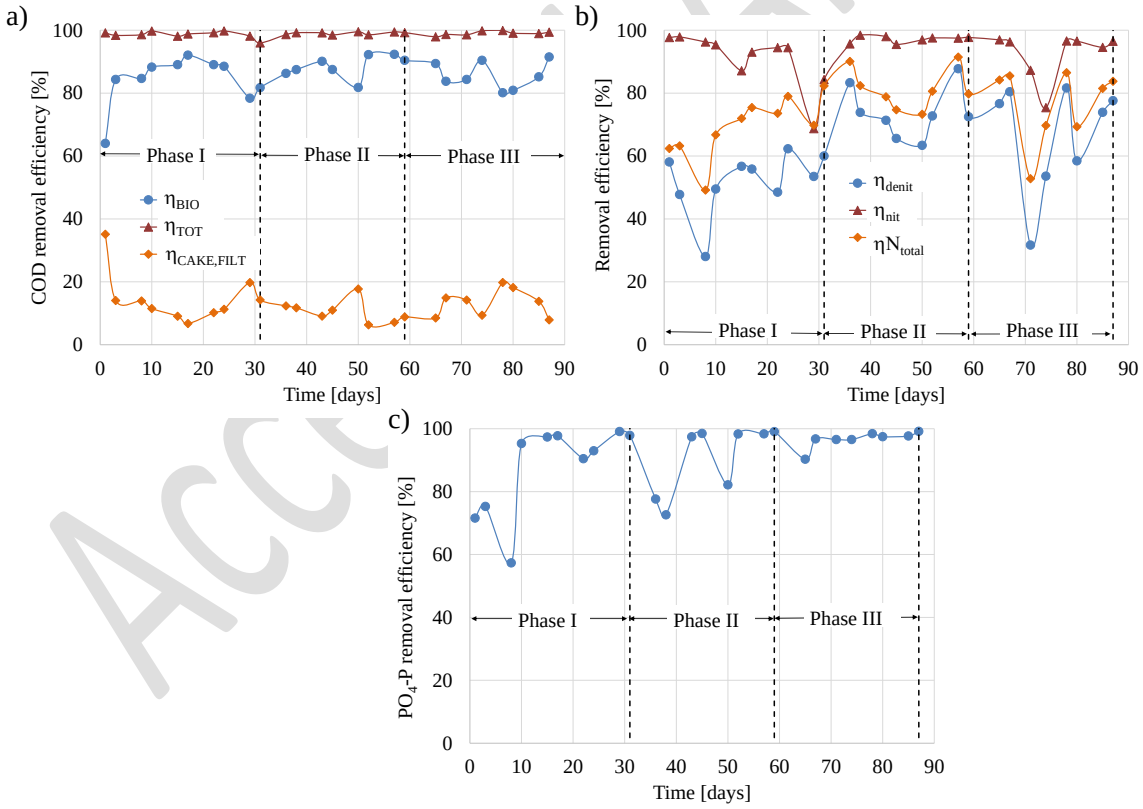

Figure 2. Trend of COD (a), N (b) and PO_4-P (c) removal efficiencies

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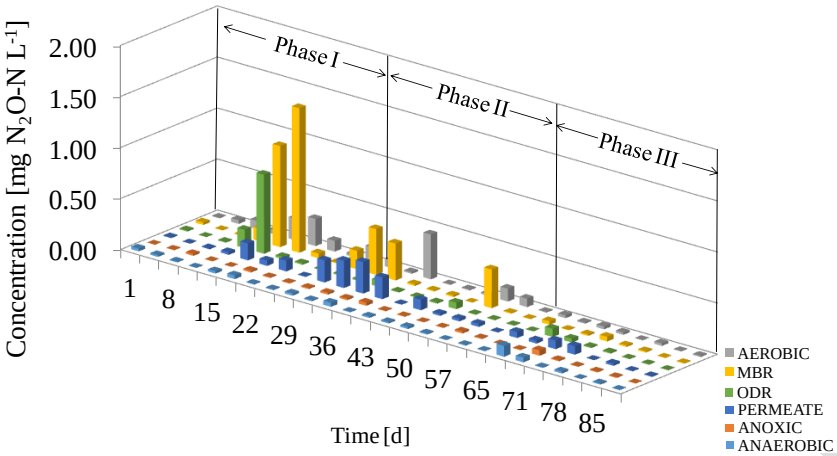

Figure 3. Nitrous oxide concentrations in the liquid phase for each experimental phase (Phases I, II and III)

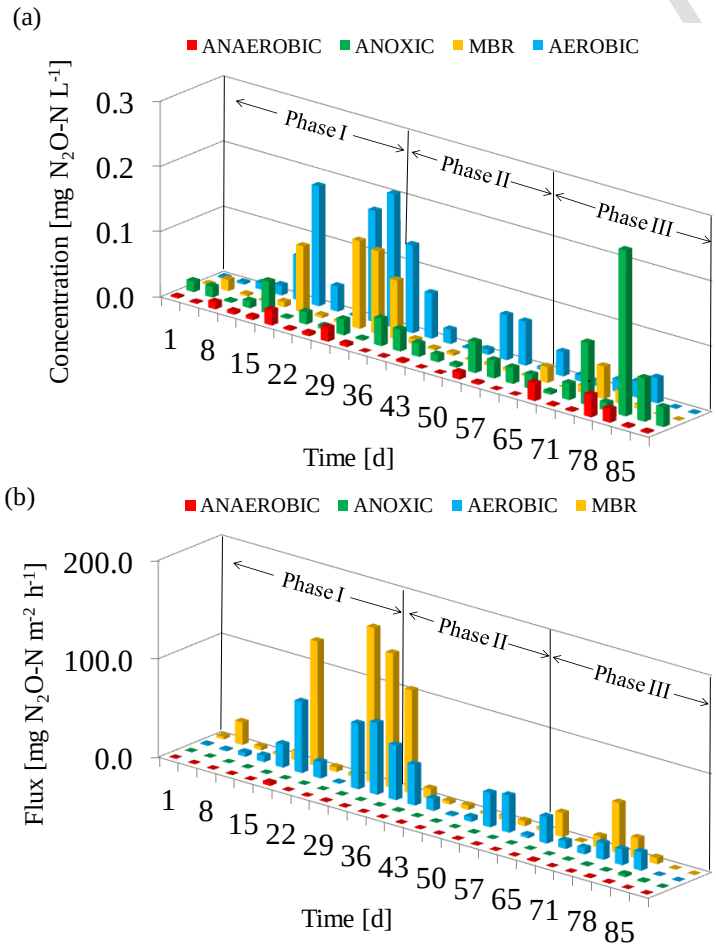

Figure 4. N_2O-N concentration in the gas phase (a) and emitted flux (b) for each experimental phase (Phases I, II and III)

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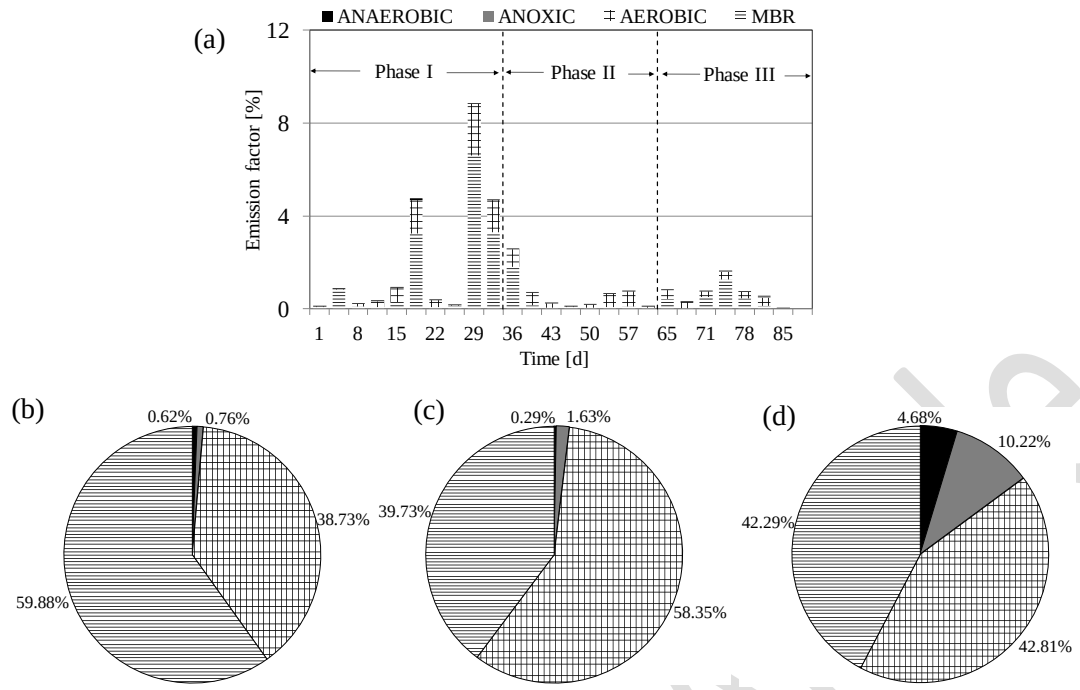

Figure 5. N_2O-N emission factor pattern during experiments (Phases I, II and III) (a); average percentage contribution of each tank for N_2O-N emission during the experimental Phase Phase I (b) , Phase II (c) and Phase III (d).

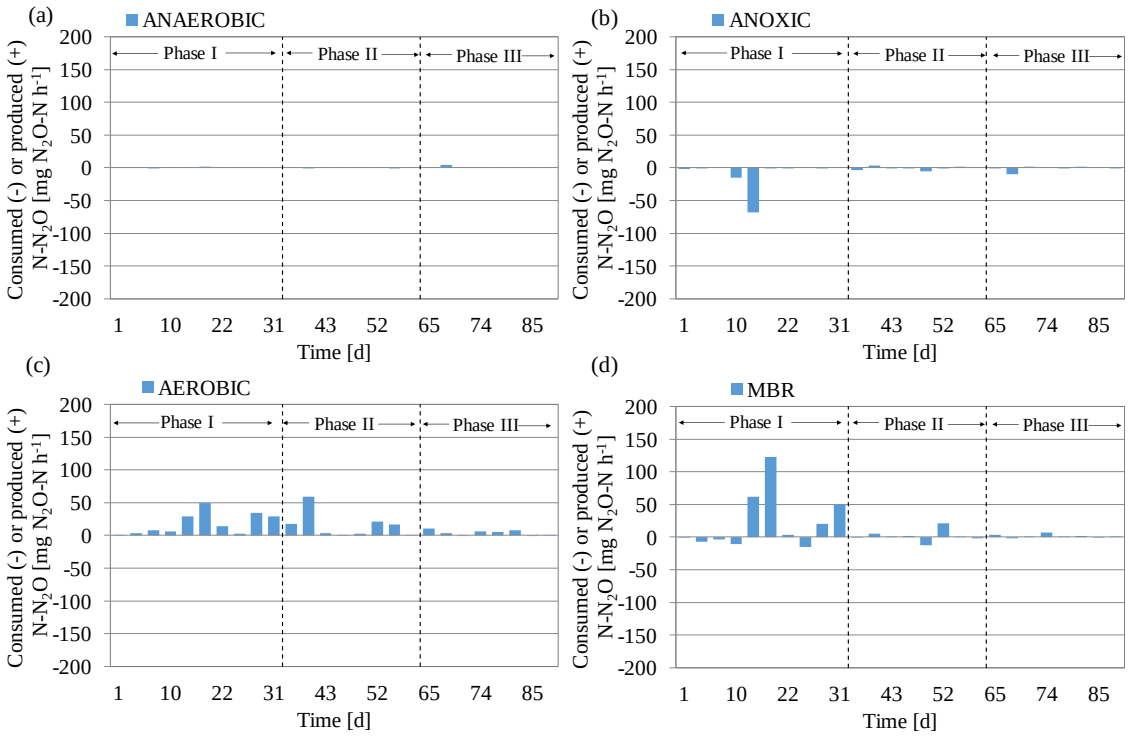

Figure 6. N_2O-N mass balance for the anaerobic (a), anoxic (b), aerobic (c) and MBR (d) tank for each experimental phase (Phase I, Phase II and Phase III).

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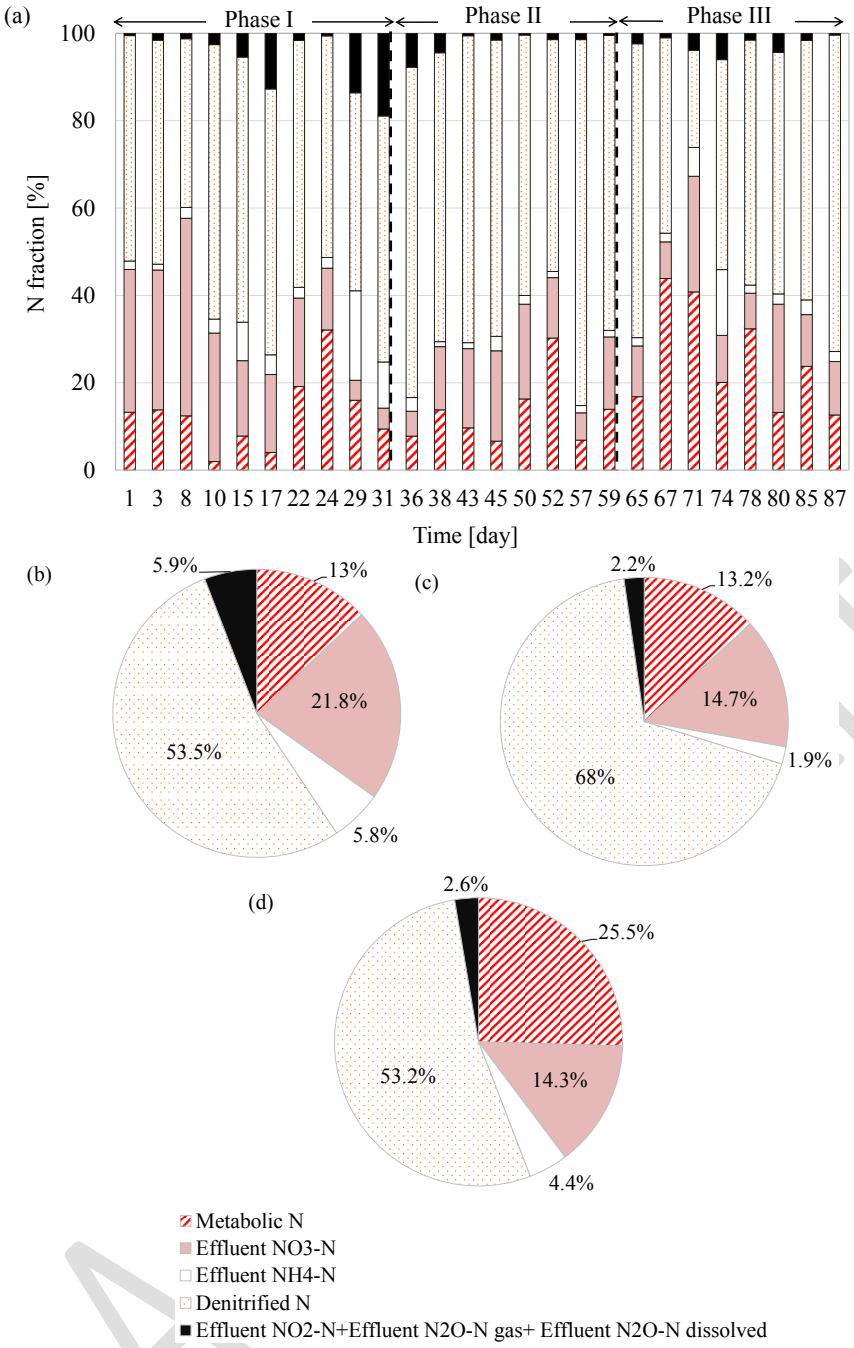

Figure 7. Trend of nitrogen forms expressed as a percentage of the total influent nitrogen throughout experiments (a); percentage of each nitrogen form (as average) referring as average to Phase I (b), Phase II (c), and Phase III (d) respectively.

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