Research article

The influence of solid retention time on IFAS-MBR systems: Assessment of nitrous oxide emission

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ABSTRACT

The aim of the present study was to investigate the nitrous oxide (N_2O) emissions from a moving bed based Integrated Fixed Film Activated Sludge (IFAS) - membrane bioreactor (MBR) pilot plant, designed according to the University of Cape Town (UCT) layout. The experimental campaign had a duration of 110 days and was characterized by three different sludge retention time (SRT) values (∞, 30 d and 15 d). Results highlighted that N_2O concentrations decreased when the biofilm concentrations increased within the aerobic reactor. Results have shown an increase of N_2O with the decrease of SRT. Specifically, an increase of N_2O-N emission factor occurred with the decrease of the SRT (0.13%, 0.21% and 0.76% of influent nitrogen for SRT = ∞, SRT = 30 d and SRT = 15 d, respectively). Moreover, the MBR tank resulted the key emission source (up to 70% of the total N_2O emission during SRT = ∞ period) whereas the highest N_2O production occurred in the anoxic reactor. Moreover, N_2O concentrations measured in the permeate flow were not negligible, thus highlighting its potential detrimental contribution for the receiving water body. The role of each plant reactor as N_2O-N producer/consumer varies with the SRT variation, indeed the aerobic reactor was a N_2O consumer at SRT = ∞ and a producer at SRT = 30 d.

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1. Introduction

Nitrous Oxide (N_2O) represents a significant greenhouse gas (GHG) with a global warming potential (GWP) 298 times higher compared to carbon dioxide (CO_2) (IPCC, 2007). Since many bacteria involved in biological nitrogen removal from wastewater are able to produce N_2O, in recent years N_2O emission from wastewater treatment plants (WWTPs) has received increasing attention by the scientific community (Stenström et al., 2014; Ni and Yuan, 2015; Mannina et al., 2016a). N_2O production mainly occurs during biological nutrient removal (BNR) processes (Kampschreur et al., 2009). Indeed, N_2O can be produced by ammonia oxidizing bacteria (AOB) during nitrification (Peng et al., 2015). Furthermore, since N_2O represents an intermediate product of the heterotrophic denitrification process, it can be produced via incomplete heterotrophic denitrification (Liu et al., 2015). Therefore, both autotrophic and heterotrophic bacteria can be responsible for N_2O production

during BNR (Kampschreur et al., 2009; Chandran et al., 2011; Law et al., 2012; Paudel et al., 2015). Moreover, during phosphorus removal process, N_2O production can also occur (Kampschreur et al., 2009; Zhou et al., 2012). Indeed, technical literature highlights that in processes aimed at biological nitrogen and phosphorous removal (BNPR), the role of polyphosphate accumulating organisms (PAOs) in the production of N_2O cannot be disregarded (Zhou et al., 2012). Indeed, PAOs can growth under anoxic conditions by using nitrate and/or nitrite as the terminal electron acceptor to oxidize their intracellular Polyhydroxyalkanoate (PHA). Therefore, under certain conditions, N_2O can be accumulated during the denitrification due to PAO_S activity (Zeng et al., 2003).

In the last years, several efforts have been dedicated to better understand the key mechanisms involved in N_2O production and emission (Kampschreur et al., 2009). Several operational conditions and influent features that might favour N_2O production/emission have been identified: low dissolved oxygen (DO) concentrations, nitrite accumulation, dynamic conditions as well as low carbon-to-nitrogen (C/N) ratio values during denitrification (Kampschreur et al., 2009; Chiu and Chung, 2000; Park et al., 2000; Zeng et al., 2003; Tallec et al., 2008; Mannina et al., 2017a). Amongst the

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main operational variables, the sludge retention time (SRT) has been recognized able to influence N_2O production. Indeed, previous studies carried out on full scale WWTP highlighted that the N_2O production increases with the decrease of the SRT (Kampschreur et al., 2009). However, as authors are aware, most of the studies dealing with N_2O production/emission are focused on conventional activated sludge (CAS) systems. This aspect must face with the spread-out of innovative technologies occurred during the last ten years (e.g., biofilm systems, membrane systems etc.).

Indeed, very recently hybrid systems, integrating biofilm within a suspended-growth system, have been proposed for BNPR (Leyva-Díaz et al., 2016). Hybrid systems have the advantages of maximizing the nitrification taking advantage of the high SRT of the biofilm, but having the potential of operating the suspended growth phase with a relatively short SRT. Moreover, in a hybrid system, biofilm and suspended biomass may have a different role referring to either nitrogen or phosphorus removal. This peculiar aspect can be of importance in terms of N_2O emissions from BNPR in hybrid systems. Among the hybrid systems, the joint use of membrane bioreactors (MBRs) and moving bed biofilm reactors (MBBRs) was recently proposed, replacing the secondary settler by means of the membrane module. The latter configuration is usually referred to as MB-MBR (Di Trapani et al., 2014) or IFAS-MBR. Regarding the biofilm influence on N_2O production, literature shows a very limited knowledge (Todt and Dörsch, 2015). Indeed, to author's knowledge, there are only few modelling studies that compare the relative effects of the biofilm and the suspended sludge on N and P removal efficiencies and N_2O emission in a hybrid BNPR system. Sen et al. (2010) developed a model aimed at investigating the differences between MBBR-based Integrated Fixed Film Activated Sludge (IFAS) and CAS in producing N_2O. Sen and co-authors found that the higher buffer on air supply in IFAS processes improve nitrification process and consequently reduce the N_2O emissions during nitrification. Recently, Peng et al. (2016) in a model survey found that the gas production increases when the biofilm thickness increases. The first attempt to gain insight on how the peculiar features of IFAS − MBR systems influence the N_2O emissions has been very recently presented by Mannina et al. (2017b). Mannina and co-workers investigated an IFAS-MBR system aimed at the biological nutrient removal and found a significant N_2O production in the anaerobic and the anoxic reactors. This was mainly due to a twofold reason: i. The occurrence of the denitrifying PAOs activity under sporadic nitrite/nitrate presence inside the anaerobic reactor; ii. The combination of both heterotrophic non-PAOs and PAOs growth inside the anoxic reactors. However, the study of Mannina et al. (2017b) was performed at established operation conditions (e.g., indefinite sludge retention time). The SRT is an important operation operational variables

which may influence N_2O emissions. To what extend does the SRT influence the N_2O from IFAS-MBR system has not yet assessed. Further, despite the results presented by Mannina et al. (2017b), knowledge on biofilm system is still immature (Todt and Dörsch, 2015). Therefore, the investigation of different operational conditions for a better understanding of the mechanisms involved in N_2O production from hybrid systems aimed at nutrient removal is imperative.

In the light of the above discussion, the aim of the present study is to investigate the N_2O production in an IFAS−MBR system for carbon and nutrients removal. To achieve such goals a University Cape Town (UCT) IFAS-MBR was monitored for 110 days and operated at different mixed liquor SRTs (namely, SRT = ∞, SRT = 30 d and SRT = 15 d). The pilot plant described in this paper is similar to the one presented by Mannina et al. (2017b) where only the SRT = ∞ was investigated. In this study the effect of the SRT was analysed assessing its short term effect with regards to the N_2O emission.

2. Materials and methods

2.1. Description of the UCT-IFAS-MBR pilot plant lay-out

A UCT-IFAS-MBR pilot plant has been monitored during the experimental campaign (Fig. 1).

In details, the pilot plant consisted of anaerobic (volume 62 L), anoxic (volume 102 L) and aerobic (volume 211 L) in-series compartments according to the UCT scheme (Ekama et al., 1983; Cosenza et al., 2013). The solid-liquid separation phase was achieved by means of an ultrafiltration hollow fibre membrane module (PURON® Triple bundle Demo Module, courtesy of Koch Membrane Systems Inc.). The membrane module (nominal pore size: 0.03 μm; membrane area: 1.4 m^2) was placed inside a dedicated aerated compartment (MBR tank, volume 36 L). An oxygen depletion reactor (ODR) allowed oxygen removal in the mixed liquor recycled from the MBR to the anoxic tank (Q_{RAS}). The membrane was backwashed every 9 min for a period of 1 min by pumping a volume of permeate back (Q_{BW} represents the backwashing flow rate) from the Clean In Place (CIP) tank; an instantaneous permeate flux of 21 L m^{-2} h^{-1} was applied ($Q_{OUT,IST}$) valid only during the filtration time. The influent flow rate was set equal to 20 L h^{-1} (Q_{IN}). During pilot plant operation, a 20 L h^{-1} flow (Q_{R1}) was continuously pumped from the anoxic to the anaerobic tank. Furthermore, 100 L h^{-1} (Q_{R2}) of mixed liquor were pumped from the aerobic to the MBR tank. A net permeate flow rate of 20 L h^{-1} was extracted (Q_{OUT}) through the membrane. Therefore, the recycled activated sludge (Q_{RAS}) from the MBR to the anoxic tank through the ODR tank was equal to 80 L h^{-1}. The anaerobic, anoxic, aerobic and MBR
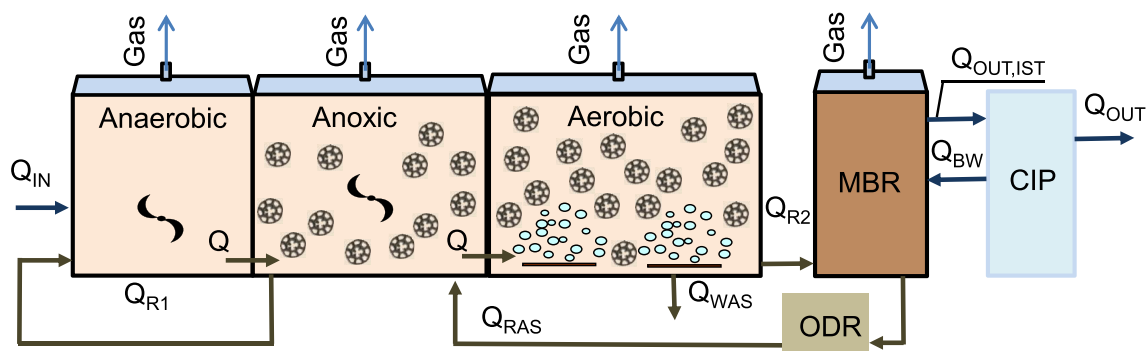

Fig. 1. Lay-out of the UCT-IFAS-MBR pilot plant (Q_{IN} = Feeding flow rate; $Q_{OUT,IST}$ = instantaneous permeate flux; Q_{OUT} = Permeate flow rate; Q_{BW} = permeate backwashing flow rate; ODR = oxygen depletion reactor; Q_{RAS} = Recycled activated sludge flux; Q_{R1} = Anoxic-anaerobic recycle; Q_{R2} = Aerobic-MBR recycle; Q_{WAS} = waste activated sludge flow rate).

reactors were equipped with specific funnel shape covers that guaranteed gas accumulation in the headspace to capture the produced gas by sampling.

Furthermore, the anoxic and aerobic compartments were filled with suspended carriers (courtesy of Amitech Co. Ltd.) with a 15 and 40% filling ratio respectively, corresponding to a net surface area of almost 75 m^2 m^{-3} and 205 m^2 m^{-3}, respectively. The filling ratios were chosen in agreement with literature data (Leyva-Díaz et al., 2016). The mixed liquor SRT was controlled by sludge withdrawals (Q_{WAS}) from the aerobic reactor.

In order to capture the overall off-gas emitted from the pilot plant, each reactor was equipped with a specific cover as described in Mannina et al. (2017a,b) (Fig. 1).

2.2. Influent features and experimental phases

The UCT-IFAS-MBR pilot plant was fed with real wastewater (collected at the University Campus) spiked by synthetic wastewater. The synthetic and real wastewater represented almost the 60 and 40% of the overall organic loading rate, respectively. More in details, the synthetic wastewater composition was: 30% of readily biodegradable COD (RBCOD) (dosed as sodium acetate) and 70% of more slowly biodegradable (dosed as glycerol). It is worth noting that the real wastewater was collected at the University Campus and was characterized by high TN and ammonia content, due to the lack of kitchen food residues contribution.

Table 1 summarizes the average features of the influent wastewater as well as the operational conditions.

During the first 66 days, the pilot plant was operated with a complete sludge retention strategy, corresponding to indefinite SRT. From day 67th to day 95th, regular sludge withdrawals were operated from the aerobic reactor in order to set the SRT at 30 days. Furthermore, from day 96th to day 115th the sludge withdrawals were increased as far as the corresponding SRT resulted equal to 15 days. Wasting sludge operations were carried out by means of a peristaltic pump that withdrew a constant sludge flow rate from the aerobic reactor (adjusted two times per week, after TSS measurements).

2.3. Analytical procedures

Samples collected from the influent wastewater, the mixed liquor inside the anaerobic, anoxic, aerobic and MBR tanks, and the effluent permeate were analysed for TSS, volatile suspended solids (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 (TN), phosphate (PO_4-P), and total phosphorus (TP), Biochemical Oxygen Demand (BOD_5). All analyses were performed according to the Standard Methods (APHA, 2005). Carriers from anoxic and aerobic reactors were periodically sampled in order to monitor the biofilm growth during experiments. The biofilm amount on the carriers was assessed according to procedure reported in Di Trapani et al. (2015).

Dissolved and gaseous N_2O concentrations were also measured in each reactor and in the permeate by using a Gas Chromatograph (Thermo Scientific™ TRACE GC) equipped with an Electron Capture Detector (ECD). Furthermore, the N_2O-N fluxes (gN_2O-N m^{-2} h^{-1}) from all reactors were quantified by measuring the gas flow rates, Q_{GAS} (L min^{-1}). For further details on gas sampling and measurements, the reader is addressed to literature (APHA, 2005; Mannina et al., 2016b,c).

Moreover, with the aim to assess the N_2O-N production or consumption within each compartment, a nitrous oxide mass balance was calculated, according to Mannina et al. (2017b).

3. Results and discussion

3.1. Pilot plant performances

Table 2 summarizes the pilot plant removal performance. Data reported in Table 2 show that in terms of total COD removal efficiency (η_{TOT}) the SRT variation did not exert any influence. Indeed, excellent η_{TOT} removals were achieved over the entire experimental campaign. Conversely, the biological COD removal efficiency (η_{BIO}) was influenced by the decrease of the mixed liquor SRT. Indeed, with the decrease of the mixed liquor SRT from indefinite to 30 days an increase of the average η_{BIO} value took place (from 76% to 80%). This result can be likely due to the decrease of the reduced competition between the suspended biomass and the biofilm attached at lower mixed liquor SRT. However, η_{BIO} decreased to 71% in Phase III, when the mixed liquor SRT was reduced to 15 days. Nevertheless, it has to be stressed that the temperature decrease from 18.2 to 15.3 °C (from Phase II through Phase III) could slightly affect biomass activity, thus contributing to the decrease of biological COD removal.

The total nitrogen removal efficiency (ηN_{TOT}) decreased with the decreasing of the mixed liquor SRT (Table 2). In particular, the highest decrease of the ηN_{TOT} occurred when the mixed liquor SRT was reduced from 30 to 15 days despite the quite high nitrification efficiency (η_{nit}) (Table 2). Such a result could be related to the lower denitrification efficiency (η_{denit}) at the lowest SRT, likely due to a sudden increase of the inlet nitrogen that promoted a decrease of the influent C/N value.

In terms of phosphorus removal efficiency (η_{PO4}) it was noticed a slight increase with the decrease of the SRT. Indeed, η_{PO4} increased from 37% to 61% with the SRT decrease from indefinite to 15 d. This result corroborates the findings of Ge et al. (2015), underlying a high competition between PAOs and ordinary heterotrophic organisms at high SRT. Fig. 2 depicts the trend profiles of TSS/VSS concentration as well as biofilm growth in the anoxic and aerobic compartments throughout experiments. The effect of the membrane and the internal tank recycles promoted the te TSS concentrations in the tanks towards the membrane, resulting in progressively increasing TSS from the anaerobic to the MBR tank (Ramphao et al., 2005). A general increase of the suspended biomass concentration was observed in the different compartments during Phase I, likely due to the absence of sludge withdrawals. In contrast, during Phase II it remained quite constant whilst in the Phase III a significant decrease was observed due to the increased sludge withdrawals. The attached biomass was quite low over the whole study — as expected at the prevailing conditions — with relatively high MLSS SRT in all phases resulting in more favourable conditions for the suspended biomass.

It is worth noting that Phase III was interrupted abruptly due to

Table 1
Average features of the influent wastewater and operational conditions during the three experimental phases at MLSRT = indefinite, 30 d and 15 d respectively (in brackets the COD contribution of the synthetic wastewater).

Parameter	Units	Phase I	Phase II	Phase III
		Value		
COD	[mg L^{-1}]	602 (357)	583 (382)	543 (308)
Total nitrogen (TN)	[mg L^{-1}]	55.46 (0)	76.91 (0)	105.00 (0)
Total phosphorus (TP)	[mg L^{-1}]	6.98 (0)	8.8 (0)	9.86 (0)
Permeate Flux	[L m^{-2} h^{-1}]	21	21	21
Flow rate	[L h^{-1}]	20	20	20
SRT	[d]	∞	30	15
HRT	[h]	20	20	20
Duration	[d]	0–66	67–95	96–115

Table 2
Average values of removal efficiencies (in brackets the standard deviation values).

SRT [d]	η_{TOT} [%]	η_{BIO} [%]	ηN_{TOT} [%]	η_{nit} [%]	η_{denit} [%]	η_{PO4} [%]
∞	99 (±0.66)	76 (±6.24)	63 (±16.54)	91 (±11.37)	49 (±21.18)	37 (±8.20)
30	99 (±0.36)	80 (±3.72)	61 (±18.96)	91 (±10.68)	50 (±24.02)	53 (±4.61)
15	99 (±0.29)	71 (±5.49)	55 (±6.64)	90 (±8.33)	45 (±5.18)	61 (±7.78)

where: η_{TOT} = total COD removal efficiency evaluated comparing the influent COD and the permeate COD; η_{BIO} = biological COD removal efficiency evaluated comparing the influent COD and the supernatant COD in the MBR mixed liquor; ηN_{TOT} = total nitrogen removal efficiency; η_{nit} = nitrification efficiency; η_{denit} = denitrification efficiency; η_{PO4} = PO$_4$-P removal efficiency. In brackets, the standard deviation is reported.
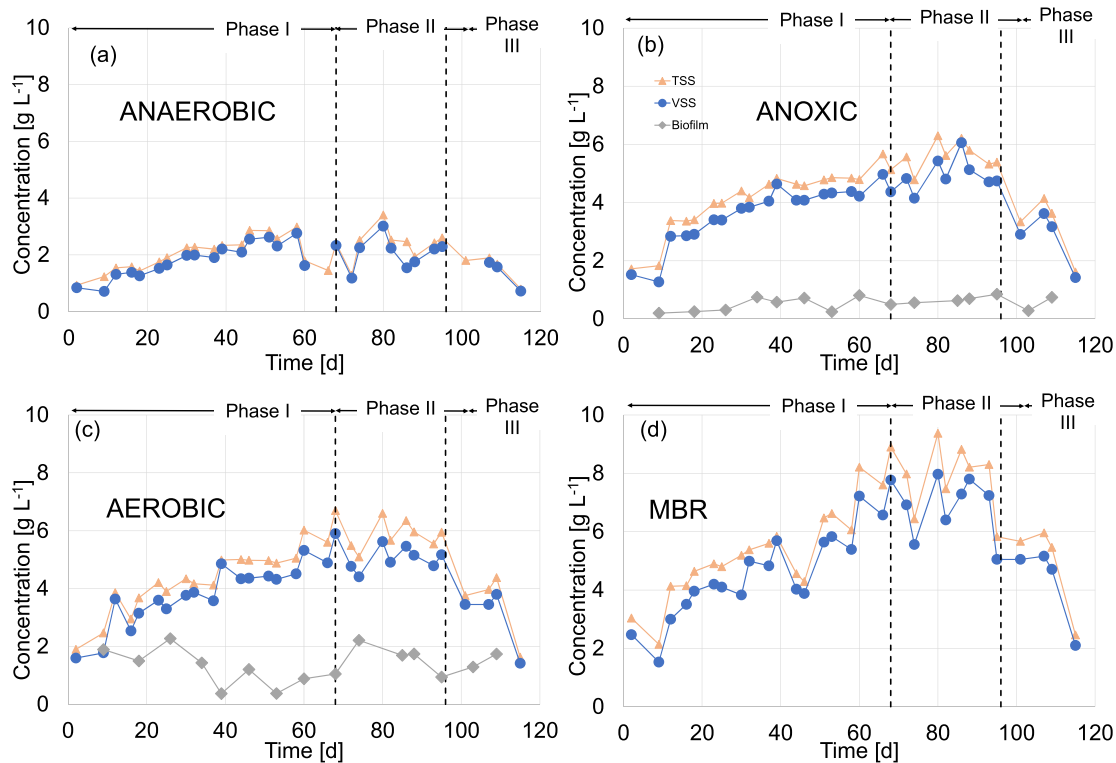
Fig. 2. Trend profiles of TSS, VSS and biofilm in the (a) anaerobic, (b) anoxic, (c) aerobic and (d) MBR compartments, respectively.

technical issues (including the lack of real wastewater feeding). Therefore, steady state conditions were not reached and future research activities must be carried out to deepen the system behaviour under these operational conditions.

3.2. Dissolved and gaseous N$_2$O concentration

Fig. 3 reports the pattern of N$_2$O-N concentration in the gas and in the liquid samples withdrawn from each reactor and in the permeate, while Table 3 summarizes the average values of gaseous and dissolved N$_2$O-N concentrations throughout experiments.

Data reported in Fig. 3 show that the SRT variation strongly influenced the N$_2$O-N concentration both in gaseous and liquid samples. More precisely, by analysing data reported in Fig. 3a one can observe that, excepting some sporadic cases, the N$_2$O-N concentration in the gas samples increased with the decrease of the mixed liquor SRT. In details, the average N$_2$O-N concentrations in the Phase III (SRT = 15 days) was 4 times higher than that of Phase I (indefinite SRT). As an example, the average N$_2$O-N concentration in the gas samples withdrawn from the aerobic reactor was 10.83 µg N$_2$O-N L^{-1} at SRT = ∞ and 23.69 µg N$_2$O-N L^{-1} at SRT = 30 d. Similarly, the average N$_2$O-N concentration in the gas samples withdrawn from the anaerobic reactor was 13.75 µg N$_2$O-N

L^{-1} at SRT = ∞ and 47.38 µg N$_2$O-N L^{-1} at SRT = 30 d. Such result is in agreement with previous literature findings obtained for CAS systems (Kampschreur et al., 2009). Indeed, Zheng et al. (1994), when studying a continuous nitrifying CAS fed with artificial wastewater, highlighted that the N$_2$O production increased when the SRT was decreased. Similarly, Noda et al. (2003) found that a SRT decrease promoted an increase of N$_2$O production in a continuous activated sludge system fed with real wastewater.

Although the nitrification efficiency resulted high throughout experiments, the total nitrogen removal efficiency decreased with the decrease of SRT (see Table 2). This efficiency decrease might have caused nitrite accumulation in the system. Indeed, the mean nitrite concentration increased in the anoxic (0.36 mg NO$_2$-N L^{-1}, 0.69 mg NO$_2$-N L^{-1} and 1.62 mg NO$_2$-N L^{-1}) as well in the aerobic reactor (0.07 mg NO$_2$-N L^{-1}, 0.08 mg NO$_2$-N L^{-1} and 0.82 mg NO$_2$-N L^{-1}) from SRT = ∞ to SRT = 30 d and SRT = 15 d, respectively. Such circumstance is likely the main cause of the N$_2$O production increase with the decrease of SRT. Furthermore, this observation is consistent with the findings of Li and Wu (2014) who identified in the higher concentration of NO$_2$-N the main reason for the increased N$_2$O emission at low SRTs. This aspect will be deepened in section 3.5 below.

The further SRT reduction (from 30 d to 15 d) did not influence
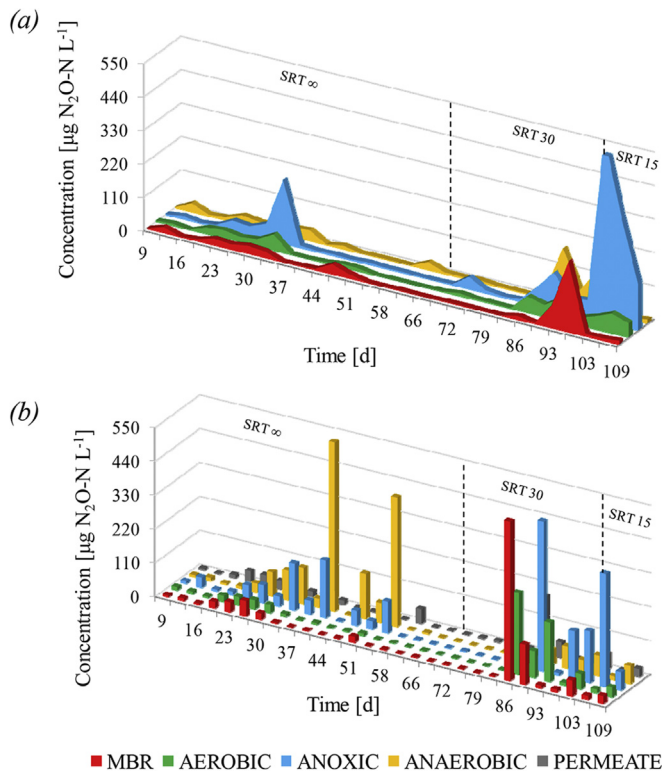
Fig. 3. Nitrous oxide concentration in the gaseous (a) and in liquid (b) samples for each SRT value.

Table 3
Average head-space and dissolved N$_2$O-N concentration for each reactor and experimental phase.

N$_2$O-N head space concentration [µg N$_2$O-N L^{-1}]	Phase I	Phase II	Phase III
Anaerobic	13.75 ($\pm$12.73)	47.38 ($\pm$66.02)	50.62 ($\pm$70.14)
Anoxic	22.84 ($\pm$50.54)	40.32 ($\pm$39.49)	377.22 ($\pm$230.58)
Aerobic	10.83 ($\pm$14.26)	23.69 ($\pm$26.54)	51.79 ($\pm$11.93)
MBR	9.79 ($\pm$10.69)	36.17 ($\pm$77.50)	8.93 ($\pm$2.90)
N$_2$O-N dissolved concentration [µg N$_2$O-N L^{-1}]	Phase I	Phase II	Phase III
Anaerobic	102.33 ($\pm$189.57)	19.56 ($\pm$26.79)	45.61 ($\pm$29.67)
Anoxic	44.85 ($\pm$54.38)	75.45 ($\pm$162.48)	197.79 ($\pm$155.64)
Aerobic	9.76 ($\pm$10.18)	62.09 ($\pm$99.97)	31.94 ($\pm$19.02)
MBR	10.39 ($\pm$13.96)	75.02 ($\pm$171.47)	30.18 ($\pm$18.99)
Permeate flux	14.22 ($\pm$14.99)	31.97 ($\pm$60.44)	28.39 ($\pm$19.59)

In brackets the standard deviation is reported.

the average N$_2$O-N gas concentration, excepting the MBR reactor. Indeed, the average N$_2$O-N gaseous concentration in the MBR tank decreased from 37.17 µg N$_2$O-N L^{-1} to 8.93 µg N$_2$O-N L^{-1} when the mixed liquor SRT was reduced from 30 to 15 d. These results are consistent with previous studies (Mannina et al., 2017b) confirming the key role played by the SRT, for the MBR tank, in the reduction N$_2$O-N gaseous concentration.

A similar trend was also obtained for the N$_2$O-N concentration dissolved in the liquid phase only in the anoxic reactor (Fig. 3b). More precisely, in the anoxic reactor the dissolved N$_2$O-N concentrations increased with the decrease of mixed liquor SRT, thus suggesting that under low SRT values there is a predominant production of N$_2$O-N inside the anoxic tank (Mannina et al., 2016c). As

an example, the average N$_2$O-N concentration dissolved in the liquid phase into the anoxic reactor increased from 75.45 µg N$_2$O-N L^{-1} to 197.79 µg N$_2$O-N L^{-1} with the decrease of the mixed liquor SRT from 30 to 15 d. This result is likely due to a twofold reason: i: the activity of suspended biomass increased due to the decrease of SRT thanks to a sort of "renewal" effect; ii: the specific biofilm contribution. Indeed, regarding this latter aspect the biofilm concentration showed fluctuations during the entire experimental duration with biofilm concentrations down to 0.4 and 0.2 g TS L^{-1} in the aerobic and anoxic compartment, respectively. This behaviour likely influenced the amount of N$_2$O-N concentration inside the anoxic and aerobic tank due to the variation of the biofilm contribution during the nitrification and denitrification processes. Indeed, during Phase I (SRT = ∞ d) a slight increase of biofilm concentration in both aerobic and anoxic reactors occurred, likely due to the simultaneous decrease of the suspended biomass (due to the increased sludge withdrawals). Indeed, the decrease of the suspended biomass could have reduced the competition between the two biomasses for the availability of the substrates, thus enhancing the growth of the biofilm. The increase of biofilm concentration could positively affect nitrification during Phase III, thus keeping the N$_2$O-N concentration both in gaseous and liquid samples of the aerobic reactor almost equal to what observed in the previous Phase II. When the SRT was reduced to 30 days a substantial decrease of the dissolved N$_2$O concentration occurred inside the anaerobic reactor. Indeed, the average dissolved N$_2$O concentration was equal to 102.33 and 19.56 µg N$_2$O-N L^{-1} for Phase I and Phase II, respectively. Such a result is likely debited to a reduced activity of PAOs as denitrifiers with the reduction of SRT.

It is worth noting that during the first 15 days of Phase II (SRT = 30 d) no significant variation in N$_2$O-N concentration (both dissolved and gaseous) occurred (Fig. 3). Such circumstance is likely due to a time lag necessary to the biological system to cope with the new SRT value.

Furthermore, it was observed that the N$_2$O concentration measured in the permeate flow rate was not negligible, in contrast to what highlighted in previous studies (Guo et al., 2012). In detail, the average N$_2$O-N concentration in the permeate samples ranged between 14.21 µg N$_2$O-N L^{-1} and 31.97 µg N$_2$O-N L^{-1} at SRT = ∞ and 30 d, respectively, thus demonstrating that the N$_2$O-N concentration in the permeate was not negligible to what measured in the other reactors. Therefore, the amount of N$_2$O discharged with the permeate in the receiving water body could represent a serious threat to the environment.

3.3. N$_2$O fluxes

Fig. 4 shows the pattern of N$_2$O-N fluxes assessed in both not aerated (a) and aerated (b) reactors, whilst Table 4 reports a summary of the average N$_2$O-N fluxes for each reactor in the different Phases.

Data reported in Fig. 4b show that the N$_2$O-N flux of the aerated reactors (aerobic and MBR) is almost 2 order of magnitude higher than that of the non-aerated reactors (anaerobic and anoxic) (Fig. 4a). This result was much more evident at the end of Phase II (SRT = 30 d) and throughout Phase III (SRT = 15 d) due to the increase of N$_2$O-N concentration in the gaseous samples. Despite similar results were also obtained in Mannina et al. (2017b), here the decrease of SRT emphasizes the role of aerated reactors in terms of N$_2$O-N flux emissions.

Significant fluxes of nitrous oxide were observed from the MBR. Due to the short hydraulic retention time (HRT) (almost 20 min), it is reasonable to assume that no biological process could occur inside the MBR tank. Although some biological processes could occur also with a so short HRT, N$_2$O fluxes up to 400 mg N$_2$O-N m^{-2} h^{-1} in
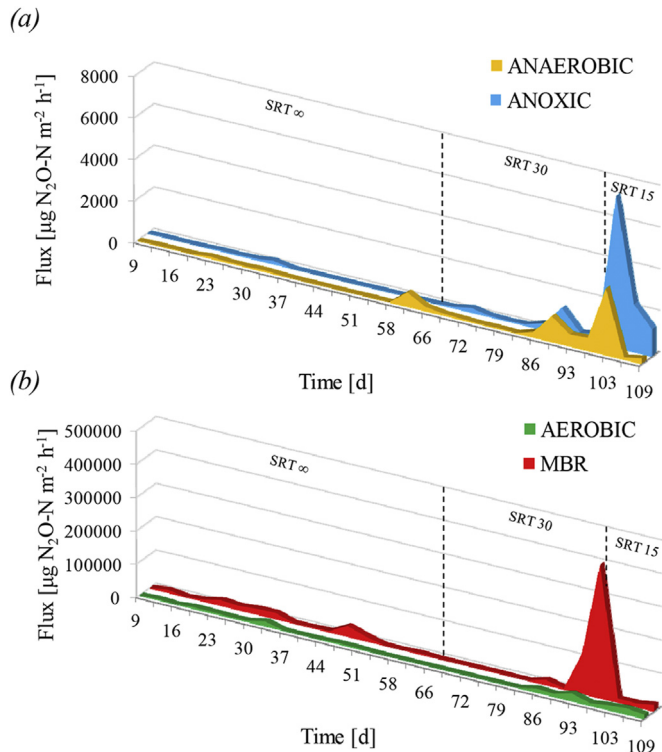
(a)

(b)

Fig. 4. N$_2$O-N flux in anaerobic and anoxic reactors (a) and in aerobic and MBR reactors (b).

Table 4
Average N$_2$O-N flux for each reactor and experimental phase.

N$_2$O-N flux [μg N$_2$O-N m^{-2} h^{-1}]	Phase I	Phase II	Phase III
Anaerobic	72 (±165)	325 (±415)	1193 (±1740)
Anoxic	22 (±38)	308 (±392)	3631 (±3205)
Aerobic	2396 (±3544)	5990 (±7786)	15352 (±3038)
MBR	7797 (±9016)	60156 (±133336)	14336 (±4667)

In brackets the standard deviation is reported.

the MBR reactor were likely produced somewhere else. It is reasonable that this huge emission might be due to the dissolved N$_2$O concentration coming from the Q_{R2} flow rate and that it stripped out in the MBR tank, thus contributing to the emission.

3.4. Emission factors

Fig. 5 shows the trend of the emission factor of each reactor. In particular, data reported in Fig. 4 show that a quite constant emission factor occurred during the entire experimental campaign, from each reactor, excepting the last days of Phase II (SRT = 30 d).

This result is mainly due to the increased air supply in the aerated reactors in the last portion of Phase II, aimed at assessing the effect of the air flow rate on both membrane fouling and N$_2$O stripping. Therefore, the N$_2$O-N emission factor assessed during days 93rd and 95th increased considerably up to the 38 and 35% of the total influent nitrogen, respectively. On average, excluding data of days 93rd and 95th the average N$_2$O-N emission factor was equal to 0.13%, 0.21% and 0.76% of the total influent nitrogen for SRT = ∞, SRT = 30 d and SRT = 15 d respectively, thus demonstrating a slight increase of the N$_2$O-N emission factor with the decrease of the mixed liquor SRT. Such result is likely due to a limitation exerted by the low SRT to the whole nitrogen removal process. Indeed, as
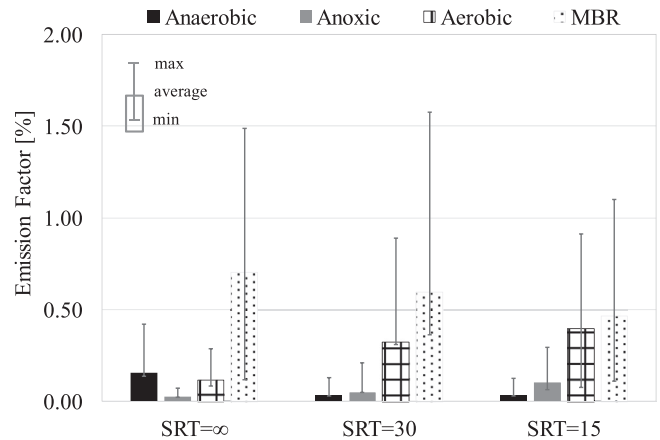

Fig. 5. N$_2$O-N emission factor pattern during experimentation during SRT = ∞ SRT = 30 d and SRT = 15 d.

reported in Table 2 slight decrease of TN removal efficiency occurred with the SRT decrease. Therefore, the observed results suggest to operate the pilot plant with higher SRT values in view to reduce the N$_2$O-N emissions.

The achieved results are in agreement with previous studies that quantified the N$_2$O emission from WWTPs. Foley and Lant (2007) derived from 11 full-scale and lab-scale wastewater systems with biological nutrient removal (BNR) a median emission factor of 0.01 kgN$_2$O−N kg^{-1} N$_{influent}$ (1% of the influent total nitrogen). Foley et al. (2010) found a high variability of the N$_2$O-N emission factor ranging between 0.006 and 0.253 kgN$_2$O−N kg^{-1} N denitrified (average: 0.035 ± 0.027). However, the emission factors obtained here are lower than that obtained for CAS by Foley and Lant (2007) even during Phase III when the maximum emission factor value (0.76% of the total influent nitrogen) was achieved. Such a result is likely due to the positive effect obtained here by the biofilm role during the nitrogen transformation processes. However, no comprehensive comparison between Phases I and II can be performed due to the aeration increase in the last days of Phase II.

3.5. Influence of nitrite accumulation on N$_2$O-N production

The influence exerted by the nitrogen forms on the N$_2$O-N emission was also investigated in the present study. In Fig. 6, the correlation between the NO$_2$-N concentration in the aerobic (Fig. 6a) and in the anoxic (Fig. 6b) reactor with the gaseous N$_2$O-N concentration in the anoxic reactor is reported.

From the observation of data reported in Fig. 6, it is worth noting a positive linear correlation between the N$_2$O-N concentration in the gas sample of the anoxic tank and the NO$_2$-N concentrations in the aerobic (Fig. 6a) as well as anoxic reactor (Fig. 6b). This result confirms that incomplete nitrification and denitrification, highlighted by the NO$_2$-N accumulation in the mixed liquor of the aerobic and anoxic tank reactors, might promote the increase of the N$_2$O-N production.

Nitrite accumulation in the anoxic reactor (Fig. 6b), up to 3 mg NO$_2$-N L^{-1}, demonstrates that the denitrification could be likely limited by the decrease of SRT. Furthermore, the high correlation (R^2 = 0.84) existing between N$_2$O-N concentration and nitrite dissolved concentration in the anoxic reactor suggests that the incomplete denitrification was the main source of N$_2$O production. Indeed, the anoxic reactor contribution to the total N$_2$O emission increased during experiments from 2.46% to 4.97% and to 10.07% in Phase I (SRT = ∞), Phase II (SRT = 30 d) and Phase III (SRT = 15 d), respectively.
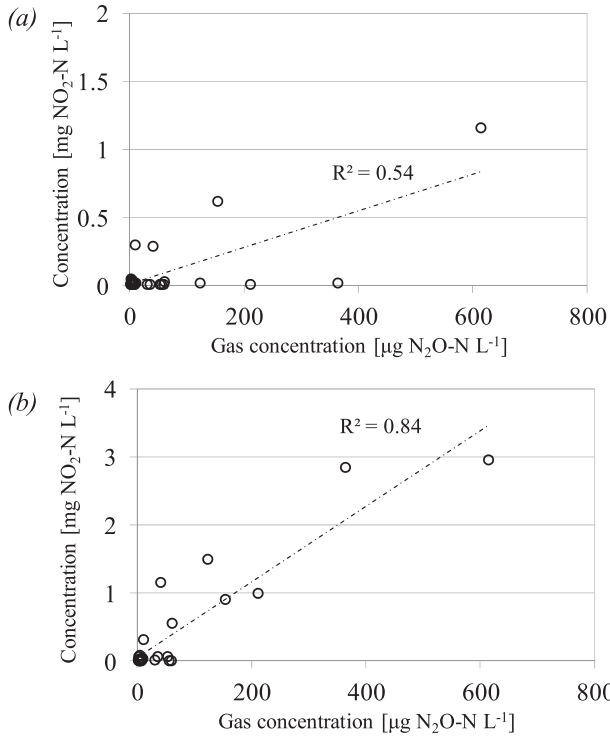
Fig. 6. Correlation between N_2O-N concentration in the gas samples of anoxic reactor and nitrite dissolved concentration in the aerobic reactor (a) and anoxic reactor (b).

3.6. N_2O-N mass balance

Fig. 7 shows the N_2O-N mass balance for each reactor, which allows the assessment of N_2O-N production/consumption in each reactor throughout experiments.

Data reported in Fig. 7a show that the N_2O-N production inside the anaerobic tank decreased with the decrease of SRT from indefinite to 30 d and 15d, respectively. Indeed, according to Mannina et al. (2017b) the anaerobic reactor is on average an N_2O-N producer. Then, with the decrease of the mixed liquor SRT from indefinite to 30 d the anaerobic reactor assume a negligible role in terms of N_2O-N consumption/production. In contrast, data of Fig. 7b–c confirm that with the decrease of the mixed liquor SRT from indefinite to 30 d the N_2O-N production both in the aerobic and anoxic tanks increased. Indeed, the N_2O-N mass balance in the anoxic tank shows that the net average production at SRT = 30 d and SRT = 15 d is almost three times higher than that at indefinite SRT (Fig. 7b). During the Phase I (indefinite SRT), similarly to previous studies Mannina et al. (2017b), the aerobic reactor was a N_2O "consumer" while during the Phase II (SRT = 30 d) it became a N_2O "producer" (Fig. 7c). Moreover, during the phase at SRT = 15 d, the aerobic reactor become again a N_2O "consumer". Finally, in the MBR reactor the production/consumption of N_2O remained quite stable, excepting for sporadic cases, over the entire experimental period.

As showed in Fig. 7, each reactor had a different behaviour towards the SRT variation. It is not easy to outline a net production or consumption pathway for each reactor. However, it is worth noting the behaviour of the anoxic and aerobic reactors, as representing the core of the nitrogen transformation processes. It is possible to affirm that the aerobic reactor was, on average, a nitrous oxide
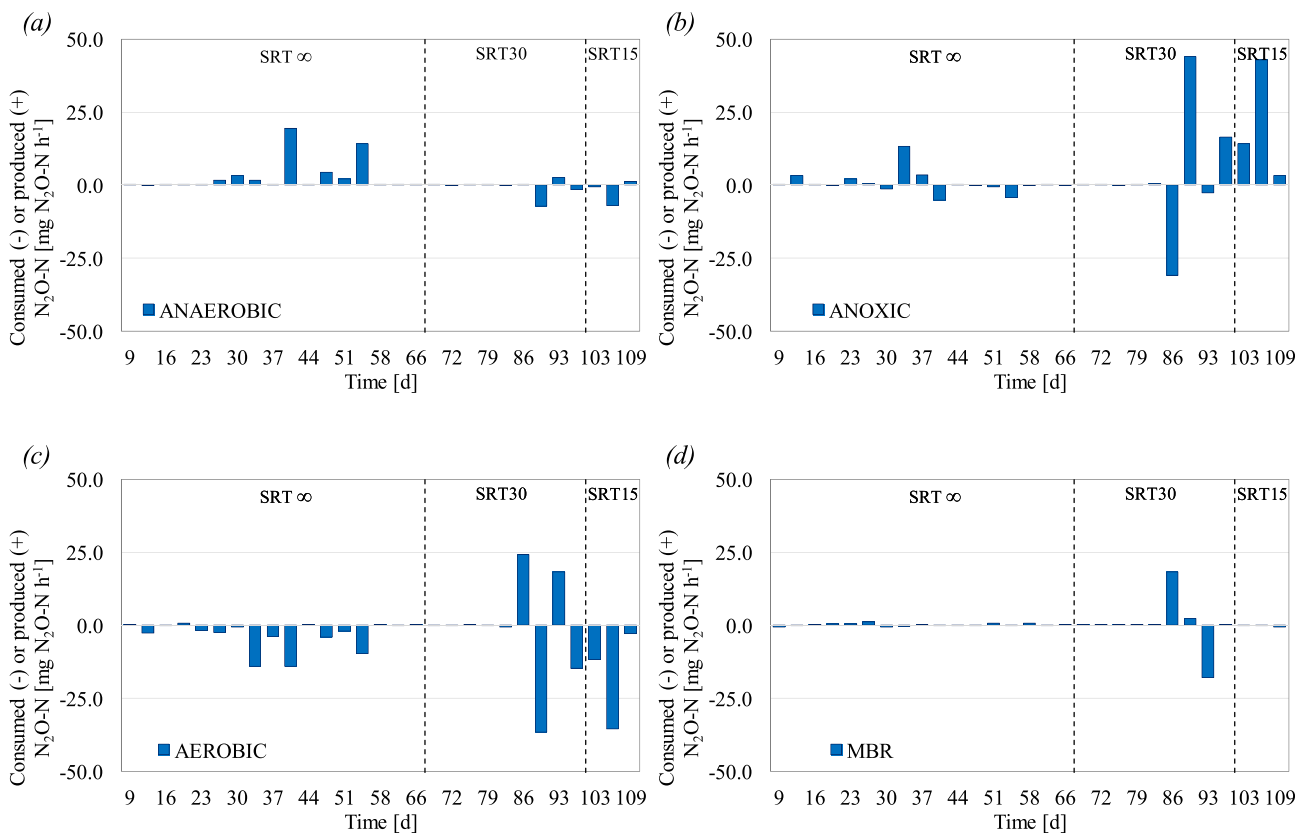
Fig. 7. N_2O-N mass balance for anaerobic (a), anoxic (b), aerobic (c) and MBR reactors (d).

consumer. Such observation can be likely due to a twofold reason: i) oxidation of dissolved nitrous oxide arriving from the anoxic; ii) stripping out of nitrous oxide coming from the anoxic and also eventually produced inside the aerobic (autotrophic denitrification). In contrast, the anoxic tank was on average a nitrous oxide producer and, as above discussed, such production increased with the SRT decrease. Such observation outlines that the main N_2O production pathway resulted the incomplete denitrification, confirmed also by the nitrite accumulation previously discussed.

However, it is difficult to point out a clear explanation for the differences that occurred in each reactor during the experimentation. Several reason could indeed affect the N_2O mass balance. Indeed in each reactor different process take place. Furthermore, each reactor is featured by different mass fluxes (that affect the mass balance). Moreover, the processes occurring in a single reactor can be transferred in the following compartments, thus affecting significantly the behaviour of the whole pilot plant.

4. Conclusions

In the present study, the influence of the mixed liquor SRT on the N_2O formation in a UCT-IFAS-MBR pilot plant was explored. In general, results showed that the SRT decrease promoted an increase of N_2O-N concentration (both in gaseous and liquid samples) and emission. The highest N_2O-N concentration was found in the off-gas of the anoxic reactor during Phase III (377.22 µg N_2O-N L^{-1}). In contrast, the highest emitted N_2O flux was achieved in the MBR tank (up to 1430 mg N_2O-N m^{-2} h^{-1}) reducing the SRT from indefinite to 30 d. This result is likely related to the high aeration provided in the MBR for fouling mitigation that might have promoted the stripping of the N_2O-N dissolved in the liquid phase. The increase of biofilm concentration has likely positively contributed to the nitrification even at low SRT value. Indeed, the N_2O-N concentration both in gaseous and liquid samples of the aerobic reactor during the phase at SRT equal to 15 d was almost equal to what observed at SRT equal to 30 d.

The emission factor highlighted a slight increase with the decrease of the SRT (0.13%, 0.21% and 0.76% of influent nitrogen in Phase I, Phase II and Phase III, respectively). Such result was likely due to the limitation of nitrification and denitrification processes with the decrease of the SRT, that likely caused a slight NO_2-N accumulation thus promoting the nitrous oxide production. Therefore, the SRT was confirmed to be a key parameter with regards to, on one hand, the nitrous oxide formation and emission while, on the other hand, the system removal efficiency. Globally, high SRT values (higher than 30 d) are suggested to mitigate the N_2O-N emissions and improve the nitrogen removal. However, the effect of the adopted SRT on the phosphorus removal has to be analysed, since low SRT values are more advisable to remove phosphorus.

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