Biochemical Engineering Journal 112 (2016) 114–122

Contents lists available at ScienceDirect

Biochemical Engineering Journal

journal homepage: www.elsevier.com/locate/bej

Regular article

Greenhouse gases from sequential batch membrane bioreactors: A pilot plant case study

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ARTICLE INFO

Article history:
Received 12 December 2015
Received in revised form 2 April 2016
Accepted 11 April 2016
Available online 13 April 2016

Keywords:
Global warming potential
Wastewater treatment
Environmental preservation
Membrane bioreactors
Sequencing batch reactor
Bioprocess monitoring

ABSTRACT

The paper reports the results of nitrous oxide (N_2O) emissions from aerobic and anoxic tank of a Sequential Batch Membrane Bioreactor (SB-MBR) pilot plant. The influence of salinity variation on N_2O emission was analyzed by gradually increasing the inlet salt concentration from 0 to 10 g NaCl L^{-1}.

The observed results showed that the N_2O concentration of the gaseous samples was strongly influenced by the salt concentration. This result was likely related to a worsening of the nitrification activity due to the effect of salinity on autotrophic bacteria. Dissolved oxygen concentration and salinity were found to be the key factors affecting N_2O concentration in the gaseous samples withdrawn from the anoxic tank. Despite the fact that the N_2O concentration in the anoxic tank was higher than in the aerobic one, it was found that the aerobic tank emitted around 25 times more N_2O than the anoxic one.

1. Introduction

During the last years the main goal of wastewater treatment plants (WWTPs) has become broader than simply to meet effluent standards for receiving water body protection: many efforts were spent with the aim to include reduction/control of greenhouse gases (GHGs) emission [1,2]. Indeed, WWTPs can produce GHGs such as nitrous oxide (N_2O), carbon dioxide (CO_2) and methane (CH_4) [2]. GHG emissions from a WWTP can have a triple nature: direct, indirect internal and indirect external [3]. Direct emissions are mainly related to the biological processes (biomass respiration; biological nitrogen removal, etc); indirect internal emissions are associated with the electric consumptions and indirect external emissions are related to the other sources not directly controlled inside the WWTP (e.g., disposal of the excess sludge). Among the GHGs produced in a WWTP, N_2O plays a key role in terms of climate change. Indeed, the global warming potential (GWP) of N_2O is 298 times higher than that one of CO_2 based on a time horizon of 100 years [4,5]. It is therefore crucial to identify potential anthropogenic sources of N_2O in order to evaluate their relevance in the global N_2O budget. The IPCC reports [6] have established that N_2O emissions from WWTP account for approximately 3% of the total anthropogenic sources. Furthermore, the global N_2O emissions from WWTP are expected to increase by approximately 13% between 2005 and 2020 [2]. Thus, it is imperative to better understand the core mechanisms connected with the N_2O production and emission in WWTPs and identify the main operating conditions affecting its formation.

During the last years, several efforts have been spent by the scientific community (*inter alia* Law et al. [2]; Kampschreur et al. [7]) with the aim to better understand processes and key operating factors promoting the N_2O emission in WWTPs.

The processes associated with biological nitrogen removal have been reported to be the key source of N_2O emission [2,7,8]. Indeed, N_2O can be produced during both nitrification (only by the ammonia oxidizing bacteria – AOB) and denitrification processes (during the NH_2OH pathways of nitrifier denitrification and/or the heterotrophic denitrification pathway). In detail, N_2O is an intermediate of the heterotrophic denitrification but it can also be produced during the ammonia oxidation process (nitrification) [9]. However, N_2O formation mechanisms have not been completely elucidated yet [2,10]. Contrasting opinions have been reported in the technical literature regarding the prevalent pathway in N_2O formation [2]. Furthermore, large variations in terms of measured N_2O emissions have been reported for different WWTPs ranging between 0.01% and 1.8%, and in some cases even higher than 10% referring to the N-loading rate [7,11–14]. These variations have been mainly ascribed to the different operational conditions (e.g.,

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http://dx.doi.org/10.1016/j.bej.2016.04.010
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dissolved oxygen (DO) concentration, C/N-ratio, pH level, ammonium (NH_4^+) loading rate, and NO_2- accumulation) applied to the plants and also in different zones of the same plant [15,16]. Therefore, the fixed emission factors, applied to estimate N_2O emissions from WWTPs, as suggested by the IPCC [6,17], may drive to erroneous quantifications. Indeed, fixed emission factors do not take into account the interrelationship between the process configurations and operating conditions. Therefore, the understanding of the key operating conditions or plant configurations affecting or promoting the N_2O emissions is imperative for the reduction of N_2O emissions.

Kampschreur et al. [7] identified the main operational conditions that promote the N_2O production during the nitrogen removal process (e.g. low DO or nitrite accumulation due to the presence of toxic compound in the aerobic reactor or the low ratio C/N required for the denitrification). Zhao et al. [8] found that high salinity or salinity variations could also promote N_2O production during nitrification. Several authors have previously studied the role of salinity on N_2O emissions [8,18–20].

In particular, Tsuneda and co-workers [18] found that an increase in salt concentration strongly influenced the N_2O emission in a conventional pre-denitrification plant due to direct inhibition of N_2O acceptor oxidoreductase activity. Furthermore, Tsuneda et al. [18] found that the high concentration of DO, transported from the oxic tank to the anoxic one through the recycling stream, promotes the N_2O formation in the anoxic tank due to the high salinity.

Shang et al. [19] investigated the effect of salt on the nitrification process comparing two plants treating ordinary municipal wastewater and saline wastewater and found that high N_2O production was related to the saline wastewater treatment and that a rapid salinity increase led to the greatest N_2O production. Therefore, they suggested to avoid huge fluctuation of salinity.

Zhao et al. [20] investigated the effect of salinity stress under various COD/N ratios on the N_2O production during the denitrification process in the presence of different terminal electron acceptors. Zhao and co-workers [20] found that the salinity was the factor that most influenced N_2O production, whilst the COD/N ratio was the sub-important one. Specifically, when the salinity was high (20 g NaCl L^{-1}), N_2O accumulated at various COD/N ratios and in the presence of different terminal electron acceptors.

Very recently, Zhao et al. [8] have investigated the salinity effect on N_2O production pathway during nitrification. They found that saline shocks led to nitrite accumulation, thus enhancing the N_2O production that can be reduced by pre-acclimatizing the activated sludge to the saline wastewater.

The literature review reported above, shows that there is a worldwide high interest in the N_2O emissions from WWTPs, as well as all factors that affect the N_2O production.

In this study, a sequencing batch reactor (SBR) was used. It is reason to suspect that the changing operating conditions of a SBR may make this type of WWTP prone to high N_2O emissions. Indeed, transient conditions in terms of DO, typical of the SBRs, should imply the increase of N_2O emission [16].

Rodriguez-Caballero et al. [21] have recently demonstrated that SBRs operated with long aerated phases provide the largest N_2O emissions. Stenström at al. [22] studied N_2O production under various C/N-ratio and DO in full-scale SBR treating digester supernatant founding that reduced DO concentrations during nitrification (<1,0–1,5 mg L^{-1}) enhanced N_2O formation. Furthermore, Stenström at al. [22] pointed out that the N_2O formed in the water phase during denitrification accumulates in the water volume until aeration starts and thereafter it is quickly stripped off. Rapid changes in operating conditions, for instance lowering the DO set point from 2.0 to 1.9 mg L^{-1}, resulted in an increase in N_2O emitted in the off-gas during nitrification by 65.6%.

To our knowledge, there has not been any study reporting the role of salinity in N_2O emissions from sequencing batch membrane bioreactors (SB-MBRs) despite their worldwide application for the treatment of wastewater. Therefore, the novelty of the present study consists in the investigation of N_2O emissions form a SBR pilot plant equipped with a membrane module (MBR) for the solid/liquid separation. The SB-MBR pilot plant was fed with domestic wastewater and was subjected to a gradual salinity increase (addition of NaCl to yield concentrations from 0 to 10 g NaCl L^{-1}), carried out at moderate steps (2 g NaCl L^{-1}). The main aim of the study was to gain insight about the short term effect of this gradual salinity increase on N_2O emission both from oxic and anoxic tanks. The present study is part of a wider research project focused on the use of a non-specialized bacterial consortium for the treatment of saline wastewater contaminated by hydrocarbons [32,33]. The present paper reports the results of a part of the study aimed at analyzing the effect of salinity up to 10 g NaCl L^{-1}, that was recognized to represent a sort of threshold value, beyond which a significant impact on bacteria might occur [27].

2. Materials and methods

2.1. SB—MBR pilot plant

The SB-MBR pilot plant consisted of two reactors in-series, one anoxic (volume 45 L) and one aerobic (volume 224 L), according to a pre-denitrification scheme (Fig. 1). An ultrafiltration hollow fiber membrane module (Zenon Zeeweed, ZW10) was installed into a separate aerated compartment (volume 50 L) while an oxygen depletion reactor (ODR) was placed in the recycling line in order to ensure anoxic conditions inside the anoxic reactor despite the intensive aeration in the aerobic tank. The aerobic, anoxic and MBR reactors were equipped with specific covers that guaranteed the gas accumulation in the headspace.

The SB-MBR pilot plant was fed discontinuously with real domestic wastewater (stored in a feeding tank of 320 L volume) according to fill-draw-batch operation approach. More in detail, 40 L of wastewater (V_{IN}) (previously mixed inside the mixing tank with salt, in order to meet the design salinity concentration) were cyclically fed in, whereas the permeate was extracted at 20 L h^{-1} (Q_{OUT}). Each cycle had the duration of 3 h that were split into 1 h of biological reaction and 2 h of MBR filtration. During the biological reaction time the permeate extraction pump was turned out, thus Q_{OUT} was equal to zero. During the cycle, 80 L h^{-1} (Q_{R1}) were continuously pumped from the aerobic to the MBR tank. Furthermore, a recycling activate sludge stream (Q_{RAS}), equal to 80 L h^{-1} during the reaction period and to 60 L h^{-1} ($Q_{R1} - Q_{OUT}$) during the filtration phase, was recycled from the MBR to the anoxic tank via the ODR tank. The SB-MBR pilot plant was operated for 3 months without sludge withdrawals (indefinite sludge retention time – SRT). The main wastewater characteristics as well as pilot plant operational parameters are summarized in Table 1. The experimental campaign was divided into six phases each characterized by a specific salt concentration from 0 up to 10 g NaCl L^{-1}. The NaCl concentration in the influent was increased at step of 2 g NaCl L^{-1} on a weekly basis. The Phase VI had a duration of 26 days.

2.2. Gas sampling

During pilot plant operation, both liquid and gaseous samples were withdrawn from the aerobic and anoxic tanks and analyzed to evaluate the N_2O concentration. Furthermore, in order to quantify the N_2O flux emitted from both the aerobic and anoxic compartment, the gas flow rate (Q_{gas}) was indirectly measured by using a hot wire anemometer.

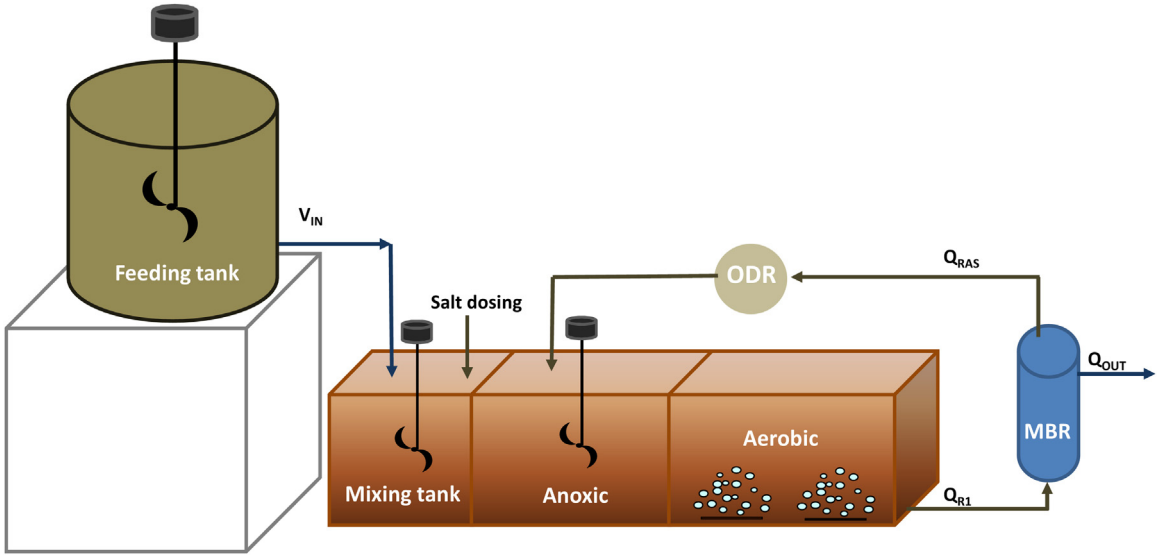

Fig. 1. Layout of the SB-MBR pilot plant (where V_{IN} = 40 L = influent wastewater volume; ODR = Oxygen Depletion Reactor; MBR = membrane Bioreactor; Q_{RAS} = 80 L h^{-1} = recycled sludge from MBR to ODR; Q_{R1} = 80 L h^{-1} = sludge feeding from aerobic tank to MBR; Q_{OUT} = 20 L h^{-1} (only during the MBR filtration phase) = effluent flow rate).

Table 1
Operational conditions and wastewater main characteristics.

Parameter	Units	Value
Duration of the biological process	[h]	1
Duration of the filtration phase	[h]	2
Volume fed for each cycle	[L]	40
Permeate Flow rate	[L h^{-1}]	20
MLSS	[g L^{-1}]	4.5
BOD	[mg L^{-1}]	82
COD	[mg L^{-1}]	240
NH4-N	[mg L^{-1}]	30
F/M	[kgBOD kgVSS^{-1} d^{-1}]	0.085
C/N-ratio	[mg L^{-1}]	8
NaCl	[g L^{-1}]	0–10

2.2.1. Gas flow rate measurement

The gas flow rate (Q_{gas}) was indirectly evaluated according to the following Eq. (1):

$$Q_{gas} = v_{gas} \times A \quad (1)$$

where A represents the outlet section (m^2) and v_{gas} ($m\,s^{-1}$) is the gas velocity, measured by using the TMA-21HW – Hot Wire anemometer. During the flow rate measurements in the anoxic compartment a sweep air flow rate (Q_{Sweep}) was supplied inside the reactor in order to promote the gas mixing and to facilitate the gas sampling at low gas flow rate condition [23]. Thus, the gas flow rate emitted from the anoxic tank was evaluated according to Eq. (2).

$$Q_{gas} = v_{gas} \times A - Q_{Sweep} \quad (2)$$

2.2.2. Gas phase sampling

Gas samples were withdrawn by means of commercial syringes and transferred into glass vials (e.g., LABCO Exetainer, 738 model) where the vacuum was previously created.

In order to guarantee the atmospheric pressure inside the vials, the ratio between the volume of the gas sample (inserted inside the vial) and the volume of the vial has to be not less than 1.25 (e.g. 15 mL of sample in vial of 12 mL).

Grab samples were collected every 15 min in a 3 h sampling period (total duration of each cycle). A number of 3 replicates were carried out for each grab sample. The N_2O concentration was then calculated as the average value among the 3 replicates.

2.2.3. Dissolved gas sampling

Dissolved gas sampling was carried out on the basis of the head space gas method derived from Kimochi et al. [24]. In detail, 70 mL of supernatant (after 5 min centrifugation at 8000 rpm) were sealed into 125 mL glass bottles. In order to prevent any biological reaction, 1 mL of 2 N H_2SO_4 was added. After 24 h of gentle stirring, the bottles were left for 1 h without moving. Then, the gas accumulated in the head space of the bottles was collected similarly to the gas sampling procedure.

Finally, by applying the Henry's Law, the dissolved gas concentration at the equilibrium with the headspace gas was calculated. In this case, a lower sampling frequency was used (1 sample per hour).

2.3. Gas flux quantification

The i-th gas flux (Fi) emitted from the j-th tank was quantified according to Eq. (3) [25].

$$F_i = p_i \times C_i \times \frac{Q_{gas,j}}{A_j} \quad (3)$$

where, ρ_i ($mol\,m^{-3}$) is the density of the i-th gas at the record temperature, C_i ($mg\,L^{-1}$) is the i-th gas concentration during the sampling period; $Q_{gas,j}$ ($L\,min^{-1}$) is the gas flow rate emitted from the j-th tank; A_j (m^2) represents the emitted surface of the j-th tank.

2.4. N_2O emission factors

The N_2O emission factors, expressed as the percentage of N_2O emitted compared to the inlet nitrogen loading rates, have been evaluated, for both aerobic and anoxic compartment, by means of the following equation derived by Tsuneda et al. [18]:

$$EF_{N2O} = \frac{N_2O_{Gas}/\Delta t + N_2O_{Dissolved}/HRT}{TN_{IN}/HRT} \quad (4)$$

where EF_{N2O} is the emission factor, N_2O_{Gas} is the nitrous dioxide in the gaseous phase, Δt is the time between nitrogen gas replacement and gas sampling, $N_2O_{Dissolved}$ is the nitrous dioxide in the

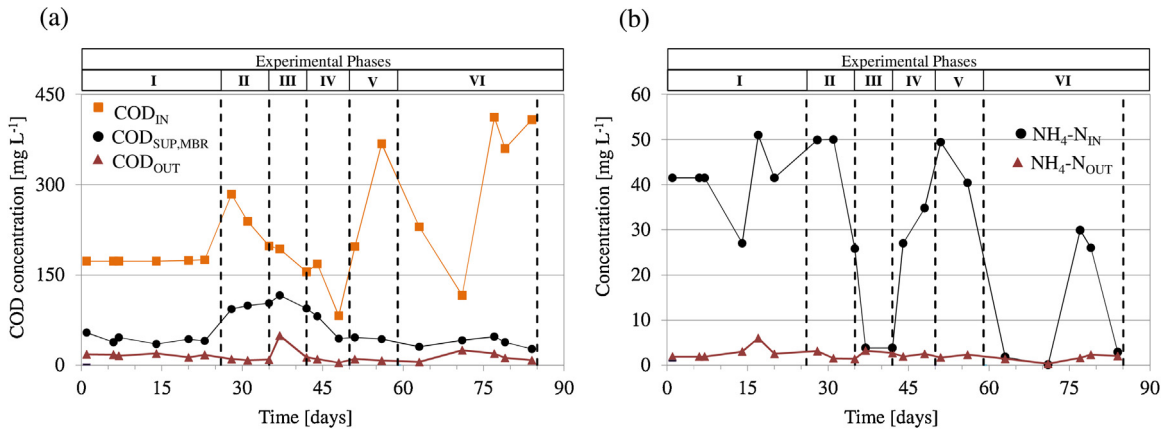

Fig. 2. Trend of influent, effluent and MBR supernatant COD concentration (COD_{IN}, COD_{OUT}, $COD_{SUP,MBR}$, respectively) (a); pattern of influent and effluent ammonia (NH_4-N_{IN} and NH_4-N_{OUT}, respectively) (b).

Table 2
Removal efficiencies during the different experimental phases.

Phase	Salinity	Removal efficiency [%]				
	[g NaCl L^{-1}]	Total COD	Biological COD	Nitrification	Denitrification	Total nitrogen
I	0	94.5	67.3	93.5	2.4	9.4
II	2	96.2	57.9	95.8	1.6	9.7
III	4	83.1	39.6	92.2	36.4	42.6
IV	6	94.6	49.1	95.7	9.9	16.6
V	8	96.4	94.1	94.4	2.8	21.4
VI	10	93.3	84.5	88.7	1.4	38.7

liquid phase, TN_{IN} is the influent total nitrogen concentration while HRT is the hydraulic retention time of the SB-MBR pilot plant.

2.5. Analytical methods

N_2O concentration was measured by using a Gas Chromatograph (Thermo Scientific™ TRACE GC) equipped with an Electron Capture Detector.

The influent wastewater and effluent permeate were also monitored in terms of total chemical oxygen demand (TCOD), supernatant COD, ammonium nitrogen (NH_4-N), nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N), total nitrogen (TN), phosphate (PO_4-P), total carbon (TC), inert carbon (IC). The measurements have been carried out according to Standard Methods [26]. Furthermore, batch respirometric tests were performed in order to evaluate the heterotrophic and autotrophic biokinetic parameters [27].

3. Results and discussion

3.1. Pilot plant performances

In MBR systems, the organic matter removal is due both to the biological removal (biomass growth on organic substrate) and physical removal (filtration through the membrane module). The sum between the biological and physical removal represents the total COD removal efficiency. Bearing in mind this consideration, both the total (evaluated between influent, COD_{IN}, and permeate, COD_{OUT}) and the biological (evaluated between influent and supernatant of the mixed liquor inside the MBR tank, $COD_{SUP,MBR}$) removal efficiencies, have been calculated. Fig. 2 shows the influent and effluent patterns for COD (a) and NH_4-N (b).

During the experimental campaign, the COD_{IN} ranged between 170 and 410 mg L^{-1} (Fig. 2a). Despite such significant fluctuations, the permeate COD (COD_{OUT}) was always lower than 25 mg L^{-1}, excepting only one day during the Phase III (37 mg L^{-1}).

Nevertheless, the SB-MBR pilot plant showed very high total COD removal efficiencies, with average value equal to 93%. The total COD removal efficiency was only slightly influenced by the increased salinity, with a minimum value of 74% at a salt concentration of 4 g NaCl L^{-1} (Phase III). Conversely, the biological COD removal efficiency (evaluated in the supernatant of the membrane compartment, prior to membrane filtration) showed a slight decrease in the Phases II, III and IV, as an effect of inlet salinity increase. Thereafter, it increased again, reaching average values of 94 and 84.5% in the Phases V and VI, respectively, suggesting a satisfactory level of biomass acclimation to salinity.

Therefore, the salinity increase did not exert a significant stress effect on the heterotrophic species, with the main kinetic/stoichiometric parameters in good agreement with literature data [28]. Only a slight decrease of the biokinetic parameters was observed during experiments, with a good acclimation level reached at the end of the experimental campaign. The respiration rates, expressed in terms of specific oxygen uptake rate (SOUR) showed an almost constant value close to 12 mgO_2 $g^{-1}VSS$ h^{-1} (as average).

In terms of ammonia, the influent value (NH_4-N_{IN}) was strongly influenced by the rain events. Indeed, as reported in Fig. 2b the NH_4-N_{IN} concentration was very low during the Phase III and VI (with minimum value of 3.8 mg L^{-1} and 0.1 mg L^{-1} for the Phase III and VI, respectively). Nevertheless, the effluent ammonia concentration (NH_4-N_{OUT}) was always lower than 6 mg L^{-1} (Fig. 2b). Indeed, the ammonia removal efficiency fluctuated in the range of 90–63% throughout the experiments. The lowest ammonia removal efficiency (63%) was obtained at the highest salinity level (10 g NaCl L^{-1}) indicating the adverse effect of salt on the nitrification process, as highlighted in previous studies [27]. This result was confirmed by the respirometric batch test that showed a significant reduction of the respiration rates (from 8.85 mgO_2 L^{-1} h^{-1} to 4 mgO_2 L^{-1} h^{-1})

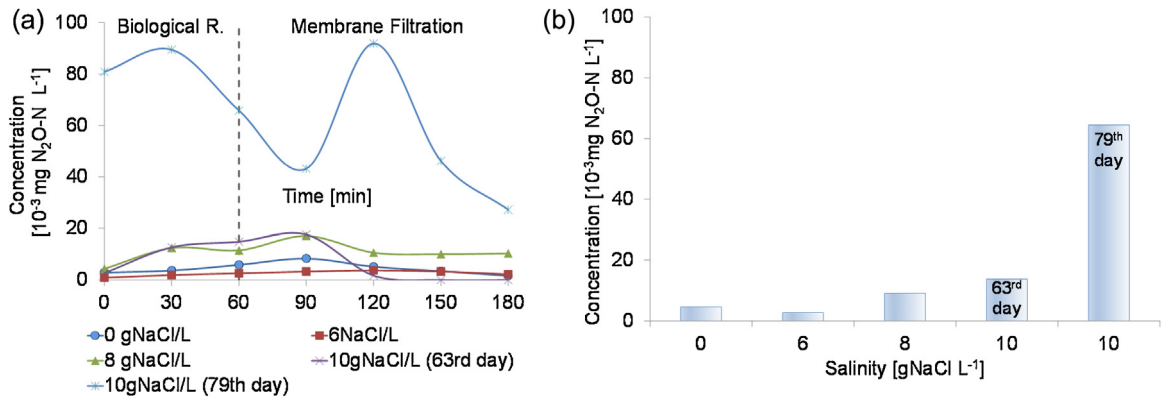

Fig. 3. N_2O-N concentration in the gas samples withdrawn from the aerobic tank during the cycle time (a); average N_2O-N concentration in the gas samples from the aerobic reactor at each salinity step (b).

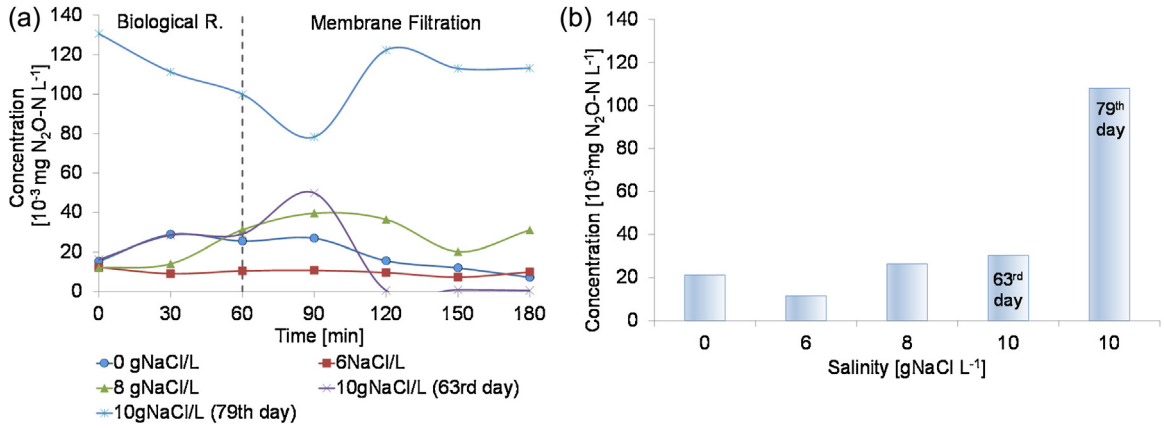

Fig. 4. N_2O-N concentration in the gas samples withdrawn from the anoxic tank during the cycle time (a); average N_2O-N concentration in the gas samples from the anoxic reactor at each salinity step (b).

with the salinity increase. However, the gradual moderate increase of salinity resulted in a gradual acclimation of autotrophic biomass at the end of the experimental period, with respiration rates that increased up to 9.3 mg O_2 L^{-1} h^{-1}. However, despite this reduction of the nitrification efficiency, no NO_2N accumulation occurred inside the system.

The denitrification removal efficiency was very low, showing an average value of 20%. This result was likely due to the quite high DO concentrations inside the anoxic tank.

Table 2 summarizes the average values of pollutants removal efficiency for each experimental sub-phase.

3.2. Salinity effect on N_2O production during the nitrification process

Fig. 3 shows the pattern of the N_2O concentration in the gas sample withdrawn from the aerobic tank during the whole cycle duration (Fig. 3a) as well as the average value for each salinity step (Fig. 3b). Data of Phase II (2 g NaCl L^{-1}) and III (4 g NaCl L^{-1}) are missing in Fig. 3 due to GC technical failure. By analyzing Fig. 3a it is worth noting that at low NaCl concentrations (0 and 6 g NaCl L^{-1}) the maximum value of the N_2O production occurred almost at the end of the biological process duration (between 90th and 100th min). The observed results highlighted in general an increasing N_2O production trend followed by a decreasing one, likely deriving from the gradual consumption of the available N source.

Furthermore, when the salinity was increased from 0 to 6 g NaCl L^{-1} a slight reduction of the N_2O concentration occurred (Fig. 3a–b). This may be due to the initial inhibition effect exerted by the saline level on the bacterial consortium, with a reduced metabolic activity. Nevertheless, with the increase of salinity from 6 to 10 g NaCl L^{-1}, no regular patterns of N_2O concentration during the entire cycle duration were found. This result was likely due to the effect of salinity on the autotrophic respiratory activity. Indeed, as discussed above, with the increase of salinity, the respiration rates of autotrophic biomass, decreased considerably. Such circumstances, coupled to the increase of salinity, led to the increase of N_2O emissions with higher concentrations in the gas samples of the aerobic tank. Indeed, as shown in Fig. 3b the maximum N_2O concentration (as average) occurred at 10 g NaCl L^{-1}. It is worth noting that after 15 days of operation at 10 g NaCl L^{-1} the average N_2O concentration increased from 13.7 10^{-3} mg L^{-1} to 64.5 10^{-3} mg L^{-1} (Fig. 3b). However, the emission measured at day 63th, significantly lower compared to that at day 79th, may be related to the very low nitrogen load at day 63th. The results suggest that a salinity concentration of 10 g NaCl L^{-1} may represent a sort of threshold value that indicates a maximum salinity stress over which a significant impact on nitrification activity takes place [27] and that a long duration might be requested for a satisfactory acclimation of autotrophic species to salinity.

3.3. Salinity effect on N_2O production during denitrification

Fig. 4 shows the N_2O concentration trend in the gas sample withdrawn from the anoxic tank during the entire cycle duration (Fig. 4a) as well as the average value for each salinity step (Fig. 4b).

Even in this case, data of Phase II (2 g NaCl L^{-1}) and III (4 g NaCl L^{-1}) are missing in Fig. 4 due to GC technical failure. Fig. 4 shows

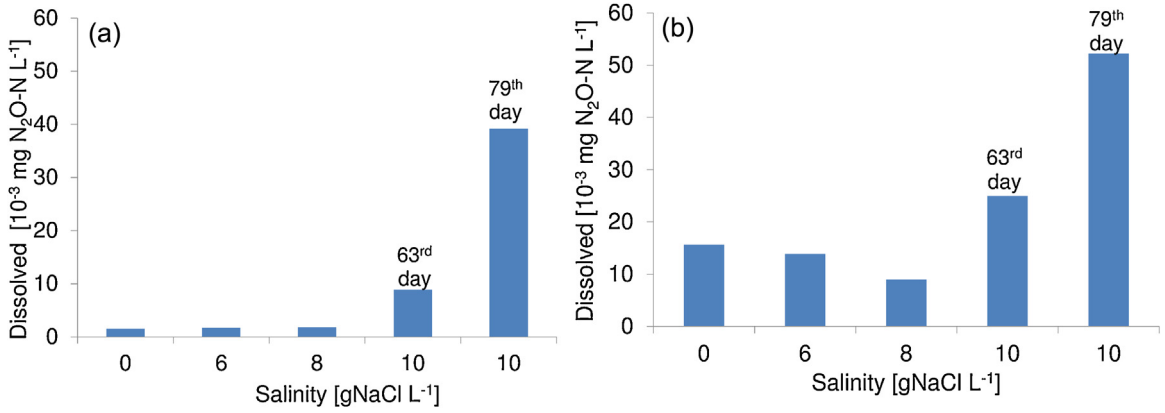

Fig. 6. N_2O concentration in the liquid samples withdrawn from the aerobic (a) and anoxic (b) at each salinity step.

Table 3
N_2O-N emission factor (% of Nitrogen loading rate).

Day	Salinity	N_2O Aerobic	N_2O Anoxic	Literature range	Reference	Type of WWTP	Remarks
	[gNaCl L^{-1}]	[%]	[%]	[%]			
20	0	0.18	0.46	0.7–13	Tsuneda et al. (2005)	Oxic-Anoxic Activated Sludge	Increasing salt concentration
44	6	0.210	0.49	0.2–0.5	Tsuneda et al. (2005)	Nitrifying activated sludge	Increasing salt concentration
56	8	0.36	0.55	0.5–20	Itokawa et al. (2001)	Oxic-Anoxic SBR Activated Sludge	Decreasing C/N ratio
63	10	0.94	1.13	>50	Lemair et al. (2006)	Oxic-Anoxic SBR Activated Sludge	Synthetic wastewater
79	10	5.11	4.46	2.8	Kampschreur et al. (2008)	Nitrifying SBR Activated Sludge	Synthetic wastewater

a trend similar to the aerobic compartment one. However, in the anoxic tank the increase of N_2O concentration with salinity (dosage from 6 to 8 NaCl L^{-1}) was likely caused by two main reasons: i. salt inhibition effect; ii. un-ability to maintain anoxic conditions inside the tank.

High amounts of DO (not used inside the aerobic tank) were recycled with the return sludge from the MBR compartment to the anoxic tank through the ODR and hence high DO concentration (2.5 mg L^{-1} on average) could not be avoided inside the anoxic tank during the last period at 10 g NaCl L^{-1}, thus depressing the denitrification enzymatic ability. However, in the present study salinity was found to be the key factor influencing N_2O production inside the anoxic tank. Indeed, no significant correlation with temperature and COD/N ratio were found in terms of N_2O concentration.

3.4. Aerobic and anoxic N_2O emission fluxes

Despite the fact that the N_2O concentrations in the gas samples from the anoxic tank were higher than that from the aerobic one, it was found that the aerobic tank produced a higher N_2O flux than the anoxic one. In Fig. 5, the trend of N_2O cumulative flux related to the aerobic (Fig. 5a) and anoxic (Fig. 5b) tanks are reported for each salinity step.

As shown in Fig. 5a the cumulative N_2O flux emitted from the aerobic tank during the cycle range between 2.8 g m^{-2} h^{-1} (at 0 g NaCl L^{-1}) and 67 g m^{-2} h^{-1} (at 10 g NaCl L^{-1}), i.e. around 25 times higher than in the anoxic tank. This finding is in agreement with previous studies that demonstrate higher N_2O production inside the aerobic tank [25]. Ahn et al. [11] have found that N_2O emissions are two to three orders of magnitude higher in aerated zones than in non-aerated ones. Such a result is due to the fact that N_2O formed in water phase during denitrification accumulates mainly in the water volume until aeration starts and thereafter it is quickly stripped off to the atmosphere [22].

3.5. N_2O concentration in the dissolved phase

Similarly to the results observed for N_2O concentration in the gaseous phase, the salinity increase promoted a considerable amount of dissolved N_2O production, especially at the highest saline concentration (10 g NaCl L^{-1}), as shown in Fig. 6. Moreover, the dissolved N_2O concentration was found to be significantly higher in the anoxic compartment (Fig. 6b) compared to the aerobic one (Fig. 6a). Indeed, as previously discussed, the N_2O production in the anoxic phase could be due to a twofold reason: the increase of salinity and the high DO concentrations that enhanced incomplete denitrification, thus promoting the production of dissolved N_2O.

3.6. Operating factors affecting N_2O concentration

Fig. 7 shows the relationship among DO and N_2O (as gas sample) average concentrations inside the aerobic (Fig. 7a) and anoxic tank (Fig. 7b), respectively. Moreover, the trend of DO and N_2O (as gas sample) concentration inside the aerobic tank during a typical cycle at 0 g NaCl L^{-1} and 10 g NaCl L^{-1} are reported in Fig. 7c and Fig. 7d, respectively. Finally, Fig. 7e reports the correlation among the N_2O concentrations in the gas sample withdrawn from the aerobic tank and the nitrification efficiency. The latter has been calculated according to Wagner et al. [29]. Data reported in Fig. 7a and Fig. 7e can be considered statistically significant. Indeed, by adopting a significance level (α) of 0.05, their p-value is lower than α. In details, the p-value of the data shown in Fig. 7a and Fig. 7e is equal to 0.007 and 0.02, respectively. Conversely, data reported in Fig. 7b are statistically less significant. Indeed, their p-value is equal to 0.35.

As shown in Fig. 7a–d the DO concentration has been found to play a key role (coupled with salinity) in affecting N_2O production during nitrification (Fig. 7). Indeed, as noticeable from Fig. 7a, an exponential correlation, characterized by an high regression coefficient (R^2), was found between the average DO and N_2O concentration in the aerobic tank. More specifically, at the lowest DO concentration (1.8 mg L^{-1}) the highest N_2O (65 10^{-3} mg N_2O L^{-1})

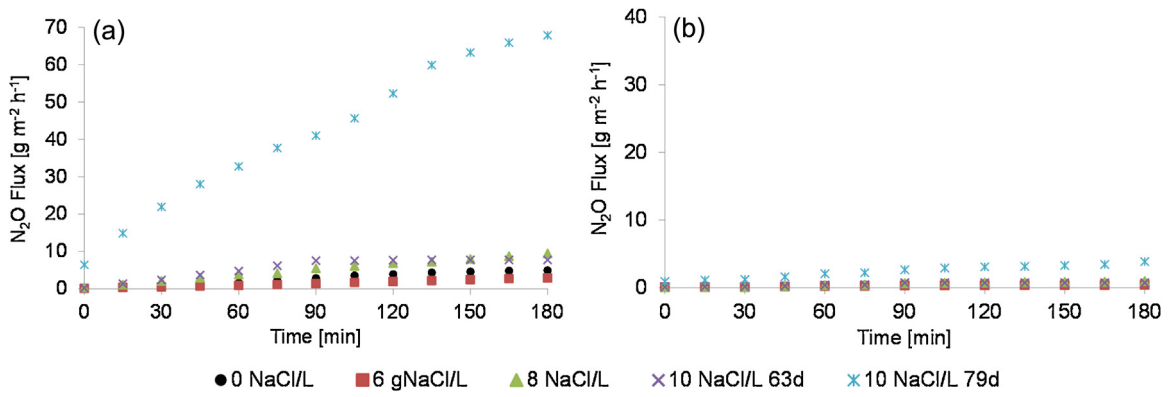

Fig. 5. Cumulative N_2O flux produced from the aerobic (a) and anoxic tank (b).

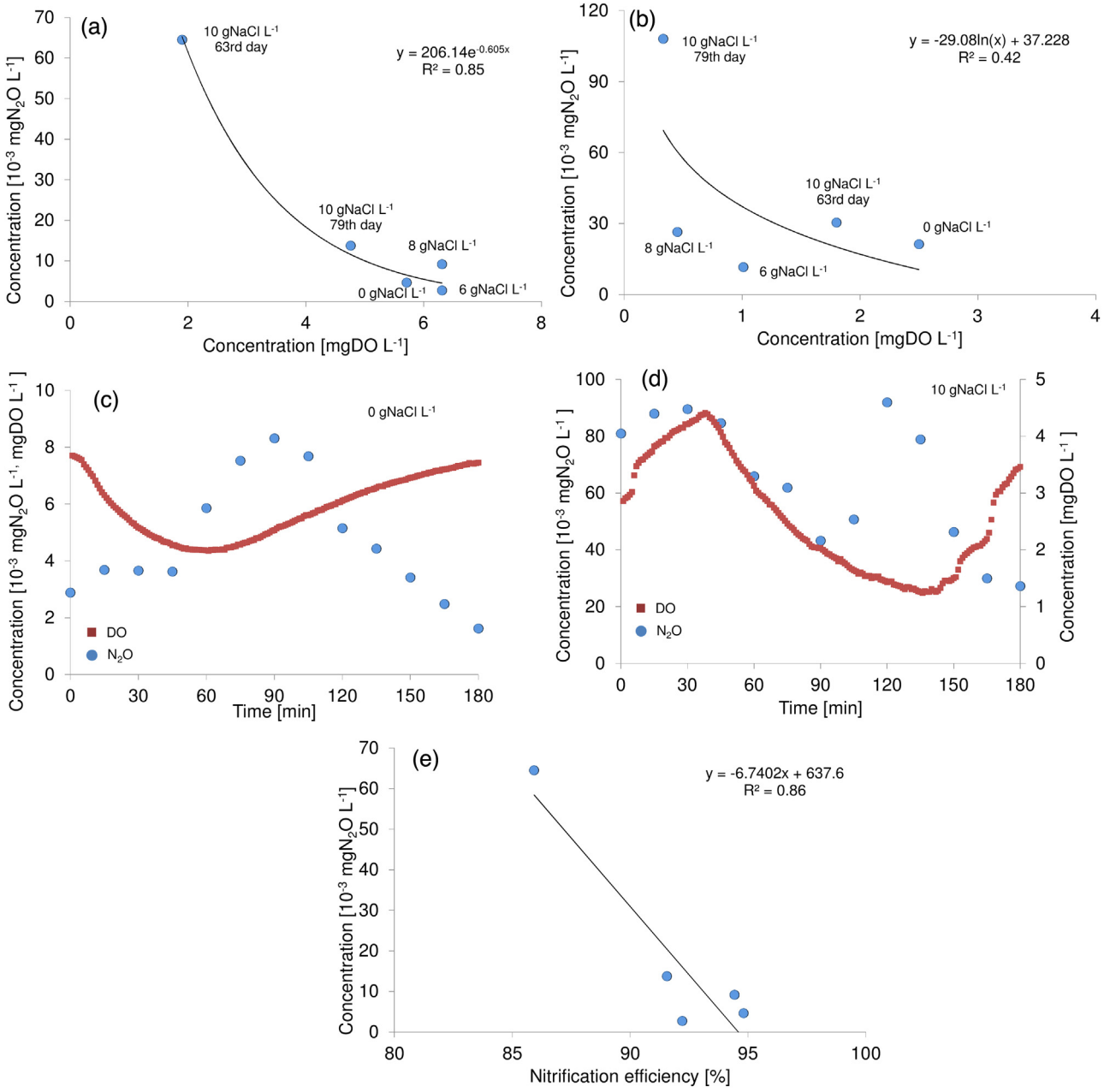

Fig. 7. Average N_2O concentration in the gas samples withdrawn from the aerobic (a) and anoxic tank (b) versus the DO concentration; DO and N_2O concentration in the gas samples withdrawn from the aerobic tank during the cycle time at 0 g NaCl L^{-1} (c) and 10 g NaCl L^{-1} (d); average N_2O concentration in the gas sample of the aerobic tank versus the nitrification efficiency (e).

was found. This result is likely due to the fact that at low DO concentration, local oxygen limitations could take place promoting the nitrifier denitrification activity [30]. Conversely, with the increase of DO inside the aerobic tank a complete nitrification took place leading to a reduction of the N_2O concentration (Fig. 7a). However, high DO concentrations inside the aerobic tank could have negative effects on the denitrification efficiency. Indeed, since significant amounts of oxygen were recycled from the aerobic to the anoxic tank it was difficult to maintain anoxic conditions within the latter. As discussed above, over the experimental period it was very hard to maintain anoxic conditions inside the anoxic tank (Fig. 7b). The data reported in Fig. 7b shows the same results similarly to the aerobic tank although with a different distribution.

Moreover, as one can notice from Fig. 7c–d the different salt concentration significantly influenced the pattern of DO and N_2O concentration profiles during a typical cycle duration. Indeed, at 0 NaCl L^{-1}, the fast DO consumption due to nitrification promoted a rapid increase of N_2O concentration, that reached its peak at the 90th minute, shortly after the DO reached its lowest value. At the end of the filtration time (between 120th and 180th min) the ammonia was almost completely nitrified thus promoting the DO increase as well as the N_2O decrease (Fig. 7c). Conversely, at 10 g NaCl L^{-1} (79^{th} day), the autotrophic activity was depressed by the high salinity, thus leading to a different behavior. Indeed, as shown in Fig. 7d the DO consumption was delayed due to the lower nitrifiers activity; consequently, the maximum N_2O concentration occurred at the 120th min indicating that a quite high amount on ammonia to be nitrified was still present at the end of the cycle. Indeed, the lowest nitrification efficiency was achieved just at 10 g Na Cl L^{-1} (Table 2).

Finally, data reported in Fig. 7e highlights that with the increase of the nitrification efficiency a decrease of N_2O occurred. This result is in good agreement with previous literature results [7].

Thus, the strong impact of the DO concentration on N_2O indicates that oxygen has to be properly controlled in order to reduce the N_2O emissions [31].

3.7. N_2O emission factor

Table 3 summarizes the N_2O emission factors, expressed as a percentage of the nitrogen loading rate, for each salt concentration.

The obtained results confirmed the previous discussed findings, thus highlighting the strong effect exerted by the salinity on N_2O production (both for aerobic and anoxic compartment).

The observed emission factors were in line with previous literature data obtained from an oxic-anoxic activated sludge pilot plant subjected to a salinity increase [18]. According to the derived results, the salt concentration caused a high increase of the N_2O emission. In order to mitigate such emissions, an equalization tank would likely attenuate the N_2O production thus reducing a potential harmful effect for the environment.

4. Conclusions

The N_2O concentration in the gaseous phase was significantly influenced by the salinity increase, which depressed the activity of autotrophic biomass within the aerobic tank, with the lowest ammonia removal efficiency (63%) obtained at the highest salinity concentration (10 g NaCl L^{-1}). Samples from the anoxic tank showed even higher concentrations of N_2O, likely due to the combined effect of salinity and high DO concentrations, that enhanced incomplete denitrification thus promoting the production of N_2O. In terms of N_2O flux, the emission from the aerobic tank was 25 times higher than the anoxic one. The salinity increase was crucial for the production of dissolved N_2O. Therefore, in order to minimize the N_2O production/emission from anoxic-oxic processes it is crucial to limit the salinity fluctuations as well as to maintain the salt concentration below 10 g NaCl L^{-1}.

Acknowledgements

This work forms part of a research project supported by grant of the Italian Ministry of Education, University and Research (MIUR) through the Research project of national interest PRIN2012 (D.M. 28 dicembre 2012 n. 957/Ric – Prot. 2012PTZAMC) entitled “Energy consumption and GreenHouse Gas (GHG) emissions in the wastewater treatment plants: a decision support system for planning and management – http://ghgfromwwtp.unipa.it” in which the first author of this paper is the Principal Investigator.

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