Journal of Urban and Environmental Engineering, v.11, n.2, p.193-201

ISSN 1982-3932
doi: 10.4090/juee.2017.v11n2.193201

Journal of Urban and Environmental Engineering

www.journal-uee.org

CASE STUDY ON NITRIFICATION RATES IN A NON-STIRRED MEMBRANE-AERATED BIOFILM REACTOR OPERATED UNDER LAMINAR REGIME

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Received 12 March 2017; received in revised form 29 May 2017; accepted 25 June 2017

Abstract: A lab-scale non-stirred membrane-aerated biofilm reactor with a volume of 14.2 L was operated under laminar flow regime with inorganic synthetic wastewater to assess tertiary nitrification rates. Nitrifying counter-diffusive biofilm grown over microporous polypropylene tubular membranes supplied with atmospheric air at low pressure (3.45 kPa). The reactor was operated at very low water-velocities (in cm/s): from 2.3×10^{-4} to 2.3×10^{-3}. In all runs, the influent ammonium concentration was kept constant (≈ 26 mg-N/L). By changing the volumetric inflow, the membrane-aerated biofilm (MAB) was tested at seven different ammonium applied loads (range: 0.57 - 6.04 g-N/m^2 d). The corresponding ammonium removal rates ranged 0.56 to 3.02 g-N/(m^2 d). The percentage of biological ammonium removal presented a range from 50% to 98%. As expected, due to passive experimental dynamic conditions to achieve an ammonium removal percentage greater than 80% a hydraulic retention time of 19 h was required. Clean membrane oxygen transfer rate was evaluated. The nitrifying MAB was found to enhance the oxygen transfer across the membrane when the surface nitrification rates were high. A significant drop in electrical conductivity that is proportional to the ammonium removed was observed. Thus, conductivity measurement can be used as a simple control method of ammonium removal extent. Effluent suspended solids were not detected, therefore a sedimentation process was unnecessary.

Keywords: Membrane-aerated biofilm reactor; counter-diffusive biofilm; nitrification; biological wastewater treatment; electrical conductivity.

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INTRODUCTION

Ammonium is an important nitrogen ion form in aqueous solution. The ammonium-nitrogen has to be removed from the wastewaters, otherwise it may cause oxygen depletion if released in too large amounts into rivers. The classical method for ammonium removal from sewage is based on aerobic biological treatment units through nitrification. Nitrification consists in the removal of soluble materials: ammonium and oxygen, for this reason, biofilm processes have proved to be very reliable for tertiary nitrification (WEF, 2000). In the membrane aerated biofilm reactor (MABR), the biofilm is supplied with oxygen across the membrane to which it is fixed, while the nutrients contribution comes from the bulk liquid (counter-current diffusion). **Figure 1** shows idealized concentration profiles of substrates being consumed (dissolved oxygen and ammonium) or produced (oxidized nitrogen) by the organisms in a nitrifying counter-diffusive biofilm. Several configurations of this type of biofilm reactor can be found in the literature (Li *et al*., 2008; Martin and Nerenberg, 2012; Chen *et al*., 2016). The MABR may encourage even higher ammonium fluxes when oxygen is also supplied from bulk liquid, allowing oxygen diffusion on both sides of biofilm (Yamagiwa *et al*., 2004; Molina *et al*., 2013).

Several studies suggest that MABR process has the potential to transfer oxygen very efficiently (Martin and Nerenberg, 2012). Operating the system with almost 100% oxygen utilization was achievable, which is one of the major advantages of a nitrifying MABR (Hwang *et al*., 2009).

In MABRs, the aeration rate may be limited to the stoichiometric supply of oxygen for aerobic oxidation reactions (Brindle *et al*., 1998; Terada *et al*., 2006).

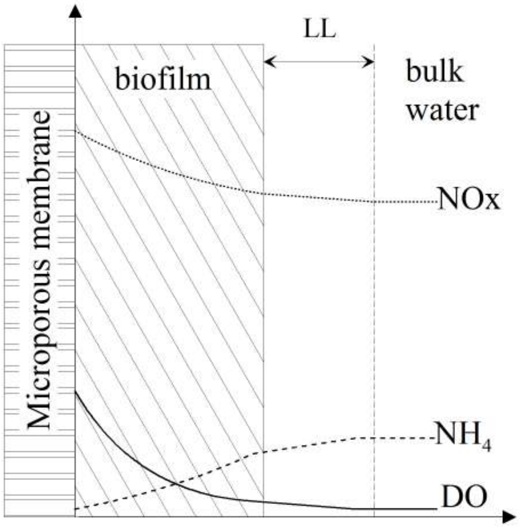

Fig. 1 Hypothetical gradients of dissolved oxygen (DO), ammonium (NH_4), and oxidized nitrogen (NO_X) in a counter-diffusive nitrifying membrane-aerated biofilm at steady state. LL is the liquid boundary layer.

In full-scale MABRs, an aeration efficiency from 6 to 8 kg O_2/kWh has been reported (Syron, 2015). Likewise, the power cost for a high liquid flow velocity may account for a significant proportion of the overall operational cost for a MABR process (Li *et al*., 2008). Thus, any reduction in liquid stirring would reduce the operating cost of MABRs. During tertiary nitrification studies at low water velocity, Walter *et al*. (2005) observed 50% ammonium removal efficiency at volumetric loading rate of 5-6 kg NH_4-N/(m^3 d) with Reynolds-number (Re) of 400, and Shanahan and Semmens (2006) observed 60% ammonium removal efficiency at a loading rate of 4.24 g-NH_4-N/(m^2 d) with Re = 253. Therefore, one advantage of MABRs is that they can reduce energy consumption because they can be operated almost passively. However, few attempts have been made to assess the overall performance of a nitrifying MABR when it is operated at very low water velocity. In several studies, the nitrification process has been postulated as one of the most promising applications of MABR (Hwang *et al*., 2009; Taskan *et al*., 2015). One trend has been to the integration of nitrifying-MABR in activated sludge reactors for simultaneous nitrification and denitrification (Wu *et al*., 2006; Downing *et al*., 2010). Given that, it may be a requirement to reduce the amount of ammonium of urban effluent discharging into sensitive receiving waters (e.g., protection of fish life in surface waters), the MABR process may be effective for tertiary nitrification in urban wastewater treatment plants (WWTPs). Even small agglomerations (< 2000 population equivalents) may require an upgrade of the WWTP to achieve a tertiary nitrification, and in these cases it is desirable that the treatment processes are simple in operation and maintenance, i.e., with fewer electromechanical equipment. In this paper, a non-stirred tubular membrane-aerated bioreactor has been operated for nitrification with very low water velocities attempting to laminar flow regime ($0.4 \leq Re \leq 4.2$). If the flow is laminar regime, liquid boundary layer (LL in **Fig. 1**) reaches a high thickness and present a high resistance to mass transfer from bulk liquid. To reduce the magnitude of this negative effect of laminar flow, the membrane module was designed with cross-flow, i.e., the water was flowing normally to the tubular membranes. The mass transfer coefficient for cross-flow is much higher than that for parallel-flow shown already (Ahmed and Semmens, 1996), and as a result reduces operational and power costs (Li *et al*., 2008).

One of the effects of biological nitrification reaction is a destruction/production of different ions (such as ammonium, bicarbonate and nitrate, mainly) with different limiting equivalent conductance values. Thus, Molina *et al*. (2013) have suggested the electrical conductivity (EC) measurement as simple and effective method of monitoring the extent of ammonia removal by nitrification. Measuring the EC has also been applied as

a control method for the detection of the breakpoint and estimation of ammonia concentration in the effluent from ion exchange columns operating to remove ammonia from domestic wastewater (Malovanyy *et al*., 2013).
The aim of this paper was to evaluate the surface nitrification rates of an air-based nitrifying MABR at different ammonium applied loadings and under almost passive operating conditions: non-stirred reactor, very low water velocity, and supply of atmospheric air into the lumen of the tubular membrane at very low pressure. In addition, the ammonium removal extent based on electrical conductivity measurement and the oxygen utilization rates were evaluated under different operations.

MATERIALS AND METHODS

Synthetic wastewater

The bioreactor was fed with synthetic inorganic wastewater consisting of (in mg/L): $(NH_4)_2SO_4$, 109; $(NH_4)_2HPO_4$, 38; $MgSO_4 \cdot 7H_2O$, 5.4; Na_2HPO_4, 0.01; KH_2PO_4, 5.5; KCl, 13.6; $CaCl_2$, 0.15; $FeSO_4 \cdot 7H_2O$, 0.3; $NaHCO_3$, 354. The composition of nutrient supplement was adapted from a recipe described by Terada *et al*. (2006).

MABR operation

The **Fig. 2** shows a schematic representation of the MABR system. The reactor tank, which houses a membrane module, was constructed using Plexiglas® sheets of 10 mm of thickness with an effective water volume of 14.2 L. The membrane module was constituted by 53 Accurel® microporous polypropylene tubular membranes, alternatively arranged in horizontal rows of 10 and 11 membranes non overlapping to induce tortuous liquid up-flow. The inner and outer diameters of the tubular membrane were 5500 and 8600 µm, respectively, and the nominal pore size was 0.2 µm. The membrane surface area available for the nitrifying biofilm growth and oxygenation was 0.27 cm^2. The specific membrane surface area (A_S) was 19.2 m^2/m^3. The synthetic wastewater was supplied to the bottom of the reactor by a peristaltic pump (Ecoline V-280, Ismatec®, Germany). Liquid in the reactor was circulated up-flow imposing flow normal to the tubular membranes at an average velocity range from 2.3×10^{-4} to 2.3×10^{-3} cm/s ($0.4 \leq Re \leq 4.2$). Given the geometry of the working volume (in cm), length × width × depth = 25.5 × 24.3 × 30.0, and the tortuous up-flow (due to the architecture of the membrane module), it was speculated that laminar-mixing condition was produced (tanks with a length-to-width ratio of nearly 1:1 are subject to a high degree of back-mixing).

The membrane module was designed as air-flow-through mode. Atmospheric air was pumped across membrane lumen with an aquarium air-pump (Rena 301, France) and regulated using a flow meter (STAG, ST-C-100-15, Spain). The air pressure drop across the membranes was insignificant (3.45 kPa) and intra-membrane pressure was close to atmospheric pressure. The reactor was covered to certificate that there would not have been oxygen entry apart from the membrane and influent. Dissolved oxygen (DO) and temperature were continually monitored and controlled with luminescence probe (LDO™ Lange, Germany) immersed at the top of reactor. Optical probes avoid the bias occurring with membrane probes when the liquid is not mixed (Stricker *et al*., 2011).

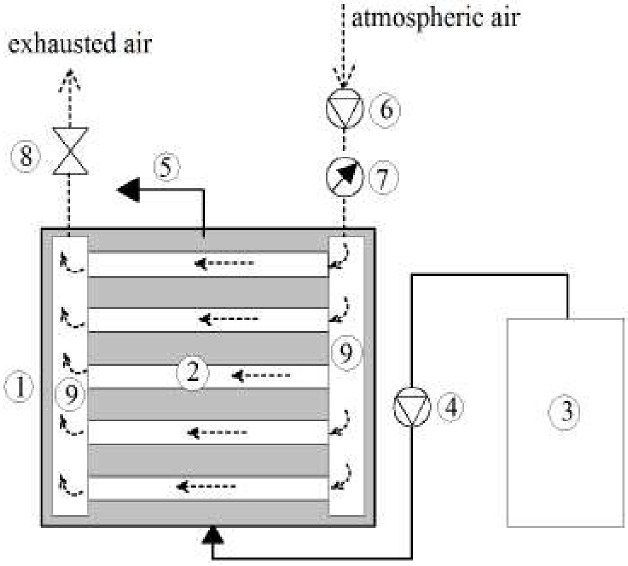

Fig. 2 Scheme of experimental system: 1-MABR, 2-horizontal tubular membranes, 3-wastewater, 4-water pump, 5-effluent, 6-air pump, 7-pressure gauge, 8-air valve, 9-PVC air pipes.

In order to colonize the membranes with nitrifying biofilm growth, inorganic synthetic wastewater seeded with a 1% inoculum of settled domestic wastewater was initially cultured in the batch-fed mode for ten days. After the initial colonization period, the reactor was operated in batch mode for fifty days for acclimatization biofilm.

Oxygen transfer tests in clean water

The oxygen transfer rate (*OTR*) of the membranes without biofilm was tested in clean water. The aeration tests were carried out at three different water velocities: 0.0, 0.1 and 0.3 cm/s, and at the inlet air pressure of 3.45 kPa. The *OTR* of clean membranes was evaluated by bubble-free aeration in transitory regime of deoxygenated water and the change in DO concentration was recorded every five minutes with HQ40d meter (Hach, Germany). As noted by the Terada *et al*. (2006) once the bulk DO concentration began to change linearly with time, the oxygen transfer rate was obtained from the slope of this line. Thus, *OTRs* (in g-O_2/m^2 d) for each water velocity were calculated from **Eq. (1)**:

$$OTR = \frac{\Delta C_{O2}}{\Delta t}\,\frac{V}{A} \qquad (1)$$

where ΔC_{O2} is the increase in DO concentration (mg/L) over the time interval (Δt) (day), *A* the membrane surface area (m^2), and *V* the liquid volume (m^3).

Analytical methods

Grab samples of the influent and effluent were analysed for process control. Ammonium (NH_4-N), nitrite (NO_2-N), nitrate (NO_3-N), total nitrogen (TN) and soluble TN (sTN) were determined colorimetrically using cuvette test (Dr. Lange, Germany) and a photometer (DR2800 Hach, Germany). Analysis of filtered concentration was performed after filtration through 1.0 µm glass microfiber filters (MFV2, Filter-lab®, Spain). Alkalinity (Alk) was analysed according to standard methods (Standard Methods, 2012). The pH was measured using a pH-meter (Crison 50-10T, Spain). Electrical conductivity was measured with a probe (CDC 401 Hach, USA).

Performance

During the experimental study, the membrane-aerated biofilm (MAB) was subjected to different surface ammonium applied loadings (B_{NH4}, as g-N/m^2 d). Since the influent wastewater had a constant concentration, the volumetric inflow was changed to vary the applied load. Reactor performance was evaluated when the steady state was reached corresponding to each of the applied loadings. According to Levenspiel (1999) it is considered that after the change of inflow, steady state is reached after allowing a period equivalent to four times the theoretical hydraulic retention time (*HRT*). During steady state, samples of influent and effluent were taken for three consecutive days. The average of measurements taken at steady state was used to calculate: applied loading rates, mass balances, removal efficiencies and nitrification rates.

RESULTS AND DISCUSSION

At the end of the tertiary nitrification study, tests were not conducted to determine biofilm thickness. However, a visual inspection was performed. A thin biofilm with light yellowish-brown colour was observed. In addition, the spacing between the MABs was maintained very similar to clean membranes. The biofilm was observed completely distributed throughout the membrane module. Therefore, it is assumed that the biofilm around the reactor was not presented enzymatic differences.

Estimation of oxygen transfer rate

The oxygen transfer capacity of the membrane module was determined in clean water. The *OTR* increased with increasing water velocity. At 0.0 cm/s (one test) the membrane supplied a flux of 1.25 g-$O_2/(m^2$ d); at 0.1 cm/s (three tests) the *OTR* was 4.68 ± 0.15 g-$O_2/(m^2$ d), and at 0.3 cm/s (three tests) the oxygen flux increased to 10.1 ± 0.8 g-$O_2/(m^2$ d). Thus, assuming that supplied oxygen would be consumed only for nitritation, i.e., oxidation of ammonium to nitrite, the maximum ammonium removal rate should be 2.97 g-N/(m^2 d) (with the stoichiometric coefficient between oxygen and ammonium equal to 3.40 g-O_2/g-NH_4-N). The global oxygen mass transfer estimated from the *OTR* tests is affected by the sum of three resistances: oxygen/membrane boundary layer, the membrane, and membrane/liquid boundary layer. By increasing the water velocity, thickness of the liquid boundary layer was reduced (i.e., the resistance of the membrane/liquid boundary layer was reduced). However, at 0.3 cm/s (Re ≈ 521), the thickness of the liquid boundary layer was not completely reduced, that is, the *OTR* test underestimated oxygen flux across the membrane. As postulated by Lackner *et al.* (2010), this is important because when the biofilm had been developed on membranes, only the oxygen/membrane boundary layer and the membrane will cause the oxygen mass transfer resistance to the membrane/biofilm interface.

Nitrification performance

After the acclimation period of 50 days, the nitrification study was conducted over 152 days at influent ammonium (Inf. NH_4-N) concentration of 26.2 ± 1.2 mg/L. **Table 1** shows the performance of the process at steady states. During the experimental period, the average bulk liquid temperature was 22.2 ± 1.4ºC. Effluent TSS concentrations remained below detection level, i.e., sludge yield was negligible. Lack of organic carbon in the synthetic wastewater and the low A_S of the tubular membranes could have played an important role in making excessive biofilm growth insignificant as Long *et al.* (2011) postulated it. The average ratio of consumed alkalinity to removed ammonium nitrogen (w/w) was 7.4. This result shows that most NH_4-N removed via nitrification and changes in the pH-Alk-carbon dioxide balance may have decreased the values for influent alkalinity. Stripping ammonia has been discarded due to moderate effluent pH values (range: 6.1-7.0) and because the bulk liquid was not stirred. The effluent remained nearly anoxic with an average DO concentration of 0.3 ± 0.3 mg/L, i.e., most oxygen that penetrated the membrane was consumed by the biofilm. Thus, the nitrification was possible due to counter-diffusion of oxygen and ammonia. Lower DO concentration was measured in bulk liquid as NH_4-N applied load (B_{NH4}) and the nitrification rate increased.

The MABR was operated at seven surface NH_4-N applied loadings rates (range: 0.57-6.04 g-N/m^2 d) by changing wastewater volumetric inflow rate. An average

Table 1. Steady state performance during tertiary nitrification of MABR operation

Run →	1	2	3	4	5	6	7
B_{NH4} (g-N/m^2 d)	1.73 ± 0.25	1.31 ± 0.09	0.77 ± 0.09	0.57 ± 0.03	2.54 ± 0.23	6.04 ± 0.10	4.14 ± 0.10
Inf. NH_4-N (mg/L)	26.3 ± 2.9	26.5 ± 1.3	25.7 ± 1.6	23.4 ± 1.3	25.2 ± 1.2	27.3 ± 0.2	26.3 ± 0.6
HRT (h)	19.2 ± 1.0	25.4 ± 1.1	41.2 ± 1.9	58.2 ± 1.6	12.4 ± 0.7	5.7 ± 0.1	7.9 ± 0.0
NH_4-N removal (%)	82 ± 8	90 ± 4	97 ± 2	98 ± 3	74 ± 4	50 ± 3	59 ± 5
Nitrification (%)	81 ± 17	84 ± 11	96 ± 8	97 ± 3	76 ± 6	52 ± 2	60 ± 1
Eff. NO_3-N (mg/L)	16.9 ± 7.4	18.5 ± 6.8	22.2 ± 1.8	26.6 ± 2.3	13.3 ± 5.6	9.6 ± 1.0	15.8 ± 0.4
Eff. NO_2-N (mg/L)	4.4 ± 2.9	4.6 ± 3.2	2.6 ± 0.8	0.9 ± 1.6	5.8 ± 3.9	4.6 ± 0.4	0.0 ± 0.0
Inf. pH	7.4 ± 0.1	7.4 ± 0.3	7.6 ± 0.2	7.4 ± 0.2	7.3 ± 0.1	7.2 ± 0.1	7.4 ± 0.1
Eff. pH	6.4 ± 0.2	6.5 ± 0.3	6.2 ± 0.1	6.1 ± 0.2	6.7 ± 0.0	7.0 ± 0.0	6.8 ± 0.1
Eff. DO (mg/L)	0.6 ± 0.2	0.7 ± 0.6	0.4 ± 0.5	0.4 ± 0.6	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
Inf. EC (µS/cm)	725 ± 30	688 ± 25	700 ± 28	695 ± 22	708 ± 8	749 ± 14	745 ± 12
Eff. EC (µS/cm)	587 ± 25	561 ± 22	556 ± 24	562 ± 25	600 ± 4	680 ± 10	660 ± 19
Inf. Alkalinity (mg/L)	190 ± 4	201 ± 13	197 ± 12	178 ± 11	190 ± 8	207 ± 14	205 ± 5
Eff. Alkalinity (mg/L)	30 ± 2	35 ± 7	32 ± 7	24 ± 2	62 ± 4	128 ± 10	104 ± 14

Inf. =influent; Eff. =effluent.

effluent ammonium (Eff. NH_4-N) concentration in a range of 1.5 to 17.4 mg/L was observed. The Eff. NH_4-N concentration showed good correlation with the B_{NH4}.The results suggest that NH_4-N removal percentage decreases linearly with increases in B_{NH4}. Nitrification efficiency reached 98 ± 3% at a loading rate of 0.57 g-N/m^2 d (at *HRT* = 58 h). Moreover, since the Inf. NH_4-N concentration was maintained approximately constant, the ammonium removal percentage was increased with increases in *HRT*. The range of *HRT* tested was 5.7 to 58 hours. In our study, the biofilm reactor was operated as an almost passive process. As expected, to achieve an ammonium removal percentage greater than 80 % a high *HRT* of 19 hours was required. It is similar to what happens in passive natural systems of wastewater treatment as constructed wetlands. With the exception of run 7, nitrite accumulation was observed in the process, without a clear relationship between the ammonium applied load and the effluent nitrite concentration. Nevertheless, the experimental results show that the nitrite accumulation percentage, i.e., Eff. NO_2-N/(Eff. NO_2-N + Eff. NO_3-N) × 100, increases with increases in B_{NH4} up to 32% (range: 3-32%). Oxygen mass transfer rates have been postulated as a crucial parameter to control nitritation in the MABRs (Terada *et al*., 2006; Lackner *et al*., 2010; Chen *et al*., 2016). However, nitrate was produced in all runs, i.e., ammonia-oxidizing bacteria (AOB) coexisted with nitrite-oxidizing bacteria (NOB). Schramm *et al*. (2000) had observed that AOB and NOB coexist in the oxic layer of nitrifying MAB, which is subject to high ammonium and nitrite concentrations. Since there was no accumulation of nitrite in the last run, we speculate that nitrifying biofilm would have taken 140 days to reach the most appropriate stratification of AOB and NOB.

Conductivity as a monitoring parameter

In general, parameters known to aid in predicting the extent of biological oxidation of ammonium include pH, DO and alkalinity. However, one of the effects of biological nitrification reaction is a destruction / production of different ions (mainly: NH_4^+, HCO_3^-, and NO_3^-) with different limiting equivalent conductance (LEC) values. An overall equation of the nitrification reaction was defined as (Henze, 1995):

$$NH_4^+ + 1.86O_2 + 1.98HCO_3^- \rightarrow 0.02C_5H_7O_2N + 0.98NO_3^- + 1.88H_2CO_3 + 1.04H_2O \qquad (2)$$

LEC values of NH_4^+, HCO_3^- and NO_3^- at 25 ºC are 73.4, 44.5 and 71.4 µS/cm per meq/L (Harned and Owen, 1964). By using the **Eq. 2**, the theoretical EC drop could be calculated as equal to 6.54 µS/cm per 1 mg/L NH_4-N removed. In this work, electrical conductivity was measured in outflow (Eff. EC) and inflow (Inf. EC) in all runs. The Eff. EC was always lower than Inf. EC. During steady state of each run, the Eff. EC remained stable. The results show a significant EC drop, which is proportional to the ammonium concentration removed. The EC drop is due to the different LEC values of the ions taking part in the nitrification reaction. When EC drop was calculated per 1 mg/L NH_4-N removed, it was in the range of 5.3 – 7.0 µS/cm (average = 6.2 ± 0.6). A similar behavior of the EC has been observed in a study on nitrification capacity of settled urban wastewater with a MABR operated in batch mode, and EC control has been suggested as a simple monitoring parameter to determine the extent of nitrification (Molina *et al*., 2013). By

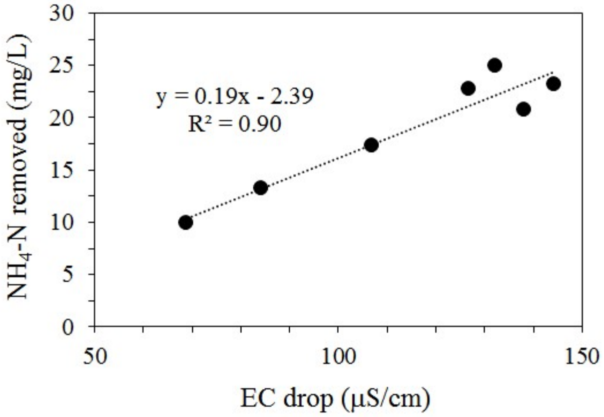

Fig. 3 Correlation of EC drop and ammonium concentration removed.

plotting EC drop versus ammonium removal (as mg-N/L removed) a linear correlation was obtained (**Fig. 3**). **Figure 4** shows the observed and predicted values of effluent NH_4-N concentration as dependent on the EC drop. The differences between observed and predicted Eff. NH_4-N concentration are considered mostly satisfactory.

Observed nitrification rate

The reaction rates, r, were calculated using:

$$r = \frac{Q\left(C_{inf} - C_{eff}\right)}{A} \qquad (3)$$

where C_{inf} and C_{eff} are the influent and effluent solute concentrations, respectively (mg/L), and Q the volumetric flow rate (m^3/day). In the case of ammonium, the reaction rate includes loss of ammonia assimilated into cell growth. The observed kinetic values are specific to the membrane, under specific conditions of transverse-flow direction, water velocity, temperature, etc. Both external and internal mass transfer resistance effects are incorporated. **Figure 5** shows that ammonium removal rate (r_{NH4}) increases almost linearly for small values of B_{NH4}, but becomes curved for large values.

In the portion of low applied load ($B_{NH4} < 1.5$ g-N/m^2 d) a high removal efficiency was observed (90-98%), while at high-applied load (i.e., low *HRT*) the reaction rate had tended towards a maximum value, therefore, the ammonium removal efficiency was decreasing. Our MABR exhibited lower volumetric nitrification rates because of the smaller specific membrane surface area, 19.2 m^2/m^3. The shortening of *HRT* had a positive effect on ammonium removal rate, which has also been observed by Rodgers *et al.* (2003) and Taskan *et al.* (2015). Therefore, as postulated by Brindle *et al.* (1998) and Terada *et al.* (2006), the volumetric nitrification rate could be significantly increased by simply adding more tubular membranes. The highest nitrification rate was 3.03 ± 0.20 g-N/(m^2 d), which is a very close result to the expected maximum rate according to the *OTR*-tests (2.97 g-N/m^2 d). That is, when the surface ammonium-applied load was high, the nitrifying MAB tended to utilize the maximum oxygen transfer capacity of the membranes. For conventional nitrifying biofilters, such as trickling filters and rotating discs, a typical maximum removal rate of 1.5 g-N/(m^2 d) has been observed (WEF, 2000). **Fig. 5** also shows the nitrification rate expressed as oxidized forms of nitrogen (NOx). The two curves were very close, which reinforced that most of the ammonia was oxidized and not assimilated in cell growth.

Table 2 presents the observed performance of nitrification studies carried out in stirred MABRs with some operating conditions similar to our study, i.e., air-based oxygenation, low specific surface area of membrane, influent ammonia concentration similar to an urban secondary effluent, and very low intra-membrane gas pressure. The results shown in **Table 2** suggest that, when the applied loading rate was low, the ammonium removal efficiency has been proved very high (> 90%) (Satoh *et al.*, 2004). Several results also suggest that, as the applied load increases, the ammonium removal rate tends to a maximum saturation value and the efficiency was reduced to 50-60% (Shanahan and Semmens, 2006; Lackner *et al.*, 2010).

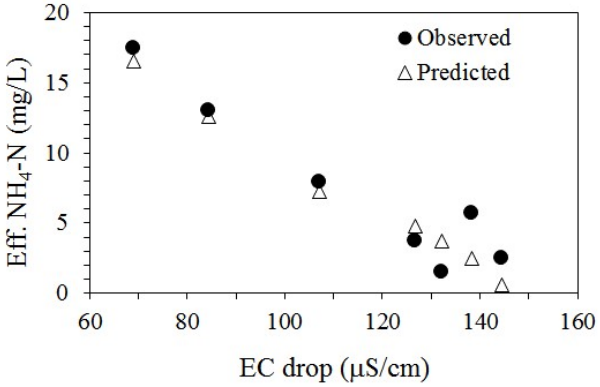

Fig. 4 Comparison between observed and predicted Eff. NH_4-N.

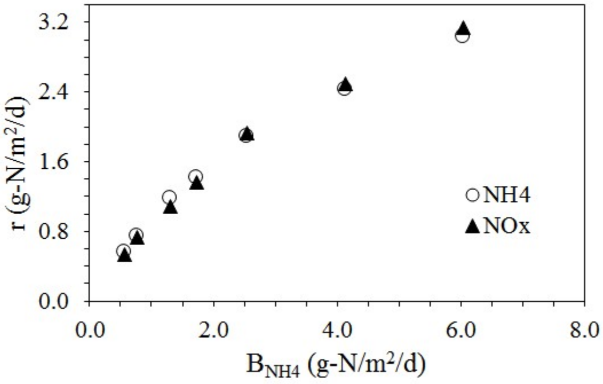

Fig. 5 Relationship between ammonium applied load and overall reaction rate ($NO_X = NO_2\text{-N} + NO_3\text{-N}$).

Table 2. Nitrification performance reported for MABRs

Membrane type	Working volume L	As m^2/m^3	HRT h	Temp. ºC	DO bulk liquid mg/L	NH_4-N influent mg/L	NH_4-N Loading $g\text{-}N/m^2/d$	NH_4-N Removal $g\text{-}N/m^2/d$
Polyurethane HF, OD: 0.275mm, OE, air[a]	4.50	55.6	53.3	20.0	0-2	34	0.54	0.5
Silicone HF, OD: 0.40mm, OE, air[b]	1.63	34.5	12.0	23.5-25.5	≥2.0	40	2.3	2.0
						160	9.3	8.0
PP flat sheet, OE, air[c]	0.305	24.4	5.8	----	<0.2	25	4.24	2.54
Polyolefin HF, OD: 0.38mm, OE, air[d]	0.23	23.2	2.2	23.0	2.0	45	10.8	9.7
			4.3		1.0		21.6	14.4
Silicone flat sheet, OE, air[e]	0.50	16	19.2	30.0	0.0	200	15.6	7.3
Composite HF, OD: 0.310mm, DE, oxygen (3.4 kPa)[f]	0.25	42.8	1.0	---	0.1	20	11.1	8.6
			7.5	---	0.1	20	4.4	4.0
PP TM, OD: 8.6mm, OE, air[g]	14.2	19.2	58.0	22.2	0.4	23.4	0.57	0.56
			5.7		0.0	27.3	6.04	3.02

Adapted from [a]Satoh *et al.* (2004); [b]Yamagiwa *et al.* (2004); [c]Shanahan and Semmens (2006); [d]Motlagh *et al.* (2008); [e]Lackner *et al.* (2010); [f]Taskan *et al.*, (2015) and [g]this study. Abbreviations: DE: dead-end lumen, OE: open-ended lumen, HF: hollow fiber, TM: tubular membrane, OD: outer diameter of membrane.

On the other hand, some results (Yamagiwa *et al.*, 2004; Motlagh *et al.*, 2008) have shown that to achieve high nitrification efficiency at high-applied load, DO concentration in the bulk liquid phase must be greater than 2 mg/L. Then, why has the ammonium removal efficiency mostly reached values similar to those of stirred MABRs despite the fact that our reactor was operated in laminar regime and with DO concentration less than 0.5 mg/L? We do not have a conclusive answer to this question, but we speculate that the crossflow added advection to diffusive transport to the biofilm, which improved mass transfer and thus increased the kinetic rate of reactions within the biofilm. Picard *et al.* (2012) have experimentally observed a mass transfer enhancement when the cross-flow over the biofilm surface exceeds a particular value.

Oxygen utilization rate

The total oxygen utilization rate (OUR_{total}) by nitrifying MAB was calculated as the oxygen consumed for the conversion of ammonium into nitrite and nitrate:

$$OUR_{total} = \frac{Q\left[3.40\left(NO_{2,eff}\right) + 4.54\left(NO_{3,eff}\right)\right]}{A} \quad (4)$$

where $NO_{2,eff}$ is the effluent nitrite-N concentration (mg/L), and $NO_{3,eff}$ the effluent nitrate-N concentration (mg/L). The OUR_{total} was calculated in the range from 2.48 to 13.07 g-O_2/(m^2 d). Other sources of oxygen came from the influent and the reduction of carbon dioxide by nitrifying bacteria. For simplicity, the oxygen utilization rate from the influent (OUR_{inf}) was calculated as:

$$OUR_{inf} = \frac{Q\left(DO_{inf} - DO_{eff}\right)}{A} \quad (5)$$

where DO_{inf} and DO_{eff} are influent and effluent DO concentrations (mg/L), respectively. The average concentrations of DO_{inf} and DO_{eff} were 6.7 ± 0.4 and 0.3 ± 0.3 mg/L, respectively. Thus, the oxygen utilization rate by nitrifying biofilm across membranes ($OUR_{mem} = OUR_{total} - OUR_{inf}$) was calculated in the range from 2.43 to 12.61 g-O_2/(m^2 d) which represents 96 to 98% of the OUR_{total}. The maximum OUR_{mem} calculated (12.6 g-O_2/(m^2 d)) is 24.8% greater than the maximum value measured for *OTR* (10.1 g-O_2/(m^2 d)). Therefore, development of a nitrifying MAB influences the *OTR* across the membrane. Under the conditions of this study, the OUR_{mem} is proportional to the nitrification rate (**Fig. 6**). When the ammonium removal rate was high (≥ 2.4 g-N/(m^2 d)), the OUR_{mem} has been able to improve the maximum *OTR* observed across the clean membranes (dashed line in **Fig. 6**). In our reactor, where the flow was normal to the long axis of the tubular membrane and a thin nitrifying biofilm was developed, the biofilm can stimulate an increase in oxygen transfer relative to clean membranes as long as the nitrification rate is high.

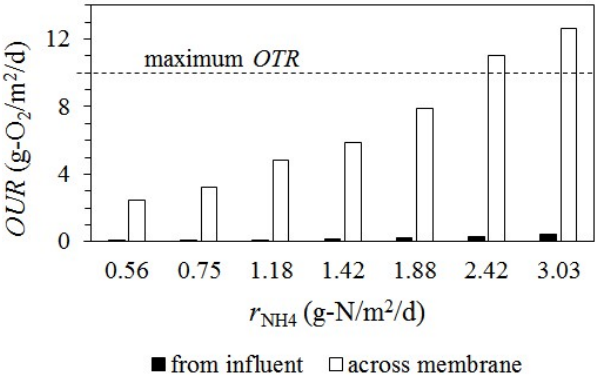

Fig. 6 Effect of the ammonium removal rate on the OUR value.

Shanahan and Semmens (2006) have reported that a nitrifying biofilm was able to enhance oxygen transfer across the membrane when the flow velocities were low. Moreover, Long *et al.* (2011) have postulated that the tertiary nitrification biofilm in MABR could increase the oxygen transfer as compared to that with clean membranes.

CONCLUSIONS

The non-stirred nitrifying MABR operated under laminar flow regime and air-based oxygenation at atmospheric pressure has shown to be effective for the removal of ammonium-nitrogen. The MABR is capable of performing an efficient nitrification process that can fully utilize the oxygen diffused across the membrane lumen. Therefore, the non-stirred MABR process can achieve high efficiency in energy consumption. However, low energy consumption is offset by a high HRT to achieve an ammonium-nitrogen removal efficiency equal to or greater than 80%. A nitrifying biofilm will improve oxygen transfer across a membrane when surface nitrification rate is high. Suspended solids have not been detected in the effluent, and therefore a final sedimentation was not necessary. Moreover, as the process can operate without pumping liquid, it would be a simple operation, which is a requirement for wastewater treatment of small agglomerations. Finally, conductivity measurement can be used as a control method of ammonium removal extent with the use of low-cost and accurate EC probe.

Acknowledgement This research was partially funded by the Council of Innovation, Industry and Commerce (Galicia - Spain) (Ref. 04PXIA11801PR).

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