High-strength ammonium wastewater treatment by MBR: Steady-state nitrification kinetic parameters

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Abstract:

In this study, a steady-state operation approach is proposed in order to accurately measure the kinetic parameters of substrate (contaminants) removal in wastewater biotreatment systems. In order to determine the kinetic parameters of a submerged membrane bioreactor (sMBR) when treating high-strength ammoniacal nitrogen wastewaters, a lab-scale sMBR was operated for 205 days with synthetic leachates (1000 mg COD L^{-1}) at 4 different ammoniacal nitrogen concentrations (220, 340, 665 and 1040 mg NH_4-N L^{-1}). Ammoniacal nitrogen oxidation rates were calculated by solving the mass balance equations when steady-state conditions were reached for each tested concentration. The Haldane model was found to be accurate when predicting the specific ammoniacal nitrogen oxidation rates with the following kinetic parameters: $r_{NH,max}$ = 854,4 mg NH_4-N L^{-1} d^{-1}, K_S = 1007 mg NH_4-N L^{-1}, and K_I = 221 mg NH_4-N L^{-1} (R^2 = 0,97). The highest ammoniacal nitrogen oxidation rate was found to be 162 mg NH_4-N L^-

^{1} d^{-1} when the effluent concentration was 472 mg NH_4-N L^{-1}. When compared to the conventional flask test approach for calculating the kinetic parameters, the steady-state approach described in this study showed a lower variability in the predicted specific nitrification rates, as well as a lower effect of the inhibition phenomena, due to the mixed liquor being adapted to each substrate concentration tested.

Keywords: kinetic, membrane bioreactor, ammoniacal nitrogen, leachate, nitrification

Declarations of interest: none

Abbreviations

AOB	Ammonia oxidizing bacteria
BOD_5	Biological oxygen demand (5 days)
CAS	Conventional activated sludge
COD	Chemical oxygen demand
CSTR	Continuous stirred tank reactor
DO	Dissolved oxygen
F:M	Food: microorganism (biomass) ratio
HRT	Hydraulic retention time
SRT	Solid retention time
MBBR	Mixed bed bioreactor
MBR	Membrane bioreactor
MLVSS	Mixed liquor volatile suspended solids
NLR	Nitrogen load rate
qPCR	quantitative polymerase chain reaction
SBR	Sequencing batch reactor
sMBR	Sumberged membrane bioreactor
TMP	Transmembrane pressure

1. Introduction

High-strength ammonium wastewater originating from anthropogenic activity, such as aquaculture water (Ling and Chen 2005), composting leachates (Roy, Azaïs et al. 2018), and landfill leachates (Ahmed and Lan 2012, Zolfaghari, Drogui et al. 2017), poses a serious threat to the preservation of clean water resources. Reported ammoniacal nitrogen concentrations measured in composting and landfill leachates range from 5 mg NH_4-N L^{-1} to more than 21 000 mg NH_4-N L^{-1} (Roy, Azaïs et al. 2018). Once discharged in the aquatic environment, ammoniacal nitrogen can have adverse effects such as promoting eutrophication, toxicity to aquatic organisms, and depletion of dissolved oxygen due to the oxidation of ammoniacal nitrogen to nitrate (He, Xue et al. 2009).

High-strength ammoniacal nitrogen wastewater treatment has become a major focus in recent years due to its negative impact on municipal wastewater biological treatment systems. Even with the co-treatment of high-strength ammoniacal nitrogen wastewater with municipal wastewater, the dilution factor is often insufficient to fade the concentration peaks that have inhibitory effects on the microbial activity in the mixed liquor (Gagnaire, Wang et al. 2011). Consequently, treatment systems have been specifically engineered to treat wastewaters with high ammoniacal nitrogen concentrations. Amongst these treatment systems, physico-chemical systems, such as stripping, are frequently used (Carrera, Jubany et al. 2004). However, recent developments in biological treatment systems have broadened their range of applications and increased their efficacy with complex wastewaters. A biotechnology that has been proven to be efficient for the removal of high concentrations of ammoniacal nitrogen, even in the presence of a high chemical oxygen demand (COD), is the membrane bioreactor (MBR).

MBRs are distinguished from conventional activated sludge systems (CAS) by the use of a micro/ultrafiltration membrane to separate the biomass from the effluent (Ng and Kim 2007). The membrane eliminates the need for large clarifying basins to settle the biomass, which consequently enables the system to be more compact. Furthermore, the membrane provides an independent control of the hydraulic retention time (HRT) and the solid retention time (SRT). Therefore, biomass can be kept in the system regardless of its ability to settle. The biomass in MBRs is composed of a complex community of microorganisms using different energy sources. Autotrophic nitrifying bacteria convert ammoniacal nitrogen to nitrates in order to obtain their energy, while heterotrophic microorganisms transform organic molecules to CO_2. When wastewater contains both ammoniacal nitrogen and organic contaminants (COD), both types of microorganisms are desired in the mixed liquor. However, due to their slow growth rate, autotrophic nitrifying bacteria are often outcompeted for nutrients and oxygen by heterotrophic bacteria in CAS. Under the conditions created by the membrane in the MBRs, slow-growing nitrifying bacteria can proliferate and survive in a population dominated by heterotrophic bacteria.(Canziani, Emondi et al. 2006). Ammoniacal nitrogen removal rates from leachates using different configurations of MBRs were reported to range from 80 to ~100%, while initial concentrations ranged from 200 to 2 800 mg NH_4-N L^{-1} (Ahmed and Lan 2012). Although there has been significant research on membrane bioreactor systems for the treatment of leachates with high COD and ammoniacal nitrogen concentrations, there remains a lack of information relative to MBR bioprocesses kinetics (Laitinen, Luonsi et al. 2006, Brown, Ghoshdastidar et al. 2013, Hashemi 2015, Hashemi, Hajizadeh et al. 2016, Zuriaga-Agustí, Mendoza-Roca et al. 2016).

Nitrification kinetics in conventional biological treatment processes such as CAS, moving bed bioreactor (MBBR), and sequential batch reactor (SBR), have been previously studied. Wastewater's characteristics and kinetic parameters from these studies are presented in Table 1. In general, the nitrification kinetic in bioreactors is modeled according to 1 of the 3 following models: 1) 0th order kinetic, 2) Michaelis-Menten (Monod), and 3) Haldane (Carrera, Jubany et al. 2004, Kaczorek and Ledakowicz 2006). With the 0th order kinetic model (Eq. 1), the ammoniacal nitrogen consumption rate is assumed constant, notwithstanding the ammoniacal nitrogen concentration in the effluent (He, Xue et al. 2009). The Michaelis-Menten model (Eq. 2) assumes an increasing consumption rate until a maximum rate is reached (Dinçer and Kargı 2000, Carrera, Jubany et al. 2004, Kaczorek and Ledakowicz 2006, Whang, Chien et al. 2009, Gagnaire, Wang et al. 2011). The Haldane model (Eq. 3) integrates an inhibition term in the Michaelis-Menten model to take into account the inhibitive effect of the substrate at high concentrations.

$$r_{NH,i} = k_{NH} \tag{1}$$

$$r_{NH,i} = r_{NH,max}\frac{N_{NH}}{K_S+N_{NH}} \tag{2}$$

$$r_{NH,i} = r_{NH,max}\frac{N_{NH}}{K_S+N_{NH}+{N_{NH}^2}/{K_I}} \tag{3}$$

With:

$r_{NH,i}$ = Ammoniacal nitrogen consumption rate at "i" concentration (mg NH_4-N L^{-1} d^{-1})

$r_{NH,max}$ = Maximum ammoniacal nitrogen consumption rate (mg NH_4-N L^{-1} d^{-1})

k_{NH} = Consumption rate constant (mg NH_4-N L^{-1} d^{-1})

N_{NH} = Ammoniacal nitrogen concentration in the reactor (mg NH_4-N L^{-1})

Ks = Saturation coefficient (mg NH_4-N L^{-1})

K_I = Inhibition coefficient (mg NH_4-N L^{-1})

Doyle et al. (2001) reported an exceptionally high nitrification rate (0^{th} order) in a SBR that treats landfill leachate. However, in order to report a 0^{th} order kinetic consumption rate, they neglected the non-linear section of their consumption curve at low concentrations, which led to a highly overestimated consumption rate. Generally, 0^{th} order kinetics are good estimations for small ranges of concentrations only (Doyle, Watts et al. 2001), while the Michaelis-Menten and Haldane models are more representative of biological kinetics over wider ranges.

The conventional experimental methods used to measure the ammoniacal nitrogen consumption rate and the kinetics parameters ($r_{NH,max}$, K_S and K_i) is the flask test (batch method). It consists of preparing flasks with different initial ammoniacal nitrogen concentrations and adding the same amount of sludge taken from the mixed liquor of the studied treatment system into each of them. Then, changes in ammoniacal nitrogen concentration are measured over a specific period of time. The measured consumption rates ($r_{NH,i}$) are expressed in mg NH_4-N L^{-1} d^{-1} or in mg NH_4-N $gMLVSS^{-1}$ d^{-1} (mixed liquor volatile suspended solids). While this technique is accurate for the measurement of cell growth and enzyme activity, it has significant limitations in terms of substrate removal kinetics measurements in wastewater treatment systems. Firstly, batch experiments tend to overestimate the inhibitive effect of secondary metabolites and products generated by microorganisms, since they accumulate in the bulk. Then, the F:M ratio in the flask is not representative of that of the reactor from which the mixed liquor was taken. For example, Whang et *al.* (2009) conducted a flask test to measure the nitrification kinetic in a SBR that treated swine wastewater. Their method consisted in taking mixed liquor from the reactor and suspending it in 1L of Bushnëll et Haas medium with ammoniacal nitrogen concentrations ranging from 1 to 600 mg NH_4-N L-1, while the SBR from which the mixed liquor originated was operated with concentrations of 215±12 mg NH_4-N L-1 (Whang, Chien et al. 2009). This method wrongly assumes that the F:M ratio ($[NH_4]$:ammonia oxidizing bacteria (AOB) concentration) has no influence on the consumption rate measured in the flask. The consequence of this assumption is that there is an excess of AOB at low ammoniacal nitrogen concentrations in the flask (in comparison to the concentration of the treated effluent) ($[F:M]_{flask} < [F:M]_{reactor}$), which leads to overestimated consumption rates. Similarly, the consumption rate is underestimated at high ammoniacal nitrogen concentrations ($[F:M]_{flask} > [F:M]_{reactor}$).

Furthermore, expressing the consumption rate as a function of MLVSS concentration with a flask test is also misleading due to the fact that the MLVSS concentration is not representative of the microbial population consuming the specific studied substrate. In biological treatment systems dealing with complex leachates, the MLVSS contains a mixture of heterotrophic and autotrophic microorganisms. Therefore, since other substrates (ex: BOD_5, COD, etc.) can significantly influence the MVLSS concentrations, the ratio MVLSS:specific substrate is not constant from one study to another. For example, Kaczorek et Ledakowicz (2006) reported a MLVSS concentration of 3.75 g L^{-1} in a SBR that treated an effluent containing 1740 to 2240 mg NH_4-N L^{-1}; on the other hand, He et *al*. (2009) reported a higher MLVSS (5.5 g L^{-1}) in a sMBR that treated an effluent with over 35 times less ammoniacal nitrogen (11 – 62 mg NH_4-N L^{-1}) (Kaczorek and Ledakowicz 2006, He, Xue et al. 2009).

To address these issues, we propose a novel approach to accurately estimate the ammoniacal nitrogen removal kinetic parameters in wastewater biotreatment systems, without having to model all biological processes. The method consists in operating a lab-scale continuous reactor (sMBR) under steady-state conditions at different effluent ammoniacal nitrogen concentrations. Then, the mass balance equations of the system are solved to calculate the kinetic parameters. The main advantage of this method over the flask test is that the AOB steady-state concentrations in the mixed liquor are in accordance with the tested ammoniacal nitrogen concentrations (the F:M ratio is respected for each measurement). Furthermore, inhibitive products such as secondary metabolites that could influence nitritation or nitratation kinetic rates are found in realistic concentrations within the reactor.

The main objectives of this study were to: 1) define the mass balance equations of a submerged membrane bioreactor (sMBR), 2) provide an accurate experimental method of measuring kinetic parameters in environmental bioprocesses that treat specific contaminants, and 3) fill the gap in information regarding the kinetics parameters for sMBRs that treat high-strength ammoniacal nitrogen wastewater. Furthermore, a critical comparison between the kinetic parameters measured in this study using the steady-state approach and those measured by the flask test method reported in the literature is presented.

Table 1 Nitrification kinetic parameters for different process treating high-strength ammoniacal nitrogen wastewaters found in the literature

Treatment process	Substrate	[Ammonia] (mg NH_4-N L^{-1})	[COD] (mg O_2 L^{-1})	[MLSS] (mg MLSS L^{-1})	Model	r_{NH} (0^{th} order) (mg NH_4-N L^{-1} d^{-1})	$r_{NH, max}$ (mg NH_4-N L^{-1} d^{-1})	K_s (mg NH_4-N L^{-1})	K_I (mg NH_4-N L^{-1})	Authors
Suspended growth activated sludge	synthetic wastewater	0 - 100	0 - 100	-	Monod		600	5,14		(Dinçer and Kargı 2000)
Sequencing batch reactor	Mature landfill leachate (8 years)	0 - 880	600 - 1400	9 590	0^{th} order	5910				(Doyle, Watts et al. 2001)
				3 840	0^{th} order	1770				(Doyle, Watts et al. 2001)
				4 960	0^{th} order	4380				(Doyle, Watts et al. 2001)
Suspended growth activated sludge	Synthetic	-	-	900	Haldane		806,4	13	284	(Carrera, Jubany et al. 2004)
Immobilized growth activated sludge	Synthetic	-	-	7 300	Haldane		273	33	1910	(Carrera, Jubany et al. 2004)
Sequencing batch reactor	Synthetic landfill leachate	1740 - 2 240	2 480 - 4 850	3 750	Haldane		2 381	8,45	37	(Kaczorek and Ledakowicz 2006)
Simultaneous nitrification/denitrification submerged MBR (SND-sMBR)	Synthetic	11 - 62	210 - 650	5 500	0^{th} order	161,8				(He, Xue et al. 2009)
Activated sludge	Municipal wastewater	0 - 600	-	1 200	Haldane		135,4	59	199	(Whang, Chien et al. 2009)
Sequencing batch reactor	Swine wastewater	0 - 600	-	3 200	Monod		169	5		(Whang, Chien et al. 2009)
Membrane bioreactor	municipal (50%) and industrial (50%) wastewater	5,6 - 86,2	150 - 3000	8 000 - 11 000	0^{th} order	238				(Dvořák, Svojitka et al. 2013)

1. Material and methods

1.1. Membrane bioreactor

The aerated submerged membrane bioreactor (sMBR) and experimental set-up used in this study are shown schematically in Fig. 1.

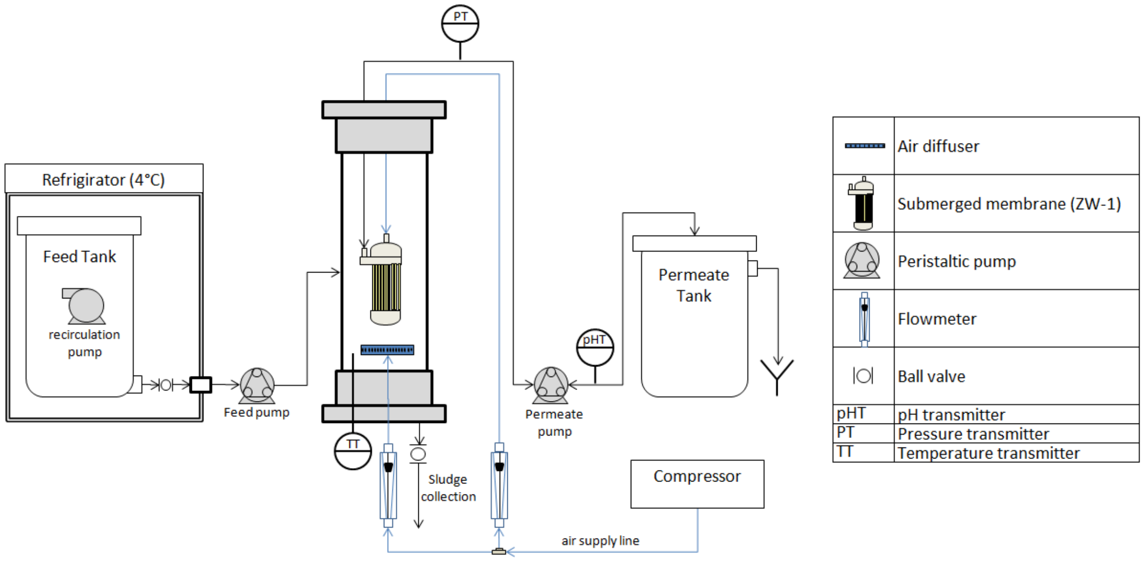


Figure 1 Scheme of the lab-scale sMBR

The wastewater was contained in a 50 L polyethylene tank placed in a refrigerator to maintain its temperature at 4°C in order to avoid any biological activity that could alter its composition. The retention time in the tube between the feed tank and the reactor was sufficient for the wastewater temperature to reach room temperature (20±1°C) before it was fed to the reactor. A submersible pump was placed at the bottom of the tank to mix the wastewater and avoid the settling of suspended solids.

The reactor was made of a 146.33 mm I.D. clear PVC tube (schedule 80), with a total net capacity of 10 L. Wastewater was fed into the reactor through its side by a peristaltic pump (Masterflex, model #7528-10). The membrane was a submerged ultrafiltration hollow-fiber membrane module (Zee-Weed, ZW-1). The membrane's specifications are presented in Table 2.

Table 2 Zee-Weed ZW-1 membrane module specifications

Nominal pore diameter (μm)	0,04
Fiber diameter (mm)	2
Membrane surface area (m^2)	0,047
Maximum transmembrane flux ($L*m^{-2}*h^{-1}$)	32

A constant permeate flow-rate was obtained by controlling the vacuum applied at the membrane (5 to 50 kPa) with a peristaltic pump (Masterflex, model #7528-10). To prevent the accumulation of a cake layer on the membrane surface, the sMBR was operated in filtration/backwash cycles (Filtration: 300 s, flux 7.4 L m^{-2} h^{-1}, Backwash: 20 s, flux 46.4 L m^{-2} h^{-1}) and air was introduced between the membrane fibers through a perforated pipe within the module (2.5 L air min^{-1}). Chemical cleaning of the module was conducted when the transmembrane pressure (TMP) reached -50 kPa. It consisted of an oxidation step (NaOCl, 1000 mg L^{-1} active Cl, recirculation for 3h), and an acidic step (Citric acid, 3 g L^{-1}, recirculation for 1.5h).

The sMBR was operated in oxic conditions (D.O. > 7 mg O_2 L^{-1}) at room temperature (20±1°C). Compressed air was introduced through a perforated tube placed at the bottom in the reactor (2.5 L min^{-1}) and arranged in such way as to create a homogeneous internal mixing of the reactor from the rising bubbles. Solid retention time (SRT) control was achieved by discharging excess sludge on a daily basis. Sludge was discharged from the bottom of the reactor in the form of mixed liquor. Hydraulic retention time (HRT) was controlled by adjusting the flow rates of the feed and the permeate pump, and it was calculated by measuring the collected permeate and mixed liquor volume on a daily basis. The pH value in the permeate, the TMP, and the activated sludge temperature were measured on-line by the built-in sensors of the experimental set-up and logged every minute.

1.2. Experimental program

The operating conditions of the sMBR during the four different experiment stages are shown in Table 3. During the initial condition (condition #1), the sMBR was fed with a synthetic leachate containing 219±3 mg NH_4-N L^{-1}. Then, the ammoniacal nitrogen concentration in the feed was increased by increments of 120, 325, and 375 mg NH_4-N L^{-1} between conditions #1 to #4, respectively.

Table 3 Operating parameters of the sMBR (average value)

Parameters	condition #1	condition #2	condition #3	condition #4
Period length (d)	118	28	32	28
MLSS (g L^{-1})	3,9	4,2	3,9	4,5
SRT (d)	31,7	30,5	28,9	32,1
HRT (hr)	50,4	51,3	48,8	50,1
Ammoniacal nitrogen (mg NH_4-N L^{-1})	219 ± 3	340 ± 28	665 ± 33	1040 ± 33
Chemical oxygen demand (mg L^{-1})	1096	1038	1000	1047
NLR (mg NH_4-N L^{-1} d^{-1})	108	163	330	509
[C:N] ratio (mg COD : mg NH_4-N)	5.0 : 1	3.0 : 1	1.5 : 1	1.0 : 1

Condition #1 lasted for 118 days in order to adapt the mixed liquor to the synthetic leachate and reach steady-state conditions. Then, for conditions #2 to #4, the sMBR was operated for 13.5 HRTs (21 days) before taking samples, which is more than the 3 HRTs generally considered to be enough to reach steady-state. Then, samples were taken every day for 7 days. If the difference in removal rates between two samples taken with a 7-day interval was less than 5%, then the sMBR was considered to be operated at steady-state. Otherwise, the sampling period was extended until that maximum 5% difference was measured.

Once steady-state was achieved, water samples were collected on a daily basis in the feed, the mixed liquor, and the permeate of the lab-scale sMBR. Samples from the feed and permeate were analyzed for ammoniacal nitrogen (NH_4^+), nitrates (NO_3^-), orthophosphates (PO_4^{3-}), chemical oxygen demand (COD), pH, dissolved oxygen (DO), alkalinity, and solids. Mixed liquor samples were only analyzed for solids.

1.3. Determining the nitrification kinetics (mass balance)

Mass balance equations are the expression of the relation between the different operating parameters of a process (Fogler 2006). The main parameters involved in the ammoniacal nitrogen mass balance equations of a sMBR that treats high-strength ammoniacal nitrogen wastewaters are shown in Fig. 2.

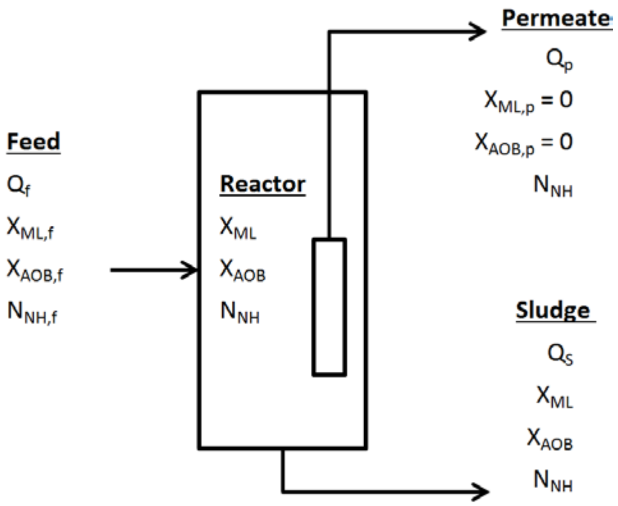


Figure 2 sMBR mass balance variables

Assuming a perfectly mixed continuous stirred tank reactor (CSTR), the ammoniacal nitrogen mass balance is defined as (Eq. 4):

$$\frac{dN_{NH}}{dt}V = Q_f N_{NH,f} - \left(Q_p N_{NH} + Q_S X_{ML} Y_{N/X}\right) + \int_0^V r_{NH} X_{AOB}\, dV \tag{4}$$

Where Q is the flow rate (L d^{-1}), N_{NH} is the ammoniacal nitrogen concentration in the reactor (mg NH_4-N L^{-1}), X_{ML} is the mixed liquor biomass concentration in the reactor (mg MLVSS L^{-1}), X_{AOB} is the AOB concentration in the reactor (mg L^{-1}), $Y_{N/X}$ is the nitrogen content of the biomass in the mixed liquor (mg N mg $MLVSS^{-1}$), r_{NH} is the ammoniacal nitrogen consumption rate (mg N-NH_4 g AOB^{-1} d^{-1}), and V is the reactor's volume (L). At steady-state conditions, biomass concentrations (X_{ML} and X_{AOB}), the reactor's volume and the ammoniacal nitrogen concentration in the reactor are constant ($dN_{NH}/dt = 0$). Eq. 4 then becomes (Eq. 5):

$$Q_f N_{NH,f} - \left(Q_p N_{NH} + Q_S X_{ML} Y_{N/X}\right) = -r_{NH} X_{AOB} V \tag{5}$$

Dividing Eq. 5 by V and rearranging, Eq.5 becomes (Eq. 6):

$$\frac{N_{NH,f}-N_{NH}}{HRT/_{24}}-\frac{X_{ML}*Y_{N/X}}{SRT}=-r_{NH}X_{AOB} \tag{6}$$

Where HRT is the hydraulic retention time (hr) and SRT is the solid retention time (d). Assuming that the AOB concentration and the consumption rate are constant for each given ammoniacal nitrogen concentration (steady-state conditions), the generation term of the equation can be simplified to (Eq. 7):

$$-r_{NH}X_{AOB} = -r_{NH,i} \tag{7}$$

Where $r_{NH,i}$ is the ammoniacal nitrogen consumption rate (mg N-NH_4 L^{-1} d^{-1}) at the ammoniacal nitrogen concentration “i”. The main advantage of using $-r_{NH,I}$ over $-r_{NH}$ is that it is does not require to know the exact concentration of AOB in the mixed liquor.

In this study, the nitrification kinetic parameters were calculated by solving using Eq. 6 for $–r_{NH,I}$ (Eq. 7) at 4 steady-state conditions (Table 3) with the lab-scale sMBR system. Then, the results were fitted to the most appropriate biological kinetic model, either Michaelis-Menten (Eq. 2) or Haldane (Eq. 3).

1.4. Synthetic wastewater

The composition of the synthetic leachate used in this study was based on the average composition of a leachate produced over the course of a year at a co-composting facility located in Quebec, Canada. The characterization results of these two leachates are summarized in Table 4.

Table 4 Co-composting facility leachate and synthetic leachate composition

Parameter	**(units)**	**Co-composting facility leachate**	**Synthetic leachate**
Ammoniacal nitrogen	mg NH_4-N L^{-1}	196	(see Table 3)

Condcutivity	mS cm^{-1}	5.11	4.11
pH		6.9	7.6
Total Hardness ($CaCO_3$)	mg L^{-1}	1386	(7.5 x [NH_4-N])
Total Organic Carbon (TOC)	mg L^{-1}	575	595
Aluminium (Al)	mg L^{-1}	0.82	0.80
Barium (Ba)	mg L^{-1}	0.092	0.07
Calcium (Ca)	mg L^{-1}	152	109
Copper (Cu)	mg L^{-1}	0.024	0.023
Iron (Fe)	mg L^{-1}	12.9	13.6
Potassium (K)	mg L^{-1}	435	232
Magnesium (Mg)	mg L^{-1}	49.4	92.4
Manganese (Mn)	mg L^{-1}	21.4	28.8
Sodium (Na)	mg L^{-1}	135	572
Nickel (Ni)	mg L^{-1}	0.06	0.08
Phosphorus (P)	mg L^{-1}	7.68	9.53
Lead (Pb)	mg L^{-1}	< 0.0045	< 0.0045
Sulfur (S)	mg L^{-1}	21	27.2
Zinc (Zn)	mg L^{-1}	0.078	0.0178

The following laboratory grade salts were used to prepare the synthetic leachate: $Al_2(NH_4)_2(SO_4)_4$, KH_2PO_4, $Na_2B_4O_7$, $BaCl_2$, $CoSO_4$, $CuSO_4$, $FeCl_3$, $MgCl_2$, $MgSO_4$, $MnCl_2$, $NiCl_2$, Na_2CO_3 and KCl. The organic carbon in the synthetic leachate was added in the form of ammonium acetate ($NH_4(CH_3COO)$), calcium propionate ($Ca(C_2H_3COO)_2$) and acetic acid (CH_3COOH). The first 200 mg NH_4-N L^{-1} of ammoniacal nitrogen consisted of only ammonium acetate ($NH_4(CH_3COO)$). Then, for each subsequent concentration increase (conditions #2 to #4), ammonium chloride (NH_4Cl) was added accordingly. In order to maintain an adequate pH for the AOB (above 6.5), the total hardness of the synthetic wastewater was adjusted at each condition using Na2CO3 in order to have a value of 7.5 mg $CaCO_3$ eq. / mg NH_4-N.

1.5. Activated sludge growth and adaptation

Activated sludge samples were obtained from a co-composting facility located in Quebec, Canada (Roy, Benkaraache et al. 2019). An initial sample volume of 40L of mixed liquor, with a concentration of approximately 0.25 g MLVSS L^{-1}, was taken from the bottom of an aerated lagoon (leachate treatment system) and left to decant for 24h. Then, the supernatant was removed and solids were transferred in a 20L batch aerated reactor filled with synthetic leachate. Then, over the duration of 4 weeks, the supernatant was replaced every week with 20L of fresh synthetic leachate. In order to maintain an adequate concentration of substrate as well as increase the concentration of the biomass in the mixed liquor, 22 g of ammonium acetate (200 mg NH_4-N L^{-1}, 343 mg C_{org} L^{-1}) and 13.3 g of calcium propionate (247 mg C_{org} L^{-1}) were added every 3 to 4 days. After 4 weeks, the mixed liquor was introduced to the MBR. For a period of 90 days prior to the kinetic experiment, the reactor was fed with synthetic leachate with an ammoniacal concentration of approximately 200 mg NH_4-N L^{-1} (Condition #1, Table 3).

1.6. Control reactor

A control sMBR was run in parallel to the nitrification kinetic experiment in order to distinguish purely chemical removal rates from those associated with the microbial activity. The control experiment was carried out over the course of 48 hours with 10L of synthetic leachate in a batch sMBR without mixed liquor. A ZW-1 membrane was used to take permeate samples. 50 mL samples were taken after 0.25, 1, 3, 6, 24, and 48 hours. Aeration was maintained at 2.5 L min^{-1} through the air diffuser and 2.5 L min^{-1} through the membrane module.

Two specific parameters were measured: 1) ammoniacal nitrogen concentration, and 2) total phosphorus concentration. Ammoniacal nitrogen is either biologically oxidized by nitrifying bacteria through the nitrification process, assimilated by bacteria in the mixed liquor during cell synthesis (microbial cell element composition: C_{60}:O_{27}:H_{94}:N_{15}:P_1), or stripped in the form of ammonia (pKa NH_4^+/NH_3 = 9.2). The equilibrium between gas and aqueous phases for the NH_3 compounds is the following:

$$NH^+_{4(aq)} \leftrightarrow NH_{3(aq)} \leftrightarrow NH_{3(g)} \; ; \; pKa \;\; NH_4^+/NH_3 = 9.2$$

Phosphorus removal is generally obtained either through co-precipitation with multivalent metals (Fe_2^+, Fe_3^+, Al_3^+), struvite formation with ammonium and magnesium (NH_4MgPO_4)(Huang, Xiao et al. 2014), adsorption on metal hydroxide colloids ($Fe(OH)_3$, $Al(OH)_3$) , or by assimilation during cell synthesis.

1.7. Analytical methods

The samples were analyzed for pH (Mettler Toledo SevenEasy), electrical conductivity (Mettler Toledo SevenCompact Conductivity), alkalinity (bromocresol green titration), solid content (total, dissolved, and volatile)(EPA Method 160.2), chemical oxygen demand (CEAEQ MA. 315 – DCO 1.1, Potassium dichromate), dissolved ammoniacal nitrogen (QuickChem Method 10-107-06-2-O, salicylate – nitroprusside colorimetric method), dissolved ortho-phosphate (QuickChem Method 10-115-01-1-B), dissolved nitrites/nitrates (QuickChem Method 10-107-04-2-B), and total metals (22 metals) and phosphorus (Varian Vista AX ICP-AES). Total metal and phosphorus contents were determined after preliminary sample digestion (15% trace metals grade HNO_3 and 5% H_2O_2 at 95°C for 2 hours).

2. Results and discussion

2.1. Control reactor experiment

The evolution of the ammoniacal nitrogen concentration in the control reactor over a 48 hour period is presented in Fig. 3. The initial ammoniacal nitrogen concentration measured in the control sMBR was 946 ± 7 mg NH_4-N L^{-1}. Over the duration of the experiment, the concentration of ammoniacal nitrogen decreased by approximately 7 mg NH_4-N L^{-1}, which corresponds to a 0.7% loss. With an initial pH of 7.6, the quantity of ammonia ($NH_{3(aq)}$) is negligible in the aqueous phase and gaseous phase. Furthermore, the nitrification reaction in the presence of mixed liquor acidifies the solution, which reduces even further the pH and favors the $NH_4^+{}_{(aq)}$ form. Thus, the variation observed in the control reactor is most likely associated with a chemical precipitation in the form of inorganic salts such as struvite..

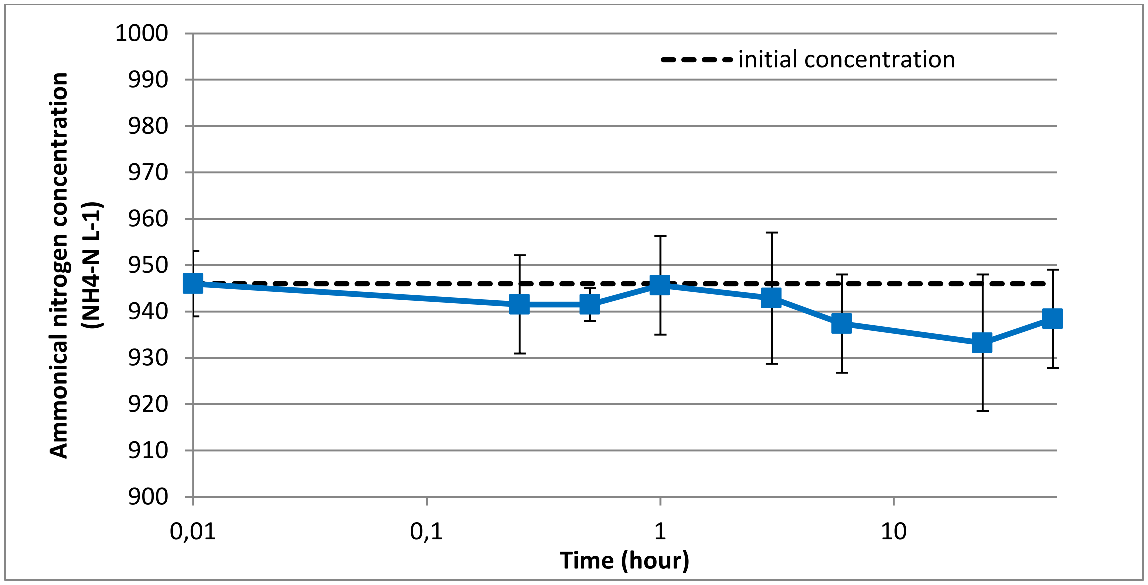


Figure 3 Evolution of the ammoniacal nitrogen concentrations in the control reactor

In terms of the phosphorus, the concentration of soluble phosphorus in the form of orthophosphate in the control sMBR decreased from 9 mg PO_4-P L^{-1} to 3.4 mg PO_4-P L^{-1} after 15 minutes, and decreased further to 0.76 mg PO_4-P L^{-1} after 48 hours. Table 5 shows the measured concentrations of the major elements present in the synthetic leachate. After 48 hours, aluminum, manganese and iron concentrations decreased by 80%, 92%, and more than 99.9%, respectively, while total phosphorus concentration decreased from 9 to 0.8 mg P L^{-1}. These results indicate the formation of insoluble inorganic molecules containing negatively charged orthophosphate ions and multivalent metal ions. The molar ratio of removed ammoniacal nitrogen (N):ortho-phosphates (P):magnesium (1:1.74:0.76) confirms that ammoniacal nitrogen reduction could be attributed to the formation of struvite. The results obtained from this control reactor experiment support the hypothesis that ammoniacal nitrogen concentration variations in the sMBR during the kinetic study are only attributed to the biological nitrification or assimilation, while phosphorus removal can only be attributed to chemical precipitation.

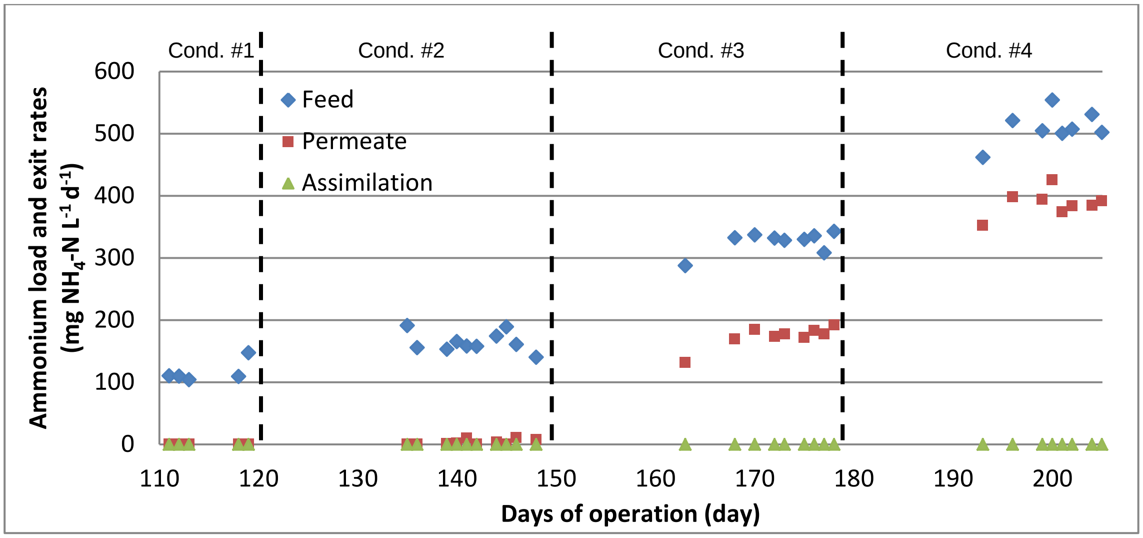
Table 5 Metals concentrations in the control reactor

	Metals (mg L^{-1})							
Time (hr)	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**P**
0	0.75	115	14.9	240	84	47	624	9.0
0.25	0.40	122	0.12	240	74	4.0	626	3.3
1	0.15	108	0.04	234	70	3.8	604	2.8
24	0.16	109	0.03	232	68	3.3	620	1.5
48	0.15	109	<0.01	218	63	3.6	630	0.8

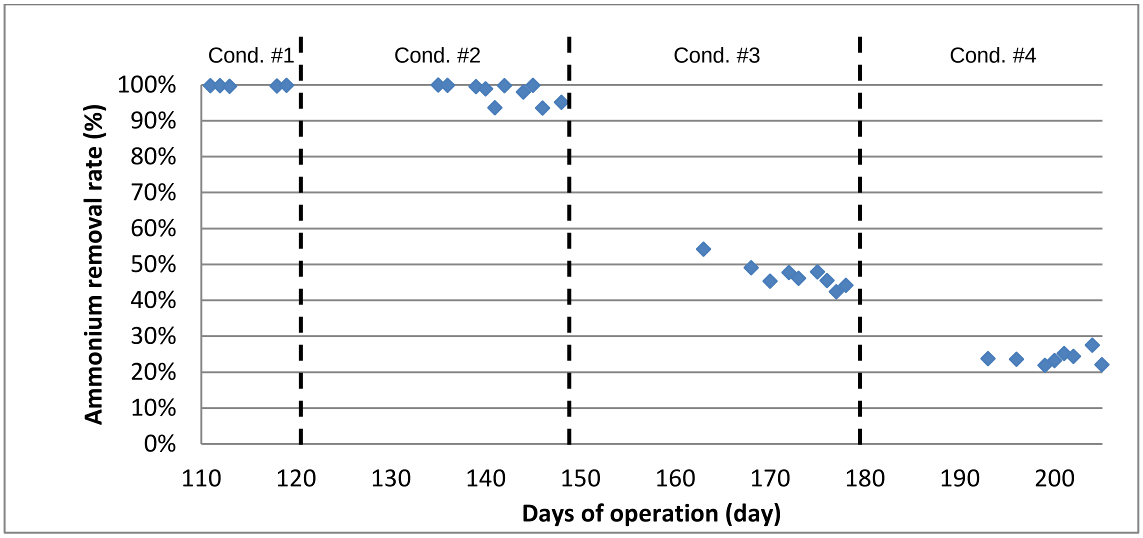
2.2. *Nitrification kinetic experiments*

2.2.1. *sMBR performances*

To define the nitrification kinetic parameters in a sMBR that treats high strength ammoniacal nitrogen wastewaters, the lab-scale submerged sMBR was fed with synthetic leachate at 4 different initial ammoniacal nitrogen concentrations (220, 340, 665 and 1040 mg NH_4-N L^{-1}) with a constant HRT. The selected ammoniacal nitrogen concentration range is based on the concentration reported in the literature for composting leachates originating from green wastes and mixed municipal solid wastes (Roy, Azaïs et al. 2018). Fig. 4 presents the ammoniacal nitrogen mass balance and removal rates obtained from this experiment. Over the first 118 days, the reactor was operated with a HRT of 48±3 hr, a SRT of 30±2 d and a NLR of 108 mg NH_4-N L^{-1} h^{-1} ($[NH_4]$ = 220 mg NH_4-N L^{-1}) to develop an acclimated mixed liquor. Toward the end of this period, the constant MLVSS measured in the sMBR indicated that the growth of new bacteria was equal to the combination of cell decay and the amount of sludge removed in order to maintain a constant SRT. With the absence in variation of MLVSS, and the entire consumption of both the ammonia and the COD, it was assumed that the heterotrophic and autotrophic bacteria populations reached their equilibrium in the mixed liquor. Therefore, the F:M ratios were constant for all substrates. Then, at day 119, 148 and 193, the NLR was increased to 163, 330 and 509 mg NH_4-N L^{-1} d^{-1}, respectively. After each increase, the reactor was operated for 28 days in order to achieve a steady-state operation, which is required to solve the mass balance equation and define the nitrification kinetic parameters. Fig. 4 a. shows the constant removal rates (<5% difference between 2 samples with a 7-day interval) observed at the end of each experimental condition, thus confirming the achievement of a steady-state operation of the sMBR.



(a)



(b)

Figure 4 Ammoniacal nitrogen load and exit rates and Fig. 4 b) Ammoniacal nitrogen removal performances of the sMBR operated at different nitrogen load rates

The ammoniacal nitrogen load and exit rates, as well as the average removal rates for each of the 4 experimental conditions are presented in Table 6. For NLRs below 165 mg NH_4-N L^{-1} d^{-1} (Conditions #1 and #2), the removal rates were of 99.7% and 97.8%, which corresponds to the range reported in the literature. However, the removal rates decreased to 46.1% and 23.8% with NLRs of 330 and 509 mg NH_4-N L^{-1} d^{-1}, respectively. These results indicate that for load rates above 160 mg NH_4-N L^{-1} d^{-1}, there is an excess of substrate for the AOB present in the mixed liquor, and any subsequent ammoniacal nitrogen fed to the reactor is not oxidized. Furthermore, the 28% decrease in ammoniacal nitrogen consumption between condition #2 (160 mg NH_4-N L^{-1} d^{-1} consumed) and #4 (115 mg NH_4-N L^{-1} d^{-1} consumed), despite an increase in NLR, indicates a significant inhibition effect of the ammoniacal nitrogen at NLRs higher than 160 mg NH_4-N L^{-1} d^{-1}.

Since all nitrogen fed to the reactor was in the form of ammoniacal nitrogen, nitrogen assimilated into the biomass/mixed liquor must be taken into account in the ammoniacal nitrogen mass balance equations. Elementary composition analyses were conducted on dried mixed liquor samples collected from the sMBR. On average, mixed liquor contains 34% C, 7,5% Ca, 6% N, 1.5% P and 7.5% of other metals (Al, Fe, K, Mg, Mn, Na, S, Si). The remaining 14% is oxygen and hydrogen. Nitrogen assimilated by the biomass in the mixed liquor (calculated from Eq. 6) corresponds to approximately 0.01% of the total nitrogen fed to the reactor. Thus, ammoniacal nitrogen is almost entirely used as a source of energy by AOB, and it is reasonable to neglect the nitrogen assimilated by the biomass when calculating ammoniacal nitrogen removal kinetics parameter in reactors treating high-strength ammonia wastewater with high NLR and long SRT (>30 days).

Table 6 Ammoniacal nitrogen mass balance for the MBR

$[NH_4]_{feed}$	**Load rate**	**Exit rates**		**Removal**	
(mg NH_4-N L^{-1})	**Feed** (mg NH_4-N L^{-1} d^{-1})	**Permeate** (mg NH_4-N L^{-1} d^{-1})	**Assimilation** (mg NH_4-N L^{-1} d^{-1})	**Assimilation** (%)	**Total** (%)
219±3	108	0,36	0,008	0,01	99,7
340±28	163	3,5	0,009	0,01	97,8
665±33	330	178	0,008	<0,01	46,1
1040±33	509	394	0,009	<0,01	23,8

2.2.2. *Nitrification kinetics modeling*

Specific ammoniacal nitrogen oxidation rates ($r_{NH,i}$) were calculated from Eq. 6 for each sample taken during the steady-state operation of the sMBR at 4 different initial ammoniacal nitrogen concentrations ($N_{NH,f}$ = [220 – 1040] mg NH_4-N L^{-1}) (Fig. 5).

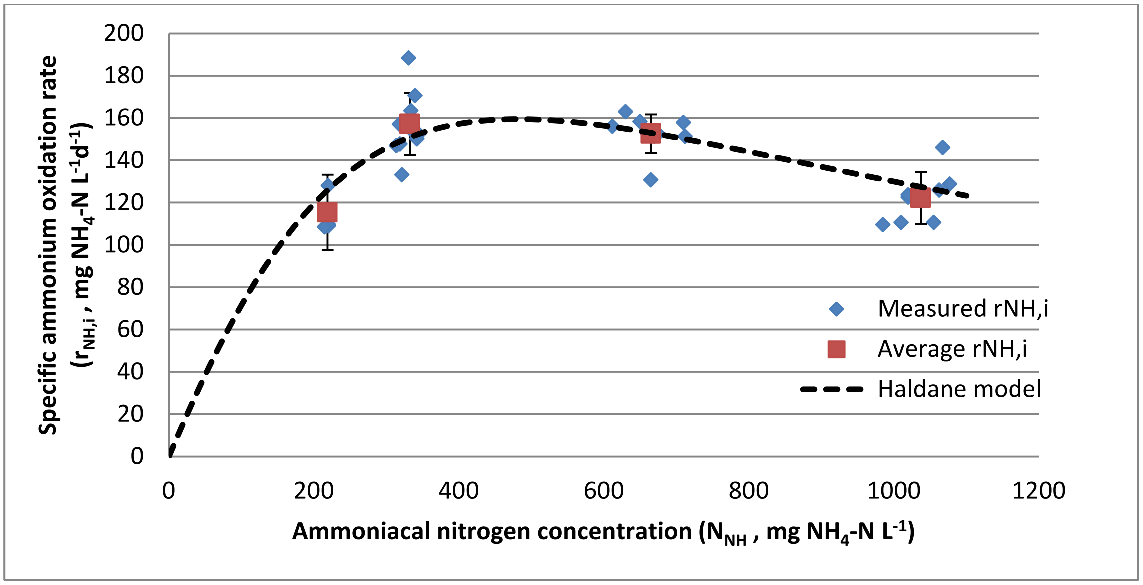


Figure 5 Specific ammonia oxidation rates measured at different ammonia concentrations

Results presented in Fig. 5 clearly indicate that the specific ammoniacal nitrogen oxidation rates were affected by the ammoniacal nitrogen concentration in the treated wastewater. For initial ammoniacal nitrogen concentrations ranging from 200 to 400 mg NH_4-N L^{-1}, the specific oxidation rates increased from 115±17 to 161±18 mg NH_4-N L^{-1} d^{-1}. Then, the specific oxidation rates decreased to 153±9 and 122±12 mg NH_4-N L^{-1} d^{-1} at initial ammoniacal nitrogen concentrations of 665 and 1040 mg NH_4-N L^{-1}, respectively. The negative variation of the specific oxidation rates at ammoniacal nitrogen concentrations above 400 mg NH_4-N L^{-1} are suspected to be caused by an inhibition phenomenon due to an excess in substrate concentration or a nitrite production which inhibits nitritation reaction, as observed by Gagnaire et al. in a flask test study(Gagnaire, Wang et al. 2011).

In order to take the inhibition phenomena into account, the Haldane model was selected to predict the specific ammoniacal nitrogen oxidation rates (Eq. 3). The 3 kinetic parameters of the model ($r_{NH,max}$, K_H and K_I) were obtained by fitting the experimental data (32 measurements) to the Haldane model equation. The calculated kinetic parameters are: $r_{NH,max}$ = 854,4 mg NH_4-N L^{-1} d^{-1}, K_S = 1007 mg NH_4-N L^{-1}, and K_I = 221 mg NH_4-N L^{-1} (R^2 = 0,97). The Haldane model is reported in Fig. 5. According to the model's equation, the lower the value of inhibition coefficient (K_I), the more significant the inhibition is. The K_I calculated in this study is in accordance with values reported in the literature for suspended growth mixed liquors. For example, Carrera et *al*. (2004) and Whang et *al.* (2009) both reported K_I values for activated sludge systems of 284 and 199 mg NH_4-N L^{-1}, respectively (Carrera, Jubany et al. 2004, Whang, Chien et al. 2009).

The ammoniacal nitrogen concentration for which the oxidation rate is at its highest is obtained by finding the root of the derivative of the model's equation ($dr_{NH,i}/dN_{NH}$ = 0). The following relationship is obtained (Eq. 8):

$$N_{NH,opt} = \sqrt{(K_S K_I)} \qquad \text{(Eq. 8)}$$

According to Eq. 8, the highest specific nitrification rate of a sMBR to treating high-strength ammoniacal nitrogen leachate is obtained at an initial concentration of 472 mg NH_4-N L^{-1}. Above this concentration, the inhibition phenomena negatively impact the nitrification rates. In terms of reactor design, this concentration corresponds to the optimal HRT:NLR ratio, and any higher ammoniacal nitrogen concentration will require a larger reactor's volume per mass of contaminants to achieve the desired treated water quality.

2.2.3. Nitrification kinetic in the literature

Kinetic parameters measured in this study were compared to those reported in the literature for systems treating high-strength ammoniacal nitrogen wastewater. Fig. 6 shows the specific ammonium oxidation rates reported for 5 flask test studies (Carrera, Jubany et al. 2004, Kaczorek and Ledakowicz 2006, He, Xue et al. 2009, Whang, Chien et al. 2009, Dvořák, Svojitka et al. 2013) and 1 continuous operation study (Dinçer and Kargı 2000), and compares them to the experimental data obtained in this study.

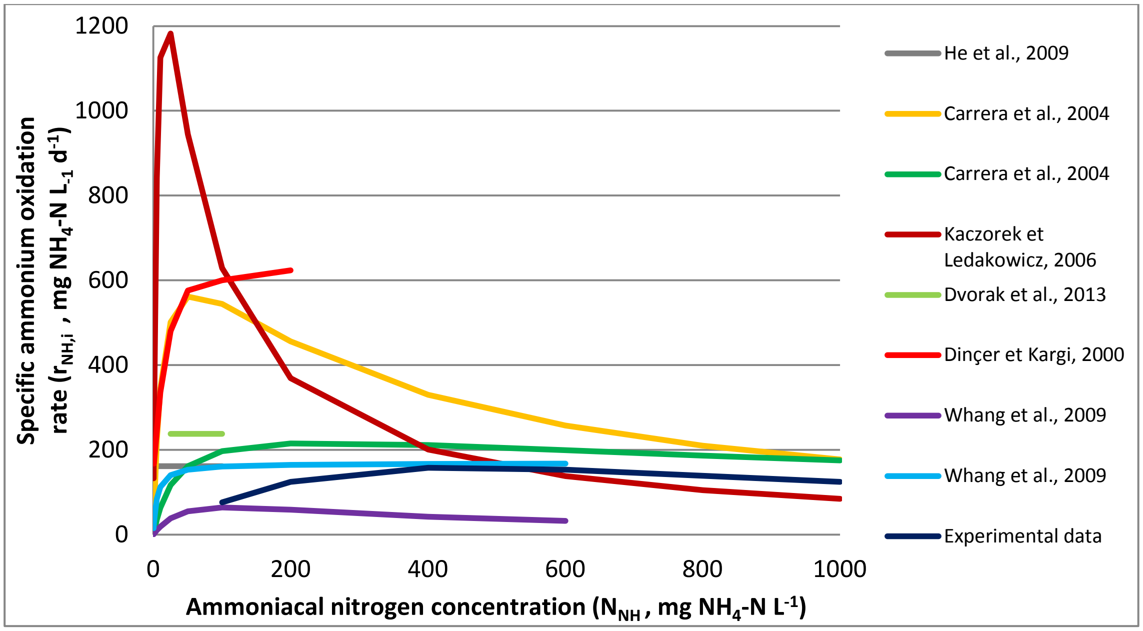


Figure 6 Comparison between ammoniacal nitrogen oxidation rates reported from the literature and those measured in this study

Dvorak et *al*. (2013) and He et *al.*(2009) both reported 0th order kinetics since, they only worked on short concentration ranges (5.6 to 86.2 mg NH_4-N L^{-1}) (He, Xue et al. 2009, Dvořák, Svojitka et al. 2013). Therefore, their reported oxidation rates are only valid for that range and cannot be compared to other reported values at higher ammoniacal nitrogen concentrations (>100 mg NH_4-N L^{-1}).

As previously mentioned, the proportion of the AOB population in the mixed liquor is directly proportional to the overall ammoniacal nitrogen oxidation rate (Eq. 7). In a previous study, Munz et *al.* (2010) showed that the AOB growth rate and concentration in the mixed liquor are proportional to the ammoniacal nitrogen concentration in the treated effluent (Munz, Mori et al. 2010). Therefore, in order to compare the mixed liquors used in the different studies reported in Fig. 6, the NLR and the corresponding ammoniacal nitrogen concentrations treated by the reactors from which the mixed liquor was taken have been summarized in Table 7.

Table 7 Ammoniacal nitrogen load rates (NLR) of reactors treating high-strength ammoniacal nitrogen

Authors	**NLR (mg NH_4-N L^{-1} d^{-1})**	**HRT (h)**	**[NH4] (mg NH_4-N L^{-1})**
Carrera et al. (2004) (Carrera, Jubany et al. 2004)(Yellow curve)	90	48	180
Kackzorek et Ledakowicz (2006) (Kaczorek and Ledakowicz 2006)	240	72	720
Dvorak et al. (2013) (Dvořák, Svojitka et al. 2013)	54 - 80	14	31 - 47
Whang et al. (2009) (Whang, Chien et al. 2009) (Blue curve)	43	10	18
Whang et al. (2009) (Whang, Chien et al. 2009) (Purple curve)	107	48	214

According to the different NLR, higher concentrations of AOB in the mixed liquor from Kaczorek et Ledakowicz (2006) would be expected when compared to any other mixed liquor reported in Table 7, since their reported NLR was the highest. This hypothesis only stands if the duration of the SRT was sufficient to maintain the AOB population within the reactor. To measure the specific ammoniacal nitrogen oxidation rate ($r_{NH,i}$), Kaczorek et Ledakowicz (2006) measured the consumption rate by exposing the mixed liquor from their reactor, which was adapted to an ammoniacal nitrogen concentration of 720 mg NH_4-N L^{-1}, to a wide range of ammoniacal nitrogen concentrations. This approach provides an accurate estimation of the specific ammoniacal nitrogen oxidation rate at concentrations close to that of the treated effluent (± 20%). However, at low substrate concentration, the F:M ratio is unrealistically low, which leads to highly overestimated rates. This is what explains Kaczorek et Ledakowicz's (2006) reported rate of 1217 mg NH_4-N L^{-1} d^{-1} with an effluent concentration of 17.7 mg NH_4-N L^{-1} (Kaczorek and Ledakowicz 2006). The mixed liquor used in their study was taken from a reactor treating a wastewater containing 720 mg NH_4-N L^{-1} with a NLR of 240 mg NH_4-N L^{-1} d^{-1}. In this case, the F:M ratio ([NH4]:AOB) in the flask at concentrations lower than 400 mg NH_4-N L^{-1} was unrealistically low, which led to a highly overestimated oxidation rate when compared to similar studies. On the other hand, the $r_{NH,I}$ that they reported at concentrations around 720 mg NH_4-N L^{-1} were in the same range as most of the reported values.

Similarly, Whang et *al.* (2009) studied the nitrification kinetics of mixed liquor taken from 2 treatment systems treating municipal wastewaters (Fig. 6, blue curve) and swine wastewater (Fig. 6, purple curve) (Whang, Chien et al. 2009). In both case, the same volume of mixed liquor was taken from each reactor to conduct the flask tests, despite the difference in NLR fed to both treatment systems. As expected, the ratio of the highest reported $r_{NH,I}$ from each reactor (168 mg NH_4-N L^{-1} d^{-1} / 65 mg NH_4-N L^{-1} d^{-1} = 2.58) is almost equal to the ratio of the NLR of the reactors (107 mg NH_4-N L^{-1} d^{-1} / 43 mg NH_4-N L^{-1} d^{-1} = 2.49). Assuming that the AOB population in the mixed liquor is proportional to the NLR, these ratios show that both reactors have a similar capacity of removing ammoniacal nitrogen from wastewaters. Therefore, by neglecting the F:M ratio ([NH4]:AOB) ratio, the flask test cannot accurately compare the kinetic parameters of treatment systems treating wastewaters with different NLR. The data reported by Whang et *al.*(2009) and Kaczorek et Ledakowicz (2006) highlights the limits of the flask test in defining kinetic parameters for contaminant removal in wastewater biotreatment systems. Reported high nitrification rates at low substrate concentrations and strong inhibition phenomenon at higher substrate concentrations are the results of the inaccurate and variable F:M ratio in flask tests. Therefore, a method that takes microbial population concentration into account when measuring the kinetic parameters for specific substrate (contaminant) removal is deemed necessary to providing accurate data and to comparing treatment systems to each other.

In general, reported specific ammonium oxidation rates range from 100 to 225 mg NH_4-N L^{-1} d^{-1} for effluent concentrations ranging from 200 to 1000 mg NH_4-N L^{-1}. In this study, measured rates ranged from 115 to 161 mg NH_4-N L^{-1} d^{-1}, which is in accordance with data reported in the literature. Furthermore, since the steady-state was achieved for each measurement, the F:M ratio (NH_4:AOB) ratio was maintained constant for each measurement; the oxidation rate measured also showed a lower variability over the range of substrate concentration tested.

The steady-state approach to measure contaminant removal kinetics addresses all the issues of the flask test method and provides more realistic data. Another option that could be considered to accurately measure those kinetic parameters would be to introduce molecular biology techniques to the flask test method. In this context, real time polymerase chain reaction (qPCR) could be used to quantify the proportions of AOB in relation to the total microbial population (Leyva-Díaz, González-Martínez et al. 2015). Then, using the qPCR results, the proper amount of sludge could be added to each flask in order to maintain the F:M ratio constant and representative of the reactor from which it was taken. While this method would be more complex than the steady-state approach, it would be much quicker (days instead of weeks).

3. Conclusion

The main objectives of this study were to provide an accurate experimental method to measure kinetic parameters in environmental bioprocesses that treat specific contaminants, as well as to fill the gap of information regarding the kinetics parameters for sMBR treating high-strength ammoniacal nitrogen wastewater. The proposed approach consisted in the operation of a lab-scale sMBR with synthetic leachate for 205 days with 4 ammoniacal nitrogen concentrations (220, 340, 665 and 1040 mg NH_4-N L^{-1}) until steady-state conditions were reached. At each steady-state, mass balance equations were solved to calculate the specific ammoniacal nitrogen consumption rates. Measured rates ranged from 115 to 161 mg NH_4-N L^{-1} d^{-1}, with the highest rate measured at an effluent concentration of 340 mg NH_4-N L^{-1}. Experimental data suggest that an inhibition phenomenon occurs at concentrations above 400 - 500 mg NH_4-N L^{-1}. Therefore, the Haldane model was selected to predict the ammoniacal nitrogen oxidation rates with the following kinetic parameters: $r_{NH,max}$ = 854,4 mg NH_4-N L^{-1} d^{-1}, K_S = 1007 mg NH_4-N L^{-1}, and K_I = 221 mg NH_4-N L^{-1} (R^2 = 0,97). According to this model, sMBRs that treat high-strength ammoniacal nitrogen are most efficacious when treating effluent with an ammoniacal nitrogen concentration of 472 mg NH_4-N L^{-1}.

The steady-state approach used to measure the kinetic parameters was found to provide more accurate estimation of the kinetic parameters in wastewater biological treatment systems than the conventional flask method. The steady-state approach takes into account the F:M ratio by adapting the mixed liquor to the substrate concentration tested, which is not the case with the flask method. When compared to other ammonia oxidation kinetic studies conducted on high-strength ammoniacal nitrogen wastewaters, results from this study showed both a lower variability in the specific nitrification rates and a lower effect of the inhibition phenomena. Therefore, this method should be favored for future contaminant removal kinetic studies in wastewater biological treatment systems.

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