

EFFECT OF DIFFERENT PARAMETERS OF THE BIOLOGICAL PROCESSES ON THE SPECIFIC GROWTH RATE OF NITRIFYING BACTERIA BY MEANS OF MATHEMATICAL MODELS

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ABSTRACT

In this study, the biological removal of nitrogen from wastewater with relatively high ammonium concentration is investigated by modelling and simulation. Specifically, the nitrification process, means the oxidation of ammonium to nitrate, which is catalysed by two types of bacteria, namely ammonium-oxidising bacteria (AOB) and nitrite-oxidising bacteria (NOB). In wastewater treatment, ammonia oxidation lowers the pH of wastewaters with in relation to total ammonia limited alkalinity. By reducing the pH, ammonia oxidation often stops just below pH 6-6.5. On the other hand, nitrification has been found to occur even at low pH in reactors that process human urine, although it was not clear which species of bacteria are involved. Against this background, this research used different mathematical models of ammonia-oxidising bacteria (AOB). The aim is to estimate those sludge residence times as a function of pH that can achieve complete nitrification of the NH₃-N load in the influent. Quantity of base that should be dosed to the system and the capacity of the bioreactor have been calculated using estimated data. The values obtained have also been compared with the values from literature.

KEYWORDS: Nitrification; Modeling; Solid retention time; Bioreactor; Wastewater treatment

1. INTRODUCTION

Recent European legislation for the reduction of total nitrogen content of wastewater treatment system effluent encourages work into new approaches for upgrading existing plants. Relevant management of internal recycling flows is getting a lot of attention nowadays (Hellinga, van Loosdrecht, & Heijnen, 1999; Kollbach & Grömping, 1996). The removal of nitrogen from wastewater is mainly achieved through biological means in wastewater treatment plants by stimulating the natural processes of nitrification and denitrification. During the biological nitrification of these wastewaters, pH plays a key role as it affects ammonia-oxidizing bacteria (AOB) and

nitrite-oxidizing bacteria (NOB) (Fumasoli, Morgenroth, & Udert, 2015). AOB growth rate declines with pH decrease, since at low pH value the real substratum of AOB which is NH₃ exists only at minimal concentrations, even though the total concentration of ammonia (NH₄ and NH₃) is high (Isamu Suzuki, Usha Dular, & S. C. Kwok, 1974).

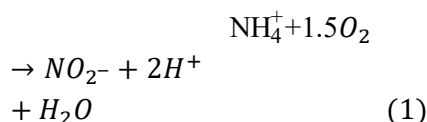
On the other hand (Antoniou et al., 1990; van Hulle et al., 2007) have proposed that pH affects AOB directly through protein damage, they have however provided no model to account for this inhibition. (Antoniou et al., 1990) investigated an optimum pH of about 7.8 and the effective maximum specific growth rate observed was increased as a function of temperature in the range of 15–25°C, while in the research study

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(EPA, 1993) it was observed that nitrification occurs in a temperature range of approximately 4-45°C, with approximately 35°C being the optimum for *Nitrosomonas* and the purpose for design, the acceptable pH range is 6.5 to 8.0 (EPA, 1993) was considered. In the end quantifying the temperature effect and optimum pH with confidence is still difficult.

Nitrification is a very oxygen hungry process; ammonia oxidation reduces the pH of wastewater with in relation to total ammonia limited alkalinity. The stoichiometric equations of nitrification are very important for understanding the mechanisms of biological nitrogen removal, which involves two steps: Equation (1) for the oxidation of ammonium to nitrite and then Equation (2) to Nitrate (Zhou, 2007) :



As seen in the above equation, the oxidation of each ammonium mole produces 2 mols of acidity, which can lead to a reduction of the pH in inappropriately buffered environments. The activity of (AOB) typically decreases with pH and sometimes stops below pH 6 (Fumasoli et al., 2017). Occasional studies (Tarre & Green, 2004) investigated that ammonia-oxidising bacteria have the ability to nitrify at low pH value such as ammonia oxidation in designed reactors using industrial wastewaters has been found at pH values of about 4.

The relationship of factors like pH, temperature, microbial numbers, acclimatisation and inhibiting compounds influence the rate at which nitrification occurs. Preliminary studies found that nitrites can accumulate in nitrifying systems. Depending on the operating condition and initial loading conditions, varied nitrite concentrations may continue without subsequent

oxidation to nitrate, especially in solutions or wastewater with high concentrations of organic or ammonia nitrogen (Anthonisen, Loehr, Prakasam, & Srinath, 1976).

For removing ammonium from municipal wastewater parameters of the biological processes need to be evaluated through modelling and simulation. Reactor design and configuration can then determine the effective use of those parameters. Common reactor configurations are at least eight Suspended growth reactor configurations has been designed with the use of different methods to incorporate nitrification process (EPA, 1993). But research on the treatment of high-strength ammonium wastewater is still a ‘hot spot’.

Only a few studies develop models of nitrification, which include explicit pH calculations based on acid-base e.g. (Hellings et al., 1999). The designed model was based on NH₃ limitation and HNO₂ inhibition and was adjusted to a pH range of 6.5-8. The pH levels in (Antoniou et al., 1990) significantly decrease the oxidation rate of ammonia between pH 7 and 6.

The relationship between biological processes, pH and nitrification, is the most critical for the N removal activated sludge system in poorly buffered wastewater or wastewater with highly N inflow (such as anaerobic digester liquors) (Sötemann, Musvoto, Wentzel, & Ekama, 2005).

To decide the level to which a biological nitrification process needs additional pH stability mechanisms to maintain the pH values of the reactor within a reasonable range and to avoid process inhibition, knowledge of the pH buffering capacity of a wastewater that contains high ammonia nitrogen, such as high-strength nitrogen wastewater, is therefore crucial.

It has been demonstrated by (Anthonisen et al., 1976) that ammonia autotroph bacteria which play an essential role in the nitrification process are specifically sensitive to the pH of their culture.

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While alkalinity provides a measure of a wastewater's overall buffering capacity, nitrifying activated sludge systems are typically operated at a pH setpoint of around 7.5-8.5, well above the 4.3 pH endpoint used for alkalinity determination through titration according to standard methods (DIN 38409-7:2005-12).

2. NITRIFICATION MODELS

The primary step in measuring the suspended growth nitrification reactor is the determination of the solid's retention time. To do this, one must account for the impacts of the different active components on the growth rate of Nitrosomonas (EPA, 1993, p. 134). From a modelling viewpoint. It is agreed in general that pH has a direct effect on the maximum growth rate of both ammonia-oxidizing bacteria and

nitrite-oxidizing bacteria (Jubany Güell, 2007; Sötemann, Wentzel, & Ekama, 2007), It was found by (Hellings et al., 1999) that AOB is more sensitive to pH changes than NOB, with the maximum growth rate of the first being considerably lower than that of the last-mentioned at acidic pH values. The models to incorporate the effect of pH in kinetic models of AOB growth are:

2.1 *Model 1:* the empirical model (Equation 2.1a), (Equation 2.1b), (Sötemann et al., 2005) including the Monod term in the model to incorporate the effect of pH in models of AOB growth. Some researchers have shown that μ can be represented as a percentage of the maximum value at optimum pH. Using this method, μ is the maximum and remains roughly constant for $7.2 < \text{pH} < 8.5$ in the pH range and decreases as the pH drops below 7.2

$$2.1A \quad (5 < \text{pH} \leq 7.2) \quad \mu' = \mu_{Am7.2} \theta^{(\text{pH}-7.2)} \cdot \left[\frac{N}{K_N + N} \right] - b_A \quad (2.1a)$$

$$2.1B \quad (7.2 < \text{pH} < 9.5) \quad \mu' = \mu_{Am7.2} * K_I * \frac{K_{max} - \text{pH}}{K_{max} + K_{II} - \text{pH}} * \left[\frac{N}{K_N + N} \right] - b_A \quad (2.1b)$$

Where:

μ' is the net specific growth rate per day for AOB, $\mu_{Am7.2}$ is the maximum specific growth rate for AOB at a pH value of 7.2 per day and K_I, K_{II} and K_{max} are empirical model coefficients, (θ) is pH sensitivity coefficient 2.35, b_A is the decay coefficient, K_N = half-saturation coefficient in mg/L, N = NH₄-N concentration in mg/L. All constants are 2.3

specified in Table 1.

2.2 *Model 2:* developed by (Antoniou et al., 1990) based on enzyme kinetics (Equation 2.2), this is a useful expression for determining the capacity of activated sludge facilities that are required for the nitrification and incorporation of wastewater into general process models, such as ASM1 (Activated Sludge model one) for different mixed liquor temperatures and pH:

$$\mu' = \frac{m * e^{-(a/T)}}{1 + \frac{b}{10^{-\text{pH}}} + \frac{10^{-\text{pH}}}{c}} * \left[\frac{N}{K_N + N} \right] - b_A \quad (2.2)$$

Where:

μ' is the net specific growth rate per day for AOB, T is the temperature in kelvin, b_A is the decay coefficient per day, and the parameters (a,b,c and m) are coefficient can be determined experimentally and depend on the wastewater specification given in Table 1.

2.4 *Model 3:* developed by (Downing A.L., Painter H.A. and Knowles G, 1964; EPA, 1993)) valid for $\text{pH} < 7.2$. The model showed that the nitrification rate could be formulated in terms of the Monod equation.

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$$\mu' = 0.47 \left[e^{0.098(T-15)} \right] * \left[\frac{N}{K_N + N} \right] * [1 - 0.833(7.26 - pH)] - b_A \quad (2.3)$$

Where:

pH = anticipated pH in nitrification reactor, μ' = net specific growth rate of Nitrosomonas per day.

$$\mu' = \mu_{max} * \left[\frac{C_{NH_3}}{K_{NH_3} + C_{NH_3}} \right] * \left[\frac{K_{I,HNO_2}}{C_{HNO_2} + K_{I,HNO_2}} \right] * \left[\frac{C_{O_2}}{K_{O_2} + C_{O_2}} \right] - b_A \quad (2.4)$$

Where:

μ' is the net specific growth rate per day for AOB, μ_{max} the maximum growth rate (d⁻¹), K_{NH_3} the affinity constant for NH₃ mg/L, K_{I,HNO_2} the non-competitive inhibition constant for HNO₂ (mg/L), and $C_{NH_3}, C_{HNO_2}, C_{O_2}$ are the concentration in mg/L of ammonia, nitrite and oxygen, and K_{O_2} the affinity constant for O₂ in mg/L given in Table 1.

2.5 *Model 4*: demonstrated by (Hellings et al., 1999), comprise a pH calculation based on acid-base equilibria, and an inhibition term has been included for the unionized HNO₂, including double Monod kinetics. The chosen substrates of AOB and NOB and their inhibitory species C_{NH_3} and C_{HNO_2} are well known (Anthonisen et al., 1976)

2.6 **Model 5**: Model developed by (WRC Report No TT16/84, 1984), considered an increase in half-saturation concentration (affinity coefficient) (Kn) with a decrease in pH, as shown in equation (2.5) as well as the overall effect of pH and temperature. But (WRC Report No TT16/84, 1984) did not consider cases of μ_N where pH > 8.5.

$$\mu' = \frac{(\mu_{nm20} \theta^{(pH-7.2)}) * (1,123^{(T-20)} * N)}{(K_{n20} \theta^{(7.2-pH)}) * (1,123^{(T-20)} + N)} * \left[\frac{N}{K_N + N} \right] - b_A \quad (2.5)$$

Table 1. Kinetic parameter for microbial growth and decay of AOB included in the nitrification models.

Parameter	Symbol	Value	Unit	Reference
Maximal growth rate	μ_{max}	2.1	d ⁻¹	(Hellings et al., 1999)
Decay rate	b_A	0.2	d ⁻¹	(Hellings et al., 1999; Jubany Güell, 2007)
pH sensitivity coefficient	θ	2.35	-	(M. Henze, 2008; Söttemann et al., 2005)
half-saturation coefficient	K_N	0.468	Mg.L ⁻¹	(M. Henze, 2008; Söttemann et al., 2005)
empirical model coefficients	K_I	1.13	-	(M. Henze, 2008; Söttemann et al., 2005)
empirical model coefficients	K_{max}	9.5	-	(M. Henze, 2008; Söttemann et al., 2005)
empirical model coefficients	K_{II}	0.3	-	(M. Henze, 2008; Söttemann et al., 2005)
empirical model coefficients	a'	9980	-	(Antoniou et al., 1990)

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empirical model coefficients	b'	2.05E-09	-	(Antoniou et al., 1990)
empirical model coefficients	c'	1.66E-07	-	(Antoniou et al., 1990)
empirical model coefficients	m'	4.70E+14	-	(Antoniou et al., 1990)
inhibition constant for HNO ₂	K_{I,HNO_2}	0.21	Mg.L ⁻¹	(Hellinga et al., 1999)
NH ₃ affinity constant	K_{NH_3}	0.468	Mg.L ⁻¹	(Hellinga et al., 1999)
O ₂ affinity constant in	K_{O_2}	1.45	Mg.L ⁻¹	(Hellinga et al., 1999)

* depend on the characteristic of wastewater

EFFLUENT AMMONIA CONCENTRATION AND SRT

1.1 Effluent ammonia concentration

To estimate the effluent ammonia concentration of wholly mixed activated sludge system, the μ' values obtained by each of the above models can be readily added in the ASM1

model's in the steady-state solution (M. Henze, 2008; Katayama, Deerberg, Londong, & Ruhr-Universität Fakultät für Maschinenbau, 2018), (Fumasoli et al., 2015) consider the dependence of NH₃'s availability on pH due to its acid-base balance with NH₄ using the following relationship between effluent TAN and pH:

$$TAN = N_{ae} = \frac{K_{nT}(b_{AT} + \frac{1}{SRT})}{\mu' - (b_{AT} + \frac{1}{SRT})} * (\frac{10^{-pH}}{10^{pKa}} + 1) \quad (3.1)$$

Where:

TAN is the effluent total ammonia Nitrogen concentration, in mg N/L, K_{nT} is the half-saturation constant of AOB, in mgNH₃/L; b_{AT} is the endogenous decay rate of AOB, in d⁻¹. pKa is the acid dissociation logarithm of the NH₄, which is 9.25 at 25 C°.

1.2 Solid retention time

The minimum sludge age for nitrification (SRT_m) at different pH and Temperature (T)

$$SRT_m = \frac{1}{[\mu'(1 - f_{xm}) - b_{AT}]} \quad (3.2)$$

$$SRT = SF * SRT_m \quad (3.3)$$

Where: f_{xm} is unaerated mass fraction <60%, (Ekama & Wentzel, 2004; M. Henze, 2008) demonstrated that increasing fraction from 0.50 to 0.60 it is not economical due to the large reactor volumes, S.F =1.25 is safety factor of 25%.

unaerated zones may have an effect on nitrification based on the assumptions:

- Nitrifiers, being compulsory aerobics, only develop in the aerobic system areas.
- Endogenous nitrifier mass loss occurs under the conditions are both aerobic and non- aerobic condition.

If ($SRT < SRT_m$) then the effluent ammonia concentration and the effluent concentration of TKN (Total Kjeldahl nitrogen) increase with increasing sludge age (WRC Report No TT16/84, 1984).

Once $SRT > SRT_m$, a high effectiveness of nitrification will be observed, but the maximum unaerated sludge mass fraction required to assure nitrification should not be exceeded.

Nevertheless, by increasing the sludge age, the Phosphorous removal is reduced because the mass of sludge wasted daily decreases as the

sludge age increases. (Hellings et al., 1999) has found that, the minimum sludge age for the growth rates of ammonium oxidisers is higher than nitrite oxidisers, causing the washout of the latter.

It is also well known that as a reactor's SRT increases, the observed yield from the growth of heterotrophic biomass decreases (M. E. Henze, 2000).

2. REACTOR VOLUME

volume of the biological reactor can be calculated from SRT, constant flow rate, Mass of Mixed Liquor Suspended Solids (MLSS), and by

$$V = \frac{Q * SRT}{X_{TSS}} * \left[\frac{Y * (S_{INF} - S_{EFF})}{f * (1 + K_d * SRT)} * (1 + f_d * K_d * SRT) + \frac{Y_A * (N_{NH4,INF} - N_{NH4,EFF})}{f * (1 + K_d * SRT)} + (TSS_{INF} - VSS_{INF}) + nbVSS_{INF} \right] \quad (4.1)$$

Where:

XTSS represent the Concentration of Total Suspended Solids; the variables $N_{NH4, INF}$, S_{INF} , TSS_{INF} , VSS_{INF} and $nbVSS_{INF}$ are the ammonia nitrogen, COD, TSS, VSS and non-biodegradable VSS concentrations in the influent, respectively; $N_{NH4, EFF}$, S_{EFF} are the COD and ammonia nitrogen concentrations in the effluent. Values for the model's stoichiometric

specifying the Concentration of Total Suspended Solids (XTSS) in the reactor by equation 4.1 with neglecting the sludge's weight in the secondary settling tank and the losses of a solid mass with effluent is also ignored. This presumption is logical when the process is maintained at a sludge age greater than three days:

the Activated Sludge Model 1 (ASM1) which consist of the set of differential equations which is based on the steady-state solution for an activated sludge system including COD removal and nitrification, given by Equations 4.1 and (Tchobanoglous, Burton, & Stensel, 2003):

kinetic parameters are listed in Table 4.1. The fraction of the total VSS given in Equation 4.2:

$$nbVSS_{INF} = f_{NB} * VSS_{INF} \quad (4.2)$$

Values were taken from (Hocaoglu et al. 2010 (M. Henze, 2008)), Who characterized sludge obtained from an MBR (Membrane Bioreactor) which operated under similar operating conditions as the system under consideration here and treated high-strength nitrogen wastewaters with a similar composition.

Table (4.1): Parameter values of the steady-state MLSS.

Parameter	Symbo l	Valu e	Unit	Referenc e
Heterotroph ic yield coefficient	Y	0.47	gVSS/gCO D	Hocaoglu et al. 2010
Heterotroph ic	K_d	0.18*	d ⁻¹	Hocaoglu et al. 2010

endogenous decay coefficient	Cell debris fraction	f_d	0.15	-	(M. Henze, 2008)
Volatile fraction in VSS		f	0.85	-	(M. Henze, 2008)
Autotrophic yield		Y_A	0.16	gVSS/gCO D	(M. Henze,

coefficient				2008)
Autotrophic	K_{da}	0.06*	d^{-1}	(M.
endogenous				Henze,
decay				2008)
coefficient				

*Temperature = 20 C°

The inflow Q and effluent COD concentration Si were considered constant, with 480 L/d and 207 mg/L respectively. The effluent NH4-N concentration was considered zero. It was taken that all the VSS present in the influent is fully biodegradable (f_{nb}=0). Based on the results obtained by (Hocaoglu et al. 2010) these assumptions made. Value of (XTSS) were taken from (M. Henze, 2008; Katayama et al.,

2018) which was about 6 (kg/m³) who characterized sludge obtained from MBR that operate under similar operating conditions as the system under consideration here and treated blackwater with a similar composition. However, the sludge concentration in the reactor varies over the day with the daily flow through the plant.

2. ALKALINITY AND BASE CONSUMPTION

2.1 Alkalinity need to compensate nitrification:

In an activated sludge process, the alkalinity consumed by microbiological activity can calculate COD removal and nitrification in a steady-state. A formula was derived to predict changes alkalinity (Searce, Benninger, Weber, & Sherrard, 1980).

$$\Delta Alk_0 = 3.57N_{ORG} - 3.57N_{Bio} - 7.14(\Delta NO_3^-) \quad (5.1)$$

Where ΔAlk_0 , is the net change in the alkalinity of a wastewater (mg/l); N_{org}, is the concentration of organic nitrogen; N_{BIO} is the concentration of N assimilated by a microorganism; ΔNO_3^- is the concentration of

ammonia nitrogen nitrified.

The mineralization of organic nitrogen to NH₄⁺-N and Denitrification leads to releases alkalinity. Then the equation (5.2) can be calculated as follow:

$$\Delta Alk_{need} = 3.57N_{ORG} - 3.57N_{Bio} - 7.14(\Delta NO_3^-) + 3.57N_{den} \quad (5.2)$$

N_{den} is the concentration of N removed by denitrification as CaCo₃, all models constant and parameter are given in table 5.1.

Denitrification is a cheap way of regulating the pH in the SHARON process (Hellings et al., 1999). The alkalinity in wastewater helps resist pH changes caused by adding acids. Wastewater is ordinarily alkaline, and receives its alkalinity from the water supply, groundwater, and

material added during domestic use (Tchobanoglous, Stensel, Tsuchihashi, & Burton, 2014). The difference between the alkalinity present in the influent (Alk_{pre}) and the alkalinity needed to compensate for the biological processes in the bioreactor (ΔAlk_{need}), is the Deficiency in alkalinity as shown by Equation 5.3:

$$\Delta Alk_{net} = \Delta Alk_{need} - Alk_{pre} \quad (5.3)$$

2.2 Alkalinity present in reactor:

In Wastewater alkalinity is determined by titrating against a standard acid that results from the presence of hydroxides $[OH^-]$, carbonates $[CO_3^{2-}]$, and bicarbonates $[HCO_3^-]$ of elements such as magnesium, calcium, sodium, ammonia and potassium. Of these, magnesium bicarbonates and calcium are most common.

Phosphates, silicates and Borates can also contribute to the alkalinity. The dominant buffering system in domestic wastewaters is a standardized titration curve of a carbonate-only buffer solution (Luklema, 1969). Then the total alkalinity in terms of molar quantities can be defined as Equation 5.4 (Stumm & Morgan, 1996) :

$$Alk, meq/L = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (5.4)$$

The concentration of the species can then be represented by $[H_2CO_3] = C\alpha_0$, $[HCO_3^-] = C\alpha_1$ and so on, where the subscript on α , refers to the number of protons lost from the most protonated species which is called the

ionization fractions, C is the total concentration of all species of the buffer system: $[HCO_3^-]$, $[H_2CO_3]$ and $[CO_3^{2-}]$, then the fraction of the titrant of weak diprotic acid is given by Equation 5.5 (Stumm & Morgan, 1996)

$$f = \alpha_1 + 2\alpha_2 + \frac{[OH^-] - [H^+]}{C} \quad (5.5)$$

Where f is equivalent fraction of the titrant, $\alpha_0, \alpha_1, \alpha_2$ values are implicit functions of $[H^+]$ can be calculated by Equation 5.6, 5.7 and 5.8 if dissociation constants K_1 and K_2 are known:

$$[H_2CO_3] = \alpha_0 = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}} \quad (5.6)$$

$$[HCO_3^-] = \alpha_1 = \frac{1}{1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}} \quad (5.7)$$

$$[CO_3^{2-}] = \alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1} \quad (5.8)$$

dissociation constants K_1 and K_2 for diprotic acid (carbonate acid) is 4.3×10^{-6} and 4.2×10^{-11} respectively ("Interactive Student Tutorial," 2010.000Z; Luklema, 1969). Then the

morphology of the titration curve (g) of weak diprotic acid is given by Equation 5.9 (Stumm & Morgan, 1996)

$$g = 2 - f = 2\alpha_0 + \alpha_1 + \frac{[H^+] - [OH^-]}{C} \quad (5.9)$$

According to (Antoniou et al., 1990) models, AOB increase between pH (5-7.2) and decline after a pH of 7.2 nitrification effectively ceases at a pH of about 9.51. While (Green et al., 2006) suggest that AOB occur at a lower pH such as in the reactors using industrial wastewaters has

been found at pH values of about 4.3. By taking this into consideration and according to (DIN 38409-7:2005-12) for the alkalinity measurement, the alkalinity of endpoint pH value of titration which is 4.3 and initial pH of wastewater which is 8.2 are subtracted from the

equivalent titrant fraction of alkalinity that should be dosed, then the adapted titrant fraction of alkalinity can be calculated by equation 5.10:

$$g_{ada} = \frac{g_{pH} - g_{8.2}}{g_{4.3} - g_{8.2}} \quad (5.10)$$

Where g_{ada} are the adapted titrant fraction of alkalinity values at the interested pH values.

2.3 Base consumption:

by using KOH as base, the concentration of K that should be added is given by equation 5.11:

$$C_K = \Delta Alk_{net} * \beta_k \quad (5.11)$$

Where C_K is K concentration in (mg/L) and β_k is the molar mass of K per equivalent in KOH, equal to 39 g/mol.

In addition, to determine the theoretical KOH dosing rate of feedstock at interested reactor P.H. can be calculated by using equation 5.12:

$$Q_{KOH} = \frac{\Delta Alk_{net} * Q}{C_{KOH}} \quad (5.12)$$

Where Q_{KOH} is the KOH dosing rate (L/day) and C_{KOH} is the concentration of the base feedstock.

Table (5.1): Parameter values of alkalinity consumption estimation.

Parameter	Symbol	Value	Unit	Reference
Inflow rate	Q	480	L/d	(Katayama et al., 2018)
NH ₄ -N initial	NH _{4_i}	170	mg/l	(Katayama et al., 2018)
TN-Initial	TN_i	270	mg/l	(Katayama et al., 2018)
alkalinity_ initial	Alk_i	0.16	mg/l	(Katayama et al., 2018)
N denitrified	N_{den}	37.5	mg/l	
N assimilated	N_{Bio}	13	mg/l	(Katayama et al., 2018)
concentration KOH solution	C_{KOH}	10	M	(Luklema, 1969)

3. ATA PROCESSING RESULTS AND DISCUSSIONS

6.1 pH limit of nitrification

Simulations of pH for all models are shown in **Figure 1**. The pH value can be used to measure AOB growth directly, since protons are

released during ammonia oxidation. Nonetheless, for the pH data to be described quantitatively, the chemical speciation model must accurately reflect the impact of the release of protons on the pH value.

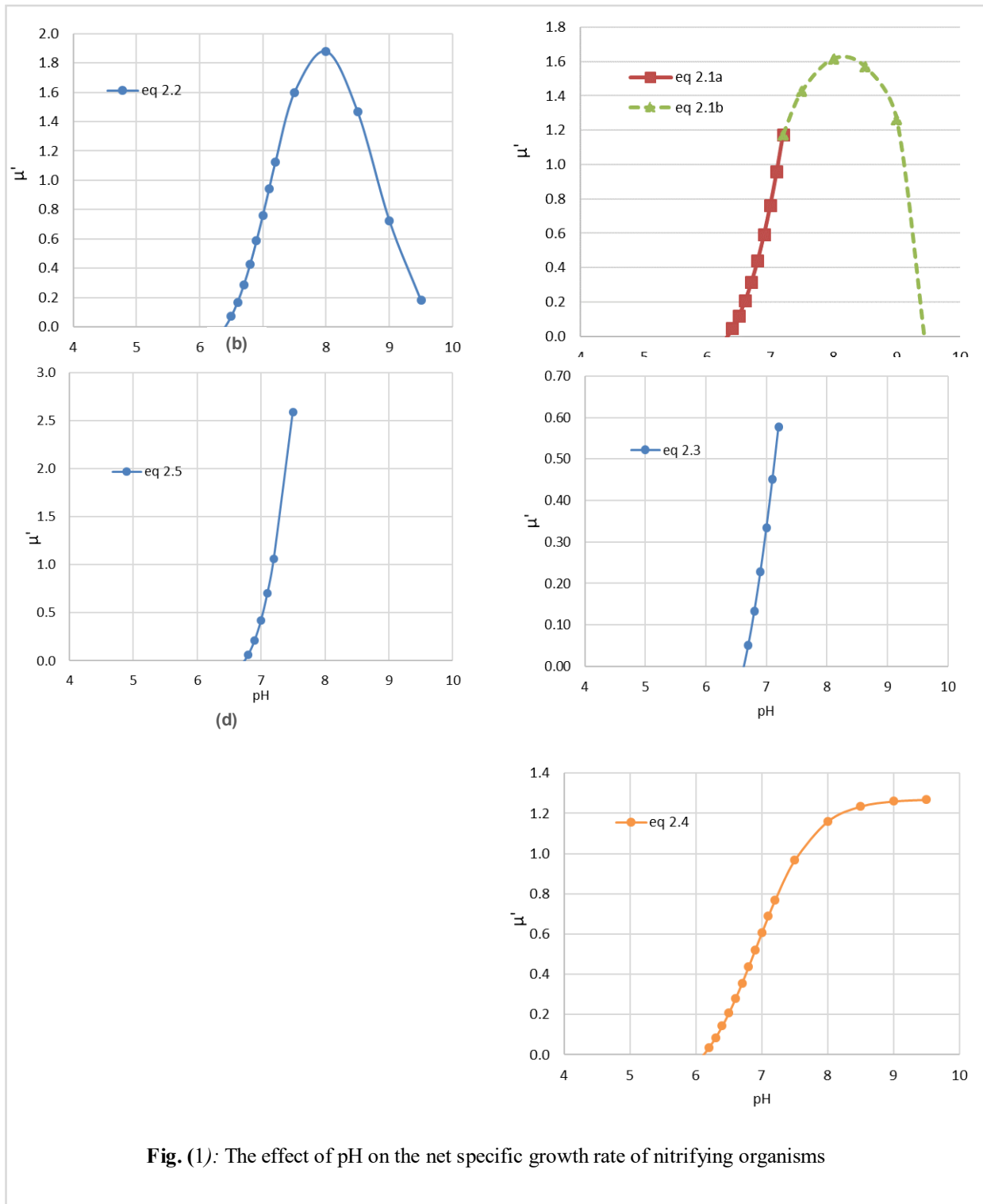


Fig. (1): The effect of pH on the net specific growth rate of nitrifying organisms

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Model 1 empirical model after including the Monod kinetics it can be seen in (Figure 1.a). in the range pH = 7.2 to 8.3, the change in μ' is small, and the model is capable of predicting the AOB in pH greater than 9, nitrification totally stopped at a pH of about 9.5. The curve of AOB has a peak value at eight start to decrease after a pH value of 8.2. The model fails to estimate the AOB in pH value less than 6.3. To provide a quantitative support for model 1, At low pH (<7.2) data from (Hellings et al., 1999) and (Antoniou et al., 1990) fit the equation reasonably well. Very few data are available for pH>8.5, but some points from (Antoniou et al., 1990) show reasonable agreement with model 1. Model 1 also capable of predicting a complete process stop. In addition, the μ' values produced by this model can be applied in the steady-state solution to calculate the minimum solid retention time for nitrification and reactor volume.

Model 2 this model is useful in establishing the volume of activated sludge reactor that is required to nitrify wastewater, the model fails to estimate the AOB in pH value less than 6.5 as shown in (Figure 1.b). Similar to Model 1, the net specific growth rate of nitrifying organisms found at pH about 8, after that by further increasing the pH value lead to decrease AOB and the growth rate of nitrifying organisms totally stopped at pH about 9.5.

Model 3 and model 5 were approximately similar. Both models fail to predict the specific growth rate of nitrifying organisms at pH less than 6.5, and greater than 7.5 (Figure 1.c) and (Figure 1.d), So these models did not consider ceases of the specific growth rate of nitrifying organisms where pH>8.5.

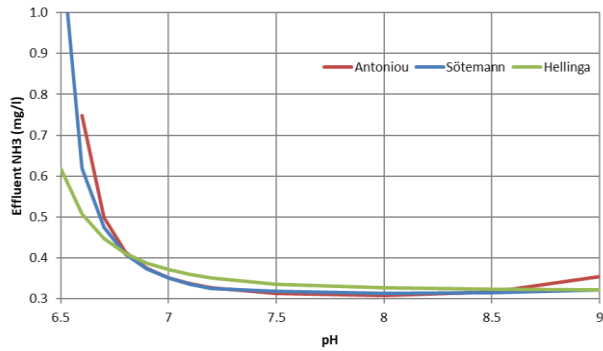
Model 4 Our model simulations were in line with the model proposed by (Hellings et al., 1999): this model was adequate to explain the ammonia oxidation in high-strength nitrogen wastewaters of pH 6 and 7. Based on Monod terms for NH₃ and HNO₂ is capable of estimating pH values above pH 6.2, but the model does not fully predict the net specific

growth rate of nitrifying organisms at pH range below 6.0 (Figure 1.e). By further increasing the pH value, the net specific growth rate of AOB is also increased; this means Model 4 fails to predict a complete process stop. In contrast to model 1 and model 2 which lead to decrease the AOB at P.H. value greater than 8, In the range of pH. value from (8-9) the data fit the estimated data of model 1 (Söttemann et al., 2005) According to model, even Adjusting the decay coefficient (b_A), bend in the AOB curve close to the pH limit cannot be represented.

In all models the net specific growth rate per day for AOB μ' at pH range (4-6.5) are zero or about to zero it can be called death stage, Since the real substratum of AOB which is NH₃ exists just at minimal concentrations at a low pH, even when the total ammonia concentration (NH₄ and NH₃) is high. In pH range of (6.5-8) it could be called growth stage, there is a quick growth in the value of μ' and it increase significantly, Ammonium oxidation to ammonia caused curve results. In pH range (8-9.5) in model 1 and 2 the value of μ' is decline. In contrast to Model 1 and 2, in the model 4 the value of μ' is increased by further increasing the pH, which means that by adding the Monod term inclusive with b_A the decay coefficient did not show the decline of the growth rate of AOB. Because in this model it was considered that not just ammonia, but ammonium too as substrate considered. While the other two model fails to indicate a pH higher than 7.5.

6.2 SRT and effluent ammonia nitrogen

The μ' values produced by either one of these models (model 1, model 2, model 4) can be readily applied in the steady-state solution of the ASM1 model (Henze et al., 2008, S. 90) to estimate SRT_m (Figure 2.a). (minimum solid retention time) and the TAN (total ammonia nitrogen) concentration in the effluent of a completely mixed activated sludge system without nitrogen removal.

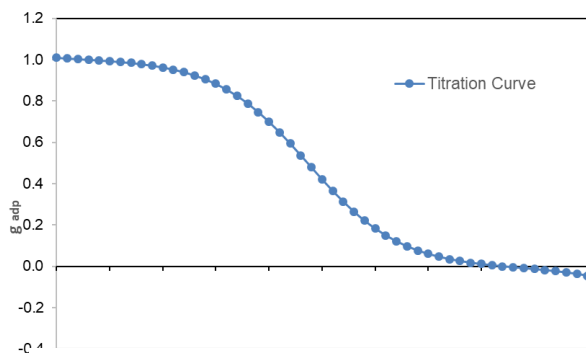


(Fig. (2.b)): minimum Solid retention time as a function of pH

The lower expected temperature it is recommended to be selected for design to determine the aerobic mass fraction and the SRT. If this is done and by using say $S_f = 1.25$, then it can be accepted from Eq.3.1 that the effluent ammonia concentration is below 1 mg/l at the highest temperature as shown in (Figure 2.b).

6.3 Reactor Volume

After the sludge mass in the reactor is calculated from a given sludge age and organic COD mass load, the volume of the reactor is determined by ‘diluting’ this sludge mass to a



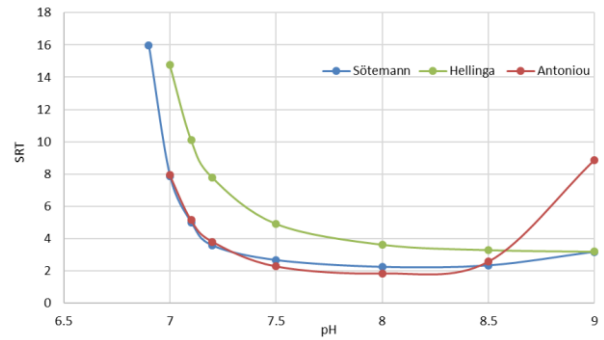
(Fig. 4): Model titration curves of a carbonate buffer solution, where $pK_{a1} = 6.35$ and $pK_{a2} = 10.33$ (25°C)

6.4 Reactor Alkalinity and titration curve

As shown in (Figure 4) the form of the theoretical adapted titration curve of the carbonate only model (weak diprotic acid), which is typically the dominant buffering system in domestic wastewaters (Tchobanoglous et al., 2014) is used to estimate the available alkalinity by a fraction of the total alkalinity consumed to bring the sample pH to any given pH value is

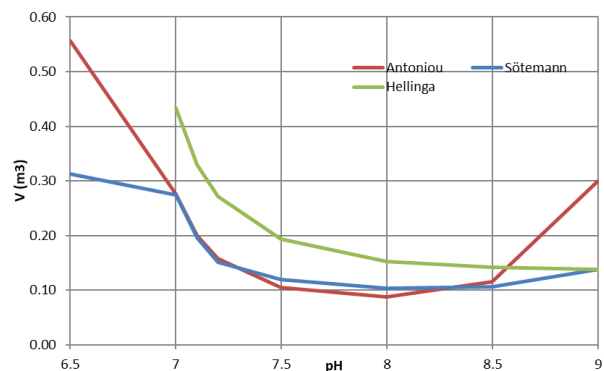
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(Fig. (2.a)): minimum Solid retention time as a function of pH

given TSS concentration. As expected, the volume of the reactor gets smaller at the point where AOB has its maximum value in the pH range of about (7.5-8.5). By further increasing the pH value of the reactor, more than 8.5 results in large reactor volume (Figure 3). It should be noted that, the SRT, temperature and concentration of total suspended solids also play a crucial role in designing the reactor volume. But in our study, we didn’t specify these factors to get optimum reactor volume design.



(Fig. 3): Reactor volume as a function of pH

calculated by the difference between the respective g_{adp} values; Alkalinity available at the setpoint can then be estimated by multiplying the difference by measured alkalinity as given in equation 5.11, where KOH was used for pH control, the remuneration of that buffering capacity deficit resulted in dosing of around 1000 mg/L of K to the solution. According to this simple calculation, it is imperative for low stefan.panglich@uni-due.de,

alkalinity wastewaters; therefore, that denitrification is incorporated in nitrifying plants even if removal of N is not necessary (Fumasoli et al., 2015). The equivalence points of the buffer system in the pH range between (4.3 and 8.2 for a carbonate system with concentration of 10 mM), at the upper end of the pH range, where the buffering system of carbonate is weak indicates that a second buffer system is needed to reasonable model the buffering capacity in that range.

4. CONCLUSIONS

The findings published here indicate that nitrification is one of the most important aspects to be taken into account when designing and operating the activated sludge systems for high-strength nitrogen wastewaters treatment. The net specific growth rate of ammonia oxidizing bacteria, minimum solid retention time and small reactor volume, found at pH about 8. This value of our model simulations were in agreement with the optimum pH suggested by (Downing A.L., Painter H.A. and Knowles G, 1964; EPA, 1993). As the pH drops below pH 6. The pH term decreases the rate of ammonia oxidation bacteria to zero. Of course, there are other factors affecting μ' like (Temperature, because temperature decreases the μ rate and increases the K_n coefficient, Unaerated zones in the reactor and Dissolved oxygen (D.O.) concentration). Low buffered wastewater nitrification is a very complex process since AOB's growth rate is highly dependent on pH, but the pH is likely to change due to the low buffer strength in these wastewaters. Therefore, nitrification models for describing these complex nitrification systems need to reflect the growth rates depending on pH accurately. The results of this research, however, show that at least the effect of Monod term should be included for a realistic AOB in high-strength nitrogen wastewaters treatment.

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Nitrosomonas are widely available in high-strength wastewaters of nitrogen at pH-limit less than 5.5. With kinetics based on NH_3 and HNO_2 inhibition, this limit and levels close to the limit cannot be modelled. Consequently, nitrification models based on Monod-type kinetics are not appropriate for understanding and enhancing the process stability of nitrification reactors operating between pH 6 and the pH limit.

The dosage of substantial quantities of an external alkalinity source is needed, with just a small portion of the buffering capacity available at the pH range between the high-strength nitrogen wastewaters mean pH (8.5-9.0) and the optimum pH for the growth of nitrifying microorganisms (around 7.5-8.0).

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