Improving titrimetric techniques by modelling pH change in activated sludge systems

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Abstract Existing titrimetric techniques rely on a well defined hydrogen ion production rate. In particular, they are only suitable in circumstances in which constant background pH influencing reactions take place. This is rarely the case due to the presence of the carbonate acid/base system. In this paper, a model, which describes the influence of the nitrification process on pH and accounts for the action of the carbonate system, is presented. The validity of the model is tested by comparison of model predictions for the important state variables with that of experimental data from a batch oxidation of ammonium nitrogen. The two cases studied are the responses of an endogenously respiring nitrifying sludge to: an ammonium chloride pulse and a pulse of both bicarbonate and ammonium chloride. The results are most encouraging as the dynamic HPR response is mirrored by the model simulation. Furthermore, using the model for data interpretation, the initial nitrogen substrate levels are recovered. It is shown that this could not have been achieved in either case using existing titrimetric techniques.

Keywords Activated sludge; pH modelling; titrimetric

Introduction

Titrimetric methods have recently been developed as an alternative to respirometry for monitoring nitrification in activated sludge systems (Ramaradori *et al*., 1980). These instruments rely on the rate of hydrogen ion production (HPR) from the oxidation of ammonia. The pH in the bioreactor is maintained at a set level. The rate of base addition required to keep a constant pH is then directly related to the hydrogen ion production rate (HPR) (Massone *et al*., 1998). The development of titrimetric sensors has led to application for the measurement of ammonium present in mixed liquor (Massone *et al*., 1998), the detection of toxicity (Gernaey *et al*., 1997) and the estimation of biokinetic parameters for the nitrification process (Gernaey *et al*., 1998). Unfortunately, the method relies on a constant background hydrogen ion production (HPR) profile, which is unlikely due to the presence of the carbonate buffering system. Researchers have made attempts to overcome this limitation through the use of a model-based data interpretation procedure (Gernaey *et al*., 2002) – but they have failed to fully describe the factors influencing pH change in the system.

In this paper, a dynamic model that describes changes in hydrogen ion concentration (and consequently pH) is presented. The model is for the oxidation of nitrogen in the aerobic phase of the activated sludge system. The model development procedure is such that further acid-base systems can be added if their presence is deemed significant. Examples of these include the phosphoric and acetic acid-base systems. The challenge is to properly integrate all of these factors into a single model that is compatible with existing measurement techniques. This has been achieved by improving a well used nitrification model to include some further process stoichiometry and descriptions of the relevant acid-base systems. Identification of the model then allows analysis of the nitrification process including quantification of the nitrogen substrate levels.

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Model development

The processes that are considered to affect the system pH are ammonia (NH_3) oxidation, ammonia uptake for biomass growth and the carbonate acid-base system (Figure 1). These processes are described in terms of the hydrogen ion production rate (HPR), carbon dioxide production rate (CPR) and oxygen uptake rate (OUR).

Nitrification is the conversion by autotrophic bacteria of ammonia nitrogen to nitrite and then nitrate. Oxygen is required by the micro-organisms as an electron acceptor for both of these processes. Inorganic carbon is used as the carbon source.

The reaction is described below (US EPA, 1993):

$$NH_3 + 1.89O_2 + 0.0805CO_2 \rightarrow 0.085CH_{1.4}O_{0.4}N_{0.2} + 0.952H_2O + 0.984NO_3^- + 0.98H^+ \quad (1)$$

where $CH_{1.5}O_{0.4}N_{0.2}$ is assumed as the composition of nitrifiers (US EPA, 1993)

As the growth rate of these bacteria is extremely low, so too is the quantity of carbon required – only 0.08 moles per mole of NH_3 nitrified. Consequently, the subsequent contribution to the CPR signal may be considered negligible relative to the contributions by other biological and physio-chemical processes. This also applies to the nitrogen required for nitrifier population growth. The contribution to the HPR signal resulting from this process is considered to be negligible.

In parallel with the important biological reactions exist many physio-chemical reactions. Many acid/base buffering systems are of particular importance with regard to titrimetric methods. In this study, the ammonium and carbonate buffering systems are most relevant.

The ammonium system describes the equilibrium between the ammonium ion and ammonia.

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad pK_a = 9.3 \quad (2)$$

In activated sludge systems (pH 6–8) most ammonia nitrogen is in the ammonium form (NH_4^+).

The carbonate system includes dissolved carbon dioxide ($CO_{2(d)}$), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and the hydrogen ion (H^+).

$$\begin{array}{l} CO_2(g) \\ \updownarrow KLaCO2 \\ CO_2(d) \longleftrightarrow H_2CO_3 \overset{1}{\longleftrightarrow} H^+ + HCO_3^- \overset{2}{\longleftrightarrow} 2H^+ + CO_3^{2-} \\ pK_{a(1)}\,6.35;\ pK_{a(2)}\,10.35 \end{array} \quad (3)$$

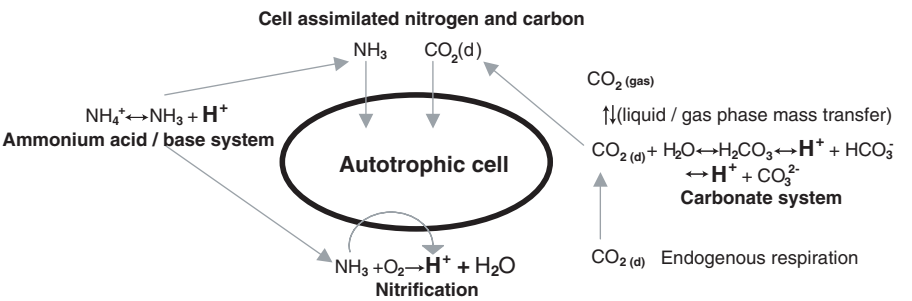

Figure 1 Schematic of dynamic processes that effect system pH

The ratio of ($CO_{2(d)}$) and carbonic acid (H_2CO_3) is fixed and equal to 99.76:0.24 at 25°C (Musvoto *et al*., 1997). The two species are generally lumped and referred to as $H_2CO_3^*$. The dissolved CO_2 or $H_2CO_3^*$ is driven, albeit slowly, to equilibrium by the partial pressure of $CO_{2(g)}$. In contrast, the acid-base reactions involving $H_2CO_3^*$, HCO_3^- and CO_3^{2-} are all extremely rapid. Even the hydration of $CO_{2(d)}$, which is considerably slower than the other acid-base reactions, is significantly faster than the physical transfer and biological processes (Van Vooren, 2000).

The dissolved CO_2 concentration is influenced by the rate of endogenous respiration of heterotrophic biomass. However, as the endogenous respiration rate remains relatively unchanged during autotrophic activity, the direct effect on the HPR signal is negligible.

Also, it is important to realise that, because the pH is controlled at a constant level, the significance of other buffering systems becomes negligible if there is no net change in the concentration of system components. For example, the phosphorus system plays no role in conditions in which there is an absence of phosphorus accumulating organisms.

The three relationships (1–3) form the foundation of the new model. The rate of the nitrification reaction is a function of the biomass characteristics and population. The rates of the two acid/base systems are known to be extremely rapid. Therefore, the strategy developed by Musvoto *et al*. (1997) was deemed suitable whereby the reactions are essentially assumed to always be in equilibrium. The equilibrium constants (pKa) are used to determine the respective concentrations at a given time. In this study, the hydrogen ion concentration has been modelled to stay constant as a result of the pH controller, which ensures a constant pH is maintained. The model, presented in matrix format, is included as Figure 2.

Materials and methods

Hardware configuration

The TOGA biosensor, shown in Figure 3, was used for the batch oxidations. A full description of the TOGA sensor can be found in Pratt *et al*. (2002). It consists of a bioreactor, a pH control system and an off-gas measurement arrangement. The custom made, cylindrical (base diameter 11.5 cm) reactor has a total volume of 3.5 L with a working liquid volume of approximately 3 L. Gas is fed to the vessel through two aluminium porous plates (Metapor, Portec Ltd). These are both located in one half of the reactor base to promote axial mixing. Further, a baffle (30 cm high) is installed to ensure thorough mixing. Liquid temperature and dissolved oxygen are both measured using a dissolved oxygen electrode (YSI model 5739, Yellow Springs USA). The reactor sits in a water bath for the purpose of temperature control.

Crucial for the acquisition of the HPR signal is the pH control system. The system consists of a pH electrode (Ionode IJ44, TPS Aus) and high accuracy dosing pumps (Prominent Beta4, Germany). The pumps are used to maintain system pH within 0.02 units of the set-point by addition of NaOH or HCl (0.0196 mol l^{-1}). The doses are fed to the vessel through nozzles, which are fitted to the reactor lid. An average pH signal (based on the final three consecutive pH readings of interval one second) is processed every 8 seconds resulting in a decision on the number of doses to be added in the following 8 seconds. The dosing rate is recorded and used as the hydrogen ion production rate (HPR) signal. For this titrimetric study, only the HPR signal was important. The oxygen uptake rate and carbon dioxide production rate measured via the off-gas arrangement could be used for further examination of the processes.

Experimental procedure

Two experiments were conducted to validate the new model. The activated sludge used was taken from a nitrifying wastewater treatment plant in South-Eastern Queensland

Component → i		1	2	4	5	6	7	7	10	Process Rate, ρ_j [$ML^{-3}T^{-1}$]
J	Process ↓	X_A	S_O	S_{NH3}	$S_{[CO2]}$	$S_{[HCO3]}$	$S_{[CO3]}$	$S_{[NH4+]}$	S_H	
1	Aerobic Growth of Nitrifiers	1	$-\frac{(4.57-Y_A)}{Y_A}$	$-\frac{i_{XB}}{14}-\frac{1}{14.Y_A}$					$i_{XB}+\frac{1}{Y_A}$	$\mu_A\left(\frac{S_O}{K_{OA}+S_O}\right)X_A$
2	Formation H_2CO_3				−1	1			−1	$\left(10^{10}\times10^{-(pK_{a1})}\times86400\right)\times S_{[CO2]}$ *fe
3	Dissociation H_2CO_3				1	−1			1	$\left(10^{10}\times86400\right)\times S_{[HCO3]}\times S_{[H]}$ *fe
4	Dissociation HCO_3^-					−1	1		1	$\left(10^{10}\times10^{-(pK_{a2})}\times86400\right)\times S_{[HCO3]}$ *fe
5	Formation HCO_3^-					1	−1		−1	$\left(10^{10}\times86400\right)\times S_{[CO3]}\times S_{[H]}$ *fe
6	Dissociation NH_4^+			1				−1	1	$\left(10^{10}\times10^{-(pK_{aN})}\times86400\right)\times S_{NH_4^+}$ *fe
7	Formation NH_4^+			−1				1	−1	$\left(10^{10}\times86400\right)\times S_{NH_3}\times S_{[H]}$ *fe
8	Carbon Transfer				−1					$K_{LaCO2}(S_{[CO2]}-S^*_{CO2})$: * is saturation conc
9	Oxygen Transfer		1							$K_{LaO2}(S^*_O-S_O)$: * is saturation coonc
Observed Conversion Rates [$ML^{-3}T^{-1}$]										$pK_{a1}=\frac{3404.7}{T}-14.8435+0.03279.T$ $pK_{a2}=\frac{2902.4}{T}-6.498+0.02379.T$ $pK_{aVFA}=\frac{1170.5}{T}-3.165+0.0134.T$ $pK_{aN}=\frac{2835.8}{T}-0.6322+0.00123.T$
Parameters: Heterotrophic yield: Y_H Nitrifier yield: Y_A Mass N / Mass COD in biomass: i_{XB}		Autotrohps [mg COD]	Oxygen [mg L^{-1}]	NH_3 nitrogen [mmoles L^{-1}]	Dissolved CO_2 [[mmoles.L^{-1}]	Dissolved HCO_3^- [mmoles.L^{-1}]	Dissolved CO_3^{-2} [mmoles.L^{-1}]	NH4 nitrogen [mmoles. L^{-1}]	Protons [mmoles.L^{-1}]]	**Kinetic Parameters:** Autotrophic growth and decay: u_A: Growth rate of autotrophs K_{NH}: half saturation concentration of ammonia K_{OA}: half saturation concentration of oxygen

Figure 2 Model matrix – including the nitrification process and the carbonate and ammonium acid/base systems

* *fe*: forced to equilibrium (a very high reaction rate is selected to ensure equilibrium is reached and the equilibrium constant used to ensure that the ratio of the rates of the forward and reverse reactions are correct)

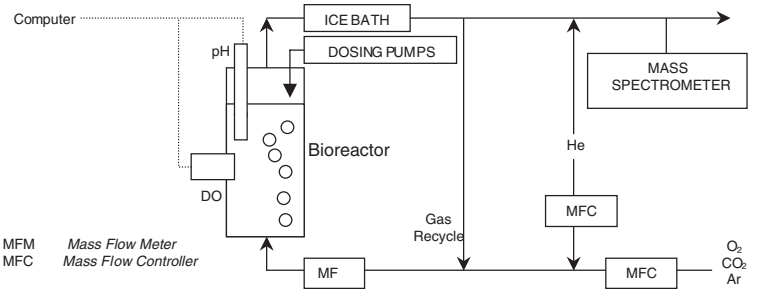

Figure 3 Hardware configuration

(Caboolture). The sludge was left aerated (with air) overnight to stabilise.

Prior to each experimental run, the reaction vessel was aerated and pH controlled at 7.5. A specialty gas (75% O_2, 1% CO_2, make-up Ar) at a flow rate of 135 ml/min was used with He (600 ml/min) for experimental aeration.

Each experimental run consisted of measurement of the signals during endogenous respiration, addition of substrate and measurement of the signals during and after substrate oxidation. Additional to on-line measurement, the mixed liquor was also sampled for Flow Injection Analysis (FIA) for soluble nitrogen. The samples were taken prior to substrate addition, immediately after addition, during oxidation and after substrate removal. The experiments were considered to be complete after the system had returned to equilibrium conditions.

In the first of the two experiments, ammonium chloride (NH_4Cl) was added to the sludge resulting in an initial condition of 13.5 mg-N/L. In the second experiment, sodium bicarbonate (15 mg/L) was added along with the ammonium chloride substrate (13.5 mg-N/L).

Results and discussion

The responses to the substrate addition are presented in Figure 4. Figure 4a shows the result of ammonium chloride addition only and Figure 4b shows the response to the addition of ammonium chloride along with bicarbonate.

Prior to the addition of the first substrate, the hydrogen ion production rate (HPR) was observed to be negative (acid dosage). This was caused by the action of the carbonate system. The removal of $CO_{2\,(d)}$ via mass transfer to the gas phase resulted in proton consumption. As expected, the oxidation of the ammonium chloride caused significant proton production. After the completion of the oxidation, the HPR did not return to the original level. The significance of the carbonate system had been reduced by this stage as the system was approaching equilibrium. Thus, the background HPR occurring prior to substrate addition differed from that observed after substrate removal. In this circumstance, traditional titrimetric techniques could not be used to accurately study the nitrification process. However, if the carbonate system is considered the contribution of nitrification to the HPR can be identified.

The response to the addition of ammonium chloride along with bicarbonate is shown as Figure 4b. In this case, the HPR prior to substrate addition was very similar to that observed after the conclusion of the oxidation. For this experiment, the initial bicarbonate load was known. Using this information, along with typical biological parameters reported by Henze *et al*. (1987), the model was simulated in order to identify the initial nitrogen concentration and nitrification rate (as a function of $\mu_A.X$). The identification was achieved by fitting the model-predicted HPR to the measured HPR (Figure 5). The nitrogen recovered is shown in Table 1. The result demonstrates the validity of the model in describing the nitrification process in the presence of a buffering system.

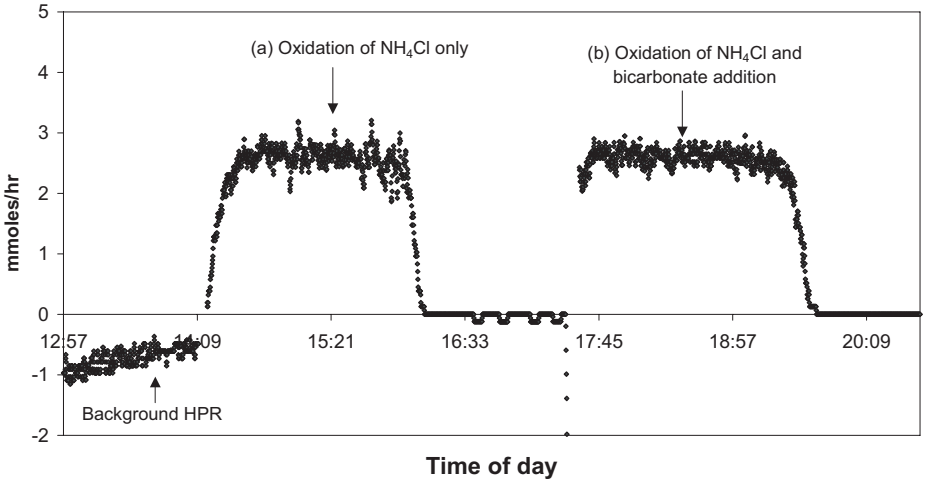

Figure 4 Measured HPR for nitrification. (a) addition of NH_4Cl only, (b) addition of NH_4Cl and bicarbonate

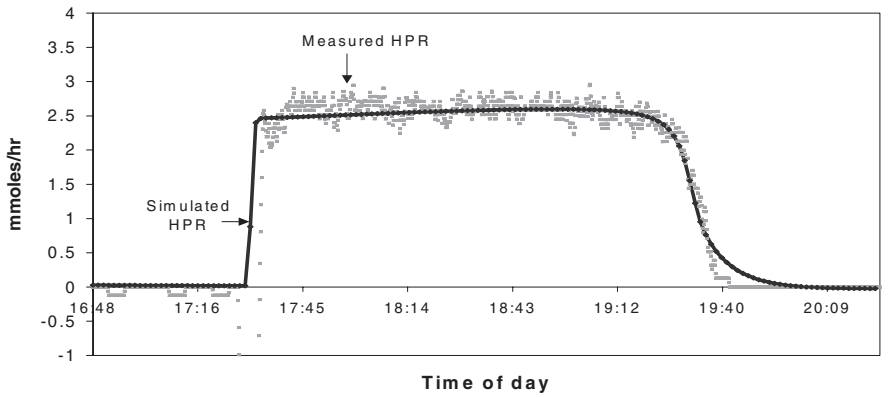

Figure 5 Comparison of simulated and measured HPR using known initial loads

Again, traditional titrimetric techniques would not have been suitable to study this process, as the presence of the carbonate system was significant during the early stages of the oxidation. It is shown that the initial nitrogen load is underestimated when using the traditional technique (Table 1). The stoichiometric load was calculated in the traditional titrimetric manner (based on Eq. (4)). The stoichiometric nitrogen load was measured as:

$$nitrified\_N = \frac{(moles\_hydrogen\_ions\_produced)}{(1.98 protons\_per\_mole\_N)} \times (molar\_mass\_nitrogen) \quad (4)$$

Table 1 Nitrogen balance

Experiment (*addition of...*)	Measured nitrogen addition *from model identification*	Stoichiometric nitrogen addition	Comments
13.5 mg/L NH_4-N		10.6 mg N	* background HPR changing so result is subjective
13.5 mg/L NH_4-N	13.5 mg N	12.1 mg N	* presence of carbonate system masked

Conclusion

Titrimetric methods provide valuable information for the study of activated sludge processes. However, the presence of a number of acid/base buffering systems – in particular the carbonate system – make the methods unsuitable on most occasions. In this paper, it has been shown that the influence of these buffering systems can be accounted for, provided that proper description of the systems is used. It has been demonstrated that for the nitrification process, the action of the carbonate system would have rendered existing tirimetric methods unworkable on two counts. Firstly, the motion towards equilibrium of the system resulted in a continuous change in the background HPR. And secondly, even in cases where the background HPR appeared constant, the presence of bicarbonate in the wastewater resulted in an underestimation of the nitrogen load.

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