

Calculating pH in pig manure taking into account ionic strength

A. M. Nielsen, H. Spanjers and E. I. P. Volcke

ABSTRACT

Models such as the Anaerobic Digestion Model No. 1 (ADM1) assume that pH can be calculated directly from the concentration of hydrogen ions. However because pH is, by definition, the negative logarithm of the hydrogen ion activity, and thus pH measurements represent hydrogen ion activities, this approach may lead to a bias between measured and predicted pH values. Implementing ionic strength effects into the charge balance equation and the calculation of pH is a theoretical improvement to this. In this study a model, implementing a procedure for calculating pH, was developed to analyse the effect of ionic strength on pH in a pig manure. By adding KCl to samples of pig manure, experimental results could be analysed with help from the model. A modified form of the Davies equation was found to give the most accurate prediction of pH in the pig manure studied in this paper with changing ionic strength.

Key words | activity coefficients, ADM1, ionic strength, modelling, pH, pig manure

A. M. Nielsen
Faculty of Agricultural Sciences,
University of Aarhus,
Schüttesvej 17, DK-8700 Horsens,
Denmark
E-mail: andersm.nielsen@agrsci.dk

A. M. Nielsen
H. Spanjers
E. I. P. Volcke
Department of Applied Mathematics,
Biometrics & Process Control,
Ghent University, Coupure links 653,
B-9000 Ghent,
Belgium
E-mail: eveline@biomath.ugent.be

H. Spanjers
Lettinga Associates Fdn, NL-6700,
AM Wageningen,
The Netherlands
E-mail: Henri.Spanjers@wur.nl

E. I. P. Volcke
INRA, LBE,
Avenue des Etangs,
F-11100 Narbonne,
France

INTRODUCTION

Pig manure can be digested to produce methane (CH₄) under anaerobic conditions. The production of CH₄ is governed by a number of factors such as concentration of substrates, biomass, rates of growth and degradation, concentration of inhibitory compounds and the osmotic and physical stress imposed on the specific micro-organisms in the anaerobic processes.

In anaerobic digesters pH varies as substrates are degraded and process conditions change as a consequence of fresh manure fed to the reactor and changes in the operation of the digester. If pH in digesters can be controlled and predicted better, it may be possible to improve individual processes in the digester when needed and avoid process breakdowns.

Models such as the ADM1 model (Batstone *et al.* 2002) have been developed to study anaerobic processes in detail,

but they do not include the effect of ionic strength in their pH calculations. As pH is a key parameter in the ADM1 and a number of biological and chemical processes depend on pH, improved modelling of pH in the ADM1 and other models may lead to better model calibration and simulation results and further progress in the field of modelling physiological and biochemical processes.

Söttemann *et al.* (2005) implemented ionic strength effects into a model of anaerobic digestion of sewage sludge, by correcting ionisation constants using apparent ionic strength corrected ionisation constants calculated in a previous study.

Smith & Chen (2006) focused on one of the Davies Equations (Davies 1962) in defined media and suggest that activity corrections should be a standard component in all pH calculation algorithms of wastewaters media given their high ionic strengths. In their study they mention the ADM1

model as an example where correction for activities should be applied. Indeed it would be relevant to implement ionic strength effects into the ADM1 model since the concentration of volatile fatty acids (VFAs) changes as a consequence of production and degradation of VFAs.

This study aims at testing the Davies equations and finding the most accurate equation for predicting ionic strength effects in a pig manure by analysing experimental results of changing ionic strengths on pH. For this purpose a procedure for calculating pH is proposed that is based on the charge balance equation. By increasing ionic strength in pig manure through the addition of KCl to the manure, we have investigated whether the change in pH can be explained by the Davies equation.

METHODS

Theory for taking into account ionic strength

pH is defined as the negative, base 10 logarithm of the activity of hydrogen ions $\{H^+\}$:

$$\text{pH} = -\log_{10}\{H^+\} \quad (1)$$

The activity of hydrogen ions $\{H^+\}$ is measured with a hydrogen-sensitive electrode (pH-meter). At infinitely dilute solutions, pH can be approximated by the concentration of hydrogen ions ($[H^+]$), but in anything from very dilute solutions this approximation is not valid.

In non-ideal solutions such as manure, $[H^+]$ is not the same as $\{H^+\}$. The latter can be calculated using the individual activity coefficient of the hydrogen ion (f_{H^+}) and $[H^+]$ as follows:

$$f_{H^+}[H^+] = \{H^+\} \quad (2)$$

Individual ion activities

Individual ion activity coefficients can be calculated from the Extended Debye-Hückel (EDH), Güntelberg or Davies Equations (Table 1) and the ionic strength (I). I is calculated from the concentration and valence (z) of all the ions in the solution.

$$I = \frac{1}{2} \sum_i [i] \cdot z_i^2 \quad (3)$$

Both the Güntelberg and Davies equations are empirically derived forms of the Debye-Hückel theory to calculate ion activities at higher ionic strengths. The EDH is not considered in this study because it is considered useful only in dilute solutions. The experiments that allowed Davies to suggest his equation were performed in simple electrolytes. A look at the list of salts in which the value was derived (Davies 1962) reveals that no weak acid/base pairs such as NH_4^+/NH_3 and buffers such as bicarbonate (HCO_3^-) were present. This means that change in ionic strength did not change the charge balance significantly as salt concentrations changed. This is not the case in pig manure. Pig manure contains NH_4^+/NH_3 , $CO_2/HCO_3^-/CO_3^{2-}$ and VFAs that make changes in the charge balance and ionisation constants caused by the ionic strength very important. Furthermore, long- and short range ionic effects may be different in pig manure compared to simple electrolytes.

Even though the Davies equation has been recommended for higher ionic strength solutions it has to be tested if it is the best equation for use in buffered, strong electrolytes with weak acid/base pairs such as pig manure.

To calculate ionic strength corrected concentration dependent ionisation constants (K_a^C) for use in the charge balance equation, individual ion activities in each acid/base and buffer equilibrium must be calculated to correct the thermodynamic ionisation constants (K_a^T) to K_a^C .

Table 1 | Calculation of individual ion activities

Name	Equation	Ionic strength interval
Extended Debye-Hückel	$\log_{10} f = -Az^2(\sqrt{I}/(1 + Ba\sqrt{I}))$ (4)	$I \in [0;0.1]$
Güntelberg	$\log_{10} f = -Az^2(\sqrt{I}/(1 + \sqrt{I}))$ (5)	$I \in [0;0.1]$
Davies $b = 0.3$	$\log_{10} f = -Az^2(\sqrt{I}/(1 + \sqrt{I})) - (bI)$ (6)	$I \in [0;0.5]$

f is the individual ionic activity coefficient, A and B are constants; respectively ≈ 0.51 and ≈ 0.33 in water, a is the ion size parameter (Stumm & Morgan 1996). Both the Davies and the Güntelberg equation assume all ions have an ion size parameter of 3, and because $0.33 * 3 \approx 1$, a and B are not shown in these equations. Studies convinced Davies that the parameter b in (6) should be 0.3 rather than his initial suggestion of 0.2 (Davies 1962).

The relationship between K_a^C and K_a^T is specified in a notation similar to Smith & Chen (2006) but with f^* as the overall effect of individual ion activities on the specific equilibrium.

$$K_a^T = f^* K_a^C \quad (7)$$

The use of Equation (7) can be illustrated with an example showing how the K_a^C of HCO_3^- ($K_{\text{HCO}_3^-}^C$) is calculated from the K_a^T of HCO_3^- ($K_{\text{HCO}_3^-}^T$), when $I = 0.1$, using the Davies equation.

$$K_{\text{HCO}_3^-}^T = \frac{\{\text{H}^+\}\{\text{CO}_3^{2-}\}}{\{\text{HCO}_3^-\}} = \frac{f_{\text{H}^+} f_{\text{CO}_3^{2-}}}{f_{\text{HCO}_3^-}} \cdot \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = f^* K_{\text{HCO}_3^-}^C$$

f_{H^+} and $f_{\text{HCO}_3^-}$ cancel each other in the above equation, as they are equal. The individual activity coefficient of CO_3^{2-} is calculated from Equation (6): ($f_{\text{CO}_3^{2-}} = 0.38$). Calculating $K_{\text{HCO}_3^-}^C$ by dividing $K_{\text{HCO}_3^-}^T = 4.68 \times 10^{-11}$ by 0.38 yields a value of 1.23×10^{-10} or a pK_a^C of 9.91, whereas pK_a^T is 10.33.

So instead of assuming $[\text{H}^+] = \{\text{H}^+\}$ and using thermodynamic ionisation constants, K_a^T , not corrected for ionic strength in the charge balance Equation (written in a shortened version and with total inorganic carbon ($\text{TIC} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$):

$$-[\text{H}^+] + [\text{TIC}] \left(1 + \frac{\{\text{H}^+\}}{K_{\text{H}_2\text{CO}_3^*}^T} + \frac{K_{\text{HCO}_3^-}^T}{\{\text{H}^+\}} \right) - [\text{NH}_4^+] \dots = 0$$

and solving for $\{\text{H}^+\}$, the charge balance equation should rather be solved using ionic strength corrected concentration dependent ionizations constants, K_a^C , and $[\text{H}^+]$ calculated from f_{H^+} and $\{\text{H}^+\}$ giving a charge balance Equation (written in a shortened version) as:

$$-[\text{H}^+] + [\text{TIC}] \left(1 + \frac{[\text{H}^+]}{K_{\text{H}_2\text{CO}_3^*}^C} + \frac{K_{\text{HCO}_3^-}^C}{[\text{H}^+]} \right) - [\text{NH}_4^+] \dots = 0$$

Finally pH should be calculated from $[\text{H}^+]$ and the individual activity coefficient of H^+ .

Pig manure

The pig manure used in the experiments was sampled at Praktijkcentrum Sterksel, The Netherlands. Total ammonium nitrogen (TAN) was determined by the Skalar method (photometric).

Concentrations of total acetate (TAce), total propionate (TPro), total butyrate (TBut) and total valerate (TVal) were determined by Gas Chromatography. The concentration of Ca^{2+} and Mg^{2+} was determined by Dutch standard NEN 6869, and K^+ , Na^+ and Cl^- was determined by Dutch Standard NEN 1483. The density of the manure was determined and its concentration of TIC was determined by the method described by Anderson & Yang (1992). Values are shown in Table 2.

Experiments

A total of 27 experiments were done. 9 experiments with 100% raw pig manure, 9 with 75% manure and 25% demineralised water and 9 with 50% manure and 50% demineralised water. Dilutions were made to increase the range in ionic strength of the samples. Dilutions were made to increase the number of samples with a ionic strength less than 0.5 after KCl was added. Samples of pig manure were transferred to 100 ml plastic containers. Samples were stirred with a magnetic stirrer and pH was measured with a Knick Portamess pH-meter in a fixed position. To reduce volatilisation of ammonia (NH_3) and carbon dioxide (CO_2) from the sample, parafilm was placed on top of the containers and the pH-sensor was let through an opening in the parafilm. Experiments were performed at 22°C. Varying quantities (0.37 g to 3.77 g) of KCl were added to (50.7 g–81.0 g) of diluted and not diluted pig manure samples. The effect on pH was monitored with the pH-meter. To minimise the effect of pH drifting before the addition of KCl, pH measurement was allowed an equilibrium time of 30–40 minutes.

Table 2 | Concentrations of compounds in the investigated pig manure

Density	1.018 g cm ⁻³	TAce	0.093 mol/L	TVal	0.006 mol/L	Na ⁺	0.030 mol/L
TAN	0.177 mol/L	TPro	0.027 mol/L	K ⁺	0.065 mol/L	Ca ²⁺	0.010 mol/L
TIC	0.191 mol/L	TBut	0.006 mol/L	Mg ²⁺	0.003 mol/L	Cl ⁻	0.036 mol/L

The drifting of pH prior to all experiments was upwards. pH was read 4–5 minutes after addition of KCl. A downward response to pH (0.01 to 0.07 pH units) was observed in all experiments. The effect began after 20–60 seconds and ceased after a few minutes.

Analysis

A model implementing a procedure for calculating pH in pig manure was developed in the programming language Java. The core of the model is a standard charge balance Equation (Stumm & Morgan 1996; Batstone *et al.* 2002) including the ions NH_4^+ , HCO_3^- , CO_3^{2-} , CH_3COO^- , $\text{CH}_3\text{-CH}_2\text{COO}^-$, $\text{CH}_3(\text{CH}_2)_2\text{COO}^-$, $\text{CH}_3(\text{CH}_2)_3\text{COO}^-$, H^+ , OH^- , K^+ , Mg^{2+} , Na^+ , Ca^{2+} , Cl^- and Z^+ to close the balance in its initial condition. It was decided to use molarities (mol/L) in all calculations.

Correction of ionisation constants for temperature was done with the van't Hoff equation as suggested in the ADM1. Values for K_a^T were found in Lide (1992). The ionic strength in the initial solution, before KCl was added to the manure, was calculated iteratively (Figure 1) (Levine 1995; Noggle 1996), because when ionic strength changes, K_a^C , f_{H^+} , and the concentration of ions change, and the ionic strength has to be calculated again. Before the calculation is started, initial pH and the concentrations of compounds are fed into

the model. It is also specified which form of the Davies Equation (6) is used for the ionic strength corrections.

When KCl is added to the manure a procedure very similar to the one described in Figure 1 is conducted to calculate a new $[\text{H}^+]$ as a consequence of the change in ionic strength. This procedure (Figure 2) is iterative as well.

Finally the pH is calculated from the final $[\text{H}^+]$ and the final f_{H^+} found from the final ionic strength. The procedure can be repeated over and over again with different values of the parameter b in (6), concentrations of compounds, pH and different amounts of KCl added to the initial solution.

RESULTS AND DISCUSSION

A total of 25 experiments (Figure 3) were used as basis for evaluating the Davies equation with different values of the parameter b in Equation (6).

The results showed that if the Davies equation was used to calculate pH in the manure after the addition of KCl, from the initial pH and the initial conditions in each of the 25 experiments, pH was erroneously predicted. Only looking at 8 of the 25 experiments where the final ionic strength did not exceed 0.50, the error in the prediction of pH using the Davies equation ranged from 0.014 to 0.028

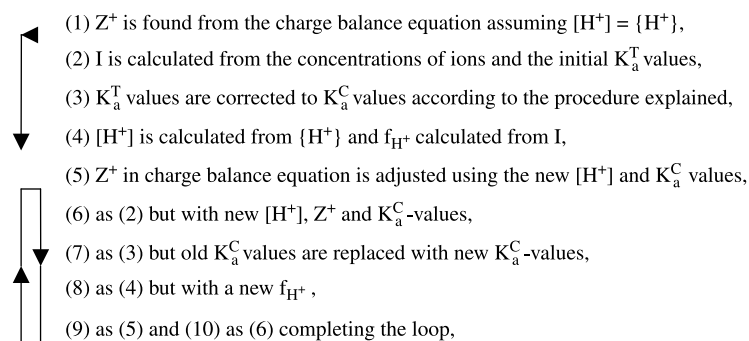


Figure 1 | When the loop from (5) to (10) has been run through 15 times, $[\text{H}^+]$, I and Z^+ changed less than 1×10^{-11} between successive iteration steps and the initial condition in the pig manure, before KCl is added, is set.

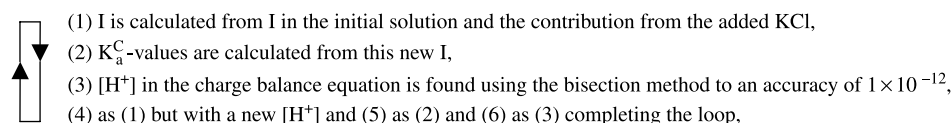


Figure 2 | The iterative procedure stops when the change in I between successive iterations is less than 0.001 and the change in $[\text{H}^+]$ smaller than 1×10^{-15} .

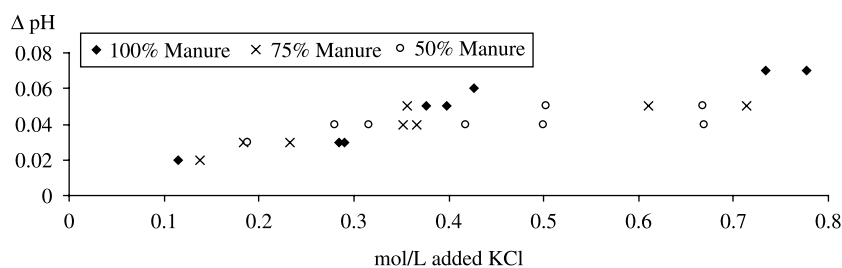


Figure 3 | The drop in pH as a function of mol/L KCl added to the pig manure. Two measurements where pH had dropped only 0.01 pH units were discarded as insignificant and removed from the dataset.

pH units with an average and standard deviation of respectively 0.021 and 0.006 pH units. Not doing ionic strength corrections at all led to an average error of 0.03 pH units compared to the experimental results.

To see which parameter b of Equation (6) would fit the data best; the b value in Equation (6) was varied to fit the experimental data in each of the 25 experiment. By running the pH model several times using the trial and error method, b values that could explain the observed change in pH were found for all 25 experiments. If only the 8 out of 25 experiments where the final ionic strength did not exceed 0.50 were considered, the b value in (6) that fitted experimental data was found to an average of $b_{\text{avg}} = 0.078$ with a standard deviation of $b_{\text{sd}} = 0.046$.

Using the 0.078 b value in all 8 the experiments where $I < 0.50$ to calculate pH after the addition of KCl resulted in an average error and standard deviation of respectively 0.003 and 0.003 pH units.

For the 17 remaining experiments the same procedure of fitting Equation (6) to experimental data was used; the average and standard deviation was $b_{\text{avg}} = 0.065$ and $b_{\text{sd}} = 0.060$.

An intrinsic standard deviation in the results caused by the pH meter was expected and confirmed in the data. A reading of, for example, a drop in pH of 0.03 units might only be a drop in pH of 0.025 units. In an example from one experiment, such an error would result in an inaccuracy of estimating b of 0.04 or $b = 0.11$ instead of $b = 0.07$.

Implementing the Davies equation or a form of the Davies equation in the ADM1 with another b value in Equation (6) may not improve the pH calculation in ADM1, since some, if not all, of the inhibition and affinity parameters in the ADM1 are derived under the assumption that $[\text{H}^+] = \{\text{H}^+\}$.

To make sense of a comparison between the current ADM1 and a version of the ADM1 taking into account ionic strength, inhibition and affinity parameters in the current ADM1 should be corrected together with the pH algorithm. When this is done, the precision of the modelling of the pH dynamics in the ADM1 should improve, as this would be the right way of calculating pH.

CONCLUSION

This study shows that using the Davies equation for calculating the effect of ionic strength in the pig manure investigated in this study is not accurate. The Davies equation was however more accurate than if no ionic strength corrections were done.

Furthermore it was shown, that changing the parameter b in Equation (6) to 0.078 was even more accurate than both the Davies equation with the b value proposed by Davies, and if no ionic strength corrections were done.

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Erratum

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We regret that as a result of an error in production equation (6) in Table 3 on p1786 was incorrectly reproduced. The correct version of the equation is shown below:

$$\log_{10}f = -A \cdot z^2 \cdot \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - bI \right) \quad (6)$$