

Dynamic Simulation of pH in Anaerobic Processes

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Abstract

With the objective of contributing to the buildup of mathematical tools for anaerobic process simulation, an algorithm for the dynamic simulation of pH was developed. The dynamic simulation of the gaseous phase variables was also considered. The pH algorithm was validated for a watery system, obtaining good agreement between predicted and experimental data. The applied methodology provides a differential equation that allows the inclusion of pH as a state variable of the system that can be easily included in a general mathematical model of anaerobic digestion using matrix notation. This methodology also allows a noticeable decrease in computing time in simulations. A dynamic anaerobic digestion model of complex substrates taken from the literature was completed with the developed algorithms, and it was used to predict the response of an anaerobic reactor against overloading and against the presence of pH-dependent inhibitors with satisfactory results.

Index Entries: Anaerobic digestion model; pH simulation; ammonia inhibition; physical-chemical processes; dynamical modeling.

Introduction

Anaerobic digestion processes have been frequently used in wastewater treatment, especially for highly polluted wastewaters. Its main advantages are low production of sludge, reduction of odorous materials, and energy production. It is a complex process that involves different groups of microorganisms, and, therefore, structured models constitute an important tool for the comprehensive study of microbial ecology. However, comprehensive mathematical modeling of anaerobic reactors is a rather complicated task because the entire process includes complex

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dynamics of biological, chemical, and physical subsystems with many interrelations among them (1). The Anaerobic Digestion Model No. 1 constitutes an attempt to combine the different models that are described in the literature (2), including main processes occurring in anaerobic reactors.

Inside the physicochemical subsystem, pH is one of the most important variables. pH has an important effect on the growth rate of acetogen and methanogen microorganisms, which reach the optimum at a pH value of about 7.0 (3). Furthermore, pH has an important role in some dynamic processes occurring in anaerobic reactors. It has an important role in the ammonia inhibition phenomena. Ammonia nitrogen has been described as an important inhibitor of methanogenic microorganisms (4), and free ammonia has been described as the real inhibitor species (5–7). Therefore, ammonia inhibition is a phenomenon that depends on temperature and pH, increasing with an increase in both variables (5). The free ammonia inhibition of methanogenic microorganisms produces accumulation of volatile fatty acids (VFA), especially acetate. This accumulation produces a related pH decrease and a later decrease in the toxic effect of ammonia, leading to lower but stable methane yield, as has been reported in the literature (6). Moreover, the accumulation of some kinds of VFA, such as acetate, produces inhibition in acetogenic populations and accumulation of other VFA, propionate, and butyrate (8). The pH value also determines the toxic effect of some VFA on the acetogenic population, increasing the inhibitory effect at low pH values (9), owing to the stronger toxic effect of undissociated acids.

As shown, pH is a dynamic variable, and in order to develop realistic mathematical models of anaerobic processes, algorithms capable of dynamically predicting pH evolution are needed. Many previous models of anaerobic digestion have taken pH into account. A summary of some of these models is presented in Table 1. In general, these models approximate the pH value at every step of numerical integration, and only two of them (2,12) consider pH as a state variable, but taking into account only the HCO_3^- - CO_2 equilibrium. Models that consider pH as a parameter and not as a state variable have obtained good agreement with experimental data, but if pH is included as state variable and if its derivative is expressed in matrix form, the accuracy of the results could be improved at lower computing time.

The objective of the present work was to develop the ordinary differential equation (ODE) for describing pH evolution, considering it as a state variable of the system, and to introduce it in a general dynamic structured model of anaerobic digestion process. An additional objective was to include the dynamic simulation of liquid-gas transfer in the general model.

The pH Model Framework

The pH can be calculated from the charge balance equation (13)

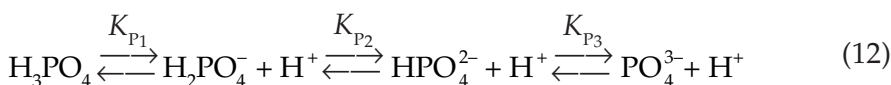
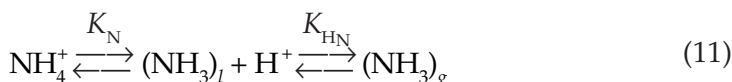
$$[H^+] - [OH^-] = Ch(pH) = [HCO_3^-] + 2[CO_3^{2-}] + \sum_j [A_i^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [Z^-] + 2[Z^{2-}] - [NH_4^+] - [Z^+] - 2[Z^{2+}] \quad (7)$$

in which $\sum A_i^-$ is the sum of the ionic species concentration of every VFA (acetate, propionate, butyrate, and valerate). The charge balance equation (Eq. 7) can be written in matrix notation as

$$Ch(pH) = \sum_{i=1}^n \left[s_i \cdot \sum_{j=1}^6 (f_{ij} \cdot c_j) \right] = S^t \cdot F \cdot C \quad (8)$$

in which S is the vector of total concentrations for the system components; F is the matrix of factors that determine the concentration of every ionic species, function of pH, and dissociation constants (Table 2), and C is the charge weighing vector, whose values depend on the charge of the ion (Table 2).

The ionic species concentration for every component is defined from the corresponding acid-base equilibrium:



The acid-base equilibrium constants are a function of temperature (T), following a polynomial form:

$$pK_i^0 = pK_i^0(0^\circ) + a_i \cdot T + b_i \cdot T^2 + c_i \cdot T^3 \quad (14)$$

The coefficients used are shown in Table 3, which have been calculated from data found in the literature (16). The acid-base equilibrium has been modified by the corresponding activity coefficients. The activity coefficients depend on the ionic strength, which depends on the concentration

Table 1
Summary of Currently Used pH Calculation Methods

Method / reference	pH calculation solving the equation ^a
pH calculation in every step of numerical integration (10)	$[\text{HCO}_3^-] = [\text{Z}^+] - [\text{A}_\text{H}^-]$ $\frac{d[\text{CO}_{2,D}]}{dt} = \frac{Q}{V} ([\text{IC}]_\text{in} - [\text{IC}]) + R_{\text{Biol}} + R_{\text{TG-L}} +$ $[\text{H}^+] = K_1 \left[\frac{\text{CO}_{2,D}}{\text{HCO}_3^-} \right] \quad (1)$
pH calculation in every step of numerical integration (11)	$[\text{A}_\text{T}] = [\text{A}_\text{T}^-] + [\text{AH}]$ $\frac{d[\text{IC}]}{dt} = \frac{Q}{V} ([\text{IC}]_\text{in} - [\text{IC}]) + R_{\text{TG-L}}$ $\frac{d[\text{A}_\text{T}]}{dt} = \frac{Q}{V} ([\text{A}_\text{T}]_\text{in} - [\text{A}_\text{T}]) + r_{\text{AT}}$ $[\text{HCO}_3^-] + \sum [\text{acid}^-] + \left[\frac{K_\text{w}}{[\text{H}^+]} \right] = [\text{H}^+] + [\text{Na}^+] \quad (2)$
ADM1 (2); dynamic model for pH calculation (12)	$\text{HCO}_3^- + \text{H}^+ \xrightleftharpoons[\rho_{15}]{\rho_{14}} \text{CO}_2 + \text{H}_2\text{O}$ $\rho_{14} = k_{14} [\text{HCO}_3^-] \cdot [\text{H}^+] \quad \rho_{15} = k_{15} [\text{CO}_2]$ $\frac{d[\text{H}^+]}{dt} = \sum (\nu_i \rho_i) = -\rho_{14} + \rho_{15} \quad (3)$

pH calculation
in every step
of numerical integration (13)

$$Ch(pH) = [HCO_3^-] + 2[CO_3^{2-}] + \sum_j [A_i^-] + [H_2PO_4^-] + 2[H_2PO_4^{2-}] - [NH_4^+] - [Z^+]$$
$$\text{for } Ch(pH) > 0 \quad [H^+] = \frac{Ch + \sqrt{Ch^2 + 4K_w}}{2}$$
$$\text{for } Ch(pH) < 0 \quad [H^+] = \frac{2K_w}{-Ch + \sqrt{Ch^2 + 4K_w}} \quad (4)$$

pH calculation
in every step
of numerical integration (14)

$$[A_i^-] + [HA_i] = S_{A_i} \quad K_{HA_i} = \frac{[A_i^-] \cdot [H^+]}{[HA_i]}$$
$$[A_k^{2-}] + [HA_k^-] + [H_2A_k] = S_{A_k}$$
$$[B_j^+] + [BOH_j] = S_{B_j} \quad K_{BOH} = \frac{[B_j^+] \cdot [OH^-]}{[BOH_j]} \quad (5)$$

pH calculation
in every step
of numerical integration (15)

$$[HCO_3^-] = [Z^+] + [NH_4^+] + [A_H^-]$$
$$\frac{d[CO_2]_b}{dt} = \frac{Q}{V} ([IC]_{in} - [IC]) + R_{Biol} + R_{TG-L} + \frac{d[A_H^-]}{dt} - \frac{d[Z^+]}{dt} - \frac{d[NH_4^+]}{dt}$$
$$[H^+] = K_1 \left[\frac{CO_{2,D}}{HCO_3^-} \right] \quad (6)$$

^aNote: $[IC] = [HCO_3^-] + [CO_2]$.

Table 3
Coefficients for Dissociation Constant Expressions Related to Eq. 14

	pK (0°)	<i>a</i>	<i>b</i>	<i>c</i>
Acetate	4.7803	-0.0023	6.00E-05	-2.00E-07
Propionate	4.8063	-0.0011	8.00E-05	-4.00E-07
Butyrate	4.8947	-0.0024	7.00E-05	-3.00E-07
Carbonate (1)	6.5787	-0.0133	0.0002	-8.00E-07
Carbonate (2)	9.2839	-0.0133	9.00E-05	-2.00E-07
Phosphate (1)	2.0473	0.0019	5.00E-05	0
Phosphate (2)	7.3144	-0.0073	0.0001	-6.00E-07
Phosphate (3)	12.6576	0	0	0
Ammonium	10.072	-0.0356	9.00E-05	4.00E-08
Water	14.934	-0.0425	0.0002	-6.00E-07

and charge of the ionic species (17). To introduce the activity, the dissociation constants can be modified as follows:

$$K_i = K_i^0 \cdot f_{ac_i}; f_{ac_i} = 10^{-0.5 \cdot \frac{\sqrt{I}}{1 + \sqrt{I}} \cdot z_i}; I = \frac{1}{2} \cdot \sum_{i=1}^n \left\{ s_i \cdot \sum_{j=1}^6 [f_{ij} \cdot (c_j)^2] \right\} \quad (15)$$

in which f_{ac_i} is the activity factor, I is the ionic strength, and z_i is a charge factor that depends on the specific equilibrium (17).

The $[H^+]$ concentration, derived from Eq. 7, can be expressed as a function of Ch :

$$[H^+] - [OH^-] - Ch = 0 \Rightarrow [H^+] = \psi(Ch) = \psi(S^t \cdot F \cdot C) \quad (16)$$

The function $\psi(Ch)$ adopts different forms as a function of the Ch value (Table 1):

$$\begin{aligned} \text{if } Ch \geq 0 \Rightarrow [H^+] - \frac{K_w}{[H^+]} - Ch = 0 \Rightarrow [H^+]^2 - Ch[H^+] - K_w = 0 \Rightarrow \\ [H^+] = \psi_1(Ch) = \frac{Ch + \sqrt{Ch^2 + 4K_w}}{2} \end{aligned} \quad (17)$$

$$\begin{aligned} \text{if } Ch < 0 \Rightarrow \frac{K_w}{[OH^-]} - [OH^-] - Ch = 0 \Rightarrow [OH^-]^2 + Ch[OH^-] - K_w = 0 \Rightarrow \\ [OH^-] = \frac{-Ch + \sqrt{Ch^2 + 4K_w}}{2} \Rightarrow [H^+] = \psi_2(Ch) = \frac{2K_w}{-Ch + \sqrt{Ch^2 + 4K_w}} \end{aligned} \quad (18)$$

The pH can be calculated from the equations using the secant rule (13).

From Eq. 16, the $[H^+]$ concentration can be derivated obtaining the following differential equation:

$$\frac{d[H^+]}{dt} = \frac{d\psi(Ch)}{dCh} \cdot \frac{dCh}{dt} = B \cdot \frac{dCh}{dt} \quad (19)$$

in which B is the derivative of ψ respect to Ch , and it can be calculated depending on the Ch value:

$$\begin{aligned} &\text{if } Ch(\text{pH}) \geq 0 \equiv [H^+] \geq [OH^-] \\ B &= \frac{d\psi(Ch)}{dCh} = \frac{1}{2} \left(\frac{Ch(\text{pH})}{\sqrt{Ch^2 + 4K_w}} + 1 \right) \end{aligned} \quad (20)$$

$$\begin{aligned} &\text{if } Ch(\text{pH}) < 0 \equiv [H^+] < [OH^-] \\ B &= \frac{d\psi(Ch)}{dCh} = -\frac{[H^+]^2}{2 \cdot K_w} \cdot \left(\frac{Ch(\text{pH})}{\sqrt{Ch^2 + 4K_w}} - 1 \right) \end{aligned} \quad (21)$$

The derivative of the Ch function respect on time is

$$\frac{dCh(\text{pH})}{dt} = \frac{d(S^t \cdot F \cdot C)}{dt} = \left(\frac{dS^t}{dt} \cdot F \cdot C \right) + (S^t \cdot F' \cdot C) \cdot \frac{d[H^+]}{dt} \quad (22)$$

The derivative of the F matrix, F' , is calculated based on the derivative of every matrix component:

$$F' = \frac{dF}{d[H^+]} \Rightarrow F' = \left(\frac{df_{ij}}{d[H^+]} \right) \quad (23)$$

and results are shown in Table 4.

From Eqs. 19 and 23, an ordinary differential equation for $[H^+]$ is derived:

$$\frac{d[H^+]}{dt} = \frac{B \cdot \left[\left(\frac{dS^t}{dt} \right) \cdot F \cdot C \right]}{1 - B \cdot (S^t \cdot F' \cdot C)} \quad (24)$$

Liquid-Gas Transfer

The liquid-gas transfer and pH are clearly affected by each other: a pH change will affect the nonionized concentration and, therefore, the liquid-gas transfer. The molar flow $N_{g,i}$ of the component i is driven by the differ-

Table 4
F' Matrix (rows corresponding to ionic species)

j	1	2	3	4	5	6
Ion charge	+2	+1	0	-1	-2	-3
Organic acids	f'_{ij}	0	$\frac{K_{A_i}}{([H^+] + K_{A_i})^2}$	K_{A_i}	0	0
Carbonate	f'_{ij}	0	$(1)f'_{C_3}$	$(2)f'_{C_4}$	$(3)f'_{C_5}$	0
Ammonia	f'_{ij}	0	$-\frac{K_{N_1}}{([H^+] + K_{N_1})^2}$	0	0	0
Orthophosphate	f'_{ij}	0	$(4)f'_{P_3}$	$(5)f'_{P_4}$	$(6)f'_{P_5}$	$(7)f'_{P_6}$
Z ⁺	f'_{ij}	0	0	0	0	0
Z ²⁺	f'_{ij}	0	0	0	0	0
Z ⁻	f'_{ij}	0	0	0	0	0
Z ²⁻	f'_{ij}	0	0	0	0	0

Note: $(1)f'_{C_3} = \frac{1}{K_{P_2}K_{P_3}} \left(\frac{[H^+]^2}{K_{C_1}K_{C_2}} + \frac{2[H^+]}{K_{C_1}} \right)^2, (2)f'_{C_4} = \frac{1}{K_{C_2}} \left(-\frac{[H^+]^2}{K_{C_1}K_{C_2}} + 1 \right)^2, (3)f'_{C_5} = -\frac{2[H^+] + \frac{1}{K_{C_2}}}{\left(\frac{[H^+]^2}{K_{C_1}K_{C_2}} + 1 \right)^2}, (4)f'_{P_3} = \frac{1}{K_{P_3}K_{P_2}K_{P_3}} \left(\frac{[H^+]^4}{K_{P_1}K_{P_2}K_{P_3}} + \frac{2[H^+]^3}{K_{P_2}K_{P_3}} + 3[H^+]^2 \right)^2,$

$(5)f'_{P_4} = \frac{1}{K_{P_2}K_{P_3}} \left(-\frac{[H^+]^4}{K_{P_1}K_{P_2}K_{P_3}} + \frac{[H^+]^2}{K_{P_3}} + 2[H^+] \right)^2, (6)f'_{P_5} = \frac{1}{K_{P_3}} \left(-\frac{2[H^+]^3}{K_{P_1}} - \frac{[H^+]^2}{K_{P_2}K_{P_3}} + 1 \right)^2, (7)f'_{P_6} = \frac{3[H^+]^2}{K_{P_1}K_{P_2}K_{P_3}} + \frac{2[H^+]}{K_{P_2}K_{P_3}} + \frac{1}{K_{P_3}} \left(\frac{[H^+]^3}{K_{P_1}K_{P_2}K_{P_3}} + \frac{[H^+]^2}{K_{P_2}K_{P_3}} + 1 \right)^2$

ence between the concentration of the nonionic form $S_i f_{i,3}$ in the bulk liquid and the equilibrium concentration S_i^* at the phase boundary. The latter value can be expressed in terms of the corresponding gas-phase partial pressure P_i and the Henry coefficient He_i (2,11,18):

$$N_{g,i} = K_{La,i} \cdot (S_i \cdot f_{i,3} - S_i^*) = K_{La} \cdot (S_i \cdot f_{i,3} - He_i \cdot P_i) \quad (25)$$

The Henry coefficient depends on temperature. The coefficient values were taken from the literature (16,18,19). Oversaturation and gas bubble formation were not considered.

Precipitation of Solids

Precipitation of solids was not considered in the present work. Precipitation is a very complex process that includes nucleation, crystallization, and ripening. The precipitation phenomenon is especially important for high-rate anaerobic digesters, in which the precipitated solids are retained together with biological solids, but it has a relative low importance in continuous-flow stirred tank reactor (CSTR) (2). Dynamic modeling of solids precipitation was developed in refs. 20 and 21, and it could be considered in further improvements of the present work.

Validation of pH Algorithm

A watery solution of different acid and alkali substances was considered. Variation in every component was known precisely. Concentrated solutions of different components were added to the initial watery solution at a certain and well-known flow rate without extraction. Neither biologic processes nor salt precipitation phenomena were considered. Ammonium, acetate, phosphate, carbonate, and anions were the considered components. The ordinary differential equation for the system is

$$\frac{dS}{dt} = \frac{F_L}{V} \cdot (S_0 - S) + v \cdot r \quad (26)$$

in which V is the volume of water solution that depends on time, F_L is the influent flow rate, S_0 is the vector of influent concentrations, S is the vector of system component concentrations, r is the vector of rate process, and v is the matrix of coefficients that relates the rate of every process to the variation of every component. Three variables related to the gaseous phase were taken into account: partial pressure of CH_4 , CO_2 , and NH_3 . The considered processes were liquid-gas transfer (11,18), especially important for taking into account stripping of CO_2 and variation in $[H^+]$. The rest of the $v_{i,j}$ coefficients were assumed to be zero. The $[H^+]$ is a component of the S vector, and its ODE is defined by Eq. 24.

The system of ODE was integrated by the Runge-Kutta-Fehlberg adaptive method of fifth order (22).

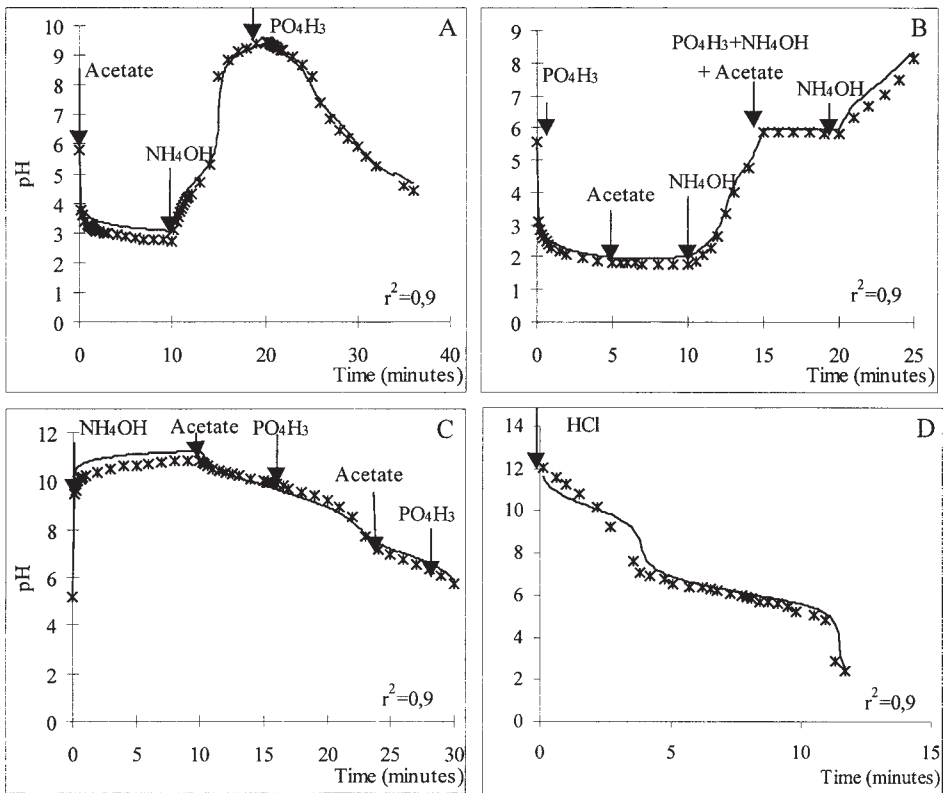


Fig. 1. Comparison of measured and predicted pH values, indicating moments at which every component was added. (A–C) Initial solution: pure water; (D) initial solution of CaCO_3 (0.23 M).

Experimental Procedure

The system was tested for sequential mixtures of the following components: ammonia base, orthophosphate, acetate, sodium carbonate, and chloride acid. Four experiments were performed in which different components were added in different ways, in order to induce abrupt changes in the pH value and to study the model responses in transitory states.

In experiments A to C (Fig. 1A–C), the flow rate, F_L , of addition of influent solution was fixed at 1 mL/min, and the initial volume, V_0 , was 100 mL in all cases. The initial concentration of watery solution, s_i , was zero for all components. The temperature was 20°C. Influent concentration, s_{i0} , was 0.5 M for acetate and H_3PO_4 solutions and 1 M for NH_4OH solution. Temperature and pH were measured in a continuous way. The order and moment in which the different influent solutions were added are indicated in Fig. 1.

Experiment D (Fig. 1D) consisted of adding 1 M chloride acid to an initial solution of calcium carbonate in water (0.23 M). In this case, the flow

rate was variable on time. The atmospheric CO_2 was neglected, since it was negligible vs the CO_2 concentration of the watery solution.

Results of Simulations

The comparison of experimentally measured values and predicted values of pH is shown in Fig. 1. Precipitation processes were not observed. In all cases, the experimental and predicted values for pH present very good agreement (Fig. 1), with determination coefficients r^2 higher than 0.9. Therefore, it can be concluded that the developed pH simulation algorithm is valid for predicting pH evolution in watery solutions in transitory states.

pH Algorithm in a General Dynamic Anaerobic Digestion Model

The pH simulation algorithm and the liquid-gas transfer equations were included in a general model of an anaerobic digestion system of complex substrate adapted from ref. 23, in order to illustrate the application of the developed algorithms. A CSTR system was considered, with a total of 33 state variables and 22 processes. The processes are those considered in ref. 23, with the addition of equations for dynamic pH calculation (Eq. 24) and dynamic liquid-gas transfer for the considered components (Eq. 25). All kinetic and physical-chemical parameters depended on temperature, and all stoichiometric, kinetic and physical-chemical coefficients were adapted from the literature (1,23,24).

Numerical Methods Applied

The solution of the system of ODE defining the evolution of the considered 33 state variables has been numerically approximated by means of the Runge-Kutta-Fehlberg adaptive step-size integration method (22). To compare results, the solution of the general model of anaerobic digestion without considering the developed pH algorithm has also been approximated, by using the secant procedure for pH calculation at every time step of integration, using Eq. 17 or 18 (13).

Simulations with Anaerobic Digestion Model

With the aim of characterizing the capability of the system of equations to explain experimental results, to guide startup processes, and to obtain fast and accurate response values against changes in feeding composition, some numerical experiments were conducted. These numerical experiments consisted of simulating CSTR performance operated with pig slurry at different nitrogen ammonia concentrations and at different temperatures, and mixtures of pig slurry and olive oil bleaching earth (OOBE) from an oil refinery factory, with different addition rates of OOBE (data not shown).

The main organic components of OOBE are lipids, especially glyceride trioleate, whose hydrolysis produces long chain fatty acids (LCFA), which are described as important inhibitors of all anaerobic steps (25,26).

By using the two numerical methods described, it was concluded that values obtained for evolution of the state variables are very similar, and with the same level of accuracy when the integration interval time is short enough. Computing time is much longer when pH is calculated at every time step, by the secant rule, since the implicit equation to be solved requires multiple iteration. In some simulations characterized by large transitory variations in state variable values, convergence problems with the secant procedure were found.

Results from numerical experiments with different ammonia loads were in accordance with experimental results obtained in other research works (27), confirming previous results found in the literature (6,7). Results from numerical experiments with different OOB loading rates demonstrated the convenience of increasing gradually the OOB contents in the feeding flow, in order to allow adaptation and to prevent accumulation of LCFA. This result was in accordance with that of Angelidaki and Ahring (26), and it has been experimentally proven in simulated conditions (27).

Conclusion

The developed dynamic algorithm simulates pH in transitory states with high determination coefficients. The methodology applied provides a differential equation that allows including pH as state variable of the system, and it can be included in a general anaerobic digestion model using matrix notation. This methodology also allows a noticeable decrease in computing time in simulation processes. The algorithm has been tested including it in a general and dynamic anaerobic digestion model of complex substrates, using kinetic parameters and stoichiometric coefficients found in the literature. Numerical simulations have provided a satisfactory explanation of the experimental results and useful indications about critical steps of the process, guiding operational strategies.

Acknowledgments

We acknowledge Rosa Teira for her comments and support in translating the manuscript into English. This research was supported by a grant from CIRIT (Generalitat de Catalunya).

References

1. Kalyuzhnyi, S. and Federovich, V. (1997), *Water Sci. Technol.* **36**(6–7), 201–208.
2. Batstone, D. J., Keller, J., Angelidaki, R. I., Kalyuzhny, S. V., Pavlostathis, S. G., Rozzi, A., Sanders, W. T. M., Siegrist, H., and Vavilin, V.-A. (2002), Scientific and Technical Report No. 13, International Water Association, London.
3. Clark, R. H. and Speece, R. E. (1970), in *Advances in Water Pollution Research, Proceedings of the 5th International Conference*, vol. II(27), Jenkins, S. H., ed., Pergamon, Oxford, pp. 1–14.
4. Zeeman, G., Wiegant, W. M., Koster-Treffers, M. E., and Lettinga, G. (1985), *Agric. Wastes* **14**, 19–35.
5. Hashimoto, A. G. (1986), *Agric. Wastes* **17**, 241–261.

6. Angelidaki, I. and Ahring, B. K. (1993), *Appl. Microbiol. Biotechnol.* **38**, 560–564.
7. Hansen, K., Angelidaki, I., and Ahring, B. K. (1998), *Water Res.* **32**, 5–12.
8. Ahring, B. K. and Westermann, P. (1988), *Appl. Environ. Microbiol.* **54**, 2393–2397.
9. Fukuzaki, S., Nishio, N., Shobayashi, M., and Nagai, S. (1990), *Appl. Environ. Microbiol.* **56**, 719–723.
10. Andrews, J. F. and Graef, S. P. (1971), in *Anaerobic Biological Treatment Processes, Advances in Chemistry Series 105*, Pohland, F. G., ed., American Chemical Society, Washington, DC, pp. 126–162.
11. Costello, D. J., Greenfield, P. F., and Lee, P. L. (1991), *Water Res.* **25**, 847–858.
12. Siegrist, H., Renggli, D., and Gujer, W. (1993), *Water Sci. Technol.* **27(2)**, 25–36.
13. Angelidaki, I., Ellegaard, L., and Ahring, B. K. (1993), *Biotechnol. Bioeng.* **42**, 159–166.
14. Vavilin, V. A., Vasiliev, V., Rytov, S., and Ponomarev, A. (1995), *Water Res.* **29**, 827–835.
15. Kiely, G., Tayfur, G., Dolan, C., and Tanji, K. (1997), *Water Res.* **31**, 534–540.
16. Lide, D. (1993), *CRC Handbook of Chemistry and Physics*, 73rd ed., CRC Press, Boca Raton, FL.
17. Aguilar Sanjuán, M. (1993), *Introducción a los equilibrios iónicos*, Cpd-a-etseib, Barcelona.
18. Merkel, W. and Krauth, K. (1999), *Water Res.* **33**, 2011–2020.
19. Costello, D. J., Greenfield, P. F., and Lee, P. L. (1991), *Water Res.* **25**, 859–871.
20. Van Langerak, E. P. A., Hamelers, H. V. M., and Lettinga, G. (1997), *Water Sci. Technol.* **36(6–7)**, 341–348.
21. Musvoto, E. V., Wentzel, M. C., Loewenthal, R. E., and Ekama, G. A. (2000), *Water Res.* **34**, 1857–1867.
22. Sewell, G. (1988), *The Numerical Solution of Ordinary and Partial Differential Equations*, Academic, London.
23. Angelidaki, I., Ellegaard, L., and Ahring, B. K. (1999), *Biotechnol. Bioeng.* **63**, 363–372.
24. Angelidaki, I., Ellegaard, L., and Ahring, B. K. (1997), *Water Sci. Technol.* **36(6–7)**, 263–269.
25. Hanaki, K., Matsuo, T., and Nagase, M. (1981), *Biotechnol. Bioeng.* **23**, 1591–1610.
26. Angelidaki, I. and Ahring, B. K. (1992), *Appl. Microbiol. Biotechnol.* **37**, 808–812.
27. Campos, E. (2001), PhD thesis, University of Lleida, Lleida, Spain.