Microbial interaction during the anaerobic treatment of swine manure slurry in a sequencing batch reactor

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Massé, D.I. and Droste, R.L. 1997. **Microbial interaction during the anaerobic treatment of swine manure slurry in a sequencing batch reactor.** Can. Agric. Eng. **39**:035-041. A simple model that simulates the Psychrophilic Anaerobic Digestion (PAD) of swine manure slurry in a Sequencing Batch Reactor (SBR) is developed and verified. The model predictions have been compared with corresponding laboratory results. The trends in volatile acids and soluble chemical oxygen demand (COD) accumulation as well as the methane production rate were reasonably well predicted. The percent error of estimate ranged between 12 and 37. The model is a useful tool to study the influence of SBR operating strategies on the dynamic interaction between the acid and methane formers. Keywords: anaerobic digestion, methane production, modelling, process kinetics.

Un modèle mathématique est proposé pour simuler la digestion anaérobie du lisier de porc en milieu psychrophile dans un bioréacteur à opérations séquentielles (BOS). Les prédictions du modèle ont été comparées avec des résultats expérimentaux. Le % d'erreur sur l'estimation de l'accumulation des acides volatiles, la demande chimique en oxygen soluble (DCO) ainsi que la production de méthane variait entre 12 et 37. Le model est un outil pratique pour étudier l'influence des différentes stratégies d'opération du BOS sur l'intéraction dynamique entre les différents groupes de bactéries anaérobies qui transforment le lisier de porc.

INTRODUCTION

A comprehensive study on Psychrophilic Anaerobic Digestion (PAD) of swine manure slurry in Sequencing Batch Reactors (SBR) was conducted by Massé (1995). The temperature range for growth of psychrophilic bacteria includes the range of temperatures normally found in manure storage gutters in animal shelters in Canada (5 to 20°C). An SBR anaerobic process occurs in a tank or a reservoir in the sequences given in Fig. 1: fill; react; settle; draw; and idle. During the fill and react phases, the soluble organics and some of the suspended organic particulates are removed by the anaerobic microorganisms. During the settling phase there is no mixing; this provides quiescent settling conditions (Dague et al. 1992) for the separation of treated manure and suspended solids. SBR operation retains a very high concentration of microorganisms in the digester. During the draw phase the treated manure is removed. The idle phase allows some flexibility for the operation and maintenance of the SBRs.

Massé (1995) indicated that PAD of swine manure slurry in SBR was very stable. The anaerobic bioreactors were not affected by high concentrations of volatile acids (6500 mg/L) and ammonia nitrogen (NH_3 + NH_4^+ = 3700 mg/L). The proposed process stabilized and deodorized swine manure slurry and also produced a significant amount of high quality biogas (0.33 to 0.66 L CH_4 /g of volatile solids added). These results indicated that PAD in SBR has the potential to be a stable, easy-to-use, and cost effective process to treat swine manure slurry on Canadian farms. But before this process can be recommended, additional laboratory tests are required to investigate the effect of other factors such as loading rates, temperature variation, solids content, animal diets, and manure handling practices. One problem is that laboratory tests require substantial amounts of time, especially when they are carried out at low temperatures.

The objective of this work was to develop a simple comprehensive model to predict the bioreactor performance under different operating and environmental conditions. Such a model would be useful to:

1. gain a better knowledge of PAD in SBR;
2. predict the rate limiting steps during fill and react phases;
3. reduce the number of experimental tests; and
4. optimize the bioreactor design and control strategy.

MODEL DEVELOPMENT

The authors opted for a comprehensive model that involved some simplifying assumptions. As a result, the model does not require a large number of kinetic constants. A dynamic model similar to the models developed by Hill and Barth (1977), Droste and Kennedy (1988), Jones (1989), and Jones and Hall (1989) was developed for PAD in an SBR process. These previous models considered the two phases (acid and methane formation) in anaerobic digestion, but apply to only continuous flow or steady state bioreactors.

PAD in SBR not only has different flow regimes but also has transient conditions that always prevail during the fill and react phases. The bioreactor operates as a semi-batch system during the feed phase and as a batch system during the reaction phase. The rate limiting steps during the transient feed and reaction phases also differ (Massé 1995). The model presented below makes use of different assumptions and

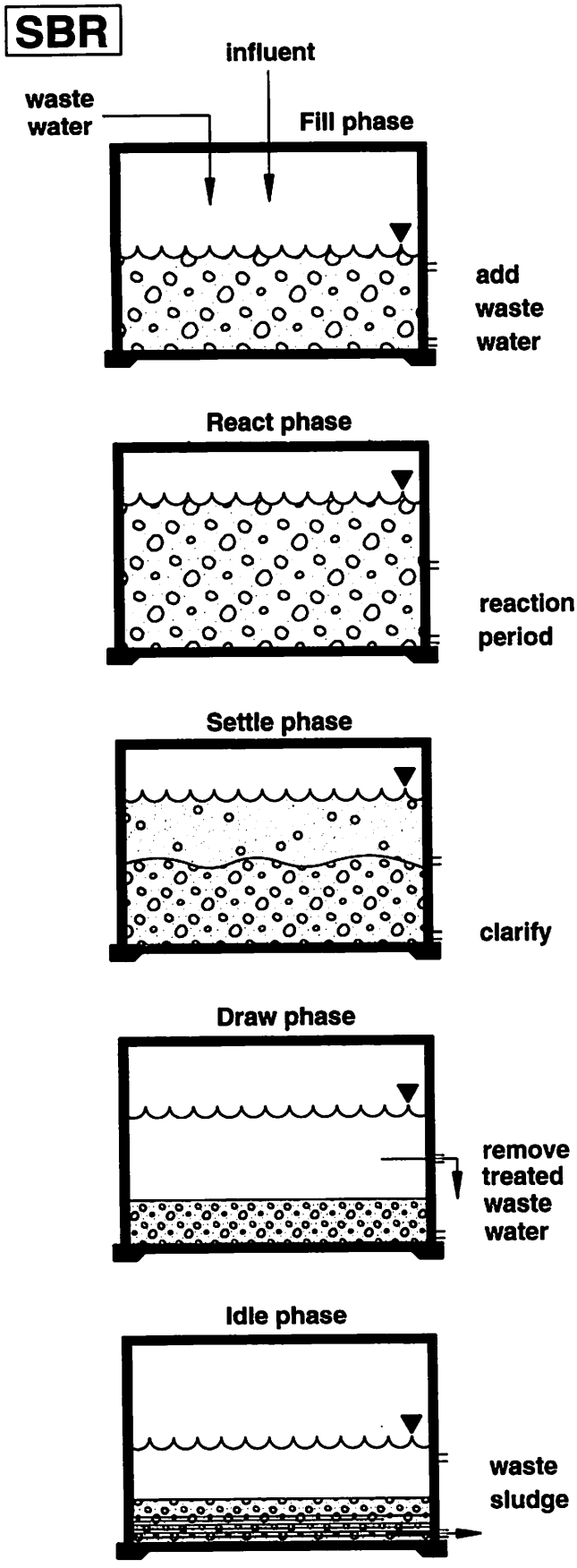


Fig. 1. Operation of the anaerobic SBR process.

non-linear differential equations.

The simplified scheme of PAD in SBR used in this study to develop the model (Fig. 2) includes the two major microbial groups (the acid formers and methane formers). The proposed model will be used to simulate the biological phase only. The parameters considered are soluble chemical oxygen demand (SCOD), volatile acids (VA), and methane production. Removal of volatile solids (VS) and total COD (TCOD) are not considered because in a SBR their removal is due to both biological degradation and settling; but hydrolysis of particulate matter to SCOD is considered.

Model assumptions

The model proposed for the simplified scheme is based on the following assumptions:

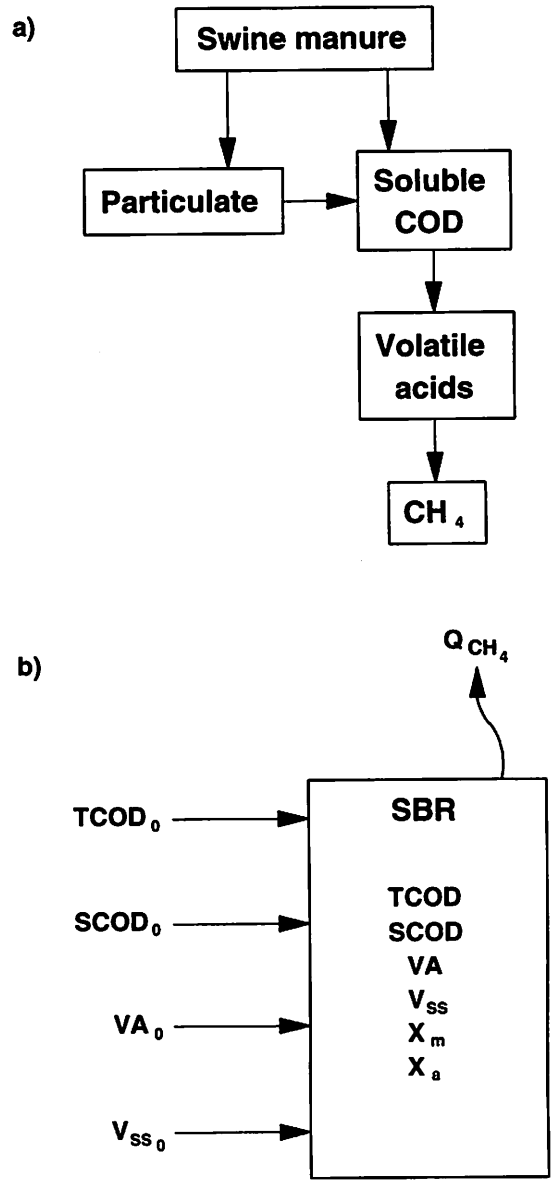


Fig. 2. a. Simplified scheme for anaerobic digestion b. Parameters considered in simple model development.

1. Swine manure contains both particulate and soluble substrates.
2. Particulates are converted to SCOD.
3. SCOD is converted to VA and acid formers.
4. VA are converted to methane and methane formers.
5. pH, VA, NH_3-N, and NH_{4+}-N concentrations do not have an effect on PAD in SBR process kinetics as supported by Massé (1995).
6. Soluble substrate utilization follows Monod kinetics.
7. Both acid former and methane former populations change during the simulation.
8. Methane solubility in the liquid phase is negligible. The rate of methane leaving the SBR with the biogas is equal to that produced by the methane formers.
9. Only one population of acetoclastic methanogens is present in the digesters.
10. Psychrophilic conditions (T=20°C) are maintained in SBRs.

Particulate organics Droste and Kennedy (1988) used a soluble substrate and, therefore, did not consider hydrolysis of particulates. In the manure slurry, hydrolysis of particulates is important. During the fill phase the material mass balance for particulates is:

$$\frac{d(PV_L)}{dt} = QP_0 - r_p V_L \qquad (1)$$

where:
- P = particulate COD concentration in the SBR (mgL),
- V_L = SBR liquid phase volume (L)
- t = time (d),
- Q = influent flow rate (L/d),
- P_0 = particulate COD concentration in influent (mg/L), and
- r_p = utilization rate of particulates (mg COD•L^{-1}•d^{-1})

In an SBR during the fill phase, both the particulates concentration and liquid phase volume are functions of time.

$$\frac{d(PV_L)}{dt} = P\frac{dV_L}{dt} + V_L\frac{dP}{dt} \qquad (2)$$

It is known that:

$$\frac{dV_L}{dt} = Q \qquad (3)$$

Substituting Eq. 3 into Eq. 2 gives:

$$\frac{d(PV_L)}{dt} = PQ + V_L\frac{dP}{dt} \qquad (4)$$

Substituting Eq. 4 into Eq. 1 and simplifying further yields:

$$\frac{dP}{dt} = \frac{Q(P_O - P)}{V_L} - K_P P \qquad (5)$$

where: K_p = first order solubilization rate (d^{-1}).

Gujer and Zehnder (1983), indicated that a first-order hydrolysis rate for particulate solubilization may be the most appropriate expression for complex wastes and this was therefore used in this study.

The mass balance for a SBR during the fill phase is identical to the mass balance for a continuous flow stirred tank reactor (CSTR). The term PQ in Eq. 4 does not represent the effluent output, instead it represents the reduction in concentration due to dilution caused by the increase in SBR liquid phase volume.

Similar mass balances for the fill phase were also developed for SCOD (Eq. 6), volatile acids COD (Eq. 7), acid and methane formers (Eqs. 8 and 9, respectively), as well as methane production (Eq. 10).

Soluble COD

$$\frac{dS}{dt} = \frac{Q(S_O - S)}{V_L} + K_P P - \left(\frac{Vmax_a X_a S}{K_{sa} + S}\right) + (K_{da} X_a + K_{dm} X_m) F \qquad (6)$$

where:
- S = SBR SCOD concentration (mg COD/L),
- So = influent SCOD concentration (mg COD/L),
- $Vmax_a$ = maximum specific SCOD uptake rate (mg COD•mg^{-1} X_a•d^{-1}),
- X_a = acid formers concentration (mg/L),
- K_{sa} = saturation constant (mg SCOD/L),
- Kd_a = decay rate constant for acid formers (d^{-1}),
- Kd_m = decay rate constant for methane formers (d^{-1}),
- X_m = methane formers concentration (mg/L), and
- F = theoretical COD equivalent of VSS (mg COD/mg VSS)

Volatile Acids COD

$$\frac{dVA}{dt} = \frac{Q(VA_Q - VA)}{V_L} + Y_A\left(\frac{Vmax_a X_a S}{K_{sa} + S}\right) - \left(\frac{Vmax_m X_m VA}{K_{sm} + VA}\right) \qquad (7)$$

where:
- VA = SBR VA COD concentration (mg COD/L),
- V_{Ao} = influent VA COD concentration (mg COD/L),
- Y_A = true yield of VA COD from substrate,
- $Vmax_m$ = maximum specific VA uptake rate (mg VA COD•mg^{-1} X_m•d^{-1}), and
- K_{sm} = saturation constant (mg VA COD/L)

Acids Formers

$$\frac{dX_a}{dt} = -\frac{Q X_a}{V_L} + Y_a\left(\frac{Vmax_a X_a S}{K_{sa} + S}\right) - K_{da} X_a \qquad (8)$$

where: Y_a = acid formers yield factor.

Methane Formers

$$\frac{dX_m}{dt} = -\frac{Q X_m}{V_L} + Y_m\left(\frac{Vmax_m X_m VA}{K_{sm} + VA}\right) - K_{dm} X_m \qquad (9)$$

where: Y_m = methane formers yield factor.

Methane Production

$$Q_{CH_4} = \left[\left(\frac{Vmax_m X_m VA}{K_{sm} + VA}\right) - F\,Y_m\left(\frac{Vmax_m X_m VA}{K_{sm} + VA}\right)\right] V_L \qquad (10)$$

where: Q_{CH_4} = methane production rate (g COD/d).

Mass balances for SCOD, VA, acid, and methane formers (Eqs. 6 to 9) were developed using Monod kinetics (Monod 1949) for substrate removal. The mass balance for methane production (Eq. 10) depends on the total conversion of VA less the conversion of VA used for the growth of the biomass. The mass balances for the react phase are similar to Eqs. 5 to 10. The only difference is that the influent flow rate term is equal to zero. The Runge Kutta method (Carnahan et al. 1969) was used to evaluate these equations.

The liquid zone volume changes with time during the fill phase. Therefore, in the Eqs. 5 to 10 the liquid phase volume is determined as:

$$V_L = V_o + \int Q\,dt \qquad (11)$$

where: V_o = SBR initial volume (L).

EXPERIMENTAL PROCEDURE

Experimental design and procedures have been previously reported (Massé 1995). Only a summary is given in this paper. Experiments were carried out in 12 laboratory scale bioreactors located in a controlled temperature room. All the tests were carried out at a temperature of 20°C.

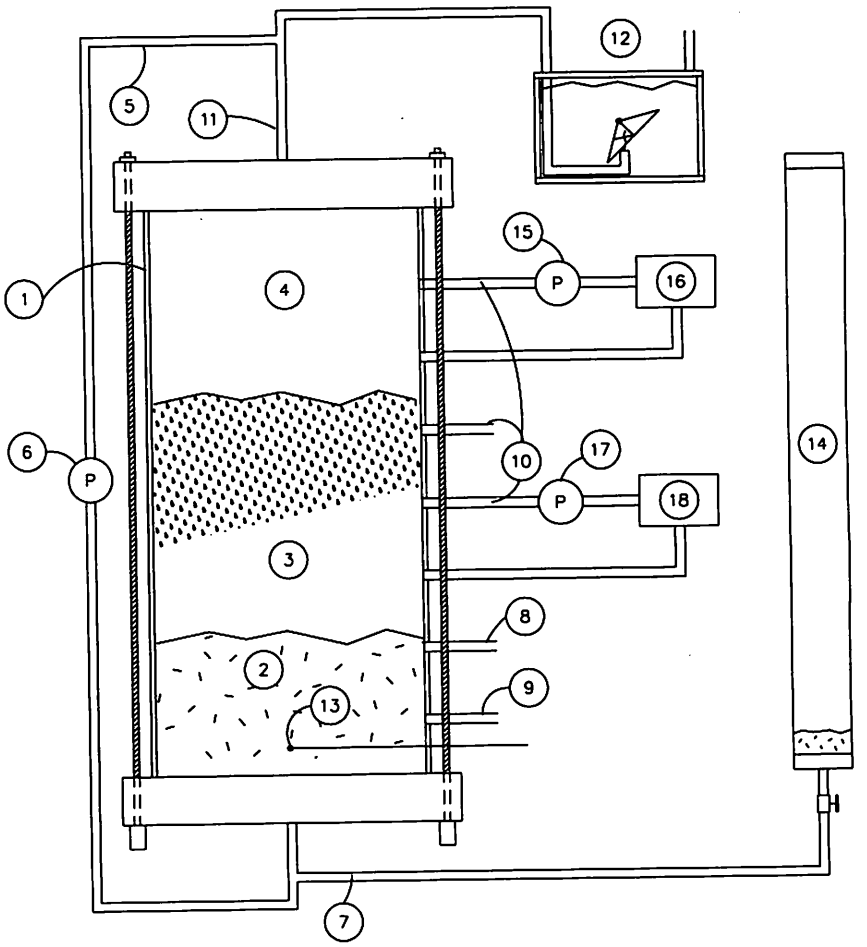
Experimental equipment

Figure 3 is a schematic diagram of the bench scale SBRs and feeding system used in this study. The plexiglass SBRs provided mixing by recirculating the biogas 10 min every 30 min through an inlet located at the bottom of the digesters. Manure slurry was obtained from storage gutters under a partially slatted floor in a growing-finishing barn at a commercial swine operation. The manure was as old as four days at the time of collection.

A mixed liquor sample of 100 mL was withdrawn from each SBR at the beginning of the experiment and once a week during the experimental run. At the end of the test, after the sedimentation phase, additional 100 mL samples were withdrawn from the supernatant and settled sludge bed zones. Swine manure slurry was sampled immediately before it was fed to the SBRs. The samples were analysed for pH, alkalinity, solids, VA, total Kjeldahl nitrogen (TKN), ammonia nitrogen ($NH_3 + NH_4^+$), TCOD, and SCOD. The biogas production was monitored daily and its composition was analysed weekly.

Analytical techniques

SCOD was determined by analysing the supernatant of centrifuged slurry. The SCOD was determined according to the method developed by Knechtel (1978). The pH, redox potential, alkalinity, total solids, total suspended solids, volatile solids, volatile suspended solids, ammonia nitrogen ($NH_3 + NH_4^+$), and TKN were determined using standard methods (APHA 1992). TKN and ammonia nitrogen were determined using a kjeltec auto-analyser model TECATOR 1030. The



1 300 mm diameter plexiglas digester
2 sludge bed zone (7.5 L)
3 variable volume zone (28.0 L)
4 head space zone (6.5 L)
5 gas recirculation line
6 biogas recirculation pump
7 influent line
8 effluent line
9 sludge sampling port, also use for sludge wastage
10 mixed liquor or supernatent sampling port
11 gas outlet
12 gas meter
13 thermocouple
14 feeder tube
15 gas pump
16 hydrogen gas monitor
17 liquid pump
18 dissolved hydrogen gas monitor

Fig. 3. Schematic of laboratory scale SBRs used for test runs 5, 6 and 7.

Table I: SBR operating conditions

Run number	Digester number	Mixing	Fill phase (week)	React phase (week)	Number cycle
5	11 -12	Yes	4	4	1
6	5 -6	No	2	2	2

Table II: Initial values of biological kinetic constants used in the simple model

Constant	Acidogens	Methanogens
$Vmax_i$ ($mg \cdot mg^{-1} \cdot d^{-1}$)	0.4*	1.0*
Ks (mg/L)	800*	200*
Y_i (mg/mg)	0.12*	0.05*
k_{di} (d^{-1})	0.025*	0.025*
Kp (d^{-1})	0.05**	0.05**

* from Droste and Kennedy (1988)
** from O'Rourke (1968)

Table III: Range of values considered for each kinetic constant in the grid analysis

Constant	Range		Incremental values
	Acidogens	Methanogens	
$Vmax_i$ ($mg \cdot mg^{-1} \cdot d^{-1}$)	0.04-0.80	0.04-1.4	0.01
Ks (mg/L)	100-2500	50-3000	10.0
Y_i (mg/mg)	0.05-0.25	0.01-0.20	0.01
k_{di} (d^{-1})	0.0005-0.04	0.0005-0.04	0.0001
Kp (d^{-1})	0.01-0.08	0.01-0.08	0.005

VA concentrations were determined by a Perkin Elmer gas chromatograph model 8310, that had a DB-FFAP high resolution column. The biogas composition was determined by using a Carle 400 AGC gas chromatograph.

Model validation

This section examines the adequacy of the model in predicting the dynamic behaviour of the PAD of swine manure slurry in SBR. Experimental data from digesters 11 and 12 in test run 5 (cycle length of 56 days) and digesters 5 and 6 in test run 6 cycle 1 and 2 (cycle length of 28 days) were compared to the dynamic model prediction. These runs were selected because they had the most comprehensive data set (Massé 1995). The organic loading for those ASBRs was 1.63 g $COD \cdot L^{-1} \cdot d^{-1}$. The other operating conditions for the runs selected for simulation are given in Table I. The parameters used in this evaluation were VA, SCOD, and methane flow rate.

Model kinetic constants in Table II were obtained from the literature (Droste and Kennedy 1988; O'Rourke 1968). These kinetic constants were determined for bioreactor operated

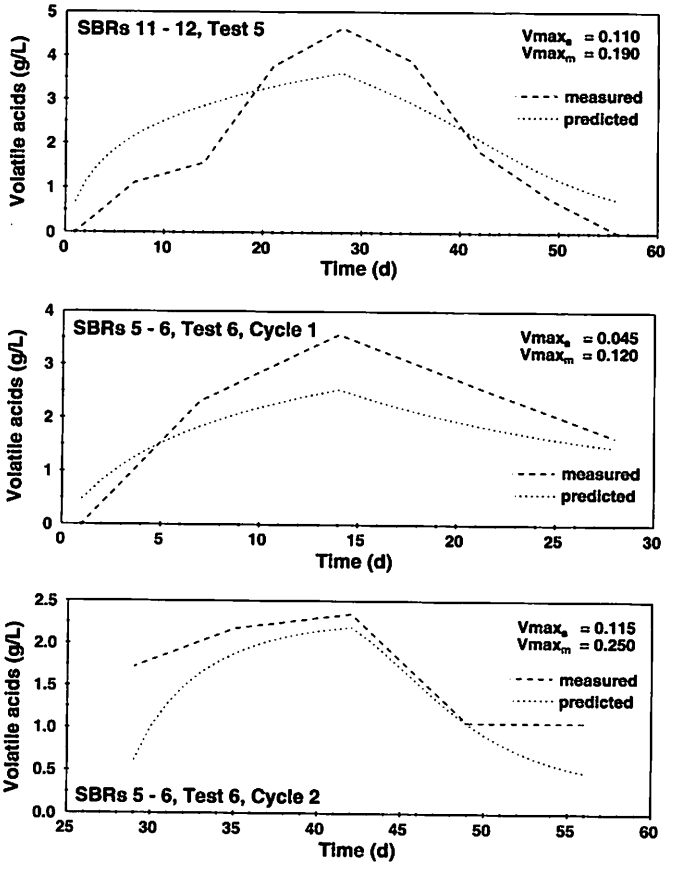


Fig. 4. Comparison between the experimental measurement of volatile acids and the simple model prediction, Ksa = 1500 mg/L, Ksm = 2500 mg/L, Kp = 0.04 d^{-1}, Kdi = 0.001 d^{-1}.

under different environments (pH, temperature, alkalinity, mixing level, etc.) and hydraulic flow regimes. The kinetic constants in this study were expected to be lower because the process took place at a lower temperature. A grid search around these values was used in the model prediction. The range considered for each kinetic constant is given in Table III. The incremental value used for each biological kinetic constant during the simulation runs is also given in Table III. The error of estimate and percent error of estimate for each Parameter (VA, SCOD, and methane flow rate) were calculated according to Eqs. 12 and 13.

$$EE = \sqrt{\frac{\sum (Calculated\,Value_i - Experimental}{N}} \qquad (12)$$

$$PEE = \left(\frac{EE}{\frac{\sum Experimental\,Value_i}{N}} \right) * 100 \qquad (13)$$

where:
EE = error of estimate,
PEE = percent error of estimate (%),

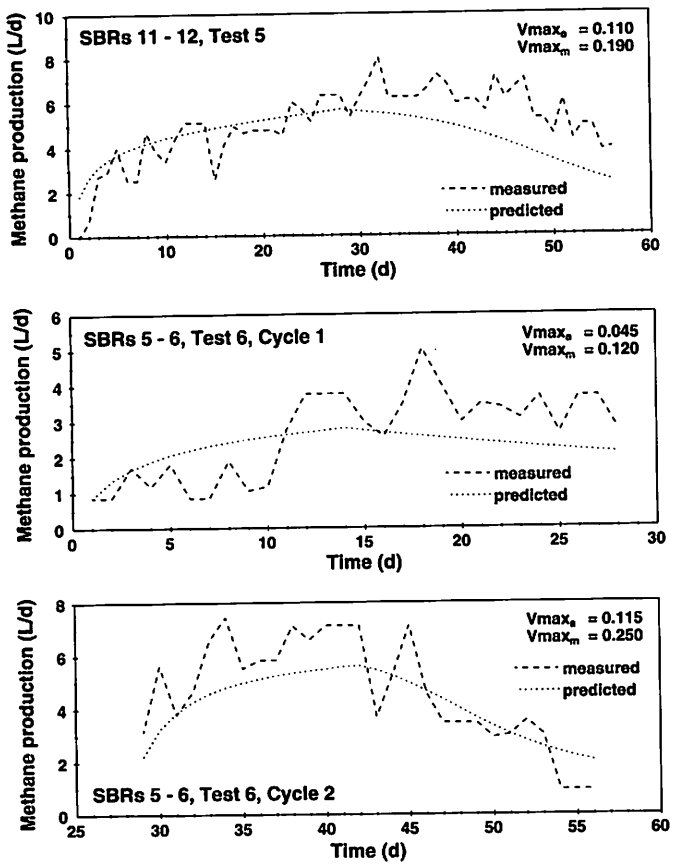


Fig. 5. Comparison between the experimental measurement of methane production and the simple model prediction, Ksa = 1500 mg/L, Ksm = 2500 mg/L, Kp = 0.04 d^{-1}, Kdi = 0.001 d^{-1}.

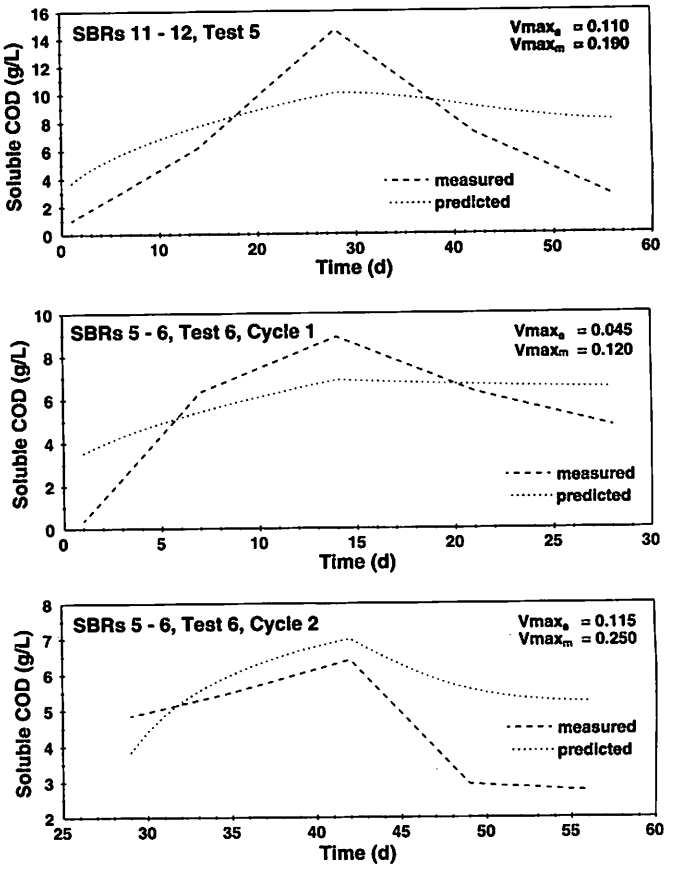


Fig. 6. Comparison between the experimental measurement of soluble COD and the simple model prediction, Ksa = 1500 mg/L, Ksm = 2500 mg/L, Kp = 0.04 d^{-1}, Kdi = 0.001 d^{-1}.

N = number of estimates, and
i = day number

The best fit yield factors for the acidogens and methanogens were 0.1 and 0.05 mg/mg, respectively. The other best fit kinetic constants are presented in Figs. 4, 5, and 6. Some of these kinetic constants are slightly different for each test run because sludge acclimation was still taking place and the operating strategies were different.

Quantitative sensitivity analysis has not been carried out to quantify the relative influence of each kinetic parameter on the prediction accuracy. Observations during simulation clearly indicate that the maximum specific substrate utilization rates of the acids and methane formers had the largest influence on the model prediction. The second most influential group of parameters was the yield factors for the acidogens and methanogens.

Table IV gives the lowest *PEE* obtained for the kinetic constants that provided the best fit in each test run. The PEE values for VA, SCOD, and Q_{CH_4} are similar and within a reasonable range. These differences between measured and predicted parameters were expected. In this study it was not possible to determine the relative contributions to the errors between the measured and predicted values due to the simple model limitations or sludge acclimation. Independent sets of experimental data would be required to clarify this.

Figures 4 to 6 compare the calculated and measured concentrations of VA, SCOD, and Q_{CH_4} as a function of time.

Table IV: Lowest PEE for the final values of kinetic constant used with the simple model

Parameter	*PEE*		
	Test run 5 digesters 11-12	Test run 6 digester 5-6 cycle 1	Test run 6 digester 5-6 cycle 2
VA	37	20	23
SCOD	37	12	34
Q_{CH4}	27	30	28

These figures show that the simple model predicted reasonably well (PEE ranged between 12 and 37) the general trend in methane production as well as VA and SCOD accumulations during the fill and react phases. This model provides a useful tool to better understand the dynamics of PAD in SBR process operated under different operating conditions.

CONCLUSIONS

A dynamic model based on a simplified scheme for the PAD of swine manure slurry in a SBR was developed and verified. Considering the overall complexity of this process, ongoing sludge acclimatization and different operating strategies, the model was judged to be acceptable for predicting the accumulated VA and SCOD in the SBR as well as the methane flow rates. The sets of kinetic constants that provided the best fit for each experimental run were of the same order. This model is a useful tool to gain better knowledge of: 1) the dynamic interaction between the acid and methane formers; and 2) microorganism response to different operating strategies.

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NOMENCLATURE

EE	error of estimate
F	theoretical COD equivalent of VSS (mg COD/mg VSS)
i	day number
Kd_a	decay rate constant for acid formers (d^{-1})
Kd_m	decay rate constant for methane formers (d^{-1})
K_p	first order solubilization rate (d^{-1})
K_{sa}	saturation constant (mg SCOD/L)
K_{sm}	saturation constant (mg VA COD/L)
N	number of estimates
P	particulate COD concentration in the SBR (mg/L)
PEE	percent error of estimate (%)
Po	particulate COD concentration in influent (mg/L)
Q	influent flow rate (L/d)
Q_{CH_4}	methane production rate (g COD/d)
r_p	utilization rate of particulates (mg COD•L^{-1}•d^{-1})
S	SBR SCOD concentration (mg COD/L)
So	influent SCOD concentration (mg COD/L)
t	time (d)
VA	SBR VA COD concentration (mg COD/L)
Vao	influent VA COD concentration (mg COD/L)
V_L	SBR liquid phase volume (L)
$Vmax_a$	maximum specific SCOD uptake rate (mg COD•mg^{-1} X_a•d^{-1})
$Vmax_m$	maximum specific VA uptake rate (mg VA COD•mg^{-1} X_m•d^{-1})
V_o	SBR initial volume (L)
X_a	acid formers concentration(mg/L)
X_m	methane formers concentration (mg/L)
Y_a	acid formers yield factor
Y_A	true yield of VA COD from substrate
Y_m	methane formers yield factor