



THE INFLUENCE OF pH ON THE PERFORMANCE OF A TWO-STAGE ANAEROBIC TREATMENT SYSTEM: MODEL PREDICTION AND VALIDATION

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ABSTRACT

The effect of lowering the pH of the acidification reactor on the overall performance of a two-stage anaerobic wastewater treatment system was determined both experimentally and through simulation of a dynamic structured model. The system operated at low pH was then subjected to a short-term step increase in feed concentration. The measured and the predicted dynamic responses of reactor variables to the shock load were evaluated. The result indicated that lowering the pH setpoint from 6.0 to 5.3 led to a reduction in the external alkali addition by 30% without any significant deterioration in the final effluent quality. The model prediction showed good agreement with the experimental results for most reactor variables. The dynamic response of the system to a concentration shock load indicated a decrease in effluent quality during the disturbance, but the system did recover quickly as soon as the shock load terminated. The comparison between the experimental and the simulation results demonstrated the feasibility of the model to be applied for reactor design and operational evaluation purposes.

KEYWORDS

Alkali, carbohydrate-based wastewater, concentration shock load, acidification, methanogenic, dynamic response, two-stage anaerobic treatment system.

INTRODUCTION

The high consumption of alkali in anaerobic wastewater treatment operations is usually the main obstacle for the application of this technology. For carbohydrate-based wastewater, buffer formation in the form of bicarbonate alkalinity as a result of the reaction of bicarbonate with cations (naturally occurring in protein decomposition) does not take place (Jeris and Kugelman, 1985). Therefore, the system requires a considerable amount of external alkali addition to maintain the reactor pH.

The manipulation of the operating conditions of a two-stage anaerobic treatment system can provide a more economically effective treatment operation. One such variable is the recycle of effluent from the methanogenic reactor into the acidification reactor which has been shown to minimise the operational

costs of treatment due to alkali saving (Romli *et al.*, 1994). Another variable of interest is the pH setpoint of the acidification reactor. It is expected that lowering the pH will result in the reduction of the external alkali required to maintain the pH of both reactors.

An improved version of a dynamic structured model of the anaerobic degradation process which was developed by Costello *et al.* (1991) has been shown to predict the steady state and dynamic responses of a two-stage anaerobic treatment system as a function of the extent of recycle of effluent from the methanogenic reactor to the acidification reactor (Romli *et al.*, accepted; Keller *et al.*, 1993).

In this study, the measured and the predicted results of lowering the acidification reactor pH on the reactor variables will be presented. Furthermore, the ability of the model to predict the dynamic responses of the system to a step increase in feed concentration at low pH will also be discussed.

MATERIALS AND METHODS

The laboratory scale two-stage anaerobic wastewater treatment system used in this study consisted of a continuous stirred tank reactor (CSTR) as the acidification reactor and a fluidised-bed reactor (FBR) as the methanogenic reactor (Fig. 1). The liquid volume of the first reactor was 1.64 litres and that of the second reactor was 3.3 litres. Both reactors were operated at a constant temperature of 35°C and at a recycle to feed rate ratio of 1. The feed used was based on diluted molasses with the addition of nitrogen, phosphorous, and trace metal elements to ensure good bacterial growth. A volumetric organic loading rate of approximately 22 kg COD/m³/day was used as the base loading rate. The details of the reactor system, feed composition, and analytical methods can be found elsewhere (Romli *et al.*, in press).

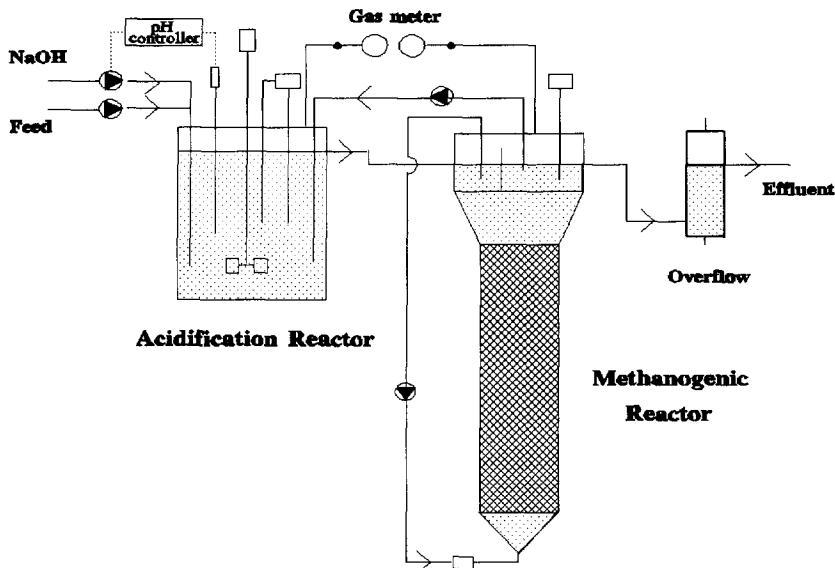


Fig. 1. Reactor configuration

The experiment on the effect of lowering the pH of acidification reactor was conducted by gradually decreasing the pH setpoint of the controller from 6.0 to 5.3. The concentration shock load experiment was carried out at pH 5.3, by introducing an eight hour step increase in feed concentration from 3.7 to 6.2 g TOC/litre. Reactor variables such as pH of the methanogenic reactor, alkali flow rate, gas

production rate and composition, and effluent organic acids concentration were measured hourly during the course of the disturbance.

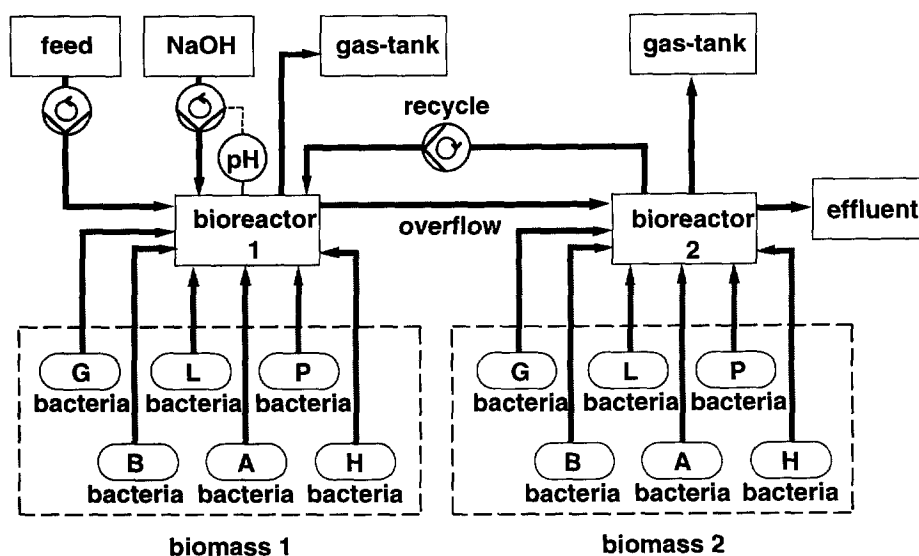


Fig. 2. Model schematic of a two-stage anaerobic treatment process in NIMBUS

The improved version of the dynamic model of anaerobic degradation processes used in this study was implemented in a recently developed simulation package NIMBUS (Newell and Cameron, 1991). The model set-up for the two-stage anaerobic reactor configuration is depicted in Fig. 2. Further details regarding the model development are described elsewhere (Costello *et al.*, 1991; Keller *et al.*, 1993; and Keller *et al.*, in preparation). The model parameters used to simulate the reactor behaviour throughout this study are presented in Tables 1 and 2.

TABLE 1 Physico-Chemical Parameters Determined at 35°C

Physico-chemical parameters		Value	Unit
Equilib.coeff.	lactic acid	0.1332	mole/m ³
	propionic acid	1.310 x 10 ⁻²	mole/m ³
	butyric acid	1.439 x 10 ⁻²	mole/m ³
	acetic acid	1.728 x 10 ⁻²	mole/m ³
	carbon dioxide	4.90 x 10 ⁻⁴	mole/m ³
Ionisation constant of water		2.09 x 10 ⁻⁸	(mole/m ³) ²
Vapour pressure of water		0.05623	bar
Ideal gas law constant R		8.314 x 10 ⁻⁵	bar m ³ /mol K
Henry's constant for CO ₂		0.041	bar m ³ /mole

TABLE 2 Biological Parameters Used for Simulation

Bacterial Groups	k	K_s	Y	b	pH_{UL}	pH_{LL}^{**}
	C-mole S/ C-mole X/h	C-mole S/ m^3	C-mole X/ C-mole S	h^{-1}		
Glucose	5.0	40	0.0636	0.83×10^{-3}	6.0	4.0
Lactic	3.8	1.14	0.1272	0.83×10^{-3}	6.0	4.0
Propionic	0.524	10	0.0636	0.42×10^{-3}	6.0	4.0
Butyric	4.0	7	0.0716	1.25×10^{-3}	6.0	4.0
Acetic	0.393	6	0.0477	0.83×10^{-3}	6.0	4.5
Hydrogen	3.6	$5.5e^{-3}$	0.03	0.38×10^{-3}	6.0	4.5

*unit in bar, ** pH_{LL} and pH_{UL} : lower and upper limits of pH inhibition

EFFECT OF LOWERING pH OF ACIDIFICATION REACTOR

The effect of lowering the pH of the acidification reactor on some reactor variables are shown in Figs. 3-6. Both the measured and the predicted results are presented. The experimental results are represented with symbols and the simulation results with lines. Error bars in the figure indicate the measurement uncertainty at a 95% confidence level. Fig. 3 shows that by decreasing the acidification reactor pH, the consumption of alkali could be reduced. It is shown that more than 30% alkali reduction could be achieved by changing the pH setpoint from 6.0 to 5.3. A similar response is shown by the model prediction.

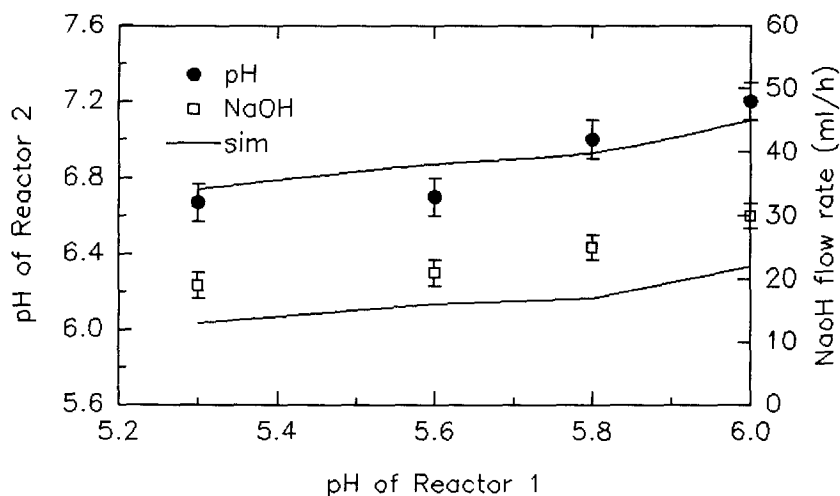


Fig. 3. pH influence on the alkali and pH of Reactor 2

The changes in the pH setpoint of the first reactor, however, led to a decrease in the final effluent pH. The above change was observed to decrease the pH of the methanogenic reactor to approximately 6.7. Nevertheless, the COD removal efficiency of the methanogenic reactor was still high (more than 90%) both in steady state as well as during the shock load situation. This pH level is considered to be within the optimal pH value for methanogenic reactors (Zoetemeijer *et al.*, 1982; Attal *et al.*, 1988).

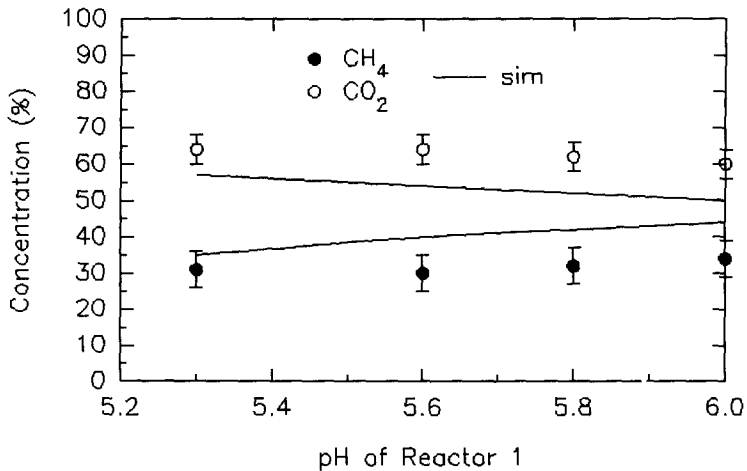


Fig. 4. pH influence on the gas composition of Reactor 1

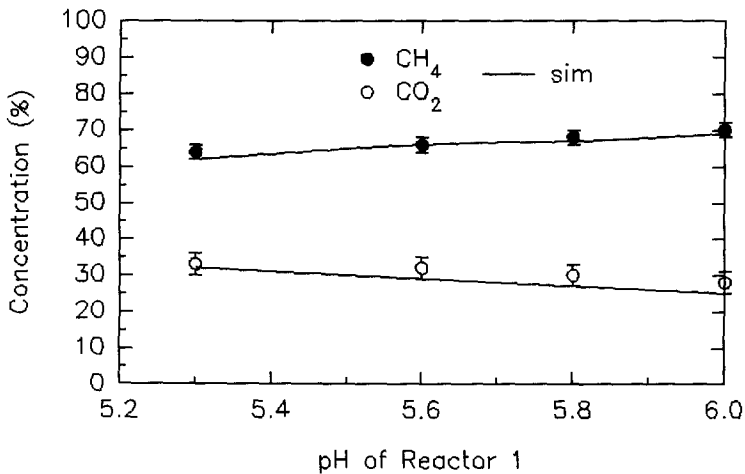


Fig. 5. pH influence on the gas composition of Reactor 2

The change in pH setpoint did not significantly affect the gas production rates, but decreased the concentration of methane in both reactors as shown in Figs. 4 and 5. The reason for this apparent decrease in the methane concentration was most likely due to the dilution effect from the increased carbon dioxide concentration in the gas phase. The analysis of effluent dissolved carbon dioxide (data

not shown) indicated that at lower pH, a proportion of the dissolved carbon dioxide will strip off to the gas phase. This behaviour is also confirmed by the model predictions, especially in the second reactor where the gas flow rate is significantly higher than in the first reactor. The hydrogen concentration increased with lowering the pH setpoint (Fig. 6). The hydrogen levels in the methanogenic reactor were all below the detection limit, but the model simulation predicted a similar tendency.

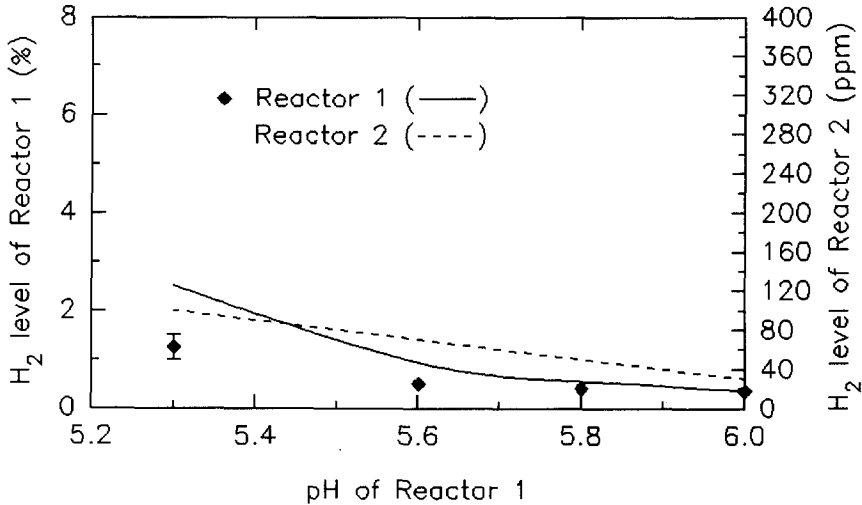


Fig. 6. pH influence on the hydrogen concentration of both reactors

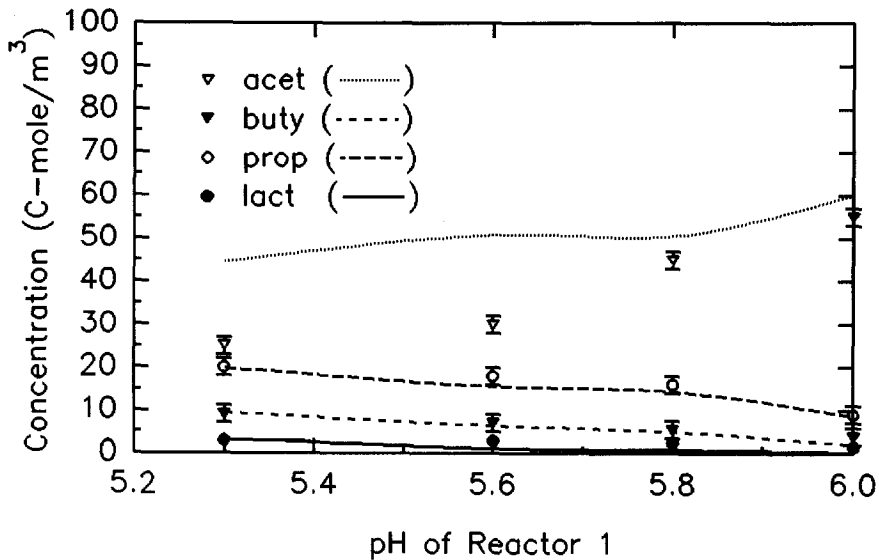


Fig. 7. pH influence on the concentration of organic acids in Reactor 1

The effect of lowering the pH of the acidification reactor on the concentration of organic acids in the first reactor is shown in Fig. 7. Except for acetic acid, the concentrations of all other organic acids increased with decreasing pH. It should be noted here that other minor intermediate fermentation products, such as succinic acid, formic acid, and ethanol were also detected in the first reactor. These species, however, were not modelled. With regard to acetic acid, a similar conclusion was also reported by Dinopoulou *et al.* (1988), who found a decrease in the percentage of acetic acid production relative to total volatile fatty acids with decreasing pH. The accumulation of lactic and propionic acids probably occurred as a response of the hydrogen increase at lower pH. The hydrogen level in the first reactor as high as 10000 ppm was observed during the steady state operation at pH 5.3. The production of lactic acid, which in turn converted to propionic acid, in such a condition is an easy solution for finding the electron acceptor. The accumulation of propionic and butyric acids could also be attributed to the pH inhibition of the acetogenic bacteria. Attal *et al.* (1988) showed that the increase in the fraction of unionised form of volatile fatty acids was the cause of this pH inhibition. Fig. 7 shows that the model predicts well the behaviour of effluent organic acids in the first reactor. A slight increase in the total concentration of organic acids was also observed in the final effluent with decreasing pH. However, a high substrate removal still could be maintained even during the shock load situation as shown later.

SYSTEM RESPONSE TO THE CONCENTRATION SHOCK LOAD

The dynamic responses of some of the reactor variables to a step increase in feed concentration are presented in Figs. 8-11. Again, both the experimental and the simulation results are displayed. The vertical dotted line at time 8 indicates the time at which the feed concentration is returned to normal. The step increase in feed concentration, as expected, increased the alkali flow rate during the course of the shock load, but decreased very quickly to pre-shock level in less than 4 hours. This behaviour is in general predicted by the model, although some discrepancies in the maximum values of alkali flow rate are observed. The step increase slightly dropped the pH of the final effluent, but it recovered even before the shock load was terminated. As shown in Fig. 8, the pH behaviour in response to the shock load is predicted quite well by the model.

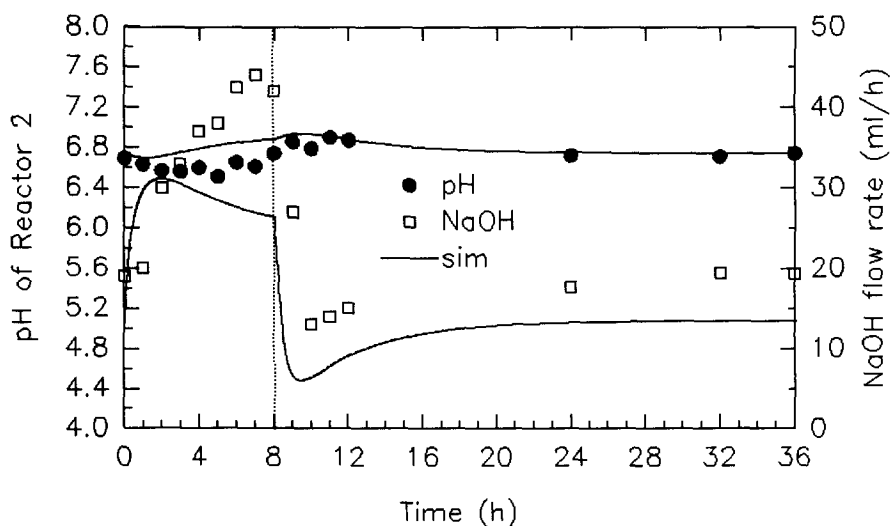


Fig. 8. Effect of a step increase in feed concentration on the alkali flow rate and pH of Reactor 2

A good prediction is also observed for gas production rates in both reactors (Fig. 9). The increased gas generation rate in the first reactor was only marginal, but more than a 100% increase was demonstrated in the second reactor. This variable was also returned to the pre-shock value at a relatively short time. The shock load increased the concentration of carbon dioxide in the gas phase of both reactors, thus decreased the methane concentration. In the methanogenic reactor, however, the methane concentration only dropped during the first 4 hours of the shock load from 65% to 58% and then gradually recovered and reached the previous steady state value before the feed concentration was returned to normal.

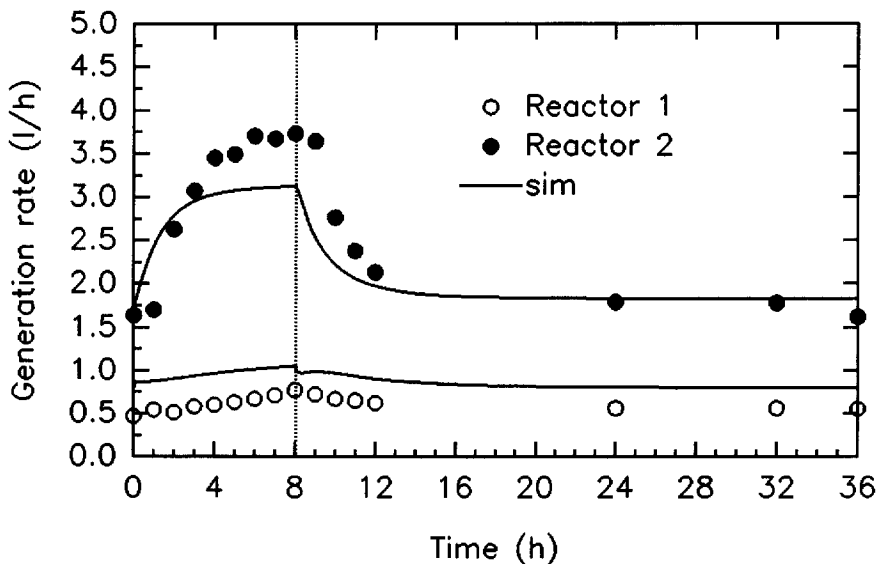


Fig. 9. Effect of a step increase in feed concentration on the gas production rate

Figs. 10 and 11 respectively show the dynamic behaviour of effluent organic acids concentration of the first and second reactor in response to the shock load. As soon as the high feed concentration was introduced, the lactic acid concentration (less than 5 C-mole/m³ at steady state as shown before) increased markedly and reached a maximum level of 70 C-mole/m³ at the end of the shock load period. Similarly, the fraction of undegraded feed (as glucose) also increased quite considerably (50 C-mole/m³). This undegraded feed, however, was quickly utilised after 4 hours of shock load commencement and reached below the detected level soon after the normal feed was restored. The accumulated lactic acid was also consumed rapidly in less than 4 hours. Other organic acids (acetate, propionic and butyric acids) only increased marginally. A notable increase in propionic and acetic acids shortly after the feed shock load termination was the result of the lactic acid degradation. Overall, the dramatic increase in the total effluent organic acids concentration was rapidly consumed and returned to the pre-shock level in less than 12 hours. The accumulation of undegraded feed, lactate, propionate, and butyrate was modelled quite accurately. The apparent overestimation of acetate concentration was perhaps due to the model simplification which includes only those four acid species. As shown in Fig. 11, although the feed shock load led to an increased concentration of the final effluent total acids, the level of these acids were rapidly decreased to the pre-shock value in less than 12 hours.

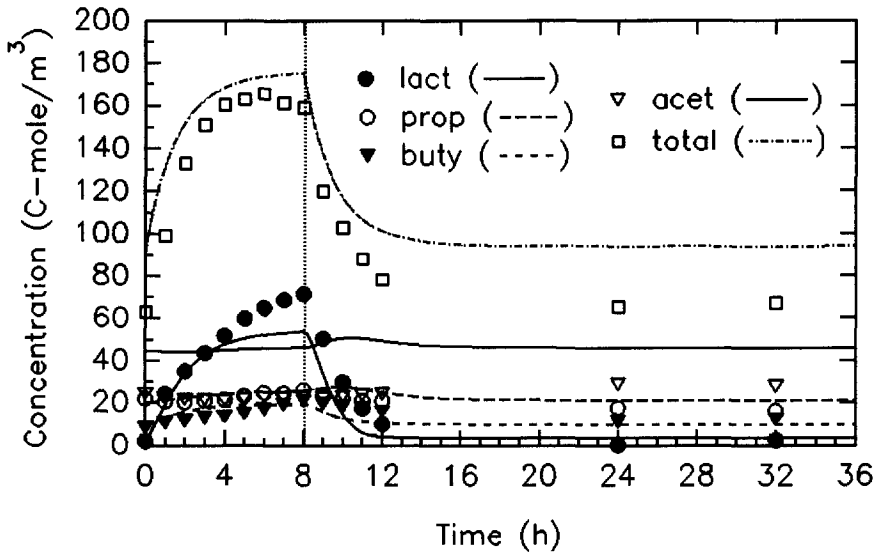


Fig. 10. Effect of a step increase in feed concentration on the effluent organic acids concentrations in Reactor 1

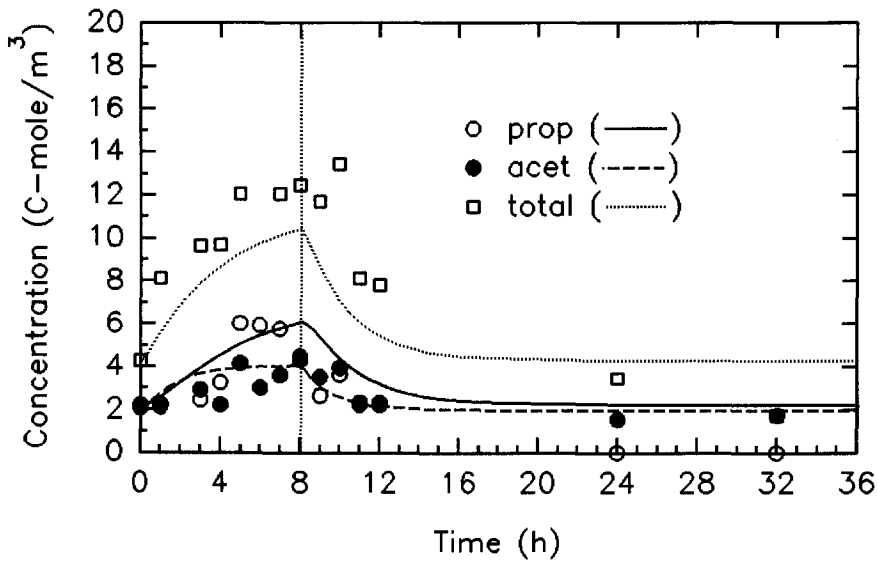


Fig. 11. Effect of a step increase in feed concentration on the effluent organic acids concentration in Reactor 2

CONCLUSIONS

This study shows that lowering the pH of the acidification reactor in two-stage anaerobic treatment processes could result in the reduction of alkali requirement. By decreasing the pH setpoint of the first

reactor from 6.0 to 5.3, an approximate 30% saving in alkali addition could be achieved without significantly deteriorating the final effluent quality. The model prediction has been shown to confirm this observation. It has also been shown that the model predicts well the effect of lowering the pH of the acidification reactor on other reactor variables.

The dynamic response of the two-stage system operated at low pH shows the ability of the reactors to withstand a short-term concentration shock load. Despite the fact that the shock load leads to an increase in the final effluent total acids, the system does recover as soon as the normal load is restored. Good agreement between the measured and the predicted results for most of reactor variables shows the applicability of the model to be used as a tool for design and operational evaluation of two-stage anaerobic reactor configurations.

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