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SLUDGE DIGESTION BY ANAEROBIC FLUIDIZED BEDS. II: KINETIC MODEL

By Bill T. Ray,¹ Member, ASCE, Ju-Chang Huang,² Fellow, ASCE, and Brian A. Dempsey³

ABSTRACT: A model has been developed to describe the gas production and soluble-COD variations from the digestion of waste-activated sludge in the anaerobic fluidized-bed reactor. It indicates that a substantial rate increase can be attained by prehydrolysis of the biological sludge, external to the reactor. The model indicates that the rate-limiting step is in the sludge hydrolysis. The model is developed from an assumption of first-order kinetics in a set of series and parallel, irreversible reactions. That is, the formation of soluble substrate is first order with respect to the particulate biomass present, and that the production of methane is first order with respect to the soluble substrate present. The amount of particulate biomass can be approximated by the sludge-suspended solids and that the amount of soluble substrate can be approximated by the soluble COD present in the reactor. The model correlates well with the laboratory data observed in the study.

INTRODUCTION

Anaerobic digestion processes have been used for many years in the treatment of wastewater. The advantages include low energy input, low biomass synthesis, low nutrient requirements, and production of methane gas as a useful by-product. The feasibility and the performance data of using an attached-film, anaerobic fluidized-bed system to achieve an accelerated stabilization of waste-activated sludge are described in Part I of this paper (Huang et al. 1989). The fluidized-bed reactors were batch fed with continuous sludge recirculation for fluidization. It was found that at 35°C, an adequate degree of stabilization could be obtained within a 1–2 day hydraulic retention time (HRT) if the influent sludge was presolubilized with 17.5 meq/L of NaOH. On the other hand, if no presolubilization was used, the necessary HRT would be increased to 10 days. Presolubilization is beneficial mainly because the rate-limiting step in the anaerobic digestion of waste-activated sludge (WAS) is cellular hydrolysis of the bacterial capsule (Gossett and Belser 1982).

The present paper evaluates the steady-state-performance data reported in the aforementioned paper (Huang et al. 1989), and also examines the kinetics in a series of sequential reactions during the sludge-digestion process. The objective of the present study was to formulate a model from the observed experimental data. This paper presents the model development, and then compares the model with the actual laboratory results.

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LITERATURE REVIEW

The literature review is divided into two sections. One is concerned with the rate-limiting step and the other with the ultimate sludge biodegradability in the anaerobic digestion process. Both of these factors are important to the overall performance of anaerobic sludge digestion. The rate-limiting step will, of course, determine the rate of sludge stabilization. The ultimate biodegradability will determine the extent to which the sludge can be stabilized. The reader may wish to refer to Part I of this paper (Huang et al. 1989) for other literature relevant to fluidized-bed reactors.

Rate-Limiting Step of Anaerobic Sludge Digestion

Gossett and Belser (1982) presented a first-order model for the decay of the activated sludge into a usable substrate for the anaerobic organisms present in a digester. They showed cellular hydrolysis to be the rate-limiting step in the digestion of WAS. In contrast to this, the rate of acetate formation was shown by O'Rourke (1968) to be the rate-limiting step in the digestion of primary settled sludge. Fig. 1 illustrates the generally accepted three-step model for anaerobic digestion. The findings by Gossett and Belser (1982) are important to anaerobic digestion of WAS since the rate of digestion can be improved by increasing the rate of cellular hydrolysis. Such hydrolysis can even be accomplished external to the digester.

Haug et al. (1978) digested thermally pretreated sludge, and found that pretreatment greatly improved the digestibility of WAS, but had almost no effect with primary sludge. The thermal pretreatment resulted in a substantial amount of cellular hydrolysis, thus increasing the soluble chemical oxygen demand (COD). Similarly, Stuckey and McCarty (1978) used thermochemical pretreatment to increase the soluble portion of WAS to improve its digestibility. The thermochemical-pretreatment process increased the sludge biodegradability from approximately 50% to 85%.

Ghosh et al. (1987) investigated a two-stage digestion process in which acidogenesis was performed separately from methanogenesis. The feed sludge was an unspecified sludge from the Chicago Metropolitan Sewer District. The upflow digesters were used to increase the solids-retention time above the hydraulic-retention time. They found that the system greatly improved the digestion process. When compared with a conventional single-stage complete-mix digester, the performance of the two-stage system was almost always superior. At an operating temperature of 35° C, the two-stage system had a volatile solids (VS) removal of 53.8% at a 15 day HRT, 42.8% at a 7 day HRT, and 28.5% at a 3 day HRT. The conventional system had VS removals of 29.1%, 28.8%, and 14.9%, respectively.

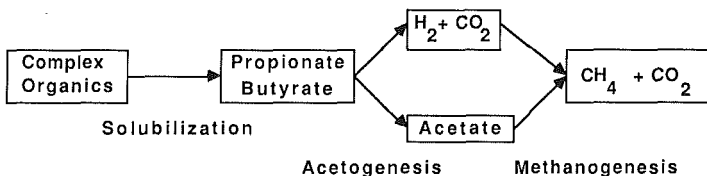


FIG. 1. Three-Step Model of Methane Conversion

Hall and Jovanovic (1983) performed a field study using different anaerobic processes to treat thermally conditioned sludge liquor. One of the systems involved a fluidized bed, which was able to achieve a total COD removal of 50% at an HRT of 13 hr. This indicates that the fluidized-bed reactor is capable of treating solubilized-sludge waste streams at very high loading rates. Sludge presolubilization, by whatever means, seems to reduce the influence of sludge hydrolysis as the rate-limiting step in the digestion process. This concept is supported by the work of Gossett and Belser (1982), Haug et al. (1978), Stuckey and McCarty (1978), and Hall and Jovanovic (1987). Recently, a simplified algebraic expression for biofilm kinetics was developed for a single-substrate system condition (Suidan and Wang 1985). The algebraic expression relates the substrate-utilization rate to its concentration at the biofilm surface and the thickness of biofilm. However, in a system that digests sludge solids, the modeling of kinetics is considerably more complex than the single-substrate system.

Sludge Biodegradability

A portion of wastewater-treatment sludge consists of refractory organics, which may be biodegradable, but not under the normal environmental conditions existing in an anaerobic digester (Gossett and Belser 1982; Ghosh et al. 1987; Hall and Jovanovic 1983; Malay and Fadrus 1971). Malay and Fadrus (1971) found that only 50% of the volatile solids from a mixed primary-secondary sludge were biodegradable. However, they did not specify the proportions of primary and secondary sludge. Their laboratory evaluation consisted of taking the mixed sludge and allowing it to digest for extended periods of time, after seeding with an initial acclimated inoculum. The digesters were then monitored for 105–186 days. In all cases, the ultimate destruction of VS was approximately 50% of the initial amount. They also found that temperature affected the digestion rate in the range of 20–50° C, but not the ultimate extent of VS destruction or methane-gas production.

Hindin and Dustan (1960) describe the effects of detention time on the anaerobic digestion process. Using a mixed primary-trickling-filter sludge, they studied HRTs from 5 days to 90 days. With a detention time of 20–90 days they were able to obtain a VS reduction of approximately 80%. When the HRT was reduced to below 20 days, the VS removal was greatly reduced. As expected, the shorter the HRT, the lower the VS removal and gas production.

Ghosh et al. (1987) also investigated the ultimate biodegradability of sludge. At temperatures ranging from 35° C to 55° C and HRTs from 3 days to 15 days, the ultimate VS removals were estimated to be from 56% to 59%.

In addition to their findings on cellular hydrolysis, Gossett and Belser (1982) also noted that the sludge age in the activated-sludge reactor significantly affected the required digestion time. Generally, a longer sludge age required a longer digestion time to achieve a given level of VS destruction, and this also resulted in a lower net-sludge production.

It thus appears that although the relative amount may vary among different digesters, a substantial portion of the sewage sludge is resistant to anaerobic biological degradation. The reported amount of COD and volatile suspended solids (VSS) not amenable to anaerobic degradation seems to vary from 15% (Stuckey and McCarty 1978) to as high as 50% (Malay and Fadrus 1971).

REACTION MODEL

The experimental results obtained in this study can be used to develop a simple model that describes the reaction kinetics and also adequately explains the limiting step in the digestion process. The model is intended to give an insight into the sequential reactions inside the AFB reactor. Several simplifications and assumptions have been made in developing this model. For example, the attached and suspended biomass have not been incorporated into the model since there is no practical way to differentiate quantitatively among the hydrolytic heterotrophs, acid and methane formers. The model assumes first-order, irreversible, parallel, and series reactions. Mass transfer of substrate is considered to be fast relative to the rate of biological conversion (ultimately) to methane. Therefore, this is one reason mass transfer is not included in the model.

Three different feed sludges were used in the project, as described in Part I (Huang et al. 1989). In general, the untreated sludge (with a low initial soluble COD of 350 mg/L) in Reactor 1 had the lowest initial, but the highest final, gas-production rate in a feeding cycle (Fig. 2). In contrast, the presolubilized sludge in Reactor 3 (with the initial soluble COD of 3,300 mg/L) had the highest initial, but the lowest final, gas-production rate. The reactor receiving the partially presolubilized sludge had intermediate gas-production rates at both the beginning and end of each cycle. These generalizations are true for all the HRT data at 35° C.

In the comparison of the graph of cumulative gas production versus time (Fig. 2) and the graph of soluble COD versus time (Fig. 3) there are strong indications that beyond the first six hours after feeding there is no substantial further reduction of soluble COD, while the methane production continues to proceed at a slow, yet steady rate. This suggests that inert soluble COD is continuously produced through sludge hydrolysis at a rate equal to the biodegradable soluble COD's being converted to methane gas. For practical purposes most of the soluble COD remaining after the first six hours of feeding can be considered recalcitrant. Upon a new feeding, the soluble COD in Reactor 1 increases only slightly, but the gas-production rate increases sharply. This indicates that immediately after feeding, an appreciable amount of new biodegradable soluble COD is again made available to the methane bacteria. It is also significant to note that both Reactors 2 and 3 have an initial soluble COD of only 1.5–2.5 times greater than the final soluble COD, but their initial gas-production rates are 5–10 times greater than their final gas-production rates. Again toward the end of the feeding cycle, most of the remaining soluble COD is relatively inert; only a small fraction is biodegradable, and it is still being converted to methane while an equal amount of new inert soluble COD is added to the system through sludge hydrolysis. As a result, the overall soluble COD remains relatively constant. Thus, to construct a reasonable model of the AFB process, it is necessary to divide the sludge matter (both particulate and soluble) into biodegradable and inert fractions. It is also reasonable to postulate that: (1) The rate of biodegradable soluble COD production is first order with respect to the amount of particulate COD in the system; (2) the rate of methane-gas production is first order with respect to the amount of biodegradable soluble COD in the system; and (3) the two reactions occur in series. A further division of the particulate COD is accomplished by dividing this fraction into a readily hydrolyzable

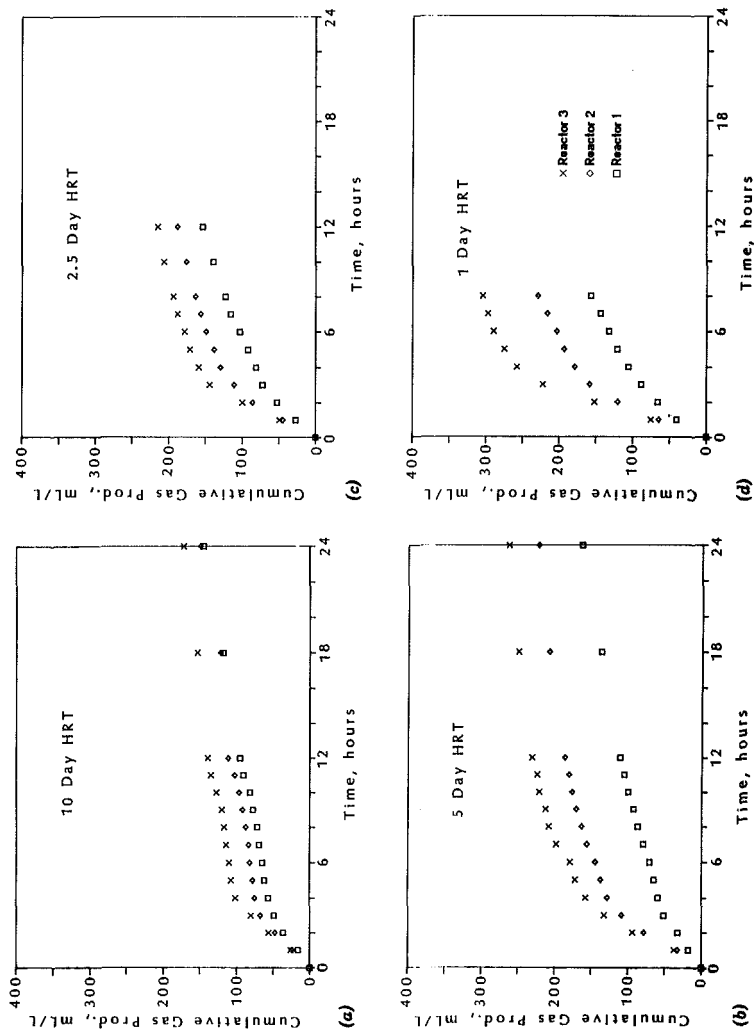


FIG. 2. Actual Gas Production

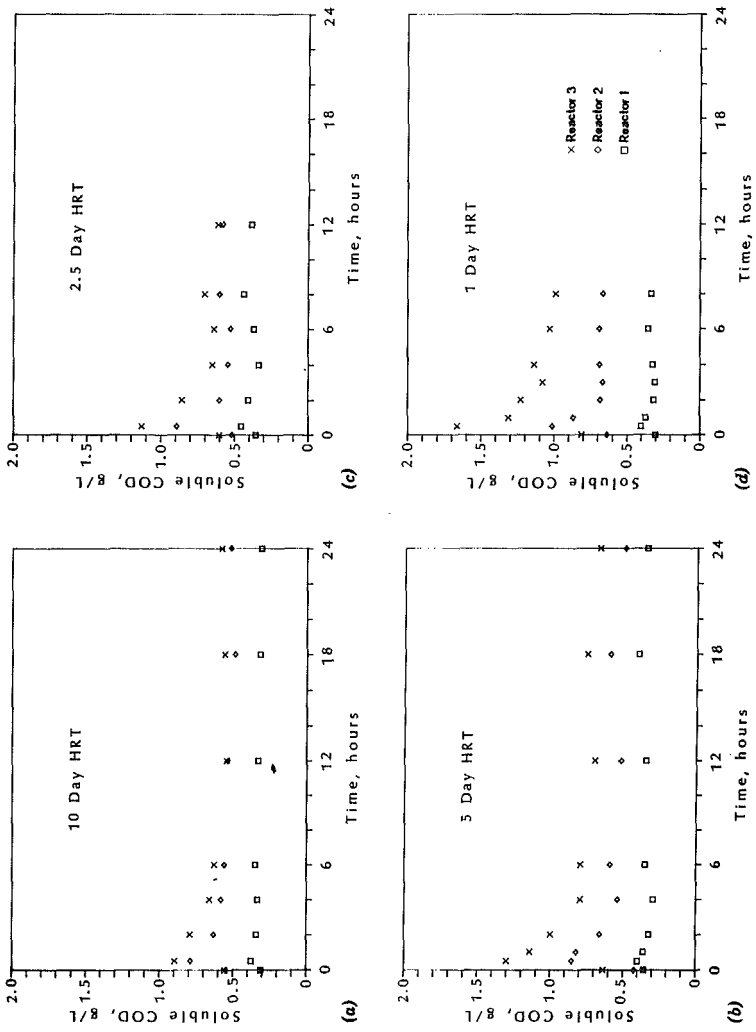


FIG. 3. Actual Soluble COD

portion, possibly cell wall, cell membrane, glycocalyx, and other material external to the cell membrane (Costerton et al. 1978) and a slowly hydrolyzable portion, cellular contents.

MODEL DEVELOPMENT

Using the concept of a two-substrate feed (soluble COD and particulate COD), a model was developed that predicts the gas production as a function of time. The currently accepted three-step reaction is shown in Fig. 1. This model assumes that the complex organic matter is first converted to acetate precursors (butyrate, propionate), and that the precursors are then converted to acetate, which in the final step is converted to methane. This is a three-step reaction, which can be represented by the following lumped reactions:

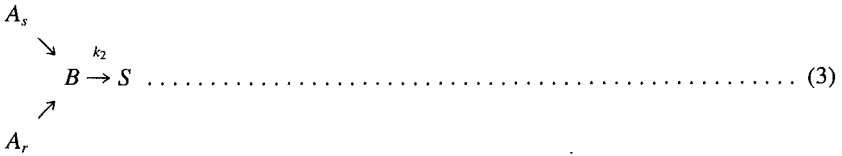


where A = complex organics; B = acetate precursors; R = acetate; and S = methane. It should be noted that this is a very simplified approach to the actual process. There may be multiple series and parallel reactions that are actually occurring, but it is postulated that this may represent, in a lumped sense, the more complex chemical-reaction network. Also, this model does not account for the methane produced by the hydrogen-carbon-dioxide pathway; Lawrence and McCarty (1969) have found that 70% of the methane generated in an anaerobic digester is produced by the acetate path.

A slightly different kinetic model than the one given by Eq. 1 has been constructed to describe the results of these fluidized-bed experiments. In this model it is assumed that the conversion of acetate to methane is very fast in relation to the conversion of the acetate precursors to acetate. This assumption is supported by two observations. First, the organic-acid concentration in the reactor was usually below 75 mg/L, indicating that organic acids were being consumed as rapidly as they were formed. Second, O'Rourke (1968) found that the maximum specific rate of substrate utilization for acetate was 6.7 g BOD/g VSS per day. With VSS concentrations in the reactors of this study in the range of 5–10 g VSS/L, this would mean k_3 is much greater than either k_1 or k_2 . Additionally, since the AFB digester is a fixed-film system, the concentration of active methanogenic bacteria should be higher in this system than in a conventional suspended-growth digester. Therefore, the assumption of the very fast reaction from acetate to methane is more appropriate here than in a conventional suspended-growth system. Thus the model can be reduced to the form



However, although our final gas-production rate can easily be modeled using the reaction set (Eq. 2), the initial gas-production rates are underpredicted by this model. This led to the concept that the particulate matter is composed of materials having two different reaction rates. Thus it is necessary to divide the particulate biodegradable matter (A) into two fractions, one rapidly biodegradable (A_r) and the other slowly biodegradable (A_s). With this provision, the reaction can then be depicted as



Also, it was assumed that the acetate precursors (*B*) could be approximated by the soluble biodegradable COD. Thus, the concentrations of the reactants and products are *A_s* = slowly biodegradable particulate (nonfilterable) COD, mg/L; *A_r* = rapidly biodegradable particulate (nonfilterable) COD, mg/L; *B* = soluble (filterable) COD, mg/L; and *S* = methane COD, mg/L.

Assuming that the reactions are first-order irreversible, that 40% of COD (both soluble and particulate) is inert (Ghosh et al. 1987; Hall and Jovanovic 1983; Malay and Fadrus 1971), and that *A_r* represents 5% of the particulate biodegradable COD, the reaction set can be solved explicitly. The apparent reactions (Eqs. 1–3) are being modeled as elementary reaction steps, and their rates are given as follows:

$$r_{A_s} = -k_{1s}C_{A_s} \dots\dots\dots (4)$$

$$r_{A_r} = -k_{1r}C_{A_r} \dots\dots\dots (5)$$

$$r_B = k_{1s}C_{A_s} + k_{1r}C_{A_r} - k_2C_B \dots\dots\dots (6)$$

$$r_S = k_2C_B \dots\dots\dots (7)$$

The initial conditions are

$$C_{A_s} = C_{A_s0} \dots\dots\dots (8)$$

$$C_{A_r} = C_{A_r0} \dots\dots\dots (9)$$

$$C_B = C_{B0} \dots\dots\dots (10)$$

$$C_S = 0 \dots\dots\dots (11)$$

For a batch reactor the reaction rate varies with time as follows:

$$r_{A_s} = \frac{dC_{A_s}}{dt} \dots\dots\dots (12)$$

$$r_{A_r} = \frac{dC_{A_r}}{dt} \dots\dots\dots (13)$$

$$r_B = \frac{dC_B}{dt} \dots\dots\dots (14)$$

$$r_S = \frac{dC_S}{dt} \dots\dots\dots (15)$$

Solution of the set of differential equations yields

$$C_{A_s} = C_{A_s0} \exp(-k_{1s}t) \dots\dots\dots (16)$$

$$C_{A_r} = C_{A_r0} \exp(-k_{1r}t) \dots\dots\dots (17)$$

$$C_B = \frac{k_{1s} C_{As0}}{k_2 - k_{1s}} [\exp(-k_{1s}t) - \exp(-k_2t)] + \frac{k_{1r} C_{Ar0}}{k_2 - k_{1r}} [\exp(-k_{1r}t) - \exp(-k_2t)] + C_{B0} \exp(-k_2t) \dots \dots \dots (18)$$

$$C_S = C_{As0}[1 - \exp(-k_{1s}t)] + C_{Ar0}[1 - \exp(-k_{1r}t)] + C_{B0}[1 - \exp(-k_2t)] - \frac{k_{1s} C_{As0}}{k_2 - k_{1s}} [\exp(-k_{1s}t) - \exp(-k_2t)] - \frac{k_{1r} C_{Ar0}}{k_2 - k_{1r}} [\exp(-k_{1r}t) - \exp(-k_2t)] \dots \dots \dots (19)$$

COMPARISON WITH EXPERIMENTAL DATA

Using the aforementioned assumptions, the model was calibrated using the gas production and soluble COD at each examined HRT. The soluble COD in the reactor prior to feeding was assumed to be inert. Best fits were determined by visual evaluation of the data points as shown in Fig. 4. The following rate constants were obtained: k_{1s} of 0.18 per day, k_{1r} of 16.8 per day, and k_2 of 12.0 per day.

The modeled gas production is compared with the observed data in Fig. 4. Data are shown for HRTs of 10 days, 5 days, 2.5 days, and 1 day. The graphs indicate a reasonably good fit. It appears that the unsolubilized influent sludge has a slightly higher initial solubilization rate than the model indicates. This is reasonable since the kinetic constants for the model were lumped for all three reactors. This indicates that in the actual biological hydrolysis, or in acidogenesis, kinetic constant k_2 varies to some extent for the three different sludges, which is not unexpected. However, the initial and final gas-production rates are predicted reasonably well for all three reactors. Also, the model is not normalized for the biomass concentrations and this may lead to error.

The model assumes that mass transfer does not limit the rate of reaction. This assumption can now be evaluated based on the derived constants. For this analysis it is assumed that solubilization of particulate COD occurs in the bulk solution and therefore the rate of mass transfer should be compared with the conversion of soluble COD to methane, for which $k_2 = 12.0$ per day, and the rate of conversion (R_s) will be $12.0C_B$. The calculated thickness of the biofilm was 10–20 μm , so that the biofilm plus stagnant film thickness may be 50 μm . The diffusion coefficient, modified by the tortuosity term, is conservatively estimated to be $10^{-6} \text{ cm}^2/\text{s}$, and the surface-area-to-volume ratio is calculated to be at least 20 cm^{-1} , giving a k_{1a} value of at least 350 per day. The rate of mass transfer across the stagnant plus biofilms is estimated to be $k_{1a}(C_B - C_{B0})$, where C_{B0} = the concentration at the sand-biofilm interface. The rate of mass transfer and biological conversion would then be equal if the concentration gradient ($C_B - C_{B0}$) were only 5% of C_B . This represents an insignificant decrease in the overall rate of bioconversion. The effects of mass transfer are expected to be even less significant than indicated since conservative estimates were used in these calculations and since some of the bioconversion takes place via suspended growth.

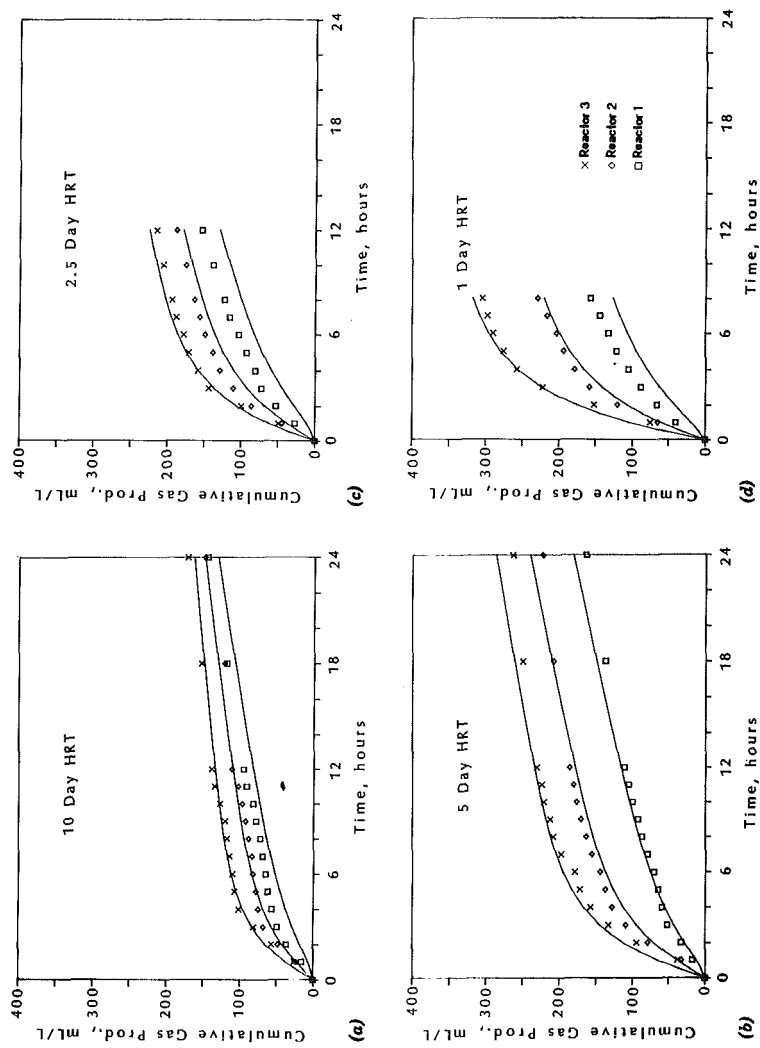


FIG. 4. Predicted Gas Production

The model can also be used to predict the COD removal (during the batch cycle) and the soluble-COD value at the end of the cycle. Fig. 5 is a plot of predicted versus actual soluble CODs for the different reactors. The soluble COD predictions agree well with the actual data.

The model gives considerable insight into the rate-limiting step in the reactor. The model predicts high initial gas production rates for the reactors receiving either solubilized or partially solubilized sludge. The model also predicts a lower secondary-gas-production rate after the soluble substrate has been utilized. Thus, the model assumes that the initial gas-production rate is proportional to the available soluble substrate and that the final gas-production rate is proportional to the particulate biomass concentration. The validity of these observations appears to be supported by the actual experimental results.

As noted, Gossett (1982) found that waste-activated-sludge digestion is rate limited by solubilization. In contrast O'Rourke (1968) found that primary sludge digestion was rate limited by methanogenesis. Gossett originally assumed that O'Rourke's model was applicable to waste-activated-sludge digestion, but later found that was not the case. Gossett hypothesized that difficulty in degrading the cellular capsule caused the solubilization step to be rate limiting. By autoclaving waste-activated sludge to rupture the cellular capsule, Gossett was able to use O'Rourke's model. The findings here tend to support Gossett's contention that solubilization is the rate-limiting step for waste-activated-sludge digestion. Other indications of this are found in studies such as Hall and Jovanovic (1983). These findings also lead to the possibility of using the AFB digester for the treatment of primary sludge. If the primary sludge is in fact rate limited by methanogenesis as O'Rourke found, then it should be well suited for digestion by this process.

MODEL SENSITIVITY

The sensitivity of the model to changes in each of four model parameters has been tested and some results are shown in Table 1. Only the percentage change in net gas production at 3 hr and at the end of the cycle are shown in the table, although each individual set of values for the four parameters results in the prediction of net gas production and the soluble and particulate COD over time for each of four HRTs and three presolubilization treatments (i.e., 36 curves are generated for each set of parameter values). It is important to note that the reactors were fed once each day for hydraulic-retention times (HRT) of 10 and 5 days, every 12 hr for an HRT of 2.5 days, and every 8 hr for an HRT of one day.

The sensitivity analysis indicates that the concentration of rapidly solubilized particulate COD (C_{Aro}) has a significant effect on the net gas production at the end of each feeding cycle. The half-time for the solubilization of C_{Aro} is 1.0 hr and the half-time for conversion of soluble COD to methane is 1.4 hr, so that most of the C_{Aro} will be converted to methane within a single feeding cycle. A +10% increase in C_{Aro} has greater effect on Reactor 1 than Reactor 3 because Reactor 1 has the highest C_{Aro} . There is very little sensitivity to k_{1s} since most of the C_{Aro} is converted to methane within one cycle. The half-time for the slowly solubilized particulate COD (C_{Asd}) is much longer, so that an increase in k_{1s} results in a large increase in the net gas-production rate, especially when the time for a single cycle is longer (the

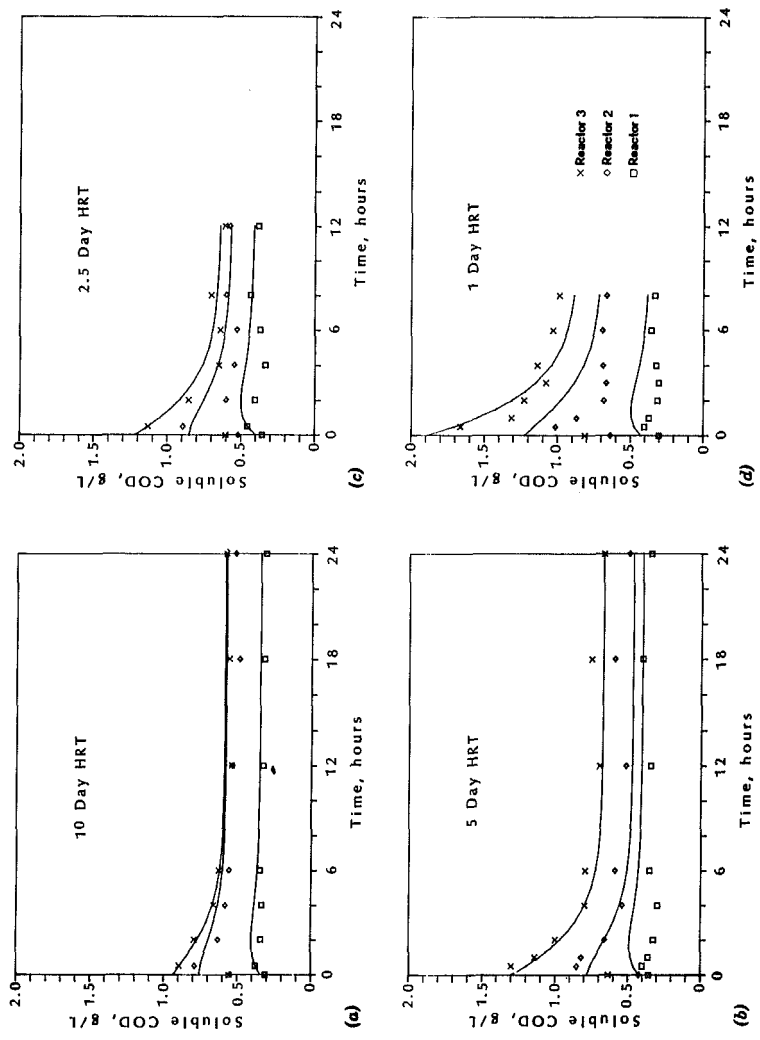


FIG. 5. Predicted Soluble COD

TABLE 1. Sensitivity Analysis Results

HRT (1)	Reactor (2)	PARAMETER							
		C_{Aro}		k_{1s}		k_{1r}		k_2	
		Change (%)		Change (%)		Change (%)		Change (%)	
		+10 (3)	-10 (4)	+10 (5)	-10 (6)	+10 (7)	-10 (8)	+10 (9)	-10 (10)
(a) Change in Net Gas Production at End of Cycle (%)									
10	1	2.1	-2.1	6.4	-6.5	0.0	0.0	0.5	-0.7
10	2	1.5	-1.4	4.5	-4.6	0.0	0.0	0.4	-0.5
10	3	1.0	-1.0	3.1	-3.1	0.0	0.0	0.3	-0.3
5	1	2.0	-2.0	6.1	-6.3	0.0	-0.1	0.5	-0.7
5	2	1.4	-1.4	4.4	-4.5	0.0	0.0	0.4	-0.5
5	3	1.0	-1.0	3.1	-3.2	0.0	0.0	0.2	-0.3
2.5	1	3.6	-3.6	5.1	-5.2	0.1	-0.1	1.1	-1.3
2.5	2	2.2	-2.2	3.1	-3.2	0.1	-0.1	0.7	-0.9
2.5	3	1.4	-1.4	2.0	-2.0	0.0	-0.0	0.5	-0.6
1	1	3.9	-3.9	3.5	-3.6	0.2	-0.4	1.6	-2.0
1	2	2.0	-2.0	1.8	-1.8	0.1	-0.2	1.1	-1.5
1	3	1.1	-1.1	1.0	-1.0	0.1	-0.1	0.9	-1.3
(b) Change in Net Gas Production at End of 3 hr (%)									
10	1	5.9	-5.6	2.4	-2.1	2.4	-2.8	5.2	-5.6
10	2	2.3	-2.3	0.9	-0.9	1.0	-1.0	4.5	-5.1
10	3	1.2	-1.2	0.5	-0.5	0.5	-0.6	4.2	-4.9
5	1	5.1	-5.1	2.1	-1.9	2.3	-2.3	5.1	-5.6
5	2	1.8	-2.2	0.8	-0.8	1.0	-1.1	4.4	-5.1
5	3	1.2	-1.2	0.5	-0.5	0.5	-0.6	4.2	-4.9
2.5	1	5.8	-5.8	2.2	-2.2	2.5	-2.9	5.2	-5.8
2.5	2	2.4	-2.4	1.0	-1.0	1.1	-1.2	4.5	-5.1
2.5	3	1.3	-1.3	0.5	-0.5	0.6	-0.7	4.3	-4.9
1	1	4.6	-4.5	1.9	-1.7	2.1	-2.2	4.9	-5.4
1	2	1.8	-1.8	0.7	-0.6	0.8	-0.8	4.4	-4.9
1	3	0.9	-0.9	0.4	-0.4	0.4	-0.4	4.2	-4.8

cycle is 1 day for HRTs of 10 and 5 days).

C_{Aro} and k_2 are the important parameters for fitting the net gas production at 3 hr, since only a few reaction half-times have occurred for the k_{1r} and k_2 reactions.

CONCLUSIONS

The following conclusions are supported from the model and the available data.

1. The gas production in the fluidized-bed reactor at varying HRTs and degrees of solubilization can be modeled by assuming that the initial gas-production rate is proportional to the soluble biodegradable substrate, while the final gas-production rate is proportional to the particulate biodegradable substrate.
2. The solids reduction and the soluble COD remaining in the reactor are also

predicted well by using the same assumptions.

3. The model confirms that the rate-limiting step in the digestion of WAS is the conversion of a particulate biomass into a soluble substrate, rather than the conversion of soluble organics to acetate or acetate to methane.

4. Other particulate or biological wastes may be amenable to treatment in a fluidized-bed reactor if a proper method of solubilization is developed.

APPENDIX I. REFERENCES

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APPENDIX II. NOTATION

The following symbols are used in this paper:

- A = complex organics;
 A_s = slowly biodegradable particulate (nonfilterable) COD, mg/L;
 A_r = rapidly biodegradable particulate (nonfilterable) COD, mg/L;
 B = acetate precursors or soluble (filterable) COD, mg/L;
 C_{Aro} = initial rapidly biodegradable particulate (nonfilterable) COD, mg/L;
 C_{Aso} = initial slowly biodegradable particulate (nonfilterable) COD, mg/L;
 k_1 = solubilization-rate constant;
 k_{1r} = solubilization-rate constant for rapidly biodegradable material, per day;

- k_{1s} = solubilization-rate constant for slowly biodegradable material, per day;
 k_2 = acetogenesis-rate constant, per day;
 k_3 = methanogenesis-rate constant, per day;
 R = acetate; and
 S = methane COD, mg/L.