The effects of hydraulic retention time and feed COD concentration on the rate of hydrolysis of primary sewage sludge under methanogenic conditions

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Abstract A series of completely mixed methanogenic anaerobic digesters have been operated to determine the rate of hydrolysis of primary sewage sludge. The hydraulic retention time was reduced from 60 d to when the system failed (~5 d), while the feed COD concentration was 40, 25, 13 and 2 gCOD/L. A steady state model based on first order kinetics was developed to simulate the hydrolysis rate at each retention time and feed concentration. With the mean value for the hydrolysis rate constant (0.992 ± 0.492 d^{-1}), this model was able to accurately predict the effluent COD for all steady state operating conditions. However, the effluent COD concentration was relatively insensitive to the exact value for this constant. The model provides a framework for analysis of anaerobic digestion experimental data, to enable meaningful comparisons.

Keywords Anaerobic digestion; feed COD concentration; first order kinetics; hydraulic retention time; hydrolysis; primary sewage sludge

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Introduction

In the anaerobic digestion of particulate organic matter such as primary sewage sludge (PSS), the rate of hydrolysis is typically the rate-limiting step. Consequently, for the design and operation of anaerobic digesters it is important that this rate be accurately quantified. Many studies have been conducted to determine the rate of hydrolysis, and to quantify the effects of system and operating parameters on this rate. However, the results from these studies are not directly comparable, due to differences in the experimental set-up or procedures, or in the aims of the individual studies. For example, O'Rourke (1968) operated a series of completely mixed anaerobic digesters at varying hydraulic retention times (HRT) and system temperatures, with a feed PSS concentration of 28.4 gCOD/L, to determine the effects of reduced temperatures on the kinetics of solids degradation. Miron *et al.* (2000) studied the effects of sludge retention time (SRT) on the rate of hydrolysis of PSS in order to determine the optimum SRT for a single or two-step UASB system. The feed concentration was 30.9 gCOD/L and the systems operated at 25 °C, but to mimic UASB systems, digesters intermittently mixed at 100 rpm for 20 s/20 min were used, introducing differences in the mass transfer of soluble components between their systems and those of O'Rourke (1968).

Izzett *et al.* (1992) aimed to determine the effects of thermal sludge pre-treatment on the kinetics of hydrolysis, and operated completely mixed digesters fed a mixture of PSS and humus sludge at 37 °C, but with a feed concentration of 40 gCOD/L (compared to 28.4 gCOD/L from O'Rourke, 1968). Veeken *et al.* (2000) studied the effects of pH and VFA on the hydrolysis of biowaste, which has a different composition to PSS, and thus it is uncertain whether a system fed PSS would respond in the same way. The study was also performed in a packed-bed type reactor with high hydraulic recycling to simulate completely mixed conditions. Eastman and Ferguson (1981) studied the effects of pH, HRT and substrate concentration on the acid-phase hydrolysis of PSS at low HRTs (9–72 h),

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acknowledging that high concentrations of hydrolysis products may inhibit the hydrolytic enzymes. Therefore, these results could not be compared to those from the other studies.

Recognising the difficulties in standardising the observations in the literature on anaerobic digestion of PSS, a study was undertaken to determine the effects of HRT, feed COD concentration, pH, methanogenesis and sulphate-reduction on the rate of hydrolysis of PSS at 35 °C in identically operated completely-mixed digesters (Ristow *et al.*, 2005). This would enable any important factors influencing the hydrolysis processes to be isolated and quantified. The results of the effects of HRT and feed concentration under methanogenic conditions will be presented in this paper.

Hydrolysis model development

The aim of the study was to determine the rate of hydrolysis of PSS under varying hydraulic retention times and feed COD concentrations. Hydrolysis is defined as the extra cellular enzymatic breakdown of polymers (particulate) into monomers and dimers (soluble), which enter the subsequent acidogenesis reactions. To determine and quantify the rate of hydrolysis for a given steady state digester, a steady state model was developed.

Model assumptions

The model was developed from mass balances for the particulate biodegradable COD, the soluble biodegradable COD (hydrolysis products), the volatile fatty acids (acidogenesis products) and the acidogenic and methanogenic biomass concentrations (Figure 1). The model was based on the following assumptions.

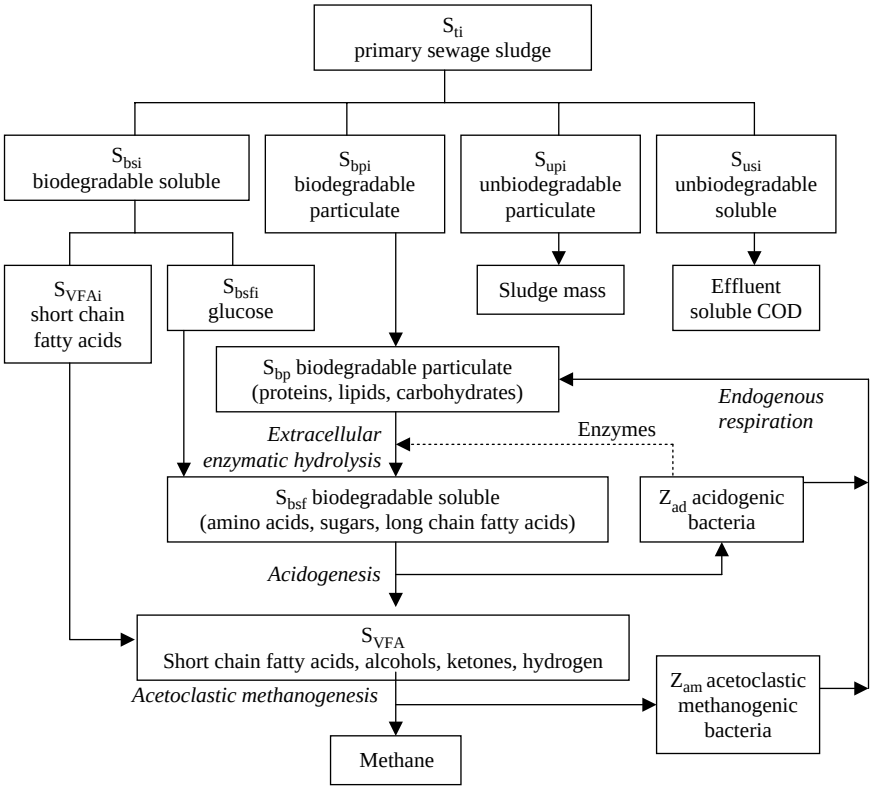

Figure 1 Schematic diagram (in units of COD) of the bulk processes involved in the anaerobic digestion of primary sewage sludge

- The PSS total COD (S_{ti}) consists of an unbiodegradable particulate fraction (S_{upi}), a biodegradable particulate fraction (S_{bpi}), an unbiodegradable soluble fraction (S_{usi}), a biodegradable soluble non-VFA fraction (S_{bsfi}) and volatile fatty acids (S_{VFAi})

$$S_{ti} = S_{upi} + S_{bpi} + S_{usi} + S_{bsfi} + S_{VFAi}. \quad (1)$$

- Under stable operating methanogenic conditions, three organism groups act on the biodegradable COD, namely acidogens (Z_{ad}), acetoclastic methanogens (Z_{am}) and hydrogenotrophic methanogens (Z_{hm}).
- Hydrogenotrophic methanogen biomass (Z_{hm}) is considered negligible compared with the other active organism biomasses.
- The effluent total COD (S_t) consists of the unbiodegradable particulate fraction ($S_{up} = S_{upi}$), biodegradable particulate fraction (S_{bp}), unbiodegradable soluble fraction ($S_{us} = S_{usi}$) and the acidogenic and acetoclastic methanogenic biomasses (Z_{ad} and Z_{am}); under stable methanogenic conditions, the effluent biodegradable soluble non-VFA fraction (S_{bsf}) and volatile fatty acids (S_{VFA}) can be accepted to be negligible

$$S_t = S_{upi} + S_{bp} + S_{us} + Z_{ad} + Z_{am}. \quad (2)$$

- Active acidogenic and methanogenic biomass concentrations in the influent are negligible ($Z_{adi} = Z_{ami} = 0$).
- Acidogenic biomass grows according to Monod kinetics, using hydrolysis products as organic substrate.
- Acetoclastic methanogenic biomass grows according to Monod kinetics, using acidogenesis products (acetate) as organic substrate.
- Endogenous respiration of acidogenic and methanogenic biomass forms biodegradable particulate COD; endogenous residue formation is considered negligible.
- Effluent soluble biodegradable and VFA concentrations are negligible ($S_{bsf} = S_{VFA} = 0$) under stable methanogenic conditions (confirmed experimentally).
- PSS hydrolysis is mediated by the acidogens and rate limiting under stable digester operation.

Reaction stoichiometry

For the purpose of mass balances, the soluble biodegradable COD (S_{bs}) was given the molecular formula of glucose, while the short chain fatty acids (S_{VFA}) were assumed to be acetic acid only. The molecular formulae for the particulate organics and the active biomasses were taken from Sötemann *et al.* (2004) as $C_{3.5}H_7O_2N_{0.196}$ and $C_5H_7O_2N$, respectively. Therefore, for hydrolysis:

$$C_{3.5}H_7O_2N_{0.196} + 0.604H_2CO_3 \rightarrow 0.684C_6H_{12}O_6 + 0.293H_2O + 0.196NH_3 \quad (3)$$

For acidogenesis:

$$C_6H_{12}O_6 + Y_{ad}NH_3 \rightarrow Y_{ad}Z_{ad} + 2\left(1 - \frac{5}{6}Y_{ad}\right)CO_2 + 4\left(1 - \frac{5}{6}Y_{ad}\right)H_2 + 2\left(1 - \frac{5}{6}Y_{ad}\right)CH_3COOH \quad (4)$$

For acetoclastic methanogenesis:

$$CH_3COOH + Y_{am}NH_3 \rightarrow Y_{am}Z_{am} + \left(1 - \frac{5}{2}Y_{am}\right)CH_4 + \left(1 - \frac{5}{2}Y_{am}\right)CO_2 \quad (5)$$

Mass balances (as COD)

In order to determine the rates of hydrolysis, acidogenesis and methanogenesis, mass balances were developed for the major groups of substrates and products (Q = volumetric flow rate, L/day; V = reactor volume, L; b = relevant organism specific endogenous respiration rate constant, 1/d; Y = relevant organism yield, mgCOD/mgCOD).

Biodegradable particulate COD (S_{bp}) mass balance:

$$dS_{bp}.V = Q.S_{bpi}.dt - Q.S_{bp}.dt - V.rate_{hydrolysis}.dt + V.b_{ad}.Z_{ad}.dt + V.b_{am}.Z_{am}.dt \quad (6)$$

At steady state:

$$rate_{hydrolysis} = \frac{Q}{V}\left(S_{bpi} - S_{bp}\right) + b_{ad}.Z_{ad} + b_{am}.Z_{am} \quad (7)$$

Biodegradable fermentable soluble COD (S_{bsf}) mass balance:

$$dS_{bsf}.V = Q.S_{bsfi}.dt - Q.S_{bsf}.dt + V.rate_{hydrolysis}.dt - V.rate_{acidogenesis}.dt \quad (8)$$

At steady state, accepting

$$S_{bsf} = 0 : rate_{acidogenesis} = rate_{hydrolysis} + \frac{Q}{V}(S_{bsfi}) \quad (9)$$

Volatile fatty acid COD (S_{VFA}) mass balance:

$$dS_{VFA}.V = Q.S_{VFAi}.dt - Q.S_{VFA}.dt + 2\left(1 - \frac{5}{6}Y_{ad}\right).V.rate_{acidogenesis}.dt - V.rate_{methanogenesis}.dt \quad (10)$$

At steady state, accepting $S_{VFA} = 0$:

$$rate_{methanogenesis} = \frac{Q}{V}(S_{VFAi}) + 2\left(1 - \frac{5}{6}Y_{ad}\right) \times \left(\frac{Q}{V}\left(S_{bpi} + S_{bsi} - S_{bp}\right) + b_{ad}.Z_{ad} + b_{am}.Z_{am}\right) \quad (11)$$

Acidogenic biomass COD (Z_{ad}) mass balance:

$$dZ_{ad}.V = Q.Z_{adi}.dt - Q.Z_{ad}.dt + Y_{ad}.rate_{acidogenesis}.V.dt - b_{ad}.Z_{ad}.V.dt \quad (12)$$

At steady state:

$$Z_{ad} = \frac{Y_{ad}.rate_{acidogenesis}.R_h}{(1 + b_{ad}.R_h)} \quad (13)$$

Acetoclastic methanogenic biomass COD (Z_{am}) mass balance:

$$dZ_{am}.V = Q.Z_{ami}.dt - Q.Z_{am}.dt + Y_{am}.rate_{methanogenesis}.V.dt - b_{am}.Z_{am}.V.dt \quad (14)$$

At steady state:

$$Z_{am} = \frac{Y_{am}.rate_{methanogenesis}.R_h}{(1 + b_{am}.R_h)} \quad (15)$$

If equations 7, 9, 11, 13 and 15 can be solved simultaneously, the rates of hydrolysis, acidogenesis and methanogenesis can be calculated for experimental data measured on stable methanogenic anaerobic digesters. Accordingly, the equations were applied to experimental data gathered from a series of completely mixed anaerobic digesters operated over a range of conditions; see below.

Materials and methods

Reactor set-up and operation

A series of six completely mixed Perspex digesters with working volumes of 16 and 20 L were batch fed once or twice daily (depending on the feed volume) to simulate continuous operation while avoiding problems relating to pumping of PSS under laboratory conditions. For feeding, a volume of mixed liquor was removed from the tap at the bottom of the digester, and the feed volume added, after which the digester was refilled with the mixed liquor to the operating volume. After feeding, the headspace was purged with nitrogen (99.999%) to remove oxygen and the digester resealed. The wasted mixed liquor was analysed further. The temperature was controlled to 35 °C by a heating coil around the walls of the digester, with a thermocouple inside the digester liquid.

Feed collection and characterisation

PSS was collected in batches from the primary settling tanks at the Athlone Wastewater Treatment Works (Cape Town, South Africa) and stored at 4 °C. Each batch served as feed source for up to 7 months. The soluble fraction of the PSS changed during storage, and this (amongst others) was monitored so that the feed to the digesters at any time could be characterised (see Ristow *et al.*, 2005 for details). The PSS was screened through a 6.7 mm square mesh to remove large particles such as rags, cigarette butts, seeds and other debris, but without changing the nature of the feed by selecting an unreasonably small PSS particle size. For each feed, the PSS was diluted by weighing the required mass of PSS (measuring PSS volumes proved problematic) and adding the required mass of warm water (to around 35 °C).

Analytical methods

The reactor pH, gas volume production, effluent volatile fatty acid (VFA) and H_2CO_3* alkalinity concentration were measured daily until steady state operation was observed. Thereafter, additionally, the effluent total COD, soluble COD, TKN, free and saline ammonia (FSA), and total and soluble P and the gas composition were analysed. The pH was measured *in situ* to prevent errors due to CO_2 loss on sampling. Gas volumes were measured by a reticulating-float gas meter with a unit volume of around 50 mL/unit (calibrated to ± 0.1 mL/unit), and the number of units per time recorded. The VFA and H_2CO_3* alkalinity were measured using the 5-point titration method of Moosbrugger *et al.* (1992). Soluble samples were prepared by vacuum filtering (0.45 μm), and filtrates analysed for COD, TKN, FSA, total and soluble P (Standard Methods, 1985).

Experimental program

The digesters were operated at four different feed COD concentrations (40, 25, 13 and 2 gCOD/L), see Table 1. This covered the range at which anaerobic digesters would be

Table 1 Steady states measured for varying hydraulic retention times and feed COD concentrations (numbers are calculated COD mass balances)

Feed COD concentration (gCOD/L)	Hydraulic retention time (d)							
	60	20	15	10	8	6.67	5.71	5
40			103.4	103.4	102.7	100.9	103.3	
25		96.0	98.6	110.3	99.6	102.6	101.4	96.0
13			100.1	97.2	98.8	100.9	104.5	
9	100.0							
2				88.4	91.9			

expected to operate. At each feed concentration, the hydraulic retention times were reduced by increasing the feeding rate until the methanogenic bacteria washed out of the system, causing system failure, observed as an increase in the effluent VFA concentration. In the reduction, at selected retention times (Table 1), the systems were allowed to attain steady state (2–3 retention times) and analysed as described above. All reported steady state points were for systems with an effluent VFA concentration below 50 mg/L as HAc. Additionally, to measure the unbiodegradable particulate COD fraction, based on O'Rourke (1968), a system was operated at a 60-d retention time, where the biodegradable particulate COD concentration was expected to be completely depleted.

Calculation procedure

As noted above, if equations 7, 9, 11, 13 and 15 can be solved simultaneously, the rates of hydrolysis, acidogenesis and methanogenesis can be calculated for the experimental data measured on the methanogenic anaerobic digesters operated above over a wide range of conditions. This requires that the COD concentrations of each organic fraction in equations 1 and 2 be quantified. For the experimental systems, total COD, soluble COD ($<0.45\,\mu m$) and volatile fatty acids (VFA) were measured on both the influent and effluent. From Lilley *et al.* (1992) and this investigation (see Ristow *et al.*, 2005), the biodegradable soluble non-VFA fraction (S_{bsf}) and volatile fatty acid (S_{VFA}) COD concentrations could be accepted to be equal. This leaves the unbiodegradable particulate fraction (S_{up}), biodegradable particulate fraction (S_{bp}) and unbiodegradable soluble fraction (S_{us}) in the influent and effluent unknown, and the acidogenic and acetoclastic methanogenic biomasses (Z_{ad} and Z_{am}) in the effluent unknown. In the effluent, the S_{us} could be determined from the measured soluble COD and S_{VFA} and determined S_{bsf}, and accepting negligible production, $S_{usi} = S_{us}$. To determine S_{up}, for the 60 d retention time system it could be accepted that the residual S_{bp} was negligible (confirmed from O'Rourke, 1968), and hence applying equations 7, 9, 11, 13 and 15 to this system the S_{up} could be determined by matching the calculated (equation 2) and measured effluent COD. This gave S_{up} as a fraction of the influent measured total COD ($f_{PS,up}$) as 33.45%. Alternative analytical procedures using the data set from all the experimental systems gave $f_{PS,up}$ as 33.3% (see Ristow *et al.*, 2005), and hence the value of 33.45% was accepted for the Athlone PSS. This value corresponds closely to the 36% obtained for the data of O'Rourke (1968). With $f_{PS,up}$ determined, the influent COD to each system could be characterised (equation 1). Accordingly, the steady state model equations were applied to each system and the rates of hydrolysis, acidogenesis and methanogenesis determined such that the measured and calculated (equation 2) effluent COD concentrations matched (see Ristow *et al.*, 2005).

Results and discussion

For each steady state of operation, a COD balance was calculated based on the feed and effluent COD concentrations and the methane production; see Table 1. With the exception of one steady state (10 d retention time at 2 gCOD/L feed), all the values are within the acceptable range (90–110% recovery) for particulate fed systems, and only three systems have a COD recovery outside the generally acceptable range of 95–105% recovery for biological systems. The COD recoveries for the systems fed at 2 gCOD/L were considerably lower (88 and 92%) than for the other systems (96–110%), due to difficulties in accurately measuring gas production volumes at the low feed concentrations (see Ristow *et al.*, 2005). The good COD recoveries strongly suggest that the methods used to analyse the various parameters are accurate and consistent, and provide confidence in

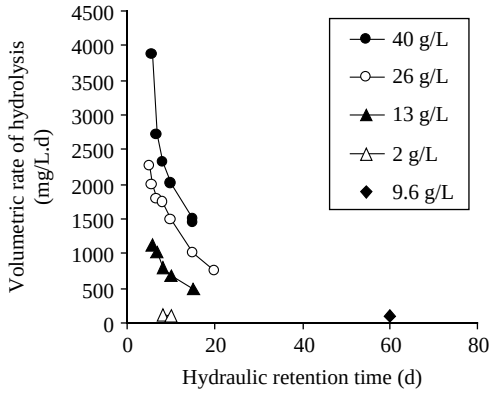

Figure 2 Plot of the calculated rate of hydrolysis for each steady state as a function of the hydraulic retention time, showing the effect of the feed COD concentration

further analysis of the measured parameters. Detailed data on the various experimental systems are provided by Ristow *et al.* (2005).

Following the procedures set out above, the volumetric rates of hydrolysis ($rate_{hydrolysis}$, equation 7) of PSS for the various experimental systems at the four different feed concentrations and the 60-d retention time system were calculated and are shown plotted vs. retention time in Figure 2.

The rate of hydrolysis (equation 8) has typically been reported as being first order with respect to the particulate biodegradable COD concentration (Ristow *et al.*, 2005):

$$rate_{hydrolysis} = k_h.S_{bp} \tag{16}$$

For each steady state in Figure 2, the value for the first order rate constant (k_h) can be calculated, since $rate_{hydrolysis}$ and S_{pb} can be calculated via equations 7, 9, 11, 13 and 15. For the 21 steady state systems operated, this gave a value of $k_h = 0.992 \pm 0.492$/d. The standard deviation is relatively large, and would suggest that first order kinetics may not be able to accurately predict the rate of hydrolysis for the different HRTs and feed COD concentrations.

In order to determine the validity of the first order model, equation 6 was recast with the first order rate formulation (equation 16) included:

$$dS_{bp}.V = Q.S_{bpi}.dt - Q.S_{bp}.dt - V.k_h.S_{bp}.dt + V.b_{ad}.Z_{ad}.dt + V.b_{am}.Z_{am}.dt \tag{17}$$

At steady state:

$$S_{bp} = \frac{S_{bpi} + b_{ad}Z_{ad}R_h + b_{am}Z_{am}R_h}{1 + k_hR_h} \tag{18}$$

Since equations 12 and 14 still apply for the calculation of the biomass concentrations, these equations were solved simultaneously with equation 18 using the determined average $k_h = 0.992$/d, based only on the influent PSS characterisation. The value of the effluent total COD concentration (S_t) was then calculated with equation 2 for all the steady state operating points from Figure 2, and plotted vs the measured effluent total COD concentration, Figure 3.

From Figure 3 it is clear that for all HRTs and influent COD concentrations, first order kinetics are capable of accurately predicting the effluent total COD concentration of a steady state methanogenic digester from the influent PSS characteristics. It is also evident that the predicted effluent total COD concentration is relatively insensitive to the exact value of the first order kinetic constant (k_h), since the difference between the k_h

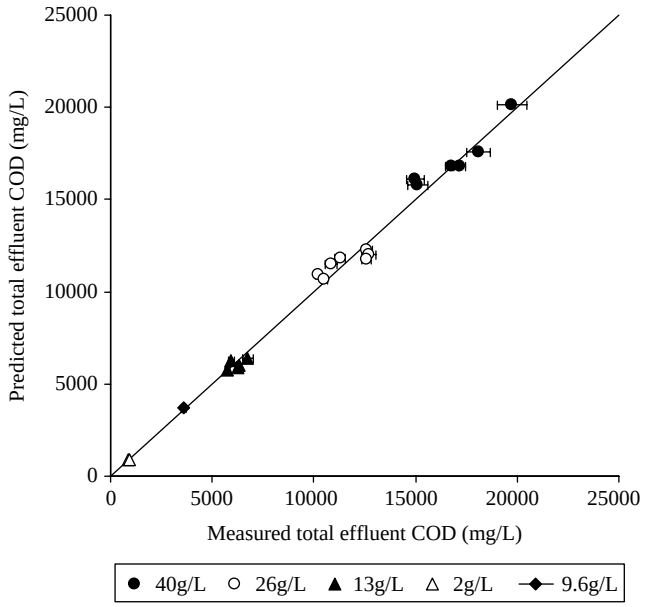

Figure 3 Plot of the calculated effluent COD concentration assuming first order kinetics with $k_h = 0.992 d^{-1}$ versus the measured effluent COD concentration

value calculated for a specific steady state was as much as 5.7 times greater than the mean k_h value used in the model, but the error in the calculated effluent total COD concentration for that steady state was only 7.1%. The largest absolute error between the measured and calculated effluent COD was 7.67% with respect to the measured value, with a mean and standard deviation of $-0.2059 \pm 4.50\%$. The model was also relatively insensitive to the biomass growth constants. However, when the biomass concentrations were removed from the model, the predictions were compromised, indicating that the structure of the model is of greater importance than the values of the kinetic and stoichiometric constants chosen.

Alternative kinetic rate formulations to describe PSS hydrolysis were evaluated, including first order specific, Monod and surface reaction (Contois); see Ristow *et al.* (2005). From an assessment of the fit of predicted to calculated values, it could be concluded that first order and surface saturation kinetics most accurately describe the rate of PSS hydrolysis under methanogenic conditions for all hydraulic retention times and feed COD concentrations. Since first order kinetics are a simplification of the hydrolysis process (the acidogenic biomass is not explicitly included, nor is there an upper limit to the rate), surface reaction kinetics are probably the most appropriate rate formulation. However, the simpler first order kinetics can be used to evaluate and compare the PSS hydrolysis rates under different operating conditions, since these kinetics have been shown to provide a good description of PSS hydrolysis rates.

The first order based hydrolysis model was applied to the experimental data of O'Rourke (1968), with the first order rate constant as determined in this study; see Figure 4. From Figure 4, the first order kinetic model with $k_h = 0.992\,d^{-1}$ could accurately predict the rate of hydrolysis for the O'Rourke systems with retention times of 7 d or longer; for the shorter retention times, O'Rourke measured significant VFA in the effluent, i.e. stable methanogenic conditions were not established. This provides substantive support validating the model developed here.

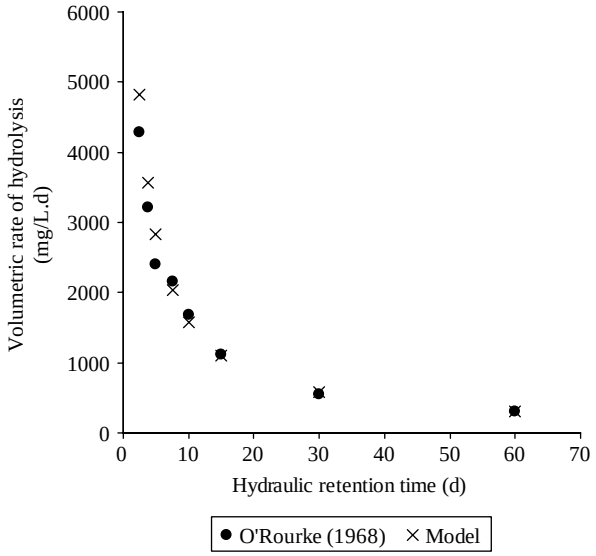

Figure 4 Calculated (from experimental data) and predicted (first order kinetics, $k_h = 0.992 d^{-1}$) rate of hydrolysis for each hydraulic retention time for the data of O'Rourke (1968)

Conclusions

- Steady state operating data were collected for methanogenic systems operating at varying retention times and PSS feed COD concentrations.
- A steady state model based on mass balances has been developed to calculate the rates of PSS hydrolysis, acidogenesis and methanogenesis at all operating conditions.
- For the kinetic rate of hydrolysis of PSS, surface reaction kinetics probably are the most appropriate, since these kinetics explicitly include the acidogen biomass concentration and impose an upper limit to the rate.
- However, first order kinetics for the rate of PSS hydrolysis have been shown to adequately predict the rate under all operating conditions; since these kinetics are simpler they can be used to evaluate and compare the PSS hydrolysis rates under different operating conditions.
- For first order kinetics, the value for the first order kinetic constant was determined as 0.992/d, but the model was relatively insensitive to the exact value for this constant.
- The model and procedures developed in this paper provide a consistent framework for the analysis of experimental data from anaerobic systems, which will enable direct comparison of hydrolysis rates for particulate organic substrates under different operating conditions.

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