A steady state model for anaerobic digestion of sewage sludges

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Abstract

A steady state model for anaerobic digestion of sewage sludge is developed that comprises three sequential parts – a kinetic part from which the % COD removal and methane production are determined for a given retention time; a stoichiometry part from which the gas composition (or partial pressure of CO_2), ammonia released and alkalinity generated are calculated from the %COD removal; and a carbonate system weak acid/base chemistry part from which the digester pH is calculated from the partial pressure of CO_2 and alkalinity generated. From the stoichiometry and weak acid base chemistry parts of the model, for a given % COD removal, the digester gas composition, ammonia released, alkalinity generated and digester pH are completely defined by the influent sludge composition, i.e. X, Y, Z and A in $C_XH_YO_ZN_A$ of the hydrolysable organics; volatile fatty acid (VFA) concentration; and pH. For the kinetic part of the model, four hydrolysis kinetic equations were calibrated against 7 to 60 d retention time anaerobic digesters treating two different sewage sludge types, viz. first order; first order specific; Monod; and saturation. Once calibrated against the two sludge type data sets and taking into account experimental error in effluent COD concentration and gas production (i.e. COD mass balance error), each of the four hydrolysis kinetic equations predicted the % COD removal versus retention time equally well, and predicted COD removal and methane production compared well with measured data. For the different sewage sludge types, viz. a primary and humus sludge mixture from a trickling filter plant, and a "pure" primary sludge, different kinetic rate constants were obtained indicating that the "pure" primary sludge hydrolysed faster and had a lower unbiodegradable particulate COD fraction ($f_{PS'up}$ = 0.33) than the primary and humus sludge mixture (0.36). With the %COD removal known from the hydrolysis part of the model, and again taking experimental error into account (i.e. C and N mass balances error), the stoichiometry and weak acid base chemistry parts of the model predicted the gas composition, effluent free and saline ammonia (FSA) concentration, alkalinity generated and digester pH well for a primary and humus sludge composition of $C_{3.5}H_7O_2N_{0.196}$. From independent measurement of primary sludge CHON composition, this model estimated composition is within 96%, 100%, 95% and 99% of the average measured composition of $C_{3.65}H_7O_{1.97}N_{0.190}$ lending strong support to the developed steady state model.

Keywords: Anaerobic digestion, steady state model, sewage sludge, hydrolysis kinetics, biodegradability

Introduction

Sötemann et al. (2005a) developed an integrated two-phase (aqueous-gas) mixed weak acid base chemical, physical and biological processes kinetic model for anaerobic digestion (AD) of sewage sludge. The COD, C and N mass balances and continuity basis of this model fixes quantitatively, via the interrelated chemical, physical and biological processes, the relationship between all the compounds of the system. Thus for a given sewage sludge COD removal the digester outputs (i.e. effluent COD, TKN, FSA, SCFA, H_2CO_3* Alk, pH, gaseous CO_2 and CH_4 production and partial pressures) are governed completely by the input sludge solids (and dissolved) constituents. In this model, the sewage sludge feed is characterised in terms of total COD, its particulate unbiodegradable COD fraction ($f_{PS'up}$), the short chain fatty acid (SCFA) COD and the CHON content, i.e. X, Y, Z and A in $C_XH_YO_ZN_A$ of the particulate organics. This approach characterises the sludge in terms of measurable parameters in conformity with the COD, C and N mass balances approach. With this approach, the interactions between the biological processes and weak acid/base chemistry could be correctly predicted for stable steady state operation of anaerobic digesters. While not validated for dynamic flow and load conditions, the model has the capability of being applied to such conditions. In this paper this complex dynamic simulation model is simplified to a steady state one for integration into a steady state mass balance model of the whole wastewater treatment plant (Sötemann et al., 2005b).

Steady state models are based on the slowest process kinetic rate that governs the overall behaviour of the system and relates this process rate to the system design and operating parameters. Therefore, steady state models allow the system design and operating parameters, such as reactor volume and recycle ratios, to be estimated reasonably simply and quickly from system performance criteria specified for the design, such as effluent quality. Once approximate design and operating parameters are known, these can serve as input to the more complex simulation models to investigate dynamic behaviour of the system and refine the design and operating parameters. A steady state AD model is therefore useful to:

- estimate retention time, reactor volume, gas production and composition for a required system performance like COD (or VSS) removal,
- investigate the sensitivity of the system performance to the design and operation parameters,
- provide a basis for cross-checking simulation model results, and
- estimate product stream concentrations for design of down- (or up-) stream unit operations of the wastewater treatment plant.

Anaerobic digestion of organics require a consortium of four organism groups (Mosey, 1983; Massé and Droste, 2000;

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Batstone et al., 2002; Sötemann et al., 2005a) viz.:

(i) acidogens, which convert complex organics to SCFA acetic and propionic (HAc, HPr), carbon dioxide (CO_2) and hydrogen (H_2),
(ii) acetogens, which convert HPr to HAc and H_2,
(iii) acetoclastic methanogens, which convert HAc to CO_2 and methane (CH_4) and
(iv) hydrogenotrophic methanogens, which convert H_2 and CO_2 to CH_4 and water.

The two methanogenic groups are very sensitive to pH and so the acetogens and acetoclastic methanogens must utilise the HAc and HPr respectively as soon as they are produced to maintain a near neutral pH for optimal operation. Because the hydrolysis/acidogenesis process mediated by the acidogens ((i) above), is the slowest process in the system, high SCFA concentrations and therefore low pH, arise only under unstable and digester upset operating conditions caused by a shock load in organics, a rapid decrease in temperature or a methanogen inhibitor in the influent. A steady state model, therefore, need only consider the kinetics of this process (Vavilin et al., 2001). The processes following hydrolysis/acidogenesis, being much more rapid (usually), can be accepted to reach completion. This implies that in stable AD systems the intermediate products of the processes following after hydrolysis/acidogenesis such as SCFAs and H_2, do not build up in the system and their concentrations are sufficiently low to be considered negligible. Consequently, in the steady state AD model, the products of hydrolysis/acidogenesis can be dealt with stoichiometrically and converted to digester end products. In effect, it can be assumed that the hydrolysis/acidogenesis process generates directly the digester end-products biomass, CH_4, CO_2 and water. Thus the steady state anaerobic digester model developed below considers three aspects:

(1) the kinetics of the hydrolysis/acidogenesis process,
(2) stoichiometric conversion of the products from (1) to digester end-products and
(3) the effect of the end products on the digester pH (weak acid/base chemistry).

Hydrolysis/acidogenesis kinetics

Hydrolysis rate equations

Since the hydrolysis/acidogenesis process is the slowest one in the sewage sludge anaerobic digester and does not reach completion within the normal range of the principal digester design parameter of hydraulic retention time, a kinetic expression describing this process rate is required for the steady state model. Sötemann et al. (2005a) considered four kinetic equations for this process, viz.:

- first order with respect to the residual biodegradable particulate organic (COD) concentration S_{bp},
- first order with respect to S_{bp} and the acidogen biomass concentration (Z_{AD}) which mediates this process,
- Monod kinetics and
- saturation (or Contois) kinetics (see Eqs 1 to 4 in Table 1).

All these equations have been used to model various biological processes for many years; the first to describe the hydrolysis/acidogenesis of sewage sludge solids in AD (e.g. Henze and Harremoës, 1983, Bryers, 1985, Vavilin et al., 2001), the second for modelling the conversion of readily biodegradable organics to short chain fatty acids in the anaerobic reactor of biological P removal systems (e.g. Wentzel et al., 1985), and the last two for the utilisation of soluble readily and particulate slowly biodegradable organics respectively in activated sludge models (Dold et al., 1980; Henze et al., 1987) and hydrolysis of complex organics in AD (e.g. McCarty, 1974 and Vavilin et al., 2001). Sötemann et al. (2005a) were unable to determine which equation was superior for modelling hydrolysis/acidogenesis process in AD because for the experimental data evaluated, the unbiodegradable particulate COD fraction ($f_{PS'up}$) of the sewage sludge (primary+humus) organics was not sufficiently well known - by changing $f_{PS'up}$ in a fairly narrow range from 0.32 to 0.36, each of the equations gave a better correlation coefficient than the other equations at different specific $f_{PS'up}$ values. They accepted the saturation kinetics for the integrated model (UCTADM1) because this equation gave a similar $f_{PS'up}$ value (0.36) to O'Rouke (1967) (0.34) working with AD of "pure" primary sludge (no trickling filter humus or waste activated sludge) and has been successfully used to model hydrolysis/utilisation of the same particulate biodegradable organics in activated sludge kinetic models. In their comparison of first order and saturation (Contois) kinetics for modelling anaerobic hydrolysis, Vavilin et al. (2001) state that the latter is preferable from a modelling perspective (and is another reason these kinetics were included in the dynamic AD model of Sötemann et al., 2005a), but the uncertainty that the unknown unbiodegradable COD fraction of the influent organics casts over hydrolysis kinetics selection is not mentioned. In their evaluation of the four hydrolysis/acidogenesis equations, Sötemann et al. (2005a) included the effect of the acidogen (Z_{AD}) and acetoclastic methanogen (Z_{AM}) biomass formation, because these two organism groups have the highest yield coefficients and so contribute significantly to the effluent organics (COD) concentration and decrease the gas production.

In steady state models, detail is not required – in fact, it is undesirable. From the simulation model, sufficient accuracy for a steady state model is obtained by selecting any of the four hydrolysis/acidogenesis equations and increasing the acidogen biomass yield to include the acetoclastic methanogens. The acidogens have the highest yield coefficient (Y_{AC}=0.089 gCOD biomass/gCOD substrate hydrolysed) and make up more than 77% of the total biomass formed. Increasing Y_{AD} from 0.089 to 0.113 very closely takes into account the biomass formation of the other organism groups (see Fig. 4 of Sötemann et al., 2005a). A consequence of accepting this approach is that in kinetic rate formulations that include the acidogen biomass concentration (first order specific, Monod and saturation), the specific rate constants in the steady state model here will be lower compared with the corresponding values in the dynamic model of Sötemann et al. (2005a) but the predicted performances (e.g. %COD removal) will be the same.

The steady state model will be derived using the COD to quantify the organics and biomass concentrations and the Monod equation for the hydrolysis/acidogenesis rate. However, the model equations for all four hydrolysis kinetics rate expressions have been derived and are summarised in Table 1.

Steady state model development – hydrolysis kinetics

Consider a flow through digester of volume V and influent flow Q giving a hydraulic retention time or sludge age of R = V/Q days (Fig. 1).

Defining the unbiodegradable fraction of the influent total particulate sewage sludge COD (S_{ti}) as $f_{PS'up}$, then the particulate biodegradable (S_{bpi}) and unbiodegradable (S_{upi}) COD concentrations in the influent are (see Fig. 2):

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TABLE 1

Steady state anaerobic digester kinetic equations for the residual biodegradable particulate organics concentration (S_{bp}), acidogen biomass concentration (Z_{AD}), unbiodegradable organics concentration (S_{up}) and methane production in gCOD/ℓ influent (S_m) for four different hydrolysis kinetic rate equations. Kinetic constants of the four hydrolysis equations for unbiodegradable particulate COD fraction ($f_{PS,up}$) = 0.36.

Hydrolysis kinetic equation	**1st order with respect to (wrt) S_{bp}**	**1st order specific (wrt to S_{bp} & Z_{ad})**	**Monod kinetics**	**Saturation kinetics**
Hydrolysis rate r_h gCOD/(ℓ·d)	$r_h = K_h S_{bp}$ (1)	$r_h = K_H S_{bp} Z_{AD}$ (2)	$r_h = \frac{K_m S_{bp}}{(K_s + S_{bp})} Z_{AD}$ (3)	$r_h = \frac{K_M (S_{bp}/Z_{AD})}{[K_S + (S_{bp}/Z_{AD})]} Z_{AD}$ (4)
Residual biodegradable organics concentration gCOD/ℓ S_{bp}	$S_{bp} = \frac{S_{bpi}}{\left\{1 + K_h R \frac{[1 + b_{AD} R(1 - Y_{AD})]}{(1 + b_{AD} R)}\right\}}$	$S_{bp} = \frac{1/R + b_{AD}}{Y_{AD} K_H}$	$S_{bp} = \frac{K_s (1/R + b_{AD})}{Y_{AD} K_m - (1/R + b_{AD})}$	$S_{bp} = \frac{S_{bpi}}{\left\{1 + \frac{[Y_{AD} K_M - (1/R + b_{AD})][1 + b_{AD} R(1 - Y_{AD})]}{Y_{AD} K_S (1/R + b_{AD})}\right\}}$
Acidogen biomass concentration Z_{ad} gCOD/ℓ	$Z_{AD} = \frac{Y_{AD}(S_{bpi} - S_{bp})}{[1 + b_{AD} R(1 - Y_{ad})]}$			
Unbiodegradable organics concentration S_{up} gCOD/ℓ	$S_{up} = S_{upi}$			
Methane production concentration S_m gCOD/ℓ	$S_m = (1 - Y_{AD}) R r_h$			
Kinetic constants (Izzett et al., 1992 data)	$K_h = 0.515 \pm 0.041$ /d $^*K_h = 0.481 \pm 0.040$ /d	$K_H = 0.322 \pm 0.047$ $^*K_H = 0.379 \pm 0.056$ ℓ/(gCOD biomass·d)	$K_m = 3.34$ (*3.72) gCOD organics/(gCOD biomass·d) $K_s = 6.76$ (*6.38) gCOD/ℓ	$K_M = 5.27$ (*5.58) gCOD organics/ (gCOD biomass·d); $K_S = 7.98$ (*8.89) gCOD/ℓ
COD balance	$S_{ti} = S_{te} + S_m = S_{bp} + Z_{AD} + S_{up} + S_m$; $S_{ti} = COD in$; $S_{te} = S_{bp} + Z_{AD} + S_{up} = COD out as sludge solids$; $S_m = COD out as methane gas$			

*Determined with the more complex hydrolysis model of Sötemann et al. (2005a) at $f_{PS,up}$ = 0.36.

Figure 1
Schematic diagram of the flow through anaerobic digester of retention time R = V/Q showing symbols used in the steady state AD model.

$$S_{bpi} = (1 - f_{PS'up})\, S_{ti} - S_{bsai} \quad (5)$$

$$S_{upi} = f_{PS'up}\, S_{ti} \quad (6)$$

where:

S_{bsai} = Influent volatile fatty acid (VFA) concentration (mgCOD/ℓ)

Sewage sludge comprises two additional dissolved COD fractions, i.e. the unbiodegradable soluble COD (S_{usi}) and the fermentable (non-VFA) readily biodegradable soluble COD (S_{bsfi}) (Fig. 2). The S_{usi} is very low in relation to the S_{upi} and so can be assumed zero for the purposes of this steady state model. The S_{bsfi} goes through the same hydrolysis/acidogenesis processes as the particulate biodegradable COD (S_{bpi}) and so is included with the S_{bpi}. Because the steady state model is based on the hydrolysis process as stated in Eq. 5, the S_{bsai} is not included with the COD passing through this process. However, the S_{bsai} does generate methane and CO_2 (but negligible sludge mass) mediated by the two methanogenic species. Hence S_{bsai} can be excluded in the hydrolysis part of the model but needs to be included in the stoichiometry part of the model due to its effect on gas composition and digester pH. Hence S_{ti} is given by $S_{upi}+S_{bpi}+S_{bsai}$ (Fig. 2).

The net acidogen growth rate from the hydrolysis/acidogenesis and endogenous processes is given by:

$$\frac{dZ_{AD}}{dt} = Y_{AD}\, r_h - b_{AD}\, Z_{AD}$$

where:

r_h = volumetric hydrolysis/acidogenesis rate in gCOD/(ℓ·d) (Eqs. 1 to 4 in Table 1)

Y_{AD} = pseudo acidogen yield coefficient (gCOD biomass/ gCOD organics hydrolysed)

b_{AD} = acidogen endogenous respiration rate (/d).

The steady state model is derived by applying the general mass balance equation (Eq. 7) over the system (Fig. 1) to the four system variable compound concentrations (all gCOD/ℓ), i.e. S_{bp}, S_{up}, Z_{AD} and methane

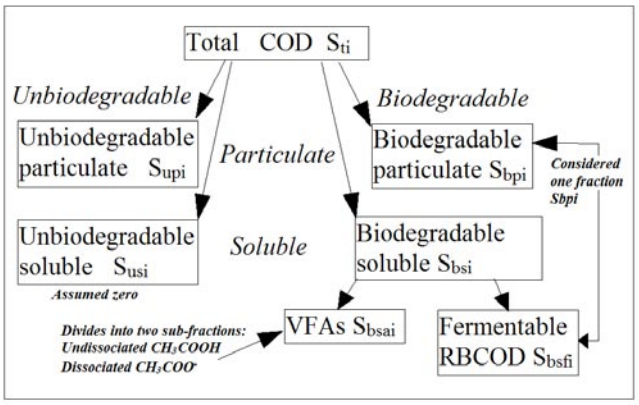

Figure 2
Influent primary sludge COD fractionation for the steady state anaerobic digestion model

(S_m) concentrations. For the flow through system, the effluent compound concentrations are equal to the reactor concentrations. For example, the mass balance for S_{bp} over a time interval dt is:

$$\begin{bmatrix}\text{Mass change in system}\end{bmatrix} = \begin{bmatrix}\text{Mass flow into system}\end{bmatrix} - \begin{bmatrix}\text{Mass flow out of system}\end{bmatrix} - \begin{bmatrix}\text{Mass loss by bio-process}\end{bmatrix} + \begin{bmatrix}\text{Mass gain by bio-process}\end{bmatrix} \quad (7)$$

$$dS_{bp}V = +QS_{bpi}dt - QS_{bp}dt - r_hVdt + b_{AD}Z_{AD}Vdt \quad (8)$$

In Eq. 8, the first and second terms on the right hand side are the biodegradable organics flowing in and out of the digester, and the third and fourth terms the decrease in biodegradable organics due to hydrolysis and the increase from the biodegradable part of the acidogen biomass that dies. Dividing Eq. 8 through by Vdt yields:

$$\frac{dS_{bp}}{dt} = +\frac{S_{bpi} - S_{bp}}{R} - r_h + b_{AD}Z_{AD} \quad \text{gCOD/(ℓ.d)} \quad (9)$$

Similarly the mass balance on acidogen biomass concentration (Z_{AD}) yields:

$$dZ_{AD}V = +0 - QZ_{AD}dt + Y_{AD}r_hVdt - b_{AD}Z_{AD}Vdt$$

Again dividing through by Vdt yields:

$$\frac{dZ_{AD}}{dt} = -\frac{Z_{AD}}{R} + Y_{AD}r_h - b_{AD}Z_{AD} \quad (10)$$

At steady state the transient dZ_{AD}/dt in Eq. 10 = 0 and solving for the hydrolysis rate r_h yields:

$$r_h = \frac{Z_{AD}}{Y_{AD}}\left(\frac{1}{R} + b_{AD}\right) \quad \text{gCOD/(ℓ.d)} \quad (11)$$

Setting Eq. 9 = 0 for steady state and solving for r_h yields:

$$r_h = \frac{S_{bpi} - S_{bp}}{R} + b_{AD}Z_{AD} \quad \text{gCOD/(ℓ.d)} \quad (12)$$

Then substituting Eq. 11 for r_h into Eq. 12 and solving for Z_{AD} yields:

$$Z_{AD} = \frac{Y_{AD}(S_{bpi} - S_{bp})}{[1 + b_{AD}R(1 - Y_{AD})]} = (S_{bpi} - S_{bp})E$$

$$= \Delta S_{bp}E \quad \text{gCOD/ℓ} \quad (13)$$

Equation 13 seems to indicate that the acidogen biomass concentration (Z_{AD}) is independent of the hydrolysis kinetic rate (and hence its formulation) because r_h does not appear in it. However, it is implicitly dependent on r_h because S_{bp} appears in the equation and S_{bp} is dependent on the hydrolysis kinetic rate. Equation 13 does show that once S_{bp} is known, then Z_{AD} can be calculated for any hydrolysis rate equation.

Substituting the Monod equation (Eq. 3 in Table 1) for r_h into Eq. 11 and solving for S_{bp} yields:

$$S_{bp} = \frac{K_s(1/R + b_{AD})}{Y_{AD}K_m - (1/R + b_{AD})} \quad \text{gCOD/ℓ} \quad (14)$$

Ignoring as negligible the formation of unbiodegradable organics from the acidogens that die (i.e. endogenous residue is zero), the total unbiodegradable organics concentration in the effluent (S_{up}) is equal to the influent, i.e.

$$S_{up} = S_{upi} \quad \text{gCOD/ℓ} \quad (15)$$

The methane production in COD units is directly related to the rate of hydrolysis of biodegradable organics. If the methane concentration in the effluent in COD units is S_m, a mass balance on S_m yields:

$$dS_mV = 0 - QS_mdt + (1 - Y_{AD})r_hVdt \quad (16)$$

where:

S_m = methane concentration in the effluent in gCOD/ℓ (if it were dissolved)

Dividing Eq. 16 through by Vdt and setting $dS_m/dt = 0$ and solving for S_m yields:

$$S_m = (1 - Y_{AD})Rr_h \quad \text{gCOD/ℓ} \quad (17)$$

Because methane has a COD 64 gCOD/mol and a gas volume at ambient temperature 20°C of 22.4 (293/273) = 24.0 ℓ/mole, the methane gas production Q_m is:

$$Q_m = (1 - Y_{AD})Rr_h 24.0/64 \quad (18)$$

(ℓ methane/d) /(ℓ influent flow/d)

The partial pressure of CO_2 in the gas (p_{CO2}) and the CO_2 composition of the gas are numerically equal. Hence, if the partial pressure of CO_2 or the CO_2 gas composition are known (in atmospheres, or volume or mole fractions), then the total gas production at 20°C (Q_{gas}) is:

$$Q_{gas} = \frac{Q_m}{(1 - p_{CO2})} = \frac{(1 - Y_{AD})Rr_h 24.0}{(1 - p_{CO2})64} \quad (19)$$

(ℓ gas/d)/(ℓ influent flow/d)

A COD mass balance over the digester system (Fig. 1) yields:

$$S_{ti} = S_{te} + S_m = S_{bp} + Z_{AD} + S_{up} + S_m \quad (20)$$

Equation 20 shows that COD exits the digester only as sludge mass in the effluent (S_{te}) and as methane gas (S_m). Substituting Eq. 13 with S_{bp} as its subject for S_{bp}, Eq. 15 for S_{up}, Eq. 17 for S_m and Eq. 3 for r_h into Eq. 20 yields:

$$S_{ti} = S_{bpi} - \frac{Z_{AD}}{Y_{AD}}[1 + b_{AD}R(1 - Y_{AD})] + Z_{AD} +$$

$$+ S_{upi} + (1 - Y_{AD})R\frac{K_mS_{bp}}{K_s + S_{bp}}Z_{AD}$$

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which on simplifying gives Eq. 14 for S_{bp}, and therefore proves the input and output COD masses balance exactly.

The total (S_{tr}) and biodegradable (S_{bpr}) COD removals and methane production (S_m) are given by:

$$S_{tr} = S_{ti} - S_{te} = S_m \quad (21)$$

$$S_{bpr} = S_{bpi} - S_{bp} \quad (22)$$

The equations for the biodegradable organics (S_{bp}), acidogen (Z_{AD}), unbiodegradable (S_{up}) and methane (S_m) concentrations for all four hydrolysis rate formulations are given in Table 1.

Calibration of hydrolysis kinetics

The equations developed above were evaluated and calibrated against data from steady state anaerobic digesters.

Calculating the effluent COD concentration (S_{te})

From the steady state COD mass balance equation (Eq. 20), the effluent total particulate COD concentration, S_{te} is given by:

$$S_{te} = S_{up} + S_{bp} + Z_{AD} \text{ gCOD/}\ell \quad (23)$$

Substituting Eq. 15 for S_{up}, Eq. 6 for S_{upi} and Eq. 13 for Z_{AD} in Eq. 23 yields:

$$S_{te} = f_{PS'up} S_{ti} + S_{bp} + \frac{Y_{AD}[(1-f_{PS'up})S_{ti} - S_{bp}]}{[1+b_{AD}R(1-Y_{AD})]} \text{ gCOD/}\ell \quad (24)$$

Solving Eq. 24 for S_{bp} yields:

$$S_{bp} = \frac{S_{ti}[f_{PS'up} + E(1-f_{PS'up})] - S_{te}}{[E-1]} \text{ gCOD/}\ell \quad (25a)$$

where $E = \frac{Y_{AD}}{1+b_{AD}R(1-Y_{AD})}$ (From Eq 13) (25b)

With S_{te} and S_{ti} known from measurement, Eq. 25 defines S_{bp} in terms of the unbiodegradable fraction of the primary sludge ($f_{PS'up}$), the retention time of the digester (R) and the acidogen constants (Y_{AD}, b_{AD}). By estimating an unbiodegradable fraction of the primary sludge ($f_{PS'up}$) and selecting acidogen biomass constants (i.e. Y_{AD} = 0.113 gCOD biomass/ gCOD organics, b_{AD} = 0.041 /d), S_{bp} can be calculated with Eq. 25 from experimental data. The yield coefficient of the acidogens (Y_{AD}) has been increased from 0.089 to 0.113 to take account of the acetoclastic methanogen biomass that grows in the system. Because acidogenesis produces 61% acetic acid (and 39% hydrogen), 61% of the acetoclastic methanogen yield coefficient (Y_{AM} = 0.040) was added to Y_{AD}. This simplification is acceptable because the endogenous respiration rate is closely the same for these two organism groups (b_{AD} = 0.041 /d and b_{AM} = 0.037 /d). However, as noted above this simplification does influence the values of the constants in the hydrolysis rate equations. The hydrogenotrophic methanogen yield (Y_{HM}) is low enough (0.01 gCODbiomass/gCOD H_2) to be ignored.

Estimating the unbiodegradable COD fraction of primary sludge

For wastewater treatment plant design, the primary sludge (PS) unbiodegradable COD fraction ($f_{PS,up}$) is entirely dependent on the unbiodegradable particulate COD fractions ($f_{S'up}$) selected for the raw and settled wastewaters and the fraction of COD removed by primary sedimentation (f_{psr}). From a COD mass balance around the primary settling tank (PST), the $f_{PS'up}$ in terms of the raw and settled wastewater $f_{S'up}$ values and the PST f_{psr} is:

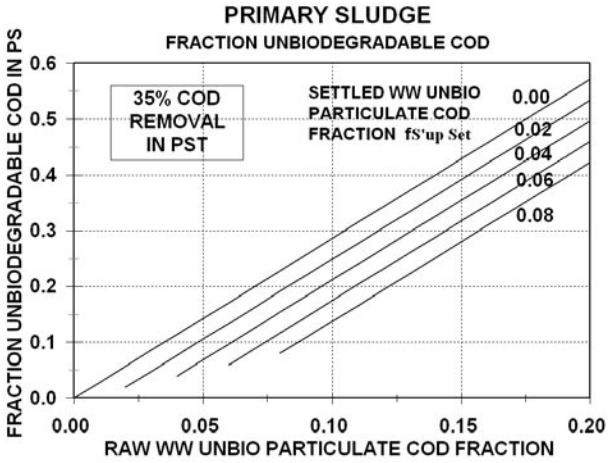

Figure 3
Fraction of unbiodegradable COD in primary sludge versus raw wastewater unbiodegradable particulate COD fraction for different settled wastewater unbiodegradable particulate COD fraction

$$f_{PS'up} = f_{S'upSet} + \frac{1}{f_{psr}}(f_{S'upRaw} - f_{S'upSet}) \quad (26)$$

where

$f_{PS'up}$ = unbiodegradable COD fraction of primary sludge (PS)

$f_{S'up\ Set}$ = Settled wastewater unbiodegradable particulate COD fraction

$f_{S'up\ Raw}$ = Raw wastewater unbiodegradable particulate COD fraction

f_{psr} = fraction of COD removed in the primary settling tank (PST)

Equation 26 has been simplified and is not strictly in conformity with a water flow balance over the PST. In Eq. 26, it has been assumed that the raw and settled wastewater flows entering and exiting the PST are equal. In practice, this is not true due to the low PST underflow, typically between 0.5 and 2% of average dry weather flow (ADWF). The error is very small on $f_{PS'up}$, but large enough to cause an error of ~1% on the COD mass balance around the whole WWTP. Mass balances are used wherever possible to verify the mathematical equations in models and errors > 1% are signals of possible errors in logic and formulae.

A graphical representation of Eq. 26 is given in Fig. 3. For the typical South African raw and settled municipal wastewaters, $f_{S'up}$ fractions of 0.15 and 0.04 respectively (WRC, 1984) and 35% COD removal (f_{psr} = 0.35), the $f_{PS'up}$ is 0.36. Literature on full-scale AD of primary sludge (PS) give maximum VS removals at long retention times at around 0.60 (Eckenfelder, 1980), suggesting an unbiodegradable fraction of around 0.35. O'Rourke (1967) determined a $f_{PS'up}$ of 0.36 in their investigation into AD of PS.

Incidently, Eq. 26 shows that the $f_{S'up}$ values selected for the raw and settled wastewaters must be consistent with observed PS characteristics; and the % removal of unbiodegradable organics (COD) in PSTs is apparently much higher (83% for the selected $f_{S'up}$ values above) than that of biodegradable organics (38%). The latter is of significant economic benefit for the activated sludge system because a large mass of burdensome unbiodegradable organics from the influent do not accumulate in the reactor. In some wastewater treatment plant simulation models, equal proportions of biodegradable and unbiodegradable

particulate organics are removed in the PST. This leads to settled wastewater and PS characteristics that deviate significantly from observed values, e.g. if equal proportions of the raw wastewater biodegradable and unbiodegradable particulate COD are removed and the %COD removal remains at 35%, then the settled wastewater $f_{S'up}$ would have to be 0.12 and $f_{PS'up}$ = 0.20. Both these values are considerably different than those observed.

TABLE 2
Experimental data measured by Izzett et al. (1992) on 14 ℓ completely mixed mesophilic (37°C) anaerobic digesters at 7 to 20 d retention time fed a mixture of primary and humus (trickling filter) sludge from the Potsdam wastewater treatment plant (Milnerton, Cape, South Africa)

Retention time (d)	7	10	12	15	20
Influent flow ℓ/d	2.00	1.40	1.17	0.93	0.70
Influent COD gCOD/ℓ	43.286	40.721	39.222	42.367	42.595
Influent VFA mgCOD/ℓ	1871	1961	2872	1824	2249
Influent TKN mgN/ℓ	1105	1100	1028	1075	1171
Influent FSA mgN/ℓ	196	203	235	221	244
Influent Alk mg/ℓ as $CaCO_3$	80	81	90	82	56
Influent pH	5.34	5.34	5.20	5.42	5.28
Effluent COD gCOD/ℓ	23.637	20.521	18.678	19.969	19.005
Effluent VFA mgCOD/ℓ	50	28	28	27	23
Effluent TKN mgN/ℓ	1041	1039	992	976	1157
Effluent FSA mgN/ℓ	511	404	430	404	511
Effluent Alk mg/ℓ as $CaCO_3$	1882	1951	2072	1994	2066
Gas composition $\%CH_4$	63.2	62.1	63.3	63.6	63.3
COD removal	19.649	20.200	20.544	22.398	23.590
Gas prod ℓ gas/ℓ influent	13.97	14.33	14.27	15.01	15.79
Gas Composition $\%CO_2$	36.8	37.9	36.7	36.4	36.7
FSA released mgN/ℓ	315	201	195	183	267
Measured digester pH	7.12	7.11	7.19	7.14	7.15
"Corrected" digester pH	6.84	6.84	6.88	6.86	6.87
COD balance (%)	108.4	108.6	109.1	106.9	107.3
Nitrogen balance (%)	94.2	94.5	96.5	90.8	98.8
Carbon balance (%)*	99.0	100.0	99.5	101.3	101.4

*Based on a sludge composition of $C_{3.5}H_7O_2N_{0.196}$ calculated from the influent COD and N masses and effluent C mass in the gas and liquid streams.

Calculating the constants in the hydrolysis kinetic equations – Izzett et al. (1992) results

Izzett et al. (1992) operated two laboratory-scale mesophilic (37°C) anaerobic digesters fed a mixture of primary and humus (trickling filter) sludge from the Potsdam wastewater treatment plant (Milnerton, Cape, South Africa) at 7, 10, 12, 15 and 20 d retention time. The steady state experimental results measured on the systems are listed in Table 2.

Accepting $f_{PS'up}$ = 0.36 from Sötemann et al. (2005a) for the Izzett data, the calculated S_{bp} concentrations from Eq. 25 are listed in Table 3. With S_{bp} known, Z_{AD} and ΔS_{bp} (= S_{bpi} - S_{bp}) can be calculated from the measured results (Table 3). Because the hydrolysis process does not reach completion in the digester, the observed hydrolysis rate r_h is given by Eq. 12 and the calculated values are listed in Table 3. With the hydrolysis rate known, the kinetic constants in the various hydrolysis rate equations can be calculated, i.e. for the first order rate with respect to S_{bp} only (Eq. 1), $K_h = r_h/S_{bp}$ (/d) and for the first order specific rate with respect to S_{bp} and Z_{AD} (Eq. 2), $K_H = r_h/(S_{bp}Z_{AD})$ [ℓ/(gCOD biomass·d)].

The calculated K_h and K_H rates for the different retention times are listed in Table 3 and plotted versus R in Fig. 4. For a hydrolysis rate equation to be reasonably general, it should take into account the major factors that influence the rate. If it achieves this, then the

TABLE 3
Izzett et al. (1992) 7 to 20 d retention time (R) anaerobic digester measured influent* (S_{ti}) and effluent* (S_{te}) COD concentrations, influent unbiodegradable (S_{upi}) and biodegradable COD (S_{bpi}) concentrations for an unbiodegradable COD fraction ($f_{PS'up}$) of 0.36, calculated residual biodegradable COD concentration (S_{bp}) (Eq. 25), change in biodegradable concentration across digester (ΔS_{bp}), observed hydrolysis rate ($r_h = \Delta S_{bp}/R + b_{AD}Z_{AD}$, Eq. 12), acidogen biomass concentration (Z_{AD}), specific hydrolysis rate [r_h/Z_{AD})] and the 1st order and 1st order specific hydrolysis rate constants (K_h and K_H). All mass units in gCOD.

R	*S_{ti}	*S_{te}	S_{upi}	S_{bpi}	S_{bp}	ΔS_{bp}	r_h	Z_{AD}	r_h/Z_{AD}	K_h	K_H
d	g/ℓ	g/ℓ	g/ℓ	g/ℓ	g/ℓ	g/ℓ	g/(ℓ·d)	g/ℓ	gCOD S_{bp}/(gCOD Z_{AD}·d)	/d	ℓ/(gCOD Z_{AD}·d)
7	43.286	23.637	15.583	25.832	6.240	19.59	2.871	1.765	1.586	0.460	0.261
10	40.721	20.521	14.660	24.100	4.142	19.96	2.064	1.654	1.207	0.498	0.301
12	39.222	18.678	14.120	22.230	3.018	19.21	1.663	1.511	1.059	0.551	0.365
15	42.367	19.969	15.252	25.291	3.065	22.23	1.548	1.625	0.912	0.505	0.311
20	42.595	19.005	15.334	25.012	2.151	22.86	1.204	1.495	0.764	0.560	0.374
									Mean**	0.515	0.322

* Measured total unfiltered COD. The VFA concentration was subtracted from this in conformity with Eq. 5 when calculating the Z_{AD} because this concentration is already hydrolysed and produces negligible biomass in the digester. The unbiodegradable soluble COD concentration was assumed zero. The fermentable (non-VFA) soluble COD (Fig. 2) was included in the S_{bpi} (in conformity with Eq. 5) because these organics pass through the hydrolysis process like the S_{bpi}. The unbiodegradable COD concentration (S_{upi}) of the sludge was calculated from the influent total unfiltered COD as listed and therefore included the soluble COD. This was done to approximate the unbiodegradable COD concentration of the "pristine" sewage sludge before any acidogenesis commenced. This is approximate because hydrogen is generated and lost in the acidogenesis that takes place in the sludge before feeding to the digester.
** Mean of all five retention time values.

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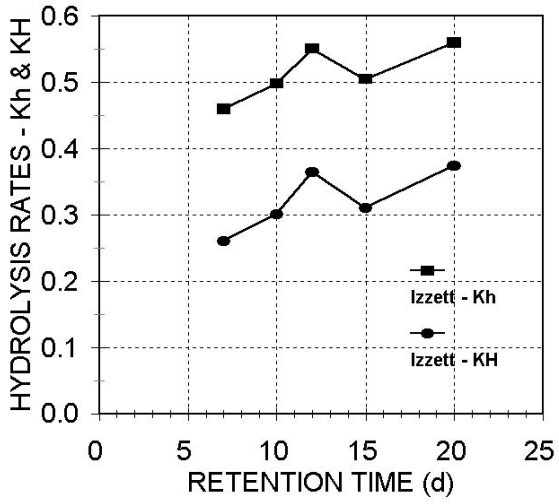

Figure 4

Hydrolysis rate constants for the 1st order (K_h, /d) and 1st order specific [K_H, ℓ/(gCOD biomass·d)] hydrolysis kinetic rate equations versus retention time for the Izzett et al. (1992) anaerobic digester data set

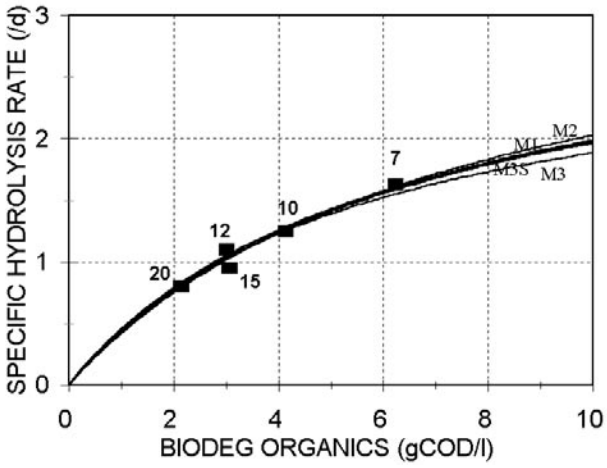

Figure 5

Specific hydrolysis rate [r_h/Z_{ad}, gCOD organics/(g COD biomass ·d)] versus residual biodegradable organics concentration (S_{bp}, gCOD/ℓ) calculated for Monod hydrolysis kinetic rate equation with constants determined from the Lineweaver-Burke (M1), inversion (M2) and Eadie-Hofstee (M3) linearisation and regression methods for the Izzett et al (1992) anaerobic digester data from 7 to 20 d retention time; experimental data (■) also shown.

K constants in the rate equation will not change with the principal design parameters, in this case, hydraulic retention time (or sludge age). For the first order and the first order specific hydrolysis rate equations (Eqs. 1 and 2 in Table 1), it can be seen that this would not appear to be the case (Fig. 4) – both K_h and K_H increase with increasing retention time. The average K_h and K_H rates over the five retention times are 0.515 /d and 0.322 ℓ/(gCOD biomass·d) respectively (Table 3, see also Table 1). Although these rate equations do not appear to be sufficiently general to describe the change in hydrolysis rate with retention time, the difference in predicted %COD removal based on the average K_h and K_H rates compared with experimental results is very small.

Determination of the K constants in the Monod and saturation kinetic rate equations require linearisation of these rate equations and linear regression over the retention time range of the experimental results, as described by Sötemann et al. (2005a). For the Monod equation, the hydrolysis rate r_h is given by Eq. 3 in Table 1, where r_h, S_{bp} and Z_{AD} are calculated from experimental data (Table 3). The linearisation can be done by three methods, viz. (i) Lineweaver-Burke, (ii) inversion and (iii) Eadie-Hofstee, each giving different K values, because each method emphasises different aspects of the Monod equation.

The specific hydrolysis rate (r_h/Z_{AD}) versus S_{bp} graphs obtained for the Monod rate equation with constants derived from the three linearisation methods (listed in Table 4) are shown in Fig. 5, together with the Izzett experimental data. Although method (i) gives the best fit with the data (highest correlation coefficient $R^2 = 0.948$), method (ii) gives marginally the best fit at the short retention time (7d). Linearisation method (iii) showed that the 15d retention time data is an outlier and is the reason for the low R^2 value (0.688) for all five retention time data. Excluding the 15d data significantly improved the R^2 value for method (iii) (0.888). The average K_m and K_s values obtained from the three methods, with the 15d retention time data excluded for method (iii), are given in Table 4 (see also Table 1). Figure 5 shows that even though different K values are obtained with the three different methods, the specific hydrolysis rate (r_h/Z_{AD}) versus biodegradable COD concentration (S_{bp}) curves obtained from each and the average are virtually the same and plot very closely to one another.

TABLE 4

Monod and saturation kinetics K constants and correlation coefficients (R^2) for the anaerobic digester data of Izzett et al. (1992) obtained from Lineweaver-Burke (M1), inversion (M2) and Eadie-Hofstee (M3) linearisation and regression methods, for the Eadie-Hofstee (M3) method without the 15 d retention time data (M3S), and the averages of the M1, M2 and M3 and the M1, M2, and M3S methods for unbiodegradable fraction ($f_{PS'up}$) of 0.36.

Kinetic rate	Monod kinetics			Saturation kinetics		
Linearisation method	K_m	K_s	R^2	K_M	K_s	R^2
Units. All mass units in COD	g organics/ (g biomass·d)	g organics/ℓ	-	g organics/ (g biomass·d)	g organics/ g biomass	-
Method 1 (M1)	3.33	6.81	0.948	5.44	8.35	0.979
Method 2 (M2)	3.55	7.49	0.876	5.61	8.69	0.823
Method 3 (M3)	2.94	5.55	0.688	4.46	6.44	0.699
Method 3S (M3S)	3.14	5.98	0.888	4.77	6.91	0.897
Average M1, M2, M3	3.27	6.62	-	5.17	7.82	-
Average M1, M2, M3S	3.34	6.76	-	5.27	7.98	-

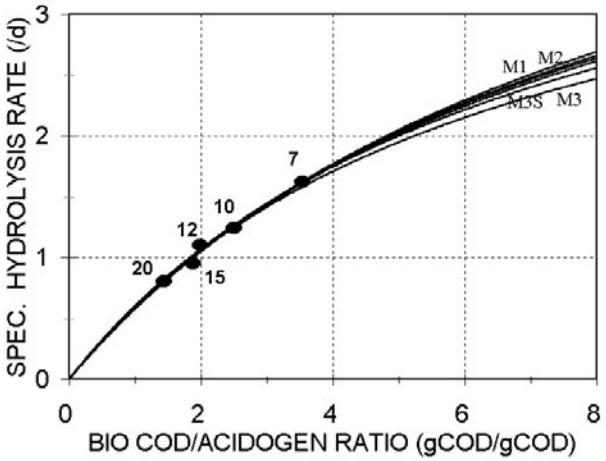

Figure 6

Specific hydrolysis rate [r_h/Z_{ad}, gCOD organics/(g COD biomass ·d)] versus residual biodegradable organics to acidogen biomass concentration ratio (S_{bp}/Z_{ad}, gCOD/gCOD) calculated for saturation hydrolysis kinetic rate equation with constants determined from the Lineweaver-Burke (M1), inversion (M2) and Eadie-Hofstee (M3) linearisation and regression methods for the Izzett et al (1992) anaerobic digester data from 7 to 20 d retention time; experimental data (●) also shown.

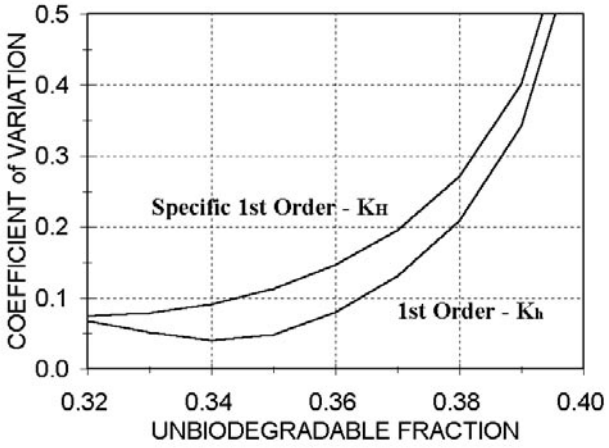

Figure 7a

Coefficient of variation versus unbiodegradable COD fraction of the primary sludge ($f_{PS'up}$) for the 1st order and 1st order specific hydrolysis equations for the Izzett et al. digester data set.

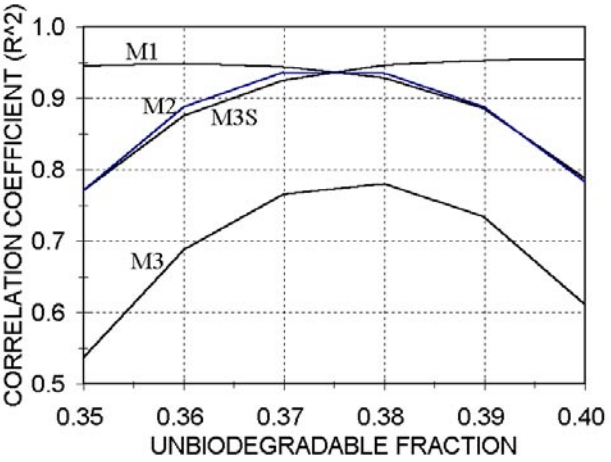

Figure 7b

Regression correlation coefficient (R^2) versus unbiodegradable COD fraction of the primary sludge ($f_{PS'up}$) for the Lineweaver-Burke (M1), inversion (M2) and Eadie-Hofstee linearisation methods, with (M3) and without (M3S) the 15 d retention time data, with the Monod hydrolysis rate equation for the Izzett et al. digester data set.

The K_M and K_S values for the saturation hydrolysis rate equation (Eq. 4 in Table 1) are found by the same linearisation methods, the only difference being that for saturation kinetics, the concentration variable is S_{bp}/Z_{AD} instead of S_{bp}. The K_M and K_S values so obtained are listed in Table 4. The specific hydrolysis rate, r_h/Z_{AD} (gCOD organics/ gCOD biomass·d) versus the saturation ratio S_{bp}/Z_{AD} (gCOD organics/ gCD biomass) graphs obtained for the saturation rate equation from the three linearisation methods are shown in Fig. 6 with the Izzett experimental data. As with the Monod kinetics, although method (i) gives the highest R^2 (0.979), method (ii) fits the experimental data marginally best at the shortest retention time (7 d). For saturation kinetics also, linearisation method (iii) showed that the 15 d retention time data is an outlier and is the reason for the low R^2 value (0.699) for all five retention time data. Excluding the 15 d data significantly improved the R^2 value for method (iii) (0.897). The average K_M and K_S values obtained from the three methods, with the 15 d retention time data excluded for method (iii), are given in Table 4. As with the Monod equations, Fig. 6 shows that even though different K values are obtained with the three different methods, the specific hydrolysis rate (r_h/Z_{AD}) versus saturation ratio (S_{bp}/Z_{AD}) curves obtained from each and the average are virtually the same and plot very closely to one another. Moreover, each of the four different hydrolysis kinetics equations yield near identical specific hydrolysis rate (r_h/Z_{AD}) versus biodegradable COD acidogen biomass concentration ratio (S_{bp}/Z_{AD}) curves.

The unbiodegradable fraction of sludge ($f_{PS'up}$) influences the calibration results of the different hydrolysis/acidogenesis rate equations. For their more complex approach, Sötemann et al. (2005a) found the lowest coefficient of variation (C_{var}, standard deviation/mean) for the first order (C_{var} = 0.017) and first order specific (C_{var} = 0.049) hydrolysis equations at $f_{PS'up}$ = 0.34 and 0.32 respectively and the highest correlation coefficient (R^2) for the Monod (R^2=0.98) and saturation (R^2=0.99) equations at $f_{PS'up}$ = 0.36. For this simpler steady state model the results are virtually the same. For the first order and first order specific hydrolysis equations, the lowest coefficient of variation (C_{var}) is at $f_{PS'up}$ = 0.34 (C_{var} = 0.040) and 0.32 (C_{var} = 0.074) respectively (Fig. 7a) and the highest correlation coefficient (R^2) for the Monod (R^2=0.945) and saturation (R^2=0.972) equations at $f_{PS'up}$ = 0.37 (Fig. 7b). It is clear that the steady state model gives almost the same results as the more complex hydrolysis model derived for UCTADM1. Even though this simpler steady state model yields different K values to the more complex model for reasons describe above, the specific hydrolysis rate (r_h/Z_{AD}) versus biodegradable COD concentration (S_{bp}) curves obtained from the model are virtually the same as for the more complex model, and similarly for the saturation kinetics.

With the hydrolysis rate kinetic constants determined from the Izzett et al. experimental results for the four different kinetic hydrolysis rate equations, plots of the %COD removal (i.e. %COD converted to methane, Eq. 21) versus retention time (R) calculated from the four hydrolysis rate equations are shown in Fig. 8. It is clear that the different rate equations give virtually identical results at long retention times (>10 d), but that critical differences between them arise at short retention times (<10 d).

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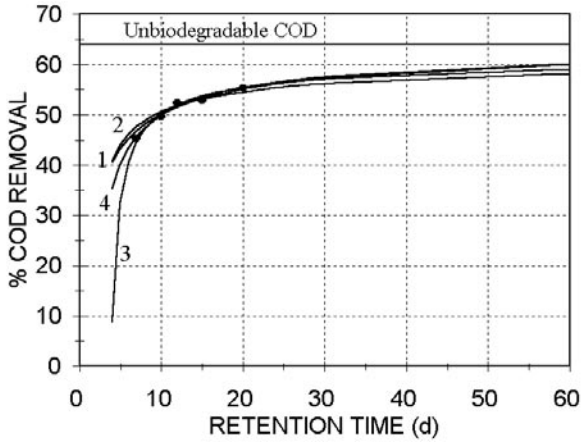

Figure 8
Percentage COD removal versus retention time for the 1st order (1), 1st order specific (2), Monod (3) and saturation (4) hydrolysis rate equations showing also the Izzett et al experimental data at 7, 10, 12, 15 and 20 d

It seems, therefore, that different digester failure retention times are predicted by different hydrolysis rate equations. However, this is not so because the hydrolysis process is not the one that causes digester failure - it is loss of methanogen species activity, usually the acetoclastic methanogens, that causes the digester pH to decrease that leads to failure. The low pH and high volatile fatty acid (VFA) concentration reduces the hydrolysis rate but does not cause it to stop (O'Rourke, 1967, Ristow et al., 2004).

From the above evaluation and Fig. 8, it can be concluded that the mixture of primary and humus sludge tested by Izzett et al. (1992) conforms very closely to both the Monod and saturation kinetics, because the % COD removal increases gradually with increasing retention time. From the Fig. 8 it can be seen that digesters at very long retention times (>60 d) are required to determine the $f_{PS'up}$ and at short retention times (<15 d) to calibrate and determine the best hydrolysis rate equation.

Calculating the constants in the hydrolysis kinetic equations – O'Rourke (1967) results

O'Rourke (1967) studied the kinetics of anaerobic sludge treatment at ambient temperatures, since at the time, most AD systems were operated at 35°C, and little was known about the performance of the systems at ambient temperatures. To determine the kinetics of AD at the ambient temperatures and the influence of temperature, digesters were fed a primary sludge concentration of 28.4 gCOD/ℓ and operated at 35, 25, 20 and 15°C and hydraulic retention times from 60 d to as low as 2.75 d, in which methanogenesis had failed. For this evaluation, only the methanogenic systems operated at 35°C are considered, of which there were five, i.e. 7.5, 10, 15, 30 and 60 d systems. The experimental results of these five systems are listed in Table 5.

Initially, all five retention time data were analysed in the identical way as the five retention time data of Izzett et al. From this analysis it was found that the validity of the hydrolysis kinetic constants obtained was very sensitive to the unbiodegradable COD fraction ($f_{PS'up}$). Values higher than 0.338 yielded negative effluent biodegradable COD concentrations (S_{bp}). This set an upper limit of 0.338 on the $f_{PS'up}$ value. A lower $f_{PS,up}$ for primary sludge seems reasonable in comparison with the 0.36 value obtained for the mixture of primary and humus sludge. Furthermore, the R^2 values for the Monod and saturation models were very low (<0.60) for all reasonable $f_{PS,up}$ from 0.32 to 0.34 and $f_{PS,up} > 0.336$ yielded negative K_s values with linearisation method (iii) (because $S_{bp} < 0$). The best $f_{PS,up}$ value was 0.334 – it yielded the lowest C_{var} for the first order and first order specific hydrolysis equations and the highest R^2 values (0.54 - 0.60) for the Monod and saturation equations. The calculated K_h and K_H rates and the Monod and saturation kinetics constants for all five retention times for $f_{PS'up} = 0.334$ are listed in Tables 6 and 7 respectively. The average K_h and K_H rates over the five retention times are 1.591 /d and 1.538 ℓ/(gCOD biomass·d) respectively. The K_h and K_H rates are plotted versus R in Fig. 9 together with the Izzett et al. data K_h and K_H rates. The O'Rourke K rates

TABLE 5
Experimental data measured by O'Rourke (1967) on completely mixed mesophilic (37°C) anaerobic digesters at 7 to 60 d retention time fed primary sludge

Retention time (d)	7.5	10	15	30	60
Influent COD gCOD/ℓ	28.4	28.4	28.4	28.4	28.4
Influent VFA mgCOD/ℓ	1 020	1 020	1 020	1 020	1 020
Influent Lipids g/ℓ	12.6	12.6	12.6	12.6	12.6
Influent Cellulose g/ℓ	4.47	4.47	4.47	4.47	4.47
Influent Proteins g/ℓ	6.4	6.4	6.4	6.4	6.4
Influent VSS g/ℓ	18.4	18.4	18.4	18.4	18.4
Effluent COD gCOD/ℓ	12.4	11.7	11.8	11.8	10.3
Effluent VFA gCOD/ℓ	0.14	0.09	0.06	0.06	0.03
Effluent Lipids g/ℓ	5.05	4.66	40.7	4.45	3.52
Effluent Cellulose g/ℓ	0.41	0.34	0.44	0.36	0.33
Effluent Proteins g/ℓ	4.32	4.33	4.35	3.78	3.67
Effluent VSS g/ℓ	8.3	8.1	7.2	7.1	6.6
Gas Composition $\%CH_4$	?	?	?	?	?
Gas prod mℓ CH_4/gCOD	308	328	330	350	347
COD balance (%)	99.7	100.9	101.6	105.3	99.4
Effluent Alk mg/ℓ as $CaCO_3$	1 800	1 600	1 800	2 000	2 300
Digester pH	6.9-7.3	6.8-7.3	6.9-7.3	7.0-7.4	7.0-7.4

TABLE 6

O'Rourke (1967) 7.5 to 60 d retention time (R) anaerobic digester measured influent* (S_{ti}) and effluent* (S_{te}) COD concentrations, influent unbiodegradable (S_{upi}) and biodegradable COD (S_{bpi}) concentrations for an unbiodegradable COD fraction ($f_{PS'up}$) of 0.334, calculated biodegradable COD concentration (S_{bp}) (Eq. 25), change in biodegradable concentration across digester (ΔS_{bp}), observed hydrolysis rate ($r_h = \Delta S_{bp}/R + b_{AD}Z_{AD}$, Eq. 12), acidogen biomass concentration (Z_{AD}), specific hydrolysis rate [r_h/Z_{AD})] and the 1st order and 1st order specific hydrolysis rate constants (K_h and K_H). All mass units in gCOD.

R	$*S_{ti}$	$*S_{te}$	S_{upi}	S_{bpi}	S_{bp}	ΔS_{bp}	r_h	Z_{AD}	r_h/Z_{AD}	K_h	K_H
d	g/ℓ	g/ℓ	g/ℓ	g/ℓ	g/ℓ	g/ℓ	g/(ℓ·d)	g/ℓ	gCOD S_{bp}/(gCOD Z_{AD}·d)	/d	ℓ/(gCOD Z_{AD}·d)
7.5	28.4	12.4	9.486	17.894	1.301	16.593	2.273	1.473	1.543	1.746	1.186
10	28.4	11.7	9.486	17.894	0.700	17.195	1.778	1.425	1.248	2.541	1.784
15	28.4	11.8	9.486	17.894	1.021	16.874	1.175	1.234	0.953	1.152	0.934
30	28.4	11.8	9.486	17.894	1.361	16.533	0.588	0.893	0.658	0.432	0.483
60	28.4	10.3	9.486	17.894	0.154	17.740	0.321	0.630	0.510	2.082	3.305
									Mean**	1.591	1.538

* See note on Table 3 . **Mean of all five retention time values.

TABLE 7

Monod and saturation kinetics K constants and correlation coefficients (R^2) for the 7.5 to 60 d anaerobic digester data of O'Rourke (1967) obtained from Lineweaver-Burke (M1), inversion (M2) and Eadie-Hofstee (M3) linearisation and regression methods and the mean values of the three methods for unbiodegradable fraction ($f_{PS'up}$) of 0.334

Kinetic rate	Monod kinetics			Saturation kinetics		
Linearisation method	K_m	K_s	R^2	K_M	K_S	R^2
Units. All mass units in COD	g organics/(g biomass·d)	g organics/ℓ	-	g organics/(g biomass·d)	g organics/g biomass	-
Method 1 (M1)	1.174	0.195	0.577	1.303	0.306	0.349
Method 2 (M2)	0.939	0.003	0.604	0.674	-0.170	0.809
Method 3 (M3)	1.177	0.127	0.108	0.690	-0.184	0.128
Average M1, M2, M3	1.097	0.108	-	0.889	-0.016	-

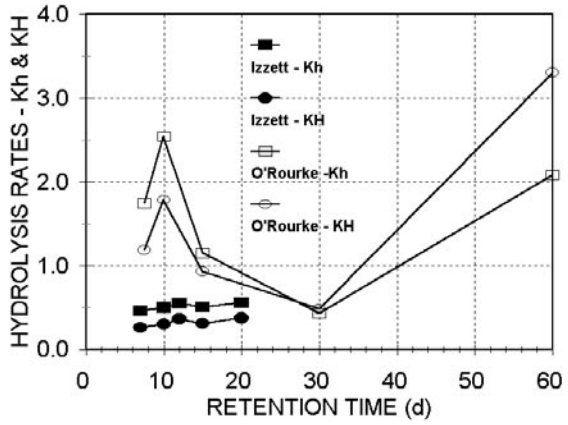

Figure 9

Hydrolysis rate constants for the 1st order (K_h, /d) and 1st order specific [K_H, ℓ/(gCOD biomass·d)] hydrolysis kinetic rate equations versus retention time for the Izzett et al. and O'Rourke anaerobic digester data sets

are significantly higher and vary widely over 7.5 to 60 d retention time. Higher K rates are expected from the O'Rourke data, because "pure" primary sludge would be expected to hydrolyse faster than a mixture of primary and humus sludge. The large variation of the K values is due to the sensitivity of the hydrolysis equations to the measured effluent total COD concentration (see Table 6), which do not decrease consistently with retention time (as anticipated by the hydrolysis equations). This is also the reason for the low correlation coefficients (R^2) obtained from the three linearisation methods for the Monod and saturation equations (Table 7).

To try and bring some consistency to the K rates obtained from the O'Rourke data, the 60 d retention time system was used to determine the $f_{PS'up}$ and the three shortest retention time systems (7.5, 10 and 15 d) to determine the K rates, i.e. the 30 d system was omitted from the analysis, which seems reasonable from Fig. 9. For the 60 d system, a $f_{PS'up}$ = 0.338 yielded a very low effluent biodegradable COD, i.e. S_{bp} = 0.041 gCOD/ℓ (0.340 makes it -ve). For this $f_{PS'up}$, determining the hydrolysis rate r_h and K rates with the 7.5, 10 and 15 d retention time systems yielded:

(i) the same r_h rates determined previously for these retention times with $f_{PS'up}$ = 0.334 (see Table 6 and 8),

(ii) the K_h and K_H rates still varied considerably, from 1.296 to 3.034 /d and 1.050 to 2.129 ℓ/(gCOD·d) at 15 and 10 d retention time respectively (Table 8) with little improvement in the coefficient of variation (C_{var}), and

(iii) lower R^2 values for the Monod and saturation kinetics (Table 9).

The reason for (ii) and (iii) for the three retention time systems compared with the five retention time systems is because the measured effluent COD concentration from the 15 d system is higher than that from the 10d system, which is contrary to the functional form of the hydrolysis equations. Furthermore, while the K_m and K_M rates increased, the increase was not large enough to indicate that primary sludge hydrolysed faster than a mixture of primary and humus sludges. Accordingly, the 15 d system data was also removed from the data set and the K rates calculated with only the 7.5 and 10 d system data (see Tables 8

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TABLE 8

O'Rourke (1967) 7.5 to 60 d retention time (R) anaerobic digester measured influent* (S_{ti}) and effluent* (S_{te}) COD concentrations, influent unbiodegradable (S_{upi}) and biodegradable COD (S_{bpi}) concentrations for an unbiodegradable COD fraction ($f_{PS'up}$) of 0.338, calculated residual biodegradable COD concentration (S_{bp}) (Eq. 25), change in biodegradable concentration across digester (ΔS_{bp}), observed hydrolysis rate ($r_h = \Delta S_{bp}/R + b_{AD}Z_{AD}$, Eq. 12), acidogen biomass concentration (Z_{AD}), specific hydrolysis rate [r_h/Z_{AD})] and the 1st order and 1st order specific hydrolysis rate constants (K_h and K_H). All mass units in gCOD. Note that r_h, Z_{AD} and r_h/Z_{AD} are identical to the values calculated in Table 6 for $f_{PS'up}$ of 0.334.

R	*S_{ti}	*S_{te}	S_{upi}	S_{bpi}	S_{bp}	ΔS_{bp}	r_h	Z_{AD}	r_h/Z_{AD}	K_h	K_H
d	g/ℓ	g/ℓ	g/ℓ	g/ℓ	g/ℓ	g/ℓ	g/(ℓ·d)	g/ℓ	gCOD S_{bp}/(gCOD Z_{AD}·d)	/d	ℓ/(gCOD Z_{AD}·d)
7.5	28.4	12.4	9.599	17.781	1.188	16.593	2.273	1.473	1.543	1.914	1.299
10	28.4	11.7	9.599	17.781	0.586	17.195	1.778	1.425	1.248	3.034	2.129
15	28.4	11.8	9.599	17.781	0.907	16.874	1.175	1.234	0.953	1.296	1.050
30	28.4	11.8	9.599	17.781	1.247	16.553	0.588	0.893	0.658	0.471	0.527
60	28.4	10.3	9.599	17.781	0.041	17.740	0.321	0.630	0.510	7.876	12.503
									Mean**	2.081	1.493
									Mean***	2.474	1.714

* See note on Table 3.
**Mean of 7.5, 10 and 15 d retention time values.
***Mean of 7.5 and 10 d retention time values only.

TABLE 9

Monod and saturation kinetics K constants and correlation coefficients (R^2) for the O'Rourke 7.5, 10 and 15 d retention time data obtained from Lineweaver-Burke (M1), inversion (M2) and Eadie-Hofstee (M3) linearisation and regression methods for unbiodegradable fraction ($f_{PS'up}$) of 0.338

Kinetic rate	Monod kinetics			Saturation kinetics		
Linearisation method	K_m	K_s	R^2	K_M	K_S	R^2
Units. All mass units in COD	g organics/(g biomass·d)	g organics/ℓ	-	g organics/(g biomass·d)	g organics/g biomass	-
Method 1 (M1)	1.35	0.100	0.026	1.17	-0.016	0.002
Method 2 (M2)	1.91	0.50	0.418	1.32	0.063	0.519
Method 3 (M3)	1.08	-0.12	0.048	1.00	-0.117	0.123

TABLE 10

Monod and saturation kinetics K constants and correlation coefficients (R^2) for the O'Rourke 7.5 and 10d retention time data for unbiodegradable fraction ($f_{PS'up}$) of 0.338. Note that all three linearisation and regression methods give the same results and perfect correlation for a pair of results.

Kinetic rate	Monod kinetics			Saturation kinetics		
Linearisation method	K_m	K_s	R^2	K_M	K_S	R^2
Units. All mass units in COD	g organics/(g biomass·d)	g organics/ℓ	-	g organics/(g biomass·d)	g organics/g biomass	-
Methods 1, 2 & 3	2.004	0.355	1.00	2.047	0.263	1.00

and 10). The calculated K_h and K_H rates at 7.5 and 10 d retention time do not change, only the average changes because it is based on only the 7.5 and 10 d system K rates (Table 8). The average 1st order K_h rate and 1st order specific K_H rate constants obtained are 2.474/d and 1.714 ℓ/(mgCOD·d) respectively (Table 8). Because there are only two systems and 2 degrees of freedom (i.e. 2 unknowns), the R^2 values for the Monod and saturation equations are 1.00 (i.e. perfect fit, Table 10). The percentage COD removal versus retention time calculated from the four calibrated hydrolysis equations for the 7.5 and 10 d system data only is shown in Fig. 10. It can be seen that with primary sludge

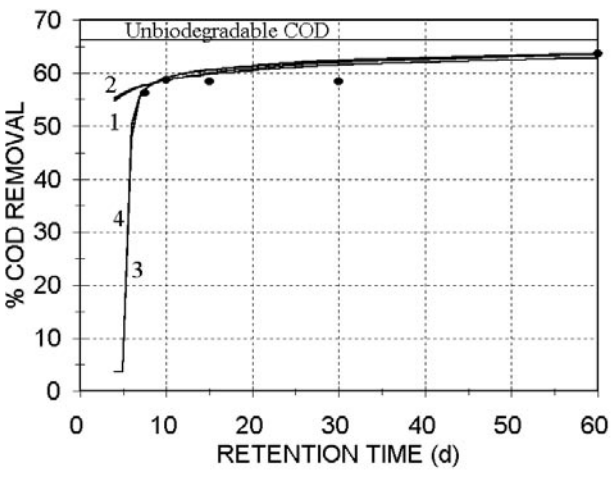

Figure 10 (right)
Percentage COD removal versus retention time for the 1st order (1), 1st order specific (2), Monod (3) and saturation (4) hydrolysis rate equations calibrated on the 7.5 and 10 d retention time systems of O'Rourke showing also the experimental data at 7.5, 10, 15, 30 and 60 d.

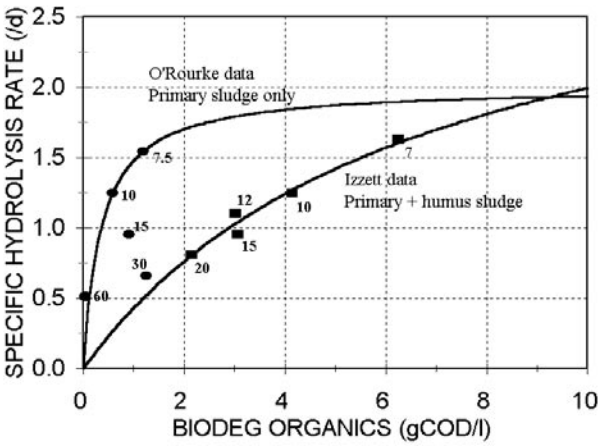

Figure 11

Specific hydrolysis rate [r_h /Z_{ad}, gCOD organics/(g COD biomass ·d)] versus biodegradable organics concentration (S_{bp}, gCOD/ℓ) calculated for Monod hydrolysis kinetic rate equation for the Izzett et al. (1992) (all 5 retention times) and O'Rourke (1967) (7.5 and 10d retention times) anaerobic digester data showing also their experimental data (■, Izzett) and (●, O'Rouke) with retention time indicated

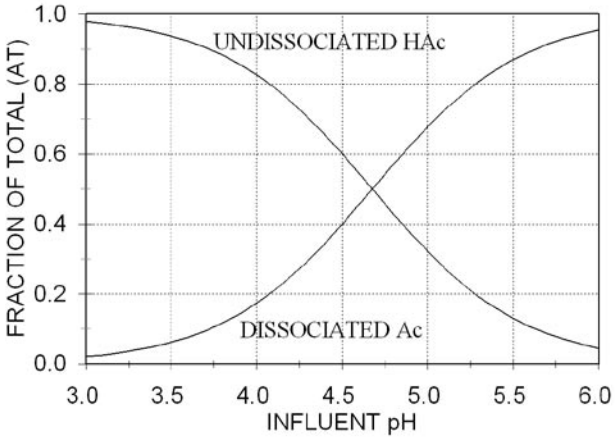

Figure 12

Fraction of undissociated and dissociated acetate species versus influent pH for a pK'$_a$ value of 4.68 for a TDS of 2500 mg/ℓ and temperature of 37°C

only, a high %COD removal (> 60%) is obtained even at short retention times (<10 d). In contrast, because humus sludge in the primary and humus sludge mixture hydrolyses more slowly than primary sludge, the %COD removal is only 55% at significantly longer retention times (>20 d) (Figs. 6 and 8). A comparison between the Monod curves obtained for the primary sludge (O'Rourke data) and the primary and humus sludge mixture (Izzett et al. data) calculated from the respective Monod K_m and K_s values is shown in Fig. 11 together with the experimental data. Figure 11 reinforces the conclusion above: With its low K_s value, higher rates of hydrolysis are maintained with "pure" primary sludge for much lower biodegradable COD concentrations, S_{bp} (and therefore shorter retention times) than for the primary and humus sludge mixture.

Steady state model development – stoichiometry

Once the concentration of hydrolysable organics utilised in the anaerobic digester is known from the hydrolysis kinetics, the sludge composition and stoichiometry of the biological processes following the hydrolysis process and the utilisation of the influent VFA concentration (S_{bsai}) define the digester gas composition and pH.

McCarty (1974) gives the following general stoichiometric reaction for the overall AD system fed an organic waste of empirical composition $C_XH_YO_ZN_A$ to methane, carbon dioxide and biomass (of composition $C_5H_7O_2N$) as final end products:

$$C_XH_YO_ZN_A + \left(2X+A-Z-\frac{9ED}{20}-\frac{(1-E)D}{4}\right)H_2O \rightarrow \left(X-A-\frac{ED}{5}-\frac{(1-E)D}{8}\right)CO_2 + \left(\frac{(1-E)D}{8}\right)CH_4 + \left(\frac{ED}{20}\right)C_5H_7O_2N + \left(A-\frac{ED}{20}\right)NH_4^+ + \left(A-\frac{ED}{20}\right)HCO_3^- \quad (27a)$$

where:

D = 4X + Y - 2Z - 3A (e$^-$ eq/mol)

In Eq. 27a, E is the fraction of hydrolysed COD utilised (S_{bp}) that is converted to biomass (Z_{AD}), which from Eqs 13 or 25 is

$$E = \frac{Z_{AD}}{S_{bpi}-S_{bp}} = \frac{Y_{AD}}{[1+b_{AD}R(1-Y_{AD})]} \quad (27b)$$

The gCOD/mol and molar mass (MM) of the influent organics $C_XH_YO_ZN_A$ are given by:

$$COD = 8[Y+2(2X-Z)-3A] \text{ gCOD/mol} \quad (28a)$$

$$MM = 12X+Y+16Z+14A \text{ g drymass/mol or gVSS/mol} \quad (28b)$$

where:

VSS = volatile suspended solids

The influent VFA concentration are assumed to be acetate species with a MM = 60 g/mol and COD=64 gCOD/mol. The stoichiometry of utilisation of the undissociated and dissociated acetate species by the methanogens, assuming zero sludge production (E=0 in Eq. 27a), is

$$CH_3COOH \Rightarrow CH_4 + CO_2 \quad \text{and} \quad (29a)$$

$$CH_3COO^- + H_2O \Rightarrow CH_4 + HCO_3^- \quad (29b)$$

The total CH_4, CO_2 and HCO_3^- species produced is the sum of Eqs. 27 and 29. The split between the undissociated and dissociated acetate species is governed by the influent pH (Eq. 30). This split is shown versus pH in Fig. 12 for a pK'$_a$ value for acetate of 4.68 obtained for an influent TDS concentration of 2 500 mg/ℓ and a temperature of 37°C (Loewenthal et al., 1989). Figure 12 shows that the higher influent pH, the higher the fraction of dissociated acetate species, the higher the alkalinity generation (Eq. 29b) and therefore the higher the digester pH.

$$S_{bsHAci} = \frac{S_{bsai}}{\left(1+10^{pH_i-pK'_a}\right)} \quad (30)$$

and $S_{bsAci} = \frac{S_{bsai}}{\left(1+10^{pK'_a-pH_i}\right)}$ mgCOD/ℓ

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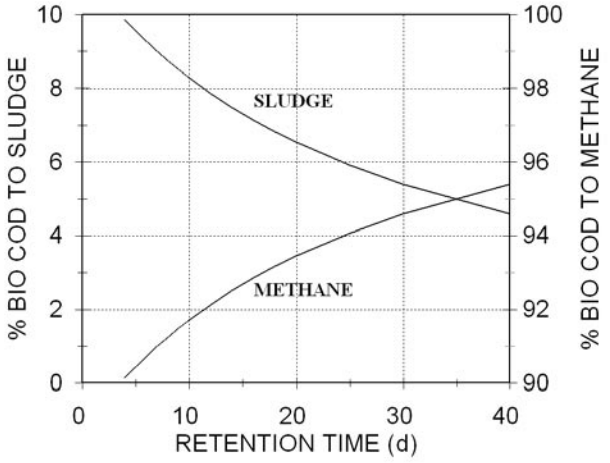

Figure 13

Percentage of biodegradable COD removed [$\Delta S_{bp}/S_{bpi} = (S_{bpi}-S_{bp})/S_{bpi}$] converted to sludge mass (E factor in Eq 27) and methane versus retention time. Although very slow, the endogenous process results in lower sludge and higher methane production at longer retention time.

where:

pH_i is the influent pH and

S_{bsHAci} and S_{bsAci} the undissociated and dissociated acetate species concentration in the influent respectively.

For acidogen organism constants Y_{AD} = 0.113 mgCOD biomass/mg COD organics degraded and b_{AD} = 0.041 /d, the fraction of COD hydrolysed converted to sludge mass (E, Eq. 27b) and methane (1-E) are shown as % in Fig. 13. One of the major advantages of anaerobic treatment is evident in Fig. 13, i.e. sludge production is extremely low compared with aerobic treatment – only 9 and 5% of COD degraded from 5 to 40 d retention time with practically all (91 to 95%) converted to useful methane gas.

Steady state model development – weak acid base chemistry

In Eqs. 27 and 29, the total CO_2 produced is the sum of the gaseous CO_2 and the dissolved CO_2, which, at the near neutral pH of AD (6.5 to 7.5), is mostly in the bicarbonate (HCO_3^-) form. The proportion of the total CO_2 that is in the bicarbonate form is governed by:

- the ammonia released in the breakdown of the hydrolysable organics (Eq. 27a), which at neutral pH, picks up a proton from the dissolved CO_2 (H_2CO_3*) to form saline ammonia (NH_4^+) and bicarbonate (HCO_3^-) according to $NH_3 + H_2CO_3^* \Rightarrow NH_4^+ + HCO_3^-$ and
- the concentration of influent dissociated acetate species utilised in the digester (Eq. 29b), which is governed by the degree of hydrolysis of the sludge prior to entry to the digester and the influent pH.

The gaseous CO_2 and CH_4 produced define the gas composition, which sets the partial pressure of CO_2 (p_{CO2}). The pH of the digester is defined by the p_{CO2} and the bicarbonate concentration (HCO_3^-) generated, which is equal to the alkalinity generated. Clearly, the N content of the influent organics and the influent VFA concentration and pH are very important because these define the HCO_3^- alkalinity concentration generated and p_{CO2} of the gas, both of which set the digester pH. If the N content of the influent organics is too low, lime may need to be dosed to augment the uptake of H^+ by the NH_3 released from the organics and establish the appropriate HCO_3^- concentration and p_{CO2} for the required digester pH (>6.5) (Capri and Marais, 1975). Accepting that:

- the pH is established predominantly by the carbonate weak acid base system and
- the bicarbonate concentration ([HCO_3^-], mol/ℓ) is generated principally from the ammonia released from the breakdown of the influent hydrolysable organics and the utilisation of influent dissociated acetate species, (i.e. low influent alkalinity with respect to that generated, see Table 2) and
- equilibrium exists between the dissolved and gaseous inorganic carbon species (reasonable at long retention times), the relationship between the bicarbonate concentration, p_{CO2} and pH is given by:

$$p_{CO2} = \frac{[HCO_3^-]\left(1 + 10^{pK'_{c1}-pH} + 10^{pH-pK'_{c2}}\right)}{10^{-pK'_{HCO2}}\left(1 + 10^{pH-pK'_{c1}} + 10^{2pH-pK'_{c1}-pK'_{c2}}\right)} \quad \text{atm or mole fraction} \quad (31)$$

where:

$[HCO_3^-]$ = bicarbonate concentration ~ H_2CO_3* alkalinity (mol/ℓ) ~ Total alkalinity (mol/ℓ)

p_{CO2} = partial pressure of CO_2 in the gas phase

pH = -ve $\log_{10}$ of the (H^+) activity

pK'_{HCO2} = -ve $\log_{10}$ of the apparent Henry's law constant for CO_2

pK'_{C1}, pK'_{C2}, = -ve $\log_{10}$ of 1st and 2nd carbonate system apparent dissociation constants where apparent means corrected for ionic strength effects (see Loewenthal et al., 1989).

Equation 31 is plotted in Fig. 14 for a temperature of 37°C and a TDS of 2 500 mg/ℓ at which pK'_{C1} = 6.211, pK'_{C2} = 9.960 and pK'_{HCO2} = +1.609 (Loewenthal et al., 1989), together with the range of normal anaerobic digester operation.

Design example

The steady state model with the Monod hydrolysis rate equation and its associated kinetic constants (Table 1) are applied to the 20 d retention time system of Izzett et al. (1992) (Table 2).

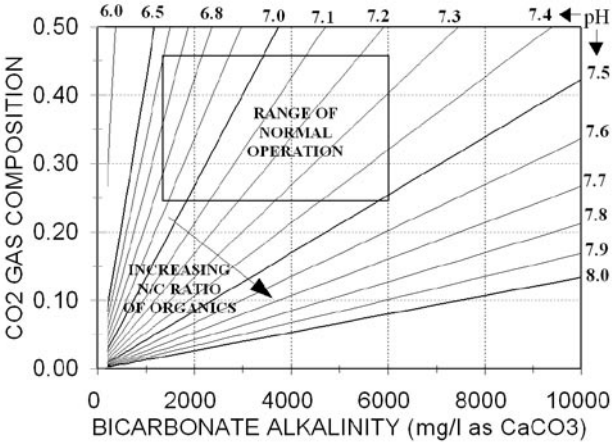

Figure 14

Fraction CO_2 gas composition versus reactor bicarbonate concentration (≈ alkalinity) for pH ranging from 6.5 to 8.0. Also shown is the range of normal anaerobic digester operation.

Calculating the COD removal and methane production – hydrolysis kinetics

Total influent COD concentration (S_{ti}) = 42.59 gCOD/ℓ (measured)
Influent VFA concentration (S_{bsai}) = 2.24 gCOD/ℓ (measured)
Unbiodegradable fraction of the primary sludge ($f_{PS'up}$) = 0.36 (determined above)
Influent hydrolysable COD concentration (S_{bpi}) = (1 - 0.36) 42.59 - 2.24 = 25.02 gCOD/ℓ (Eq. 5)
Influent unbiodegradable COD concentration (S_{upi}) = 0.36 x 42.59 = 15.33 gCOD/ℓ (Eq. 6)
Residual biodegradable COD concentration (S_{bp}) = 2.15 gCOD/ℓ (Eq. 14)
Biodegradable COD concentration removed ($S_{bp} = S_{bpi} - S_{bp}$) = 22.87 gCOD/ℓ (Eq. 22)
Acidogen biomass concentration (Z_{AD}) = 1.50 gCOD/ℓ (Eq. 13)
Unbiodegradable COD concentration (S_{up}) = 15.33 gCOD/ℓ (Eq. 15)
Total effluent COD concentration (S_{te}) = 15.33+2.15+1.50=18.98 gCOD/ℓ (Eq. 23)
Methane production concentration (S_m) = 21.38 gCOD/ℓ influent (Eq. 17)
Methane production from VFA = 2.24 gCOD/ℓ influent (Equal to VFA COD, Eq. 29)
Total methane production concentration = 21.38+2.24= 23.62 gCOD/ℓ influent
Total COD concentration out ($S_{te} + S_m$) = 18.98+23.82= 42.60 gCOD/ℓ (Eq. 20)
Hence COD balance 100(S_{te}+S_m)/S_{ti} = 100.0%
Methane production gas volume (Q_m) = 8.87 (ℓ methane/d)/(ℓ influent flow/d) (Eq. 18).
Fraction of biodegradable COD removed converted to sludge mass (E) = 0.0654 (Eq. 27b).
Fraction of biodegradable COD removed converted to methane (1-E) = 0.9346.

Calculating the partial pressure of CO_2, and the ammonia and alkalinity concentrations generated – stoichiometry

The primary sludge composition was estimated as $C_{3.5}H_7O_2N_{0.196}$ (Sötemann et al., 2005a). Hence the COD content of the sludge is 131.3 gCOD/mol (Eq. 28a) and the hydrolysable COD concentration removed 22.87/131.3 = 0.1742 mol/ℓ. From Eq. 27, with E=0.0654, the stoichiometric equation for the overall digestion process therefore is:

$$0.1742\,C_{3.5}H_7O_2N_{0.196} + 0.1530\,H_2O \rightarrow 0.2042\,CO_2 + 0.3340\,CH_4 + 0.0094\,C_5H_7O_2N + 0.0248\,NH_4^+ + 0.0248\,HCO_3^- \quad (31a)$$

The influent VFA concentration was 2.240 gCOD/ℓ, which at an influent pH of 5.28 (Table 2) comprises 20% (0.4480 gCOD/ℓ = 0.4480/64=0.0070 mol/ℓ) undissociated (Eq. 30a) and 80% (1.792 gCOD/ℓ=1.792/64=0.0280 mol/ℓ) dissociated acetate species (Eq. 30b). From Eq. 29, this yields:

$$0.0070\,CH_3COOH \rightarrow 0.0070\,CH_4 + 0.0070\,CO_2 \quad (32a)$$

and

$$0.0280\,CH_3COO^- + 0.00280\,H_2O \rightarrow 0.00280\,CH_4 + 0.00280\,HCO_3^- \quad (32b)$$

Adding Eqs. 31a, 32a and 32b yields for the total biodegradable COD utilised,

$$0.1742\,C_{3.5}H_7O_2N_{0.196} + 0.0070\,CH_3COOH + 0.0280\,CH_3COO^- + 0.1810\,H_2O \rightarrow 0.2112\,CO_2 + 0.3690\,CH_4 + 0.0094\,C_5H_7O_2N + 0.0248\,NH_4^+ + 0.0528\,HCO_3^- \quad (33)$$

Equation 33 shows that 0.0094 mol/ℓ biomass ($C_5H_7O_2N$) is formed, which is 0.0094 x 160gCOD/mol = 1.50 gCOD/ℓ and corresponds exactly with Eq. 13. It also shows that 0.2112 and 0.3690 mols gaseous CO_2 and CH_4 are produced yielding a total gas volume 0.5802 mol/ℓ influent. At 24.0 ℓ gas/mol at 20°C and 1 atm pressure (Eq. 19), this is 5.08, 8.87 and 13.95 ℓ CO_2, CH_4 and total gas volume per ℓ influent flow. It can be seen that the volume of methane production calculated from the kinetic part of the AD model is the same as that calculated from the stoichiometric part of the model, i.e. 8.87 ℓ methane/ℓ influent flow. This because the E value calculated from the kinetic model (fraction of COD removed converted to sludge mass = 0.0654, Eq. 27b) was applied to the stoichiometric model. From the CO_2 and CH_4 gas production, the CO_2 gas composition (in mol fraction or partial pressure, p_{CO2}) is 5.08/13.95 = 0.364. From Eq. 33, 0.0248 mol/ℓ ammonia and 0.0528 mol/ℓ bicarbonate alkalinity are generated. This is 0.0248 x 14 000 = 347 mgN/ℓ and 0.0528 x 50 000 = 2 640 mg/ℓ as $CaCO_3$ respectively. Adding these generated ammonia and alkalinity concentrations to the influent concentrations (Table 2) yields the predicted effluent concentrations, i.e. 244+347=591 mgFSA-N/ℓ and 56+2640=2696 mg$CaCO_3$/ℓ.

Calculating the digester pH – weak acid base chemistry

With the p_{CO2} = 0.364 and HCO_3^- concentration = 2 696 mg/ℓ as $CaCO_3$, the digester pH is 6.99 (Eq. 31, Fig. 14). Following the above procedure, a comparison between theoretically predicted and experimentally observed (a) COD removal (gCOD/ℓ) (b) gas production (ℓ gas/d per ℓ influent/d), (c) gas composition (%CO_2), (d) effluent FSA concentration (mgN/ℓ), (e) alkalinity (mg/ℓ as $CaCO_3$) and (f) digester pH are given in Figs. 15a to f respectively for the Izzett et al. 7, 10, 12, 15 and 20 d retention time digesters.

Comparison between theoretically predicted and experimentally observed results

The predicted COD removals (Fig. 15a) correspond very well to those measured. The gas production (Fig. 15b) is under predicted because the model is based on 100% COD balance and experimental data COD balances ranged between 107 and 109% (Table 2) and also due to uncertainty in the gas temperature (20°C was assumed but if it was 37°C to would be 6% higher). Because the steady state model was calibrated on COD removal (rather than on gas production, which can also be done depending on whether effluent COD or gas production data show the best consistency, i.e. sequentially decreasing or increasing respectively with retention time), the predicted COD removal conforms almost exactly to that measured (Fig. 15a) and so the error in the experimental COD balance manifests in the gas production (Fig. 15b). The gas composition (Fig. 15c) corresponds very well to that measured. The predicted effluent FSA concentration (Fig. 15d) is higher than that measured, because the model is based on 100% N balance and the N balance of experimental data range between 90 and 99% (Table 2). By decreasing

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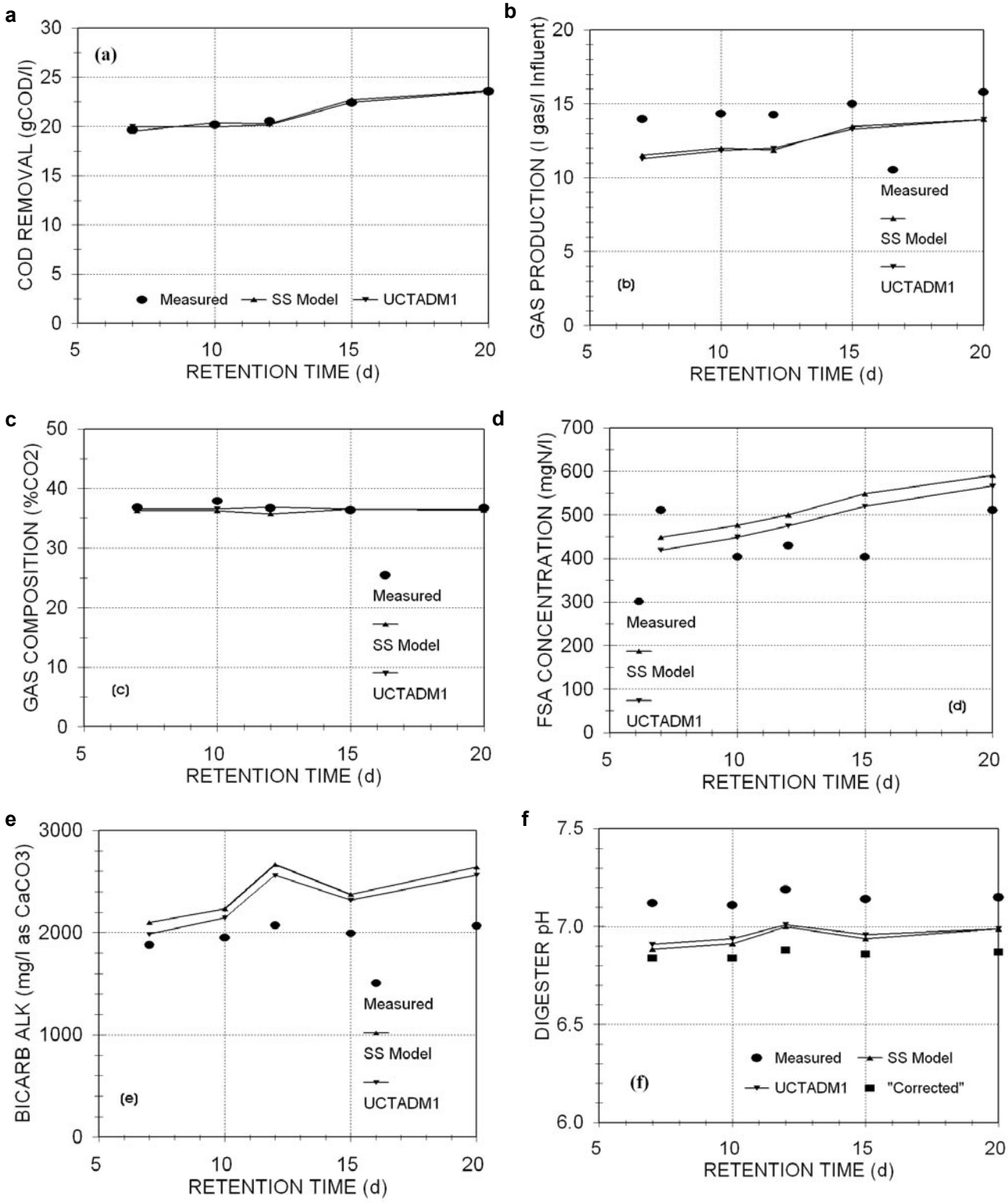

Figure 15

Comparison between steady state (SS) model and integrated simulation (UCTADM1) model predicted (lines) and measured (points) COD removal (mgCOD/ℓ, Fig. 15a, top left), gas production(ℓ/d, Fig. 15b, top right), gas composition (pCO_2, Fig. 15c, middle left), effluent FSA (mgN/ℓ, Fig. 15d, middle right), alkalinity (mg/ℓ as $CaCO_3$, Fig. 15e, bottom left) and digester pH (Fig. 15f, bottom right) versus retention time for the Izzett et al. data set.

the N content of the hydrolysable organics (A in $C_XH_YO_ZN_A$) by a small amount (5% to 0.186), the predicted effluent FSA can be made to closely fit the measured effluent FSA of the 10 to 20d retention time systems. This also will result in an improved correlation between predicted and measured alkalinity (Fig. 15e), because with a lower N content in the sludge, less alkalinity is generated. The lower alkalinity will decrease the predicted digester pH causing it to deviate further (~0.3 pH units) from the actual measured pH but closer to the "corrected" measured pH (Fig. 15f). The actual measured pH data (7.11 to 7.19) show an

inconsistency in that these pH values and the measured alkalinity and gas composition do not conform to Eq. 31 – accepting the data that are most reliably measured, i.e. gas composition (Fig. 15c) and alkalinity (Fig. 15e) with the five point titration method of Moosbrugger et al. (1992), the digester pH must be lower than that measured to conform to Eq. 31 (see Table 2 and Fig. 15f). A digester pH lower than that actually measured is quite likely because CO_2 loss during sampling and testing will increase the pH. Despite the improvement between predicted and measured results that reducing the A value to 0.186 will yield to conform to the measured effluent N mass, the A=0.196 value in $C_XH_YO_ZN_A$ was retained because it is based in the influent N mass. Further, Sötemann et al. (2005a) show that the $C_{3.5}H_7O_2N_{0.196}$ stoichiometry accepted for the primary and humus sludge composition, which was obtained from the COD, C and N mass balances over the Izzett et al. AD systems (Table 2), conforms very closely to independently measured CHON composition measurements on "pure" primary sludge, i.e. within 96%, 100%, 95% and 99% respectively. Considering the complexity of the system and the margin of error in the experimental data, overall the steady state model predicts the anaerobic digester performance over the 7 to 20 d retention time satisfactorily for steady state design. The predictions of the more detailed two phase (aqueous-gas) integrated chemical, physical and biological processes anaerobic digester model (UCTADM1) of Sötemann et al. (2005a) are also shown in Figs. 15a to f and the steady state AD model can be seen to correlate very closely also with UCTADM1. Hence, the steady state AD model provides a reliable basis for cross-checking simulation model results.

Conclusion

A steady state AD model for the treatment of sewage sludge has been developed. It comprises three sequential parts:

- a kinetic part with which the influent COD hydrolysed/utilised, gas and biomass production and effluent COD concentration are calculated for a given retention time,
- a stoichiometry part with which the gas composition (or partial pressure of CO_2), ammonia released and alkalinity generated are calculated from the COD utilised and the CHON composition of the hydrolysed COD and
- a carbonate system weak acid base chemistry part with which the digester pH is calculated from the partial pressure of CO_2 and alkalinity generated.

This model shows that for a given %COD removal, the partial pressure of CO_2 and alkalinity generated, and hence the digester pH, are governed entirely by the influent sludge composition, i.e. X, Y, Z and A in $C_XH_YO_ZN_A$ and the undissociated volatile fatty acids (VFA) species concentration of the influent.

The hydrolysis kinetic part of the model was calibrated against AD data for two types of sewage sludge:

- a primary and humus sludge mixture extending over a retention time range of 7 to 20 d and
- a "pure" primary sludge extending over a retention time range of 7.5 to 60 d.

Also, four hydrolysis kinetic rate (r_h) equations were calibrated against both sludge types, viz.

- first order ($r_h = K_h S_{bp}$),
- first order specific ($r_h = K_H S_{bp} Z_{AD}$),
- Monod [$r_h = K_m S_{bp}/(K_s + S_{bp}) Z_{AD}$] and
- saturation [$r_h = K_M (S_{bp}/Z_{AD})/(K_S + S_{bp}/Z_{AD}) Z_{AD}$].

Once calibrated against the particular sludge type and taking due account of experimental error, the %COD removals predicted by the four hydrolysis kinetic equations were closely similar, which made it difficult to select the best kinetic equation. Also, by varying the unbiodegradable COD fraction ($f_{PS'up}$) of the sewages sludges within a narrow range (~2%) changed the coefficient of variation (C_{var}) for the first order and first order specific kinetic equations, and the correlation coefficient (R^2) for the Monod and saturation kinetic equations. Within the 2% range in unbiodegradable COD fraction, the different hydrolysis kinetic equations yielded best statistical fits between theoretically predicted and experimentally measured COD removals (or gas production) at different $f_{PS'up}$ values. It is concluded that for both types of sewage sludge, taking due account of experimental error (i.e. COD mass balance errors) each calibrated kinetic equation is equally good for calculating the %COD removal and gas production versus retention time. For each sewage sludge type, different hydrolysis kinetic rates and unbiodegradable COD fractions were obtained which showed that the pure primary sludge hydrolysed significantly faster and had a lower unbiodegradable particulate COD fraction ($f_{PS'up} = 0.33$) than the primary and humus sludge mixture ($f_{PS'up} = 0.36$). Anaerobic digesters treating pure primary sludge therefore will achieve higher COD or VSS removals at shorter retention times than digesters treating a primary and humus sludge mixture.

Once the COD removal is known from the hydrolysis kinetics part of the model, the CHON composition of the COD removed and the dissociated acetate species concentration in the influent (all utilised in the digester) fixes the gas composition (or partial pressure of CO_2), the ammonia released and the bicarbonate generated (equal to alkalinity generated) through the C, H, O and N mass balances based stoichiometry part of the model. From the influent COD, C and N masses of the primary and humus sludge digesters, a sludge composition of $C_{3.5}H_7O_2N_{0.196}$ has been determined (Sötemann et al., 2005a). With this sludge composition and measured influent VFA concentration and pH, from which the dissociated acetate species concentration was calculated, the stoichiometry part of the model predicted the experimentally observed gas composition (or CO_2 partial pressure), ammonia released and alkalinity generated well, taking due account of experimental error. With the CO_2 partial pressure and alkalinity generated, the digester pH was calculated from the carbonate system weak acid base chemistry part of the model. The model predicted pH was significantly lower (by ~0.30 pH units) than that experimentally measured. From the observed CO_2 partial pressure and alkalinity, which can be measured reliably, there is an error in the measured digester pH, probably due to CO_2 gas loss in sampling and measurement. The "corrected" measured pH should be between 6.84 and 6.88 for the 7, 10, 12, 15 and 20 d retention time systems and the predicted pH is 0.08 to 0.12 pH units higher than these corrected values. A significantly closer correlation between theoretically calculated and experimentally measured digester effluent FSA, alkalinity and pH can be obtained if the N content of the feed sludge is decreased from 0.196 to 0.186 based on the measured N mass exiting the digesters rather than on that entering the digesters. Taking into consideration experimental error (C and N mass balances errors) it is concluded that the steady state model predicts very well the observed 7 to 20 d retention time primary and humus sludge digester performance. The stoichiometry and carbonate system weak acid base chemistry part of the model could not be checked against the "pure" primary sludge digester data set of O'Rourke (1967) because the N concentrations in the effluent were not measured for this data set. The steady state

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AD model also correlated very closely with the predictions of the two phase (aqueous-gas) integrated chemical, physical and biological processes dynamic simulation anaerobic digester model (UCTADM1) of Sötemann et al. (2005a). Provided the hydrolysis rate of the particulate biodegradable organics is known for a particular sewage sludge, the steady state model is useful to:

- estimate retention time, reactor volume, gas production and composition for a required system performance like COD (or VSS) removal,
- investigate the sensitivity of the system performance to the design and operation parameters,
- provide a basis for cross-checking simulation model results, and
- estimate product stream concentrations for design of down- (or up-) stream unit operations of the wastewater treatment plant.

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