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):

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±0.041 /d *K_h = 0.481±0.040 /d	K_H = 0.322±0.047 *K_H = 0.379±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.

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

$$S_{upi} = f_{PS'up}\, S_{ti} \tag{6}$$

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

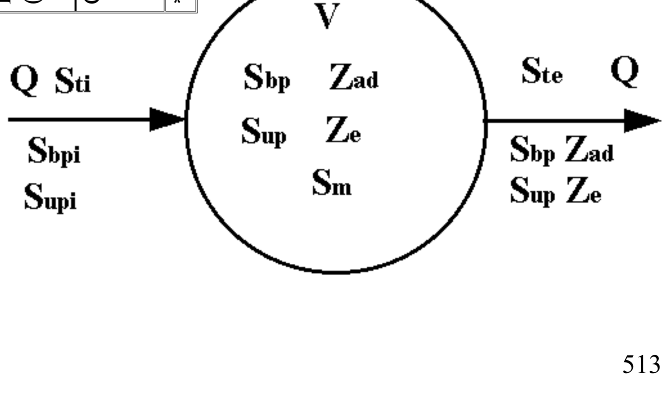

Figure 1
Schematic diagram of the flow through anaerobic digester of retention time R = V/Q showing symbols used in the steady state AD model.

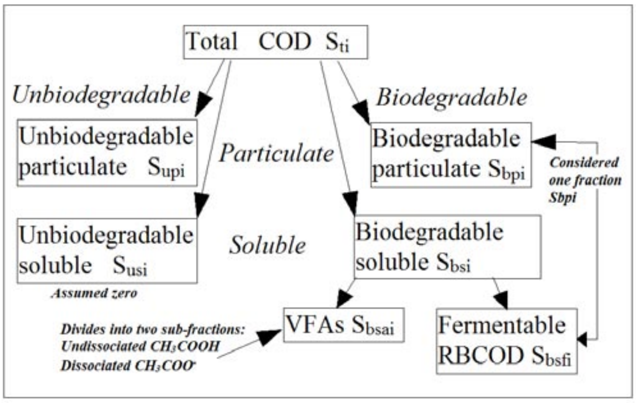

Figure 2
Influent primary sludge COD fractionation for the steady state anaerobic digestion model

(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:

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

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

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:

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

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:

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

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

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

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

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

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

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

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

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:

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

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.

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

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:

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

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:

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

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:

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

(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:

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

(ℓ gas/d)/(ℓ influent flow/d)

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

$$S_{ti} = S_{te} + S_m = S_{bp} + Z_{AD} + S_{up} + S_m \tag{20}$$

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:

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

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

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:

$$S_{tr} = S_{ti} - S_{te} = S_m \tag{21}$$

$$S_{bpr} = S_{bpi} - S_{bp} \tag{22}$$

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:

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

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

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

Solving Eq. 24 for S_{bp} yields:

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

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

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:

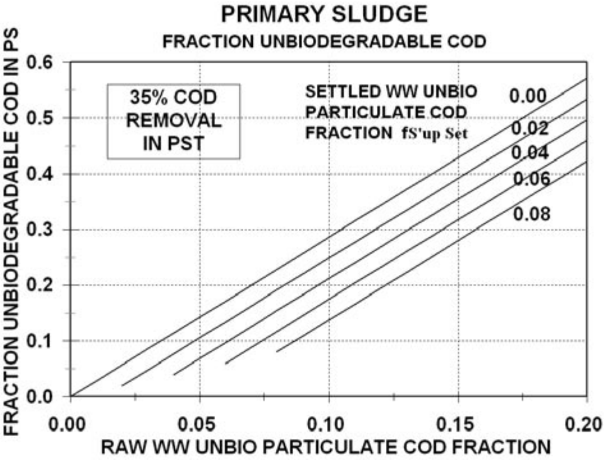

Figure 3
Fraction of unbiodegradable COD in primary sludge versus raw wastewater unbiodegradable particulate COD fraction for different settled wastewater unbiodegradable particulate COD fraction

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

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.