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 CO₂) and the digester pH is calculated from the partial pressure of CO₂; and a carbonate system weak acid/base chemistry part from which the digester pH is calculated from the partial pressure of CO₂ and alkalinity generated. From the stoichiometry and weak acid base chemistry part of the model, the COD mass balances 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 biodegradable particulate COD fraction (fᵢ₉₅₀) than the primary and humus sludge mixture. The %COD removal 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 mixture of Cᵢ₇Hᵢ₇Oᵢ₉Nᵢ₀₀. 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 Cᵢ₇Hᵢ₇Oᵢ₉Nᵢ₀₀ 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, H₂CO₃, Alk, pH, gaseous CO₂ and CH₄ 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 biodegradable COD fraction (fᵢ₉₅₀), the short chain fatty acid (SCFA) COD and the CHON content, i.e. X, Y, Z and A in Cᵢ₇Hᵢ₇Oᵢ₉Nᵢ₀₀ 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 Drosté, 2000;
acids (i.e. propionate and acetic acid) and carbon dioxide (CO₂) and hydrogen (H₂).  
ii) Acetogenic bacteria convert HPr to HAc and H₂.  
iii) Acetoclastic methanogens convert HAc to CO₂ and methane (CH₄) and  
iv) Hydrogenotrophic methanogens convert H₂ and CO₂ to CH₄ 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 H₂ 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, CH₄, CO₂ 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 \( S_{ps} \) and the acidogen biomass concentration \( Z_{ac} \) 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 (UCTADMI) because this equation gave a similar \( f_{ps,up} \) value (0.36) to O’Rourke (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 \( Z_{ac} \) and acetoclastic methanogen \( Z_{ac} \) 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 \( Y_{ac} = 0.89 \, \text{gCOD substrate hydrolysed} \) 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 \( (S_{ps}) \) as \( f_{ps,up} \), the particulate biodegradable \( (S_{ps}) \) and unbiodegradable \( (S_{up}) \) COD concentrations in the influent are (see Fig. 2):
where:

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

Sewage sludge comprises two additional dissolved COD fractions, i.e. the unbiodegradable soluble COD (\( S_{\text{usi}} \)) and the fermentable (non-VFA) readily biodegradable soluble COD (\( S_{\text{bsfi}} \)) (Fig. 2). The \( S_{\text{usi}} \) is very low in relation to the \( S_{\text{upi}} \) and so can be assumed zero for the purposes of this steady state model. The \( S_{\text{bsfi}} \) goes through the same hydrolysis/acidogenesis processes as the particulate biodegradable COD (\( S_{\text{bpi}} \)) and so is included with the \( S_{\text{bpi}} \).

Because the steady state model is based on the hydrolysis process as stated in Eq. 5, the \( S_{\text{bsai}} \) is not included with the COD passing through this process. However, the \( S_{\text{bsai}} \) does generate methane and \( \text{CO}_2 \) (but negligible sludge mass) mediated by the two methanogenic species. Hence \( S_{\text{bsai}} \) 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 \( S_{\text{a}} \) is given by \( S_{\text{a}} = S_{\text{upi}} + S_{\text{bpi}} + S_{\text{bsai}} \) (Fig. 2).

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

\[
\text{r_h} = \text{volumetric hydrolysis/acidogenesis rate in gCOD/(ℓ·d)} \\
\text{Y_{AD}} = \text{pseudo acidogen yield coefficient (gCOD biomass/ gCOD organics hydrolysed)} \\
b_{AD} = \text{acidogen endogenous respiration rate (/d)}.
\]

The steady state model is derived by applying the steady state mass balance equation (Eq. 7) to the four system variable components (Fig. 1) to the four system variable components (Fig. 1) to the four system variable components (Fig. 1) to the four system variable components (Fig. 1) to the four system variable components (Fig. 1) to the four system variable components (Fig. 1) to the four system variable components (Fig. 1) to the four system variable components (Fig. 1):

\[
\text{COD balance:} \\
S_{\text{up}} = \text{COD in:} \\
S_{\text{a}} = S_{\text{up}} + Z_{\text{AD}} + S_{\text{upi}} + S_{\text{bsai}} + S_{\text{m}}.
\]

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

TABLE 1

<table>
<thead>
<tr>
<th>Hydrolysis kinetic equation</th>
<th>1st order with respect to (wrt) ( S_{\text{bp}} )</th>
<th>1st order specific with respect to ( S_{\text{bp}} ) &amp; ( Z_{\text{AD}} )</th>
<th>Monod kinetics</th>
<th>Saturation kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis rate ( r_h ) gCOD/(ℓ·d)</td>
<td>( r_h = K_h S_{\text{bp}} ) ( (1) )</td>
<td>( r_h = K_H S_{\text{bp}} Z_{\text{AD}} ) ( (2) )</td>
<td>( r_h = \frac{K_h S_{\text{bp}}}{(K_h + S_{\text{bp}})} Z_{\text{AD}} ) ( (3) )</td>
<td>( r_h = \frac{S_{\text{upi}}}{\left[ K_h (S_{\text{bp}}/Z_{\text{AD}}) + S_{\text{upi}} \right]} Z_{\text{AD}} ) ( (4) )</td>
</tr>
<tr>
<td>Residual biodegradable organics concentration gCOD/ℓ ( S_{\text{bp}} )</td>
<td>( S_{\text{bp}} = \frac{S_{\text{upi}}}{[1 + K_H (1 - Y_{\text{AD}})]} )</td>
<td>( S_{\text{bp}} = \frac{1 + b_{AD} R}{Y_{\text{AD}} K_h} )</td>
<td>( S_{\text{bp}} = \frac{K_h R (1/Y_{\text{AD}}) - (1 + b_{AD} R)}{Y_{\text{AD}} K_h (1/R + b_{AD})} )</td>
<td></td>
</tr>
<tr>
<td>Acidogen biomass concentration ( Z_{\text{AD}} )</td>
<td>( Z_{\text{AD}} = \frac{Y_{\text{AD}} (S_{\text{upi}} - S_{\text{bp}})}{[1 + b_{AD} R (1 - Y_{\text{AD}})]} )</td>
<td>( S_{\text{upi}} = S_{\text{upi}} )</td>
<td>( S_{\text{upi}} = (1 - Y_{\text{AD}}) R r_h )</td>
<td></td>
</tr>
<tr>
<td>Unbiodegradable organics concentration ( S_{\text{up}} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kinetic constants (Izzett et al., 1992 data)</td>
<td>( K_h = 0.515 \pm 0.041 \text{ /d} )</td>
<td>( K_h = 0.481 \pm 0.040 \text{ /d} )</td>
<td>( K_h = 3.34 \text{ (*3.72) gCOD organics/(gCOD biomass·d)} )</td>
<td>( K_h = 5.27 \text{ (*5.58) gCOD organics/ (gCOD biomass·d);} )</td>
</tr>
<tr>
<td>COD balance</td>
<td>( S_{\text{up}} = S_{\text{upi}} + S_{\text{bpi}} + S_{\text{bsai}} + S_{\text{m}} )</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*VFA concentration (mgCOD/l)
(S_{bp}) 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:

\[
de S_{bp} = +Q S_{bp} - Q S_{bp} dt - r_h V dt + b_{AD} Z_{AD} V dt
\]

(7)

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:

\[
\frac{dS_{bp}}{dt} = \frac{S_{bp} - S_{bp}}{R} + b_{AD} Z_{AD}
\]

(8)

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

\[
de Z_{AD} = +Q Z_{AD} dt - Q Z_{AD} V dt - r_h V dt - b_{AD} Z_{AD} V dt
\]

(9)

Again dividing through by Vdt yields:

\[
\frac{dZ_{AD}}{dt} = -\frac{Z_{AD}}{V} + Y_{AD} r_h V - b_{AD} Z_{AD}
\]

(10)

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

\[
r_h = \frac{Z_{AD}}{Y_{AD}} \left( \frac{1}{R} + \frac{b_{AD}}{R} \right)
\]

(11)

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

\[
r_h = \frac{S_{bp} - S_{bp}}{R} + b_{AD} Z_{AD}
\]

(12)

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

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

\[
= (S_{bp} - S_{bp}) E
\]

(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 Z_{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:

\[
S_{bp} = \frac{K_s (1/Y_{AD} + b_{AD})}{Y_{AD} K_s - (1/Y_{AD} + b_{AD})} gCOD/ℓ
\]

(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.

\[
S_{up} = S_{up} gCOD/ℓ
\]

(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:

\[
de S_m = -Q S_m dt - (1 - Y_{AD}) r_h V dt
\]

(16)

where:

\[
S_m = \text{methane concentration in the effluent in gCOD/ℓ (if it were dissolved)}
\]

(17)

Dividing Eq. 16 through by Vdt and setting dS_{m}/dt = 0 and solving for S_{m} yields:

\[
S_m = (1 - Y_{AD}) R r_h gCOD/ℓ
\]

(18)

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:

\[
Q_m = (1 - Y_{AD}) R r_h 24.0/64
\]

(19)

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

\[
S_A = S_A + S_A = S_A + Z_{AD} + S_{up} + S_m
\]

(20)

Equation 20 shows that COD exits the digester only as sludge mass in the effluent (S_{bp}) 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:

\[
S_A = S_{bp} - Z_{AD} Y_{AD} (1 - Y_{AD}) + Z_{AD}
\]

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

\]

(21)

Figure 2
Influent primary sludge COD fractionation for the steady state anaerobic digestion model
which on simplifying gives Eq. 14 for $S_{u}$ and therefore proves the input and output COD masses balance exactly.

The total ($S_{r}$) and biodegradable ($S_{bp}$) COD removals and methane production ($S_{ad}$) are given by:

$$S_{r} = S_{u} - S_{m} = S_{u}$$  \hspace{1cm} (21)

$$S_{bp} = S_{ad} - S_{ps}$$  \hspace{1cm} (22)

The equations for the biodegradable organics ($S_{bp}$), acidogen ($Z_{ad}$), unbiodegradable ($S_{ps}$) and methane ($S_{ad}$) 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 ($S_{e}$)

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

$$S_{e} = S_{ad} + Z_{ad} \times gCOD/\ell$$  \hspace{1cm} (23)

Substituting Eq. 15 for $S_{ad}$, Eq. 6 for $S_{m}$ and Eq. 13 for $Z_{ad}$ in Eq. 23 yields:

$$S_{e} = S_{ps} + S_{ad} + \frac{Y_{ad}(1-f_{ad})S_{u} - S_{ps}}{[1 + b_{ad}R/(1 - Z_{ad})]} \times gCOD/\ell$$  \hspace{1cm} (24)

Solving Eq. 24 for $S_{ps}$ yields:

$$S_{ps} = \frac{S_{e} - S_{ad} + \frac{Y_{ad}(1-f_{ad})}{[1 + b_{ad}R/(1 - Z_{ad})]} S_{u}}{S_{ad} - \frac{Y_{ad}}{[1 + b_{ad}R/(1 - Z_{ad})]} (From \ Eq \ 13)}$$  \hspace{1cm} (25a)

$$\text{where } b_{e} = \frac{Y_{ad}}{1 + b_{ad}R/(1 - Z_{ad})} (From \ Eq \ 13)$$  \hspace{1cm} (25b)

With $S_{ad}$ and $S_{ps}$ known from measurement, Eq. 25 defines $S_{ps}$ in terms of the unbiodegradable fraction of the primary sludge ($f_{ps}$), the retention time of the digester ($R$) and the acidogen constants ($Y_{ps}$, $b_{sa}$). By estimating an unbiodegradable fraction of the primary sludge ($f_{ps}$) and selecting acidogen biomass constant ($i.e. Y_{ps} = 0.113 \ gCOD \ biomass/gCOD \ organics, b_{sa} = 0.041 \ /d)$, $S_{ps}$ 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 acetogenesis 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 ($b_{sa} = 0.041 /d$ and $b_{s} = 0.037 /d$). However, as noted above this simplification does influence the values of the constants in the hydrolysis rate equations. The hydrogentrophic methanogen yield ($Y_{ps}$) is low enough (0.01 gCOD biomass/gCOD H2) to be ignored.

### Estimating the unbiodegradable COD fraction of primary sludge

For wastewater treatment plant design, the primary sludge (PS) unbiodegradable COD fraction ($f_{ps}$) is entirely dependent on the unbiodegradable particulate COD fractions ($f_{ad} \times Y_{ad}$) selected for the raw and settled wastewaters and the fraction of COD removed by primary sedimentation ($f_{ps}$). From a COD mass bal-
The table and text are related to water treatment processes, specifically focusing on particulate and soluble COD removal and the calculation of hydrolysis kinetic equations. The text discusses the importance of removing particulate organics in the PST and the impact of hydrolysis on COD removal efficiencies.

### 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 $f_{up} = 0.36$ from Sötemann et al. (2005a) for the Izzett data, the calculated $S_{dp}$ concentrations from Eq. 25 are listed in Table 3. With $S_{dp}$ known, $Z_{bp}$ and $S_{bp}$ 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 $S_{dp}$ only (Eq. 1), $K_h = r_h / S_{dp}$ (d), and for the first order specific rate with respect to $S_{bp}$ and $Z_{bp}$ (Eq. 2), $K_h = r_h / S_{dp} Z_{bp}$. The calculated $K_h$, $K_h$, 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 kinetic constants $K_h$, $K_h$, 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 kinetic constants ($K_h$, $K_h$, 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 kinetic constants ($K_h$, $K_h$, 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.
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 $K_{nh}$ increase with increasing retention time. The average $K_h$ and $K_{nh}$ rates over the five retention times are 0.515 \(/d\) and 0.322 \(/(gCOD biomass\cdot d)\) 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 $K_{nh}$ 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 $r_1$, $S_{ad}$, 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 ($r_1/Z_{ad}$) versus $S_{ad}$ 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 (7$d$). Linearisation method (iii) showed that the 15$d$ retention time data is an outlier and is the reason for the low $R^2$ value (0.688) for all five retention time data. Excluding the 15$d$ data significantly improved the $R^2$ value for method (iii) (0.888). The average $K_h$ and $K_{nh}$ values obtained from the three methods, with the 15$d$ 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 ($r_1/Z_{ad}$) versus biodegradable COD concentration ($S_{ad}$) curves obtained from each and the average are virtually the same and plot very closely to one another.

### TABLE 4

<table>
<thead>
<tr>
<th>Kinetic rate</th>
<th>Monod kinetics</th>
<th>Saturation kinetics</th>
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<td>$K_{nh}$</td>
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<td>Average M1, M2, M3S</td>
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<td>6.76</td>
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The \( K_{w} \) 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 \( S_{w}/Z_{AD} \) instead of \( S_{w} \). The \( K_{w} \) and \( K_{s} \) values so obtained are listed in Table 4. The specific hydrolysis rate, \( r_{p}/Z_{AD} \) (gCOD organics/ gCOD biomass·d) versus the saturation ratio \( S_{w}/Z_{AD} \) (gCOD organics/ gCOD 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 retention time data. Excluding the 15 d data significantly improved the \( R^{2} \) value for method (iii) (0.897). The average \( K_{w} \) 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 \( r_{p}/Z_{AD} \) versus saturation ratio \( S_{w}/Z_{AD} \) 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 \( r_{p}/Z_{AD} \) versus biodegradable COD acidogen biomass concentration ratio \( S_{w}/Z_{AD} \) curves.

The unbiodegradable fraction of sludge \( f_{p,unb} \) influences the calibration results of the different hydrolysis/acidogenesis rate equations. For their more complex approach, Stötemann et al. (2005a) found the lowest coefficient of variation \( (C_{w}, \text{standard deviation/mean}) \) for the first order \((C_{w} = 0.017) \) and first order specific \( C_{w} = 0.049) \) hydrolysis equations at \( f_{p,unb} = 0.34 \) 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 \( f_{p,unb} = 0.36 \). 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 \( (C_{w}) \) is at \( f_{p,unb} = 0.34 (C_{w} = 0.040) \) and 0.32 \((C_{w} = 0.074) \) 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 \( f_{p,unb} = 0.37 \) (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 described above, the specific hydrolysis rate \( r_{p}/Z_{AD} \) versus biodegradable COD concentration \( S_{w} \) 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).
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 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_{unbiodegradable}). Values higher than 0.338 yielded negative effluent biodegradable COD concentrations (S_{e}). This set an upper limit of 0.338 on the f_{unbiodegradable} value. A lower f_{unbiodegradable} for primary sludge seems reasonable in comparison with the 0.36 value obtained for the mixture of primary and humus sludge. Furthermore, the R² values for the Monod and saturation models were very low (<0.60) for all reasonable f_{unbiodegradable} values from 0.32 to 0.34 and f_{unbiodegradable} > 0.336 yielded negative K values with linearisation method (iii) (because S_{e} < 0). The best f_{unbiodegradable} value was 0.334 – it yielded the lowest C values for the first order and first order specific hydrolysis equations and the highest R² values (0.54 - 0.60) for the Monod and saturation equations. The calculated K and K rates and the Monod and saturation kinetics constants for all five retention times for f_{unbiodegradable} = 0.334 are listed in Tables 6 and 7 respectively. The average K and K rates over the five retention times are 1.591 /d and 1.538 l/(gCOD biomass·d) respectively. The K and K rates are plotted versus R in Fig. 9 together with the Izzett et al. data K and K 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 | 4.07 | 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 %CH₄ | ? | ? | ? | ? | ? |
| Gas prod ml CH₄/gCOD | 308 | 328 | 330 | 350 | 347 |
| COD balance (%) | 99.7 | 100.9 | 101.6 | 105.3 | 99.4 |
| Effluent Alk mg/l as CaCO₃ | 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 |

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TABLE 6
O’Rourke (1967) 7.5 to 60 d retention time (R) anaerobic digester measured influent* (S<sub>i</sub>) and effluent* (S<sub>e</sub>) COD concentrations, influent unbiodegradable (S<sub>up</sub>) and biodegradable COD (S<sub>bp</sub>) concentrations for an unbiodegradable COD fraction (f<sub>up</sub>) of 0.334, calculated biodegradable COD concentration (S<sub>bp</sub>) (Eq. 25), change in biodegradable concentration across digester (∆S<sub>bp</sub>) observed hydrolysis rate (r<sub>H</sub>) (Eq. 12), acidogen biomass concentration (Z<sub>AD</sub>), specific hydrolysis rate [r<sub>H</sub>(g COD biomass·d)] hydrolysis kinetic rate equations to the measured effluent total COD concentration variation of the K values is due to the sensitivity of the hydrolysis equations. Furthermore, while the K<sub>H</sub> and K<sub>bp</sub> 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 was omitted from the analysis, which seems reasonable from Fig. 9. For the 60 d system, a f<sub>up</sub> = 0.338 yielded a very low effluent biodegradable COD, i.e. S<sub>bp</sub> = 0.041 gCOD/ℓ (0.340 makes it -ve). For this f<sub>up</sub>, determining the hydrolysis rate r<sub>H</sub> and K rates with the 7.5, 10 and 15 d retention time systems yielded:

(i) the same r<sub>H</sub> rates determined previously for these retention times (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<sub>up</sub> = 0.338 yielded a very low effluent biodegradable COD, i.e. S<sub>bp</sub> = 0.041 gCOD/ℓ (0.340 makes it -ve). For this f<sub>up</sub>, determining the hydrolysis rate r<sub>H</sub> and K rates with the 7.5, 10 and 15 d retention time systems yielded:

(ii) the K<sub>H</sub> and K<sub>bp</sub> 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<sub>v</sub>)

(iii) lower R<sup>2</sup> values for the Monod and saturation kinetics (Table 9).

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<sub>up</sub> and the three shortest retention time systems (7.5, 10 and 15 d) to determine the K rates, i.e. the

(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<sup>2</sup>) obtained from the three linearisation methods for the Monod and saturation equations (Table 7).

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, the K<sub>H</sub> and K<sub>bp</sub> 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

### TABLE 7
Monod and saturation kinetics K constants and correlation coefficients (R<sup>2</sup>) 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<sub>up</sub>) of 0.334

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<tr>
<th>Kinetic rate</th>
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<th>Saturation kinetics</th>
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</thead>
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<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
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<td>Average M1, M2, M3</td>
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* See note on Table 3. **Mean of all five retention time values.

---

**Figure 9**
Hydrolysis rate constants for the 1<sup>st</sup> order (K<sub>H</sub>/d) and 1<sup>st</sup> order specific [K<sub>bp</sub>/ℓ/(gCOD biomass·d)] hydrolysis kinetic rate equations versus retention time for the Izzett et al. and O’Rourke anaerobic digester data sets

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Download the full-text as a PDF from [http://www.wrc.org.za](http://www.wrc.org.za)
O’Rourke (1967) 7.5 to 60 d retention time (R) anaerobic digester measured influent* (S_0) and effluent* (S_e) COD concentrations, influent unbiodegradable (S_{0bp}) and biodegradable COD (S_{0sp}) concentrations for an unbiodegradable COD fraction (f_{up}) of 0.338, calculated residual biodegradable COD concentration (S_{rsp}) (Eq. 25), change in biodegradable concentration across digester (∆S_{rsp}), observed hydrolysis rate (r_0 = ∆S_{rsp}/(R+b) Z_{AD}) (Eq. 12), acidogen biomass concentration (Z_{up}), specific hydrolysis rate (r_{up}) and the 1st order and 1st order specific hydrolysis rate constants (K_s and K_r). All mass units in gCOD. Note that r_0, Z_{AD} and r_{up} are identical to the values calculated in Table 6 for f_{up} of 0.334.

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<td>16.874</td>
<td>1.175</td>
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<td>17.740</td>
<td>0.320</td>
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<td>0.510</td>
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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_{up}) of 0.338

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<th>Kinetic rate</th>
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<td>g organics/ (g biomass·d)</td>
<td>g organics/ (g biomass·d)</td>
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<tr>
<td>Method 1 (M1)</td>
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<td>Method 2 (M2)</td>
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<td>Method 3 (M3)</td>
<td>1.08</td>
<td>-0.12</td>
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Table 10

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

<table>
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<th>Saturation kinetics</th>
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<td>Linearisation method</td>
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<td>K_r</td>
</tr>
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and 10). The calculated K_s and K_r 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_r rate and 1st order specific K_r rate constants obtained are 2.474/d and 1.714 1/(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.

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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 Kₘ and Kₛ values is shown in Fig. 11 together with the experimental data. Figure 11 reinforces the conclusion above: With its low Kₛ 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_vfa) 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 CₓHᵧOᵣNₛ to methane, carbon dioxide and biomass (of composition C₅H₇O₂N) as final end products:

\[
CₓHᵧOᵣNₛ + \left(2X+2Y-2Z-3A\right)H₂O
= \left(X-A-\frac{ED}{5}\right)CH₄
+ \left(1-\frac{ED}{8}\right)CO₂
+ \left(\frac{ED}{20}\right)NH₄⁺
+ \left(\frac{ED}{20}\right)HCO₃⁻
\]

(27a)

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

\[
\text{gCOD/mol} = 27a
\]

(28a)

(28b)

where:

\[
VSS = \text{volatile suspended solids}
\]

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

\[
\begin{align*}
\text{CH₄COOH} & \rightarrow \text{CH₄} + \text{CO₂} \quad \text{and} \\
\text{CH₄COO}⁻ + \text{H₂O} & \rightarrow \text{CH₄} + \text{HCO₃⁻}
\end{align*}
\]

(29a)

(29b)

The total CH₄, CO₂ and HCO₃⁻ 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’ value for acetate of 4.68 for an influent TDS concentration of 2500 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.

\[
S_{\text{und}} = \frac{S_{\text{und}}}{\left(1 + 10^{pK’-pH}\right)} \text{mgCOD/l}
\]

(30)
where:

- $p\text{H}_i$ is the influent pH and $S_{\text{HCO}_3}^{\text{ ini}}$ and $S_{\text{HCO}_3}^{\text{ end}}$ the undissociated and dissociated acetate species concentration in the influent respectively.

For acidogen organism constants $Y_{\text{CH}_4} = 0.113 \text{ mgCOD biomass/mg COD organics degraded}$ and $b_{\text{CH}_4} = 0.041 /d$, the fraction of COD hydrolysed converted to sludge mass ($E$, Eq. 27) and methane 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$_2$ (HCO$_3^-$) to form saline ammonia (NH$_4^+$) and bicarbonate (HCO$_3^-$) according to NH$_4^+$ + HCO$_3^-$ → NH$_4^+$ + CO$_2$ and
- the concentration of influent dissociated acetate species utilised in the digester (Eq. 29a), 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$_2$ ($P_{\text{CO}_2}$). The pH of the digester is defined by the $P_{\text{CO}_2}$ 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 $P_{\text{CO}_2}$ 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$_4^+$ released from the organics and establish the appropriate HCO$_3^-$ concentration and $P_{\text{CO}_2}$ 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, $P_{\text{CO}_2}$ and pH is given by:

$$P_{\text{CO}_2} = \frac{[\text{HCO}_3^-]}{1 \times 10^{10\text{pH} - 2\text{pK}_{\text{HCO}_3^-}^\text{app}}}$$

where:

- [HCO$_3^-$] = bicarbonate concentration = H$_2$CO$_3^*$ alkalinity (mol/l) ~ Total alkalinity (mol/l)
- $P_{\text{CO}_2}$ = partial pressure of CO$_2$ in the gas phase
- pH = -ve log $P_{\text{CO}_2}$ of the (H$^+$) activity
- $\text{pK}_{\text{HCO}_3^-}^\text{app}$ = -ve log of the apparent Henry’s law constant for CO$_2$
- $\text{pK}_{\text{bic}, 1}$, $\text{pK}_{\text{bic}, 2}$ = -ve log of $1^*$ and $2^*$ 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 $\text{pK}_{\text{bic}, 1} = 6.211$, $\text{pK}_{\text{bic}, 2} = 9.960$ and $\text{pK}_{\text{HCO}_3^-} = +1.609$ (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).
Calculating the COD removal and methane production – hydrolysis kinetics

Total influent COD concentration \( (S_o) = 42.59 \) gCOD/l (measured).

Influent VFA concentration \( (S_{\text{mol}}) = 2.24 \) gCOD/l (measured).

Unbiodegradable fraction of the primary sludge \( (f_{\text{psmol}}) = 0.36 \) (determined above).

Influent hydrolysable COD concentration \( (S_{\text{hp}}) = (1 - 0.36) 42.59 - 2.24 = 25.02 \) gCOD/l (Eq. 5).

Influent unbiodegradable COD concentration \( (S_{\text{up}}) = 0.36 x 42.59 = 15.33 \) gCOD/l (Eq. 6).

Residual biodegradable COD concentration \( (S_{\text{bp}}) = 2.15 \) gCOD/l (Eq. 14).

Biodegradable COD concentration removed \( (S_{\text{bp}} - S_{\text{bp}} - S_{\text{up}}) = 22.87 \) gCOD/l (Eq. 22).

Acidogen biomass concentration \( (Z_{\text{ad}}) = 1.50 \) gCOD/l (Eq. 13).

Unbiodegradable COD concentration \( (S_{\text{up}}) = 15.33 \) gCOD/l (Eq. 15).

Total effluent COD concentration \( (S_e) = 15.33 + 2.15 + 1.50 = 18.98 \) gCOD/l (Eq. 23).

Methane production concentration \( (S_{\text{m}}) = 21.38 \) 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 \( (S_e + S_{\text{m}}) = 18.98 + 23.82 = 42.60 \) gCOD/l (Eq. 20).

Hence COD balance \( 100(S_e + S_{\text{m}})/S_o = 100.0\% \).

Methane production gas volume \( (Q_{\text{m}}) = 8.87 \) 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 \( \text{C}_6\text{H}_{10}\text{O}_{5}\text{N}_{1.96} \) (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:

\[
0.1742 \text{C}_6\text{H}_{10}\text{O}_{5}\text{N}_{1.96} + 0.1530 \text{H}_2\text{O} \rightarrow 0.2042 \text{CO}_2 + 0.0340 \text{CH}_4 + 0.0094 \text{C}_2\text{H}_5\text{O}_2\text{N} + 0.0248 \text{NH}_4^+ + 0.0248 \text{HCO}_3^-
\]

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

\[
0.1742 \text{C}_6\text{H}_{10}\text{O}_{5}\text{N}_{1.96} + 0.0094 \text{C}_2\text{H}_5\text{O}_2\text{N} + 0.0070 \text{CH}_3\text{COOH} + 0.0248 \text{HCO}_3^-
\]

\[
+ 0.0248 \text{CH}_4 + 0.00280 \text{H}_2\text{O} \rightarrow 0.2154 \text{CO}_2 + 0.0150 \text{CH}_4 + 0.0094 \text{C}_2\text{H}_5\text{O}_2\text{N} + 0.0070 \text{CH}_3\text{COOH} + 0.00280 \text{H}_2\text{O} + 0.00280 \text{H}_2\text{O} + 0.00280 \text{H}_2\text{O}
\]

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

\[
0.1742 \text{C}_6\text{H}_{10}\text{O}_{5}\text{N}_{1.96} + 0.0094 \text{C}_2\text{H}_5\text{O}_2\text{N} + 0.0248 \text{NH}_4^+ + 0.0248 \text{HCO}_3^-
\]

\[
+ 0.0248 \text{CH}_4 + 0.00280 \text{H}_2\text{O} \rightarrow 0.2154 \text{CO}_2 + 0.0150 \text{CH}_4 + 0.0094 \text{C}_2\text{H}_5\text{O}_2\text{N} + 0.0070 \text{CH}_3\text{COOH} + 0.00280 \text{H}_2\text{O} + 0.00280 \text{H}_2\text{O} + 0.00280 \text{H}_2\text{O}
\]

Equation 33 shows that 0.0094 mol/l biomass \( (\text{C}_6\text{H}_8\text{O}_6\text{N}) \) 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 \( \text{CO}_2 \) and \( \text{CH}_4 \) are produced yielding a total gas volume 5.802 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 \( \text{CO}_2 \), \( \text{CH}_4 \) 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 \( \text{CO}_2 \) and \( \text{CH}_4 \) gas production, the \( \text{CO}_2 \) gas composition (in mol fraction or partial pressure, \( P_{\text{CO}_2} \)) 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\(_3\). 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 2696 to 2640 = 2696 mgCaCO\(_3\)/l.

Calculating the digester pH – weak acid base chemistry

With the \( P_{\text{CO}_2} = 0.364 \) and \( \text{HCO}_3^- \) 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 results (a) COD removal (gCOD/l) (b) gas production (ℓ gas/d per ℓ influent/d), (c) gas composition (%\( \text{CO}_2 \)), (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 it 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...
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 (pCO₂, Fig. 15c, middle left),
effluent FSA (mgN/l, Fig. 15d, middle right), alkalinity (mg/l as CaCO₃, 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 CₓHᵧOᵢNₐ) 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 Mooshbrugger 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$_3$H$_4$O$_2$N$_6$ was retained because it is based in the influent N mass. Further, Sötemann et al. (2005a) show that the C$_3$H$_4$O$_2$N$_6$ 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 (UCTADMI) 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 UCTADMI. 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 concentrations are calculated for a given retention time, i.e. X, Y, Z and A in C$_3$H$_4$O$_2$N$_6$ 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 ($r_h = K_h S_h$),
- first order specific ($r_h = K_h S_h Z_{AD}$),
- Monod ($r_h = K_h S_h/(K_h + S_h) Z_{AD}$) and
- saturation ($r_h = K_m (S_{\text{in}}/Z_{AD})(K_m + S_{\text{in}}/Z_{AD}) Z_{AD}$).

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 ($f_{\text{unb}}$) of the sewages sludges within a narrow range (~2%), the correlation coefficient of variation ($C_v$) 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 $f_{\text{unb}}$ 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 ($f_{\text{unb}} = 0.33$) than the primary and humus sludge mixture ($f_{\text{unb}} = 0.36$). 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. The predicted COD, C and N masses of the primary and humus sludge digesters, a sludge composition of C$_3$H$_4$O$_2$N$_6$ 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
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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