Integrated chemical/physical and biological processes modelling Part 2 - Anaerobic digestion of sewage sludges

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Abstract

The development and validation of a two phase (aqueous-gas) integrated mixed weak acid/base chemical, physical and biological processes kinetic model for anaerobic digestion (AD) of sewage sludge are described. The biological kinetic processes for AD are integrated into a two phase subset of the three phase mixed weak acid/base chemistry kinetic model of Musvoto et al. (1997, 2000a,b,c). The approach of characterising sewage sludge into carbohydrates, lipids and proteins, as is done in the International Water Association (IWA) AD model No 1 (ADM1, Batstone et al., 2002), requires measurements that are not routinely available on sewage sludges. Instead, the sewage sludge is characterised with the COD, carbon, hydrogen, oxygen and nitrogen (CHON) composition. The model is formulated in mole units, based on conservation of C, N, O, H and COD. The model is calibrated and validated with data from laboratory mesophilic anaerobic digesters operating from 7 to 20 d sludge age and fed a sewage primary and humus sludge mixture. These digesters yielded COD mass balances between 107 and 109% and N mass balances between 91 and 99%, and hence the experimental data is accepted as reasonable. The sewage sludge is found to be 64 to 68% biodegradable (depending on the kinetic formulation selected for the hydrolysis process) and to have a $C_{3.5}H_7O_2N_{0.196}$ composition. For the selected hydrolysis kinetics of surface mediated reaction (Contois), with a single set of kinetic and stoichiometric constants, for all retention times good correlation is obtained between predicted and measured results for:

- COD,
- free and saline ammonia (FSA),
- short chain fatty acids (SCFA),
- $H_2CO_3^*$ alkalinity and pH of the effluent stream, and
- CO_2 and CH_4 gases in the gas stream.

The measured composition of primary sludge from two local wastewater treatment plants ranged between $C_{3.38}H_7O_{1.91}N_{0.21}$ and $C_{3.91}H_7O_{2.04}N_{0.16}$. The predicted composition is therefore within 5% of the average measured composition providing persuasive validation of the model.

Keywords: Anaerobic digestion, weak acid/base chemistry, kinetic modelling, sewage sludge

Abbreviations

Ac	Acetic acid/acetate
AD	Anaerobic digestion
ADM1	Anaerobic Digestion Model No 1
ASM1, 2	Activated Sludge Models Nos. 1 or 2
BD	Prefix for Biological anaerobic digestion processes
BEPR	Biological excess phosphorus removal
CED	Chemical equilibrium dissociation
CF	Cape Flats
CIP	Chemical ion pairing
COD	Chemical oxygen demand
CP	Chemical/physical
CPB	Chemical/physical/biological
FSA	Free and saline ammonia
IWA	International Water Association
K	Kelvin - absolute temperature scale
MW	Molecular weight
OrgN	Organic nitrogen
PGE	Physical gas exchange
pH	-ve log of the hydrogen ion activity
PMP	Physical mineral precipitation
Pr/HPr	Propionate/Propionic acid
SCFA	Short chain fatty acid
TKN	Total Kjeldahl nitrogen
TSS	Total suspended solids
UCT	University of Cape Town
UCTADM1	UCT Anaerobic Digester Model No. 1
VSS	Volatile suspended solids
WAS	Waste activated sludge
WWTP	Wastewater treatment plant

Symbols

$^{(1)}b$	Endogenous respiration/death rate of organisms
C_{disgas}	Dissolved (aqueous) gas concentration in reactor liquid (mol/ℓ)
C_{hsgas}	Head space gas concentration (mol/ℓ)
C_T	Total inorganic carbon concentration
C_{var}	Coefficient of variation
f_m	Monovalent ion activity coefficient
f_{PSR}	Fraction of COD removed by primary sedimentation
f_{PSup}	Fraction of unbiodegradable COD in the sewage sludge

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$f_{S'up}$, $f_{S'us}$	Particulate and soluble unbiodegradable COD fraction. Additional subscripts R and S denote raw and settled wastewater.
$f_{Sbsa/Sbsf}$	Fraction fermentable COD that appears as VFA (0.607) in acidogenesis
$^{(2)}H_c$	Dimensionless Henry's law constant. Additional ' (prime) denotes value adjusted for inoic strength effects.
$K_{c\ gas}$	Constant for phase change from liquid to gas
K_h, K_H	First order and first order specific hydrolysis rate constant
$^{(2)}K_H$	Henry's law constant
k_{H2}	Hydrogen gas inhibition coefficient for high p_{H2}
$^{(1)}K_I$	Hydrogen ion (H^+) inhibition constant
$^{(2)}K_{La}$	Overall liquid phase mass transfer rate coefficient
$K_{La\ gas}$	Specific gas mass transfer rate
$k_{max,HYD}$	Maximum specific rate in the saturation (Contois) hydrolysis equation
$^{(1)}K_r$, K_f	Reverse and forward kinetic reaction rate constants. Additional compound subscripts denote reactants.
$^{(1)}K_S$	Half saturation coefficient in the Monod organism growth equation
$K_{SM,HYD}$	Half saturation coefficient in Monod hydrolysis equation
$K_{SS,HYD}$	Half saturation coefficient in saturation (Contois) hydrolysis equation
$^{(1)}\mu_{max}$	Maximum specific rate in Monod organism growth equation
$\mu_{max,HYD}$	Maximum specific rate in Monod hydrolysis equation
pK	-ve log of the dissociation constant. Subscript Pr denote propionic acid. Subscripts C1 and C2 denote 1st and 2nd values of the inorganic carbon system.
p	Partial pressure (atm). Subscripts H2, CO2 denote H_2 and CO_2 gases
p_{gas}	Partial pressure of a gas (atm)
P_{atm}	Atmospheric pressure
P_{tot}	Total gas pressure in head space
q_{gas}	Vent gas flow rate from the head space
Q_i, Q_e	Digester influent and effluent flow
Q_{gas}	Total gas production
R	Universal gas constant [0.08206 (ℓ.atm)/(mol.K)]
R^2	Correlation coefficient
R_h	Hydraulic retention time
$^{(1)}r$	Volumetric growth rate of organisms (gCOD/(ℓ·d)
r_{gas}	Rate of gas diffusion across head-space bio-reactor link
r_{HYD} , r^*_{HYD}	Volumetric hydrolysis/acidogenesis rate in mole or COD units
S	General symbol for non AD biomass COD concentration (gCOD/ℓ). First subscript u, b or t denotes unbiodegradable, biodegradable or total. Second subscript p or s denotes particulate or soluble. Third subscript a or f denotes VFA or fermentable soluble COD. Last subscript i or e denotes influent or effluent.
T_k	Temperature in Kelvin = T °C + 273
V_d, V_h	Volume of anaerobic digester and its head-space respectively
$^{(1)(2)}Y$	Biomass yield coefficient
$^{(1)}Z$	Organism concentration in gCOD/ℓ
[ ]	Concentration of compound in mol/ℓ
$^{(1)}$	Additional subscripts AD, AC, AM and HM (upper-case) are for acidogenic, acetogenic, acetoclastic methanogenic and hydrogenotrophic methanogenic organisms respectively. Lower case subscripts are the anabolic equivalent values.
$^{(2)}$	Additional subscripts O2, CO2, NH3 and N2 are the constants for O_2, CO_2, NH_3 and N_2 gases respectively. Additional ' (prime) denotes value adjusted for inoic strength effects.

Introduction

Anaerobic digestion (AD) is one of the oldest biological waste treatment processes, dating back more than a century. With the development of digester heating and mixing, AD has established itself as the most common method of sludge stabilisation, and has proven to be effective also in reducing the volumes of sludge with the production of energy rich bio-gas. It has been shown that AD is an effective process for the treatment of a number of types of organic sludges, ranging from municipal waste activated (WAS) and primary sludges (Kayhanian and Tchobanoglous, 1992; Cout et al. 1994) to industrial organic sludges and agricultural slurries (Hill and Barth, 1977). In particular, the application of AD to the stabilisation of sewage sludges (primary, WAS and humus) is widespread, and this paper focuses on this application.

Despite its widespread application, the design, operation and control of anaerobic digesters treating sewage sludges is still based largely on experience or empirical guidelines. To aid the design, operation and control of (and research into) AD, a mathematical model would be an invaluable process evaluation tool. Mathematical models provide quantitative descriptions of the treatment system of interest that allow predictions of the system response and performance to be made. From these predictions, design and operational criteria can be identified to optimise the system performance. Mathematical models provide an integrated framework for the system which can give guidance to design, operation and research.

Recognising the potential usefulness of mathematical models, various researchers have developed such models to describe AD (e.g. McCarty, 1974, Hill and Barth, 1977; Gujer and Zehnder, 1983; Sam-Soon et al., 1991; Kiely et al., 1997, Batstone et al., 2002). The early models focussed primarily on the biological processes operating in an anaerobic digester. Although the importance of the interaction between the biological processes and the weak acid/base chemistry environment in which they operate was recognised early on, because of the effect of pH on the biological processes, modelling this interaction proved to be a far more complex problem than delineating the biological processes themselves. Initially the impact of the biological processes on pH was assessed graphically based on equilibrium chemistry principles of the carbonate weak acid/base system (e.g. Capri and Marais, 1975). The advent of computers and development of numerical algorithms made it easier to model the interaction based on single or two phase (aqueous-gas) weak acid/base chemistry equilibrium equations to estimate the pH in anaerobic digesters. The approach of Loewenthal et al. (1989, 1991) made it possible to include multiple mixed weak acid/base systems, both for estimating the digester pH and in the determination and interpretation of the commonly measured digester control parameters, short chain (volatile) fatty acids (SCFA) and alkalinity (Moosbrugger et al., 1992; Lahav and Loewenthal, 2000). The latest AD model (IWAADM1, Batstone et al., 2002) includes algebraic algorithms, based on equilibrium weak acid/base chemistry and continuity of charge balances, that seek to model the environment in which the biological processes operate, to predict the pH. These algebraic algorithms and calcula-

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tion of pH operate externally to the kinetic model structure. As alternative, dynamic equilibria equations for the weak acid/base systems are described (similar to the approach of Musvoto et al., 1997, 2000a). However, the weak acid/base water is not included so that pH is again algebraically calculated externally to the kinetic model, via the charge balance. Calculation of pH externally via the charge balance cannot deal simply with multiple weak acid/base systems in three phases (aqueous/gas/solid), where several minerals competing for the same species may precipitate simultaneously or sequentially (Musvoto et al., 2000a,c): In some anaerobic digestion systems precipitation of minerals is significant, either within the digester itself or in pipework leading from the digester so that the relevant chemical precipitation processes would require inclusion. For such situations, the biological processes and multiple weak acid/base systems in three phases should be modelled in an integrated way within the same kinetic model structure.

In the first paper of this series (Sötemann et al., 2005a), an integrated chemical (C), physical (P) and biological (B) processes model for the N removal activated sludge system was presented. This model was developed by integrating the biological processes of the International Water Association (IWA) Activated Sludge Model No 1 (ASM1, Henze et al., 1987) into a two phase (aqueous-gas) subset of the three phase mixed weak acid/base CP model of Musvoto et al. (1997, 2000a,b,c), and included additionally gas exchange of N_2. This paper describes the development of an integrated two phase (aqueous-gas) chemical (C), physical (P) and biological (B) processes AD model for sewage sludges, by integrating the biological processes for AD with the same two phase subset of the three phase CP model of Musvoto et al. (1997, 2000a,b,c). In a future paper, this AD model will be extended to include the third (solid) phase of mineral precipitation. In fact, the N removal activated sludge and AD models are two parts of a single larger model being developed for simulating the entire wastewater treatment plant (WWTP) on materials mass balance and continuity principles. It is planned to include also biological excess P removal (BEPR) and AD of P rich waste activated sludges in the WWTP model.

The AD model is built up in stages. First, the biological processes are defined and then these are integrated into the mixed weak acid/base model of Musvoto et al. (1997, 2000a,b,c). For ease of cross-referencing to the source papers, the same process and compound numbering system described in Part 1 will be used in this Part 2 (see Table 1 of Sötemann et al., 2005a).

Biological processes of anaerobic digestion

Conceptual model

In the literature there is considerable variation in conceptual schemes for describing the biological processes of AD with sewage sludge as influent, from simple two stage reaction schemes including only hydrolysis/acidogenesis and methanogenesis (Kiely et al., 1997) to the most commonly used six step reaction scheme as proposed by Gujer and Zehnder (1983).

In the reaction scheme of Gujer and Zehnder (1983) (Fig. 1), the hydrolysis process acts separately on three main groups of complex organics, viz. proteins, carbohydrates and lipids. These complex polymeric materials are hydrolysed by extracellular enzymes to soluble products that are small enough to allow their transport across the cell membrane. The products of the separate hydrolysis processes are amino acids, sugars and fatty acids respectively. These relatively simple, soluble compounds are fermented (acidogenesis) or anaerobically oxi-

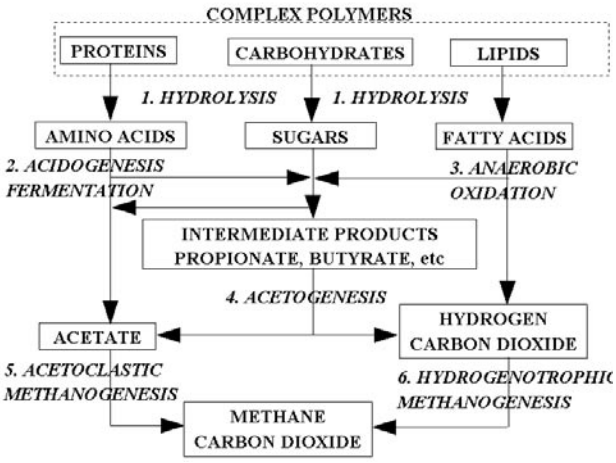

Figure 1
Anaerobic digestion processes scheme of Gujer and Zehnder (1983)

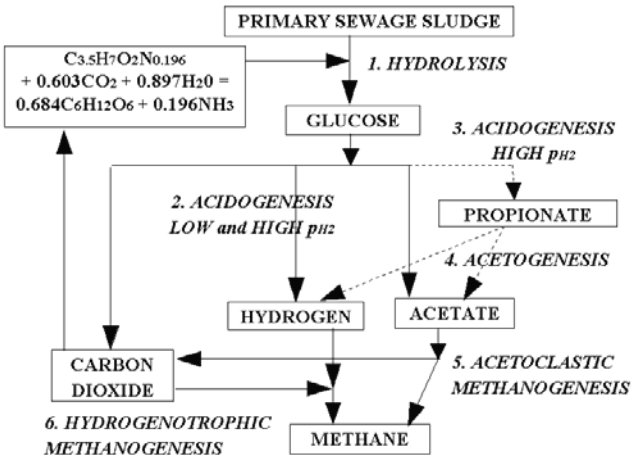

Figure 2
Anaerobic digestion processes scheme of University of Cape Town Anaerobic Digestion Model No 1 (UCTADM1) including (i) the effect of high hydrogen partial pressure on acidogenesis and (ii) COD, carbon and nitrogen mass balances with a generic CHON sludge composition.

dised to short chain fatty acids (SCFAs) (acetate), alcohols, CO_2, hydrogen and ammonia. A portion of the hydrolysis products are also converted to intermediate products (propionate, butyrate, etc.), which are then converted to acetate, hydrogen gas and CO_2 through a process called acetogenesis. Lastly, methanogenesis occurs by hydrogen reduction with CO_2 (hydrogenotrophic methanogenesis) and from acetate cleavage (acetoclastic methanogenesis).

The Gujer and Zehnder (1983) reaction scheme formed the basis for the AD model developed here, but with four main modifications (Fig. 2), viz.:

(1) Recognising that carbohydrate, protein and lipid measurements on sewage sludges are unlikely to be routinely available and indeed are difficult to do, the hydrolysis of the three separate organic materials was modified to a single hydrolysis process acting on a generic organic material representing sewage sludge ($C_XH_YO_ZN_A$, McCarty, 1974). This simplification is not unreasonable since the end products of hydrolysis and subsequent acidogenesis of the three organic groups

TABLE 1
Biological processes included in the two phase anaerobic digestion model

Process	Specific biological process	Organism group
Hydrolysis	D1. Hydrolysis of $C_XH_YO_ZN_A$ to "glucose"	Acidogens, Z_{AD}
Growth	D2. Acidogens on 'glucose' under low p_{H2}	Acidogens, Z_{AD}
	D3. Acidogens on 'glucose' under high p_{H2}	Acidogens, Z_{AD}
	D5. Acetogens on propionic acid	Acetogens, Z_{AC}
	D7. Acetoclastic methanogens on acetic acid	Acetoclastic methanogens, Z_{AM}
	D9. Hydrogenotrophic methanogens on H_2	Hydrogenotrophic methanogens, Z_{HM}
Death/ Endogenous decay	D4. Acidogens	Acidogens, Z_{AD}
	D6. Acetogens	Acetogens, Z_{AC}
	D8. Acetoclastic methanogens	Acetoclastic methanogens, Z_{AM}
	D10. Hydrogenotrophic methanogens	Hydrogenotrophic methanogens, Z_{HM}

are essentially the same, namely SCFAs. In this approach, the C, H, O and N contents of sewage sludges are needed to determine the X, Y, Z and A values in $C_XH_YO_ZN_A$; These were determined by simulation of measured data and direct measurement, see below. In follow-up work to extend the model to AD of waste activated sludges (including biological excess P removal sludges) in 3 phases (liquid-gas-solid), i.e. including mineral precipitation, the P content of sewage sludges will be added to this formulation (i.e. $C_XH_YO_ZN_AP_B$).

(2) With the proposed single hydrolysis process, recognition of three separate hydrolysis products was no longer necessary. Accordingly, a single hydrolysis process and end product were included. This end product was chosen to be the idealised carbohydrate "glucose" for a number of reasons: The subsequent biological processes on "glucose" are well established and the acidogenic/fermentation process acting on "glucose" to convert it to SCFAs is unlikely ever to be rate limiting. Accordingly, in model application accumulation of 'glucose' will not occur, even under digester failure conditions. This implies that the "glucose" acts merely as an ***intermediate*** compound, which is acidified to SCFAs as soon as it is produced. In any event, because the end products of hydrolysis and acidogenesis in the scheme of Gujer and Zehnder (1983) (Fig. 1) are the same as in the revised scheme (Fig. 2), the net result is the same in both schemes. In order to maintain the COD, C, H, O and N balances, water and carbon dioxide are taken up from the bulk liquid to generate the glucose from the sewage sludge (Fig. 2), and ammonia is released.

(3) As a consequence of accepting a single hydrolysis process, separate anaerobic oxidation of fatty acids does not need to be included.

(4) In the reaction scheme of Gujer and Zehnder (1983), a fixed proportion of hydrolysis end products are converted to intermediate SCFA (propionate, butyrate, etc.) and the balance directly to acetate. As an alternative, the influence of the hydrogen partial pressure (p_{H2}) on acidogenesis of glucose to acetate and propionate as proposed by Sam - Soon et al. (1991) was included in the revised scheme. This provides a better description of AD behaviour under failure conditions. To include the proposals of Sam-Soon et al. (1991), the acidogenesis was divided into two processes – under high p_{H2} conditions, acetic and propionic acids are generated together with H_2 and CO_2; and under low p_{H2} conditions, acetic acid only is generated together with H_2 and CO_2. In this revised scheme, generation of butyrate and higher SCFAs was not considered, because with sewage sludge as influent these usually are only found in minor concentrations, even under digester failure conditions.

Mathematical model – UCTADM1

Accepting the revised reaction scheme (Fig. 2), the biological processes mediated by the four recognised AD organism groups were included in the two phase (aqueous-gas) chemical (C), physical (P) and biological (B) anaerobic digestion model (UCTADM1, see Table 1). Following ASM1 for activated sludge systems (Henze et al., 1987), the processes were formulated either as hydrolysis or organism group growth processes. All four organism groups were accepted to be subject to endogenous respiration and so an endogenous mass loss process was included in the model for each group. It is recognised that the organism groups are not representative of a single organism species, but rather are "surrogates" representing all organism species performing a particular function of interest; this is similar to the approach followed for modelling of activated sludge systems (e.g. Dold et al., 1980, Henze et al., 1987). In formulating the model, since weak acid/base chemistry is included directly, all biological processes that act on weak acid/base species needed to be formulated in terms of the relevant dissociated or undissociated species (see below). This included both the stoichiometric consumption or production of weak acid/base species by the processes, and the formulation of the kinetic rate expressions. Whichever species is selected, in the production or consumption of weak acid/base species, because the weak acid/base chemistry is included directly, the model will automatically redistribute the weak acid/base species including the hydrogen ion (H^+) and establish a new pH.

The 10 biological processes listed in Table 1 act on 14 compounds and cause changes in their concentrations. The changes in some compound concentrations may be directly measurable, but the changes in the non-measurable compound concentrations are inferred from the conceptual model of the processes (Fig. 2) and mass balance requirements. The compounds and processes of AD based on the reaction scheme of Fig. 2 are shown in the Petersen matrix format in Table 2, in which each row represents a biological process and each column a compound, and the stoichiometric relationships between the compounds and processes are listed at their intersection blocks, the process kinetic rates on the right hand side and the units of the compounds along the bottom. Note that all the compounds in Table 2 are specified as mol/ℓ, including the sewage sludge. The mol/ℓ of the

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sewage sludge is calculated from its measured COD concentration and its gCOD/mol, which is calculated from its known composition, i.e. known X, Y, Z and A in $C_XH_YO_ZN_A$ (see below). The AD organism concentrations for all four organism groups are also specified as mol/ℓ based on a formulation of $C_5H_7O_2N$, which has a molar mass of 113 g/mol and a COD/VSS ratio of 1.42 mgCOD/mgVSS (McCarty, 1964). The gCOD, gN or gH_2CO_3* Alk per mol of the compounds as appropriate are also given along the bottom of the matrix. If the gCOD/mol ratios are multiplied by the corresponding stoichiometric value in the matrix and summed across a process, it will be found that these sums are zero, i.e. the COD mass balance applies across each process. The requirement to express the model compounds in mole units arises from the requirement to model CO_2 production/utilisation (zero COD), which is essential for the weak acid/base chemistry part of the model.

Stoichiometry of the biological processes

The stoichiometry in the model was deduced directly from the biochemical stoichiometric equations of the processes. The metabolic pathways used by fermentative organisms for the degradation of carbohydrates to SCFAs are well defined. As noted above, for this reason amongst others, the biodegradable particulate COD entering the system was directly hydrolysed to the inter-

TABLE 2

Petersen matrix representation of the biological processes and associated compounds of the University of Cape Town Anaerobic Digestion Model No 1 (UCTADM1). Influent sewage sludge concentration is in mol/ℓ. This concentration is calculated from the measured COD concentration of the sludge and the sludge composition formula $C_XH_YO_ZN_A$ with measured values of X, Y, Z and A.

	Number	C1	C2	C3	C7	C13	C28	C29	P1†	P4	D1	D2	D3	D4	D5	D6	D7	Process rates
	Compounds	NH_4^+	NH_3	$H_2CO_3^*$	H^+	HAc	HPr	Pr	CO_2	CH_4	$C_XH_YO_ZN_A$	$C_6H_{12}O_6$	H_2	Z_{AD}	Z_{AC}	Z_{AM}	Z_{HM}	
No	Processes		DsIvd	DsIvd					Gas	Gas	S_{bp}	S_{bsf}	DsIvd	Acido gens	Aceto gens	AMs	HMs	
C46	Forward dissociation of HPr				1		-1	1										$K_{fPr}[HPr]$
C47	Reverse dissociation of HPr				-1		1	-1										$K_{rPr}[Pr][H^+]$
P6†	Dissolution of CO_2 gas			1					-1									$K_{rCO2}(pCO_2)(K_{HCO2})$
P7†	Expulsion of CO_2 gas			-1					1									$K_{rCO2}[H_2CO_3^*]$
P8†	Expulsion of NH_3 gas		-1															$K_{rNH3}[NH_3]$
D1	Hydrolysis		S1	S2							-1	S3						Eq. 8d
D2	Acidogenesis (low pH_2)	-1		S4	1	S5						-1/Y_{AD}	S6	1				Eq. 9
D3	Acidogenesis (high pH_2)	-1		S7	1	S8	S9					-1/Y_{AD}	S10	1				Eq. 10
D4	Acidogen endogenous decay		S11	S12							S13			-1				$b_{AD}[Z_{AD}]$
D5	Acetogenesis	-1		S14	1	S15	-1/Y_{AC}						S16		1			Eq. 11
D6	Acetogen endogenous decay		S11	S12							S13				-1			$b_{AC}[Z_{AC}]$
D7	Acetoclastic methanogenisis	-1		S17	1	-1/Y_{AM}				S18						1		Eq. 12
D8	Acetoclastic methanogen endogenous decay		S11	S12							S13					-1		$b_{AM}[Z_{AM}]$
D9	Hydrogenotrophic methanogenesis	-1		S19	1					S20			-1/Y_{HM}				1	Eq. 13
D10	Hydrogenotrophic methanogen endogenous decay		S11	S12							S13						-1	$b_{HM}[Z_{HM}]$
	Units	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	
	g COD/mol	-	-	-	-	64	112	112	0	64	131.3‡	192	16	160	160	160	160	
	g N/mol	14	14	-	-	-	-	-	-	-	2.744	-	-	-	-	-	-	
	g H_2CO_3* as $CaCO_3$ /mol	-	-	0	-50	-	-	-	-	-	-	-	-	-	-	-	-	

† These processes and compound were included in the models of Musvoto et al. (1997, 2000a) as follows: Processes P6 was C7, P7 was C8, and P8 was C46 and compound P1 was C6.
Because the matrix units are mol/ℓ summing the stoichiometry across each process does not yield zero. However, if each stoichiometric value is multiplied by the compounds' gCOD/mol ratio and then summed across the process, zero is obtained, i.e. COD balances across each process. Also, C, N, O and H mass balances across each process.
‡ This is the g COD/mol for the primary sludge CHON content measured and predicted in this investigation, i.e. $C_{3.5}H_7O_2N_{0.196}$

TABLE 3 Stoichiometry for acetogenesis and acetogen growth (Process D5 in Table 2). The S numbers in brackets cross reference to the model Petersen matrix (Table 2).						
C1/B10 NH_4^+	C3 (S14) H_2CO^{3*}	C7 H^+	C13 (S15) HAc	C28 HPr	D3 (S16) H_2	D5 Z_{AC}
moles	moles	moles	moles	moles	moles	moles
-1	$\frac{1-2Y_{AC}}{Y_{AC}}$	1	$\frac{1-\frac{3}{2}Y_{AC}}{Y_{AC}}$	$-\frac{1}{Y_{AC}}$	$\frac{3-4Y_{AC}}{Y_{AC}}$	1

mediate "glucose", from which the remainder of the products were formed. As an example for calculating the stoichiometry, consider the process of acetogenesis:

Acetogenesis (Process D5, Table 2) is the process whereby under low hydrogen partial pressure (p_{H2}) the acetogens convert propionic acid (HPr) (generated by acidogenesis under high p_{H2}) to acetic acid (HAc). The stoichiometric equation for the acetogenesis reaction is:

$$CH_3CH_2COOH + 2H_2O \Rightarrow CH_3COOH + CO_2 + 3H_2 \quad (1)$$

During acetogenesis, growth of acetogenic organisms (Z_{AC}) takes place which can be stoichiometrically represented by:

$$3CH_3CH_2COOH + CO_2 + 2NH_4^+ \cdot \Rightarrow 2C_5H_7O_2N + 4H_2O + H_2 + 2H^+ \quad (2)$$

Note that in Eqs. 1 and 2:

- CO_2 is utilised as an additional carbon source – in all CO_2 consumption/production the undissociated carbonate species H_2CO_3* acts as source/sink respectively,
- ammonium is the nitrogen source for organism growth - under normal operating conditions and pH (6.5<pH<7.5) of an anaerobic digester, the ammonium species (NH_4^+) dominates over the ammonia species (NH_3) so that using ammonia as the N species for organism growth can cause numerical instability in solution procedures for the model,
- the undissociated propionic acid species is used as substrate source, in agreement with observations in the literature, and
- the chemical formulation for organisms is assumed to be $C_5H_7O_2N$, which is the formulation generally accepted to represent organism active mass in activated sludge (WRC, 1984).

Accepting that Y_{ac} mol of acetogen organisms are formed (i.e. the anabolic yield of acetogens), Eq. 2 can be rewritten as:

$$\frac{3Y_{ac}}{2}CH_3CH_2COOH + \frac{Y_{ac}}{2}CO_2 + Y_{ac}NH_4^+ \cdot \Rightarrow Y_{ac}C_5H_7O_2N + 2Y_{ac}H_2O + \frac{Y_{ac}}{2}H_2 + Y_{ac}H^+ \quad (3)$$

Adding Eqs 1 and 3 and dividing by Y_{ac} yields:

$$\frac{1+\frac{3Y_{ac}}{2}}{Y_{ac}}CH_3CH_2COOH + \frac{2(1-Y_{ac})}{Y_{ac}}H_2O + NH_4^+ \Rightarrow \frac{1}{Y_{ac}}CH_3COOH + C_5H_7O_2N + \frac{1-\frac{Y_{ac}}{2}}{Y_{ac}}CO_2 + \frac{3+\frac{Y_{ac}}{2}}{Y_{ac}}H_2 + H^+ \quad (4)$$

Recognising that in Eq. 4 the "true" acetogen yield (Y_{AC}, mole organism/mole propionate) is $Y_{ac}/(1+3/2Y_{ac})$, and substituting Y_{AC} into Eq. 4 and solving gives:

$$\frac{1}{Y_{AC}}CH_3CH_2COOH + \frac{(2-5Y_{AC})}{Y_{AC}}H_2O + NH_4^+ \Rightarrow \frac{1-\frac{3}{2}Y_{AC}}{Y_{AC}}CH_3COOH + C_5H_7O_2N + \frac{1-2Y_{AC}}{Y_{AC}}CO_2 + \frac{3-4Y_{AC}}{Y_{AC}}H_2 + H^+ \quad (5)$$

The stoichiometry for acetogenesis and acetogen growth was extracted from Eq. 5 directly, and is summarised in Table 3. Note that compounds that are utilised (reactants, left hand side of Eq. 5) are negative (reduction), while compounds produced (products, right hand side of Eq. 5) are positive (production), that H_2O has been included in Eq. 5 for an element balance, but is not included directly in Table 3, and that there is a net production of CO_2 expressed as H_2CO_3* in the kinetic model ($1/Y_{AC}>2$). Following this procedure, the stoichiometries for the remaining processes were derived and are summarised in Table 4.

In the hydrolysis process, the biodegradable particulate organics measured as COD (S_{bp}) in the sewage sludge are first changed to mole units "outside" of the kinetic model, i.e. matrix, by dividing by the COD/mol ratio = {(Y + 4X - 2Z - 3A)·MW_{O2}/4}, with MW_{O2} being the molecular weight of O_2 = 32 g/mol. Thereafter, the sewage sludge biodegradable particulate organics measured as moles (S_{bp}) are transformed to the intermediate organic "glucose" also as moles (S_{bs}). This process is crucial in anaerobic digestion modelling, as the amount of "glucose" formed will determine the amount of the end products (CH_4, CO_2 and biomass) in a stable digester. To develop the stoichiometry for the hydrolysis process, the stoichiometric reaction was separated into two half reactions, effectively the redox half reactions, which were added based on an electron (COD) balance. In setting up the conversion of the primary sludge COD to mole units and the two subsequent half reactions in the transformation to the intermediate "glucose", the chemical formulation for the sewage sludge was kept as a variable, i.e. $C_XH_YO_ZN_A$, to allow the composition of the influent sewage sludge to the AD to be easily changed (McCarty, 1974). The formulation for the sewage sludge was assumed to be the same for all sewage sludge fractions (i.e. biodegradable and unbiodegradable), and to remain constant with degradation. This gives the stoichiometric reaction for sewage sludge hydrolysis as:

$$C_XH_YO_ZN_A \Rightarrow \frac{Y+4X-2Z-3A}{24}C_6H_{12}O_6 \cdot + ANH_3 + \frac{Y-4X+2Z-3A}{4}H_2O + \frac{2Z+3A-Y}{4}CO_2 \quad (6)$$

In the death/endogenous decay processes for the four organism groups (Table 4), it was accepted that the organisms die releasing biodegradable particulate organics (S_{bp}), which are assumed to have the same formulation as the sewage sludge, i.e. $C_XH_YO_ZN_A$ with CO_2, H_2O and NH_3 released or taken up from the bulk

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TABLE 4
Stoichiometry for of the AD processes hydrolysis (D1), acidogenesis (D2, D3), acetoclastic methanogenesis (D7), hydrogenotrophic methanogenesis (D9) and endogenous respiration of the four organism species (D4, D6, D8 and D10). The S1 to S13 numbers cross-reference to the stoichiometry in the Petersen matrix (Table 2). Stoichiometry of process D5 is given in Table 3.

Hydrolysis (Process D1)

C2 - NH_3 (S1)	C3 - $H_2CO_3^*$ (S2)	D1 - S_{bp}	D2/B2 - S_{bs} (S3)
moles	moles	moles	moles
$+A$	$\frac{2Z + 3A - Y}{4}$	-1	$\frac{Y + 4X - 2Z - 3A}{24}$

Acidogenesis for low pH2 (Process D2)

C1/B10 NH_4^+	C3 (S4) $H_2CO_3^*$	C7 H^+	C13 (S5) HAc	D2/B2 S_{bsf}	D3 (S6) H_2	**D4 Z_{AD}**
moles	moles	moles	moles	moles	moles	**moles**
-1	$\frac{2(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	**1**	$\frac{2(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	$-\frac{1}{Y_{AD}}$	$\frac{4(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	**1**

Acidogenesis for high pH2 only (Process D3)

C1/B10 NH_4^+	C3 (S7) $H_2CO_3^*$	C7 H^+	C13 (S8) HAc	C28 (S9) HPr	D2/B2 S_{bsf}	D3 (S10) H_2	D4 Z_{AD}
moles	moles	moles	moles	moles	moles	moles	moles
-1	$\frac{(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	1	$\frac{(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	$\frac{(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	$-\frac{1}{Y_{AD}}$	$\frac{(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	1

Acetoclastic methanogenesis (Process D7)

C1/B10 NH_4^+	C3 - $H_2CO_3^*$ (S17)	C7 - H^+	C13 - HAc	P4 - CH_4 (S18)	D6 - Z_{AM}
moles	moles	moles	moles	moles	moles
-1	$\frac{(1-\frac{5}{2}Y_{AM})}{Y_{AM}}$	1	$-\frac{1}{Y_{AM}}$	$\frac{(1-\frac{5}{2}Y_{AM})}{Y_{AM}}$	1

Hydrogenotrophic methanogenesis (Process D9)

C1/B10 - NH_4^+	C3 - $H_2CO_3^*$ (S19)	C7 - H^+	P4 - CH_4 (S20)	D3 - H_2	D7 - Z_{HM}
moles	moles	moles	moles	moles	moles
-1	$-\frac{(1+10Y_{HM})}{4Y_{HM}}$	1	$\frac{(1-10Y_{HM})}{4Y_{HM}}$	$-\frac{1}{Y_{HM}}$	1

Death / Endogenous respiration Processes (D4, D6, D8, D10)

C2/B10 NH_3 (S11)	C3 $H_2CO_3^*$ (S12)	D1 S_{bp} (S13)	D4, D6, D8, D10 Z_{AC}, Z_{AD}, Z_{AM}, Z_{HM}
moles	moles	moles	moles
$\frac{Y + 4X - 2Z - 23A}{Y + 4X - 2Z - 3A}$	$\frac{5(Y - 2Z - 3A)}{Y + 4X - 2Z - 3A}$	$\frac{20}{Y + 4X - 2Z - 3A}$	-1

TABLE 5
Kinetic and stoichiometric constants at 37°C for the four anaerobic digestion organism groups. The Y, μ_{max}, K_S and b values were obtained from Sam-soon et al. (1991); the $K_{max,HYD}$ and $K_{S,HYD}$ values by calibration in this application.

Organism group	Y	μ_{max}	K_S	b
Acidogens (subscript AD)	0.1074	0.8	$7.8x10^{-4}$	0.041
Acetogens (subscript AC)	0.0278	1.15	$8.9x10^{-5}$	0.015
Acetoclastic methanogens (subscript AM)	0.0157	4.39	$1.3x10^{-5}$	0.037
Hydrogenotrophic methanogens (subscript HM)	0.004	1.2	$1.56x10^{-4}$	0.01
Hydrogen inhibition coefficient for high p_{H2}	$k_{H2} = 6.25x10^{-4}$ molH_2/ℓ			
Acidogenic hydrolysis of biodeg particulate organics				
First order	$K_h = 0.381$			
First order specific	$K_H = 40$			
Monod	$\mu_{max,HYD} = 4.529$		$K_{SM,HYD} = 0.0486$	
Surface mediated reaction (Contois)	$k_{max,HYD} = 6.797$		$K_{SS,HYD} = 10.829$	

Y= yield coefficient (mol organism/mol substrate); μ_{max} = maximum specific growth rate (/d);
K_S = half saturation coefficient (mol/ℓ); b = endogenous respiration rate (/d);
K_h = first order hydrolysis rate constant (/d)
K_H = first order specific hydrolysis rate constant (ℓ/mol Z_{AD}·d)
$\mu_{max,HYD}$ = Monod kinetics maximum specific hydrolysis rate (mol S_{bp}/mol Z_{AD}·d)
$K_{SM,HYD}$ = Monod kinetics hydrolysis half saturation coefficient (mol S_{bp}/ℓ)
$k_{max,HYD}$ = surface mediated reaction kinetics maximum specific hydrolysis rate (mol S_{bp}/mol Z_{AD}·d);
$K_{SS,HYD}$ = surface mediated reaction kinetics half saturation coefficient (mol S_{bp} /mol Z_{AD})

liquid as required to maintain the C, H, O and N mass balances. Due to the low organism yields and relatively low death rates, and the relatively large fraction of unbiodegradable particulate organics in the influent, generation of endogenous residue (Dold et al., 1980) was not included, but this can be done relatively simply if required. Hence, the stoichiometric reaction for organism death is (Table 4):

$$C_5H_7O_2N + \frac{4(2Y-2X-6A+Z)}{Y+4X-2Z-3A}H_2O \rightarrow \frac{20}{Y+4X-2Z-3A}C_XH_YO_ZN_A + \frac{Y+4X-2Z-23A}{Y+4X-2Z-3A}NH_3 + \frac{5(Y-2Z-3A)}{Y+4X-2Z-3A}CO_2 \quad (7)$$

The position of the stoichiometric formulae of Tables 3 and 4 are shown in the Petersen matrix in Table 2. By tracking through with defined organism yield values (Table 5) the stoichiometric sequence of AD processes (ignoring high p_{H2} conditions, which has no effect under stable steady state conditions, and endogenous respiration processes, which have a very small effect, <3%), degradation of 100 gCOD biodegradable particulate sewage sludge of composition $C_{3.5}H_7O_2N_{0.196}$ (see below) produces 88.3 g COD methane and 11.7 gCOD biomass (Fig. 3). Also the 100 gCOD contains 2.67 mol carbon (32.0 gC). Stoichiometrically 88.3 gCOD methane contains 1.38 molC (16.5 gC) and the 11.7 gCOD biomass of composition $C_5H_7O_2N$ contains 0.37 molC (4.4 gC). The difference between the input and output molC is the molC CO_2 produced, viz. 2.67- (1.38 + 0.37) = 0.92 molC (11.0 gC), which is equal to the model predicted net CO_2 production. This CO_2 production exits the digester as CO_2 gas and dissolved CO_2 in the effluent flow. The split between the gaseous and dissolved CO_2, or equivalently the partial pressure of CO_2 in the gas phase, is governed by the sludge feed COD concentration, i.e. the influent (and effluent) flow with which the 100 gCOD enters the digester, and the digester pH through

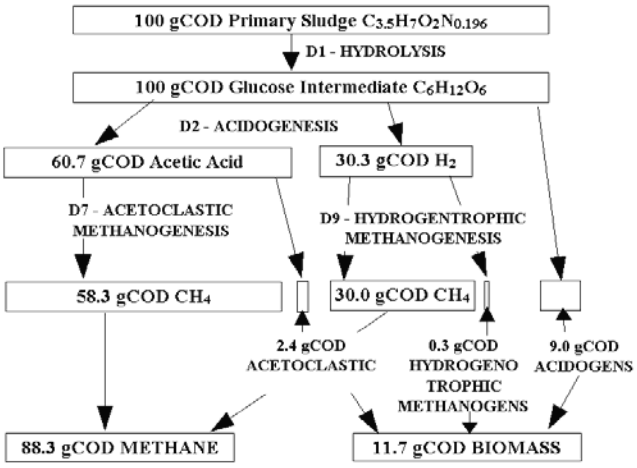

Figure 3
Stoichiometry of anaerobic digestion 100 gCOD primary sludge ignoring high partial pressure of hydrogen and endogenous respiration

the mixed weak acid/base chemistry of the system. This calculation is complex because the digester pH is unknown. The pH is affected by the mol N released as ammonia in the breakdown of the sludge organics (0.15 molN from the 100 gCOD $C_{3.5}H_7O_2N_{0.196}$ sewage sludge) and the partial pressure of CO_2 in the gas phase (p_{CO2}). While estimates of the p_{CO2} and digester pH can be obtained iteratively manually (see Sötemann et al., 2005b), the usefulness of the integrated two phase weak acid/base chemistry and biological processes kinetic model is that this calculation of the effluent gas p_{CO2} and digester pH is done seamlessly within the model structure including all the weak acid/bases in the digester influencing pH (not only the inorganic C system) and the measured (or estimated) dissolved constituents in the sludge feed as a result of prior acidogenesis. Also,

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while not validated for this yet, the integrated AD model can deal with cyclic flow and load conditions.

Kinetic equations of the biological processes

The rate equations for the 10 biological processes (Table 2) were obtained from various literature sources, where possible, and modified to describe the reactions as realistically and accurately as possible. The rate equations chosen for each of the biological processes included in the two phase CPB processes AD model are briefly described below.

Hydrolysis process (D1)

A number of different kinetic formulations for the hydrolysis process were investigated:

(i) First order kinetics

The most common way of modelling the rate of hydrolysis of particulate organic material (process D1) has been to use first order kinetics. A number of researchers (e.g. Eastman and Ferguson, 1981; Gujer and Zehnder, 1983; Pavlostathis and Giraldo-Gomaz, 1991) used simple first order equations, dependent only on the biodegradable substrate (as COD) concentration:

$$r_{HYD} = K_h\,[S_{bp}] \tag{8a}$$

where:

r_{HYD} = hydrolysis rate (mol S_{bp}/ℓ·d)
K_h = first order hydrolysis kinetic rate constant (/d)
$[S_{bp}]$ = biodegradable particulate organics concentration (mol/ℓ).

Application of the first order kinetics has been found to result in values for the first order rate constant (K_H) that are situation specific, varying with, for example, sludge age or equivalently hydraulic retention time (e.g. Henze and Harremoës, 1983; Bryers, 1985; Pavlostathis and Giraldo-Gomez, 1991; Sötemann et al., 2005b). Because the objective is to develop a kinetic model for anaerobic digestion that would be applicable over a range of sludge ages, alternative more general approaches were investigated. It is well known that the rate of hydrolysis is affected by temperature, pH, acidogen organism concentration, and type, particle size and concentration of organics. Among these, intuitively at least the acidogen organism concentration plays a major role in regulating the rate of hydrolysis and should be included in the kinetic rate expression in some way. Eliosov and Argaman (1995) included the acidogen active biomass directly into the first order kinetics:

$$r_{HYD} = K_H\,[S_{bp}][Z_{AD}] \tag{8b}$$

where:

K_H = first order specific hydrolysis kinetic rate constant (ℓ/mol Z_{AD}·d)
$[Z_{AD}]$ = acidogen active biomass concentration (mol/ℓ)

(ii) Monod kinetics

Monod kinetics are commonly used in modelling biological wastewater treatment processes (e.g. McCarty, 1974; Dold et al., 1980, Henze et al., 1987):

$$r_{HYD} = \left[\frac{\mu_{max,HYD}\,[S_{bp}]}{K_{SM,HYD} + [S_{bp}]}\right][Z_{AD}] \tag{8c}$$

where:

$\mu_{max,HYD}$ = maximum specific hydrolysis rate constant (mol S_{bp}/(mol Z_{AD}·d))
$K_{SM,HYD}$ = Monod half saturation constant for hydrolysis (mol S_{bp}/ℓ)

(iii) Surface mediated reaction (or Contois) kinetics

To model the hydrolysis of particulate slowly biodegradable COD in activated sludge systems, Dold et al. (1980) used Levenspiel (1972) planar surface mediated reaction kinetics (also known as Contois kinetics, Vavilin et al., 1996). With a single set of constant values, these kinetics gave reasonable predictions over a wide range of activated sludge system conditions including sludge age. Since the hydrolysis processes in activated sludge and anaerobic digestion could be regarded as similar and operate on the same organics (present in raw sewage), this approach also was investigated for the AD model:

$$r_{HYD} = \left[\frac{k_{max,HYD}\,\dfrac{[S_{bp}]}{[Z_{AD}]}}{K_{SS,HYD} + \dfrac{[S_{bp}]}{[Z_{AD}]}}\right][Z_{AD}] \tag{8d}$$

where:

$k_{max,HYD}$ = Maximum specific hydrolysis rate constant [mol S_{bp}/(mol Z_{AD}·d)]
$K_{SS,HYD}$ = Half saturation constant for hydrolysis (mol S_{bp}/mol Z_{AD})

Selection of the most suitable hydrolysis kinetic formulation is investigated later in this paper. Irrespective of the hydrolysis formulation used, no acidogen biomass growth takes place in this hydrolysis process, and 1 gCOD sewage sludge forms 1 gCOD "glucose" intermediate (Fig. 3, Eq. 6). Growth of acidogens arises from the acidogenic conversion of the glucose intermediate to SCFA and hydrogen, which, relative to the rate of hydrolysis, is immediate resulting in zero accumulation of glucose in the AD system.

Acidogenesis process (D2 and D3)

As noted above, acidogenesis refers to the utilisation of the model intermediate "glucose" (S_{bs}) by the acidogenic organisms, producing propionic acid, acetic acid, hydrogen, carbon dioxide and protons. Under conditions of low hydrogen partial pressure (p_{H2}), the acidogenic reaction (process D2) produces only acetic acid, hydrogen and CO_2. The process is formulated in terms of the growth rate of acidogens (r_{ZAD}), which is modelled with a Monod equation (Gujer and Zehnder, 1983; Pavlostathis and Giraldo-Gomez, 1991), as follows:

$$r_{Z_{AD}} = \frac{\mu_{max,AD}\,[S_{bsf}]}{K_{S,AD} + [S_{bsf}]}\left\{1 - \frac{[H_2]}{k_{H2} + [H_2]}\right\}[Z_{AD}] \tag{9}$$

where:

$\mu_{max,AD}$ = Maximum specific growth rate constant for the acidogens (/d)
$K_{S,AD}$ = Half saturation concentration for acidogens (mol/ℓ)
$[S_{bsf}]$ = Biodegradable soluble (glucose) substrate concentration (mol/ℓ)
$[H_2]$ = Hydrogen concentration (mol/ℓ)
k_{H2} = Hydrogen inhibition constant for high p_{H2} (mol/ℓ)

The second part of the term in { } brackets in Eq. 9, called a non-competitive inhibition function, takes account of the reduction in rate when the p_{H2} is high. At high p_{H2}, in addition to acetic acid, hydrogen and CO_2, propionic acid also is produced

(process D3). For the production of propionic acid under high p_{H2}, the growth rate of the acidogens (r_{ZAD}) is based on the same Monod kinetic equation (Eq. 9) as for low p_{H2}, viz.:

$$r_{Z_{AD}} = \frac{\mu_{max,AD}\,[S_{bsf}]}{K_{S,AD} + [S_{bsf}]} \left\{ \frac{[H_2]}{k_{H2} + [H_2]} \right\} [Z_{AD}] \qquad (10)$$

To ensure that this process only operates when the p_{H2} is high, the non-competitive inhibition function in { } switches the process "on" under conditions of high p_{H2} and "off" under conditions of low p_{H2}, controlled by switching constant k_{H2}. Additionally, to ensure that the rate of glucose (S_{bsf}) utilisation is the same under both conditions and in the intermediate condition, the rate of acetate production (Eq. 9) is reduced by subtracting the inhibition function value from 1 in Eq. 9.

Acetogenesis process (D5)

In the process of acetogenesis, the propionic acid produced under high p_{H2} conditions is degraded under low p_{H2} by acetogenic organisms to produce acetate (Eq. 1). This rate was modelled in terms of the acetogen growth rate (r_{ZAC}), also with a Monod equation for the specific growth rate:

$$r_{Z_{AC}} = \frac{\mu_{max,AC}\,[HPr]}{K_{S,AC} + [HPr]} \left\{ 1 - \frac{[H_2]}{k_{H2} + [H_2]} \right\} [Z_{AC}] \qquad (11)$$

where:

$\mu_{max,AC}$ = Maximum specific growth rate constant for the acetogens (/d)
$K_{S,AC}$ = Half saturation concentration for acetogens (mol/ℓ)
[HPr] = Undissociated propionic acid concentration (mol/ℓ)
$[Z_{AC}]$ = Acetogenic organism concentration (mol/ℓ)

Since the weak acid/base chemistry is being modelled, both the undissociated and dissociated species of propionic acid are included as compounds, and the growth rate needs to be formulated in terms of the appropriate species. In Eq. 11, the specific growth rate is a Monod function in terms of the undissociated propionic acid species, and not the more abundant dissociated species, in agreement with observations. Also, in the stoichiometry (Table 2) the undissociated propionic acid species (HPr) is used as substrate source. Should this approach lead to numerical instability in solution procedures (due to the low concentrations of HPr) , the dissociated species (Pr) can be used instead without undue difficulty, but taking due cognisance of the concentration effects in the Monod expression and the requirement of the charge balance in the stoichiometric equations.

The same non-competitive inhibition function in the { } brackets of Eq. 9 appears in Eq. 11, because the acetogenesis process is sensitive to p_{H2}, decreasing as p_{H2} increases. This means that as p_{H2} increases, not only do acidogens begin to produce propionic acid (process D3), but also the rate of propionic acid utilisation by acetogens (process D5) decreases. This causes a progressive build up of propionic acid as p_{H2} increases and contributes to the decrease in pH when the hydrogen consuming hydrogenotrophic methanogen growth rate (D9) decreases for some reason (see below).

Acetoclastic methanogenesis process (D7)

Acetoclastic methanogenesis (or acetate cleavage) is the process whereby acetic acid is converted to methane and CO_2 ($CH_3COOH \Rightarrow CO_2 + CH_4$), and growth of acetoclastic methanogens takes place. As for processes D2 and D3, the rate is modelled in terms of the rate of growth of the acetoclastic methanogens (r_{ZAM}) with a Monod equation, viz.:

$$r_{Z_{AM}} = \frac{\mu_{max,AM}\,[HAc]}{K_{S,AM} + [HAc]} [Z_{AM}] \qquad (12)$$

where:

$\mu_{max,AM}$ = Acetoclastic methanogens maximum specific growth rate constant (/d)
$K_{S,AM}$ = Half saturation concentration of acetoclastic methanogens growth on acetic acid (mol/ℓ)
[HAc] = Undissociated acetic acid concentration (mol/ℓ)
$[Z_{AM}]$ = Acetoclastic methanogen organism concentration (mol/ℓ)

As for the acetogens, the specific growth rate of the acetoclastic methanogens is a function of the undissociated acetic acid species (HAc). Also, in the stoichiometry acetic acid uptake is via the undissociated species, and CO_2 production via H_2CO_3*.

Hydrogenotrophic methanogenesis process (D9)

Hydrogenotrophic methanogenic organisms use H_2 and CO_2 to form methane and water ($CO_2 + 4H_2 \Rightarrow CH_4 + 2H_2O$). This process (D9) is also modelled in terms of the rate of growth of the hydrogenotrophic methanogens (r_{ZHM}), with a Monod equation:

$$r_{Z_{HM}} = \frac{\mu_{max,HM}\,[H_2]}{K_{S,HM} + [H_2]} [Z_{HM}] \qquad (13)$$

where:

$\mu_{max,HM}$ = Maximum specific growth rate of hydrogenotrophic methanogens (/d)
$K_{S,HM}$ = Half saturation concentration of hydrogenotrophic methanogens growth on hydrogen (mol/ℓ)
$[H_2]$ = Molecular hydrogen concentration (mol/ℓ)
$[Z_{HM}]$ = Hydrogenotrophic methanogen organism concentration (mol/ℓ)

In agreement with the other processes, CO_2 uptake for hydrogenotrophic methanogenesis is via the H_2CO_3* species.

Death/endogenous respiration of the four organism groups (processes D4, D6, D8 and D10)

Organism death in AD consists of endogenous respiration/death only, since predation apparently does not occur under anaerobic conditions. Hence, for each organism group the organism death rate is modelled with first order kinetics, viz.:

$$-r_Z = b_Z\,[Z] \qquad (14)$$

where:

b_Z = the death/endogenous mass loss rate unique for a specific organism group (/d)
[Z] = specific organism group concentration (mol/ℓ)

The organism mass that dies adds to the slowly biodegradable organics (S_{bp}) of the influent (Table 4, Eq. 7), which passes through the same hydrolysis, acidogenesis and subsequent processes as the influent biodegradable organics. Because the organism yields and endogenous respiration rates of the AD organisms are relatively very low, it was accepted that no endogenous residue (particulate unbiodegradable organics) forms and no COD (electrons) is utilised by the AD organisms for maintenance.

The stoichiometric and kinetic constants for the four organism groups (yield coefficients, maximum specific growth rates,

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half saturation concentrations, endogenous mass loss rates) were obtained from the literature and are listed in Table 5.

Aqueous chemical processes

The reaction scheme for the weak acid/base part of this two phase AD model was taken unchanged from Musvoto et al. (1997; 2000a,b,c). The 16 chemical equilibrium dissociation (CED) processes (C1-C6 and C9-C18) of the ammonia, carbonate, phosphate, short chain (volatile) fatty acid (SCFA, acetate) and water weak acid/base systems and their 13 associated compounds (C1-C5 and C7-C14) were included in the AD model (Tables 1 of Musvoto et al., 1997 and Sötemann et al., 2005a). Only the five chemical (C) and one physical (P) compounds directly associated with the 10 biological (B) and 3 physical (P) processes of AD (D1-D10 and P6-P8) are shown in the Petersen matrix in Table 2, i.e. NH_4^+ (C1/B10), NH_3 (C2), H_2CO_3* (C3), H^+ (C7), HAc (C13) and CO_2 gas (P1/C6). Two additional CED processes had to be added, viz. the reverse and forward dissociation processes for the propionate weak acid/base system (C46 and C47), together with its two associated compounds propionic acid (HPr, C28) and propionate (Pr^-, C29). The 22 chemical ion pairing processes (CIP, C20-C41) with their 13 associated chemical compounds (C15-C27) were not included in this two phase AD model, because mineral precipitation (3rd phase) is not yet included (Table 1 of Sötemann et al., 2005a).

Physical processes – gas exchange

In the three phase carbonate system weak acid/base model of Musvoto et al. (1997), the physical (P) processes for carbon dioxide gas exchange (PGE) with the atmosphere were included, by modelling the expulsion (reverse, K'_{rCO2}) and dissolution (forward, K'_{fCO2}) processes separately and linking the rates for these two processes through the Henry's law constant for CO_2 (K_{HCO2}), i.e. $K'_{fCO2} = K'_{rCO2}\ K'_{HCO2} \bullet RT$. Musvoto et al. showed that this approach yielded identical results to the usual interphase gas mass transfer equation with an overall liquid phase mass transfer rate coefficient K_{LaCO2}, where $K_{La,CO2} = K'_{rCO2}$. In their model application, the actual CO_2 expulsion rate constant value (K'_{rCO2}) was not important because they considered initial and final steady state conditions only, not the transient dynamic conditions to the final steady state. Also, the CO_2 gas concentration ($CO_2(g)$) was kept constant as calculated from a selected partial pressure of CO_2 ($CO_2(g) = p_{CO2}/RT$), since gain or loss of $CO_2(g)$ did not need to be determined.

Musvoto et al. (2000a), Van Rensburg et al. (2003) and Loewenthal et al. (2004) extended this model to include three phase mixed weak acid/base systems to simulate multiple mineral precipitation and active gas exchange of CO_2 and NH_3 during aeration of anaerobic digester liquor and swine wastewater. For CO_2, they followed the approach of Musvoto et al. (1997) above. For the NH_3, they noted that the atmospheric concentration of NH_3 is negligible (i.e. acts as an infinite sink), so that only NH_3 expulsion need be included, and dissolution could be neglected. Because they simulated transient (dynamic) conditions, the CO_2 gas exchange (as above) and NH_3 gas expulsion (stripping) (and mineral precipitation) rates were important and these were determined from the experimental results. In determining the rates for the gas exchanges, Musvoto et al. (2000a) noted that, if the dimensionless Henry's law constant of a gas, H_c [$=\{1/(K_H R T)\}$] is > 0.55, then O_2 can be used as a reference gas and the expulsion rate constant K'_r ($= K_{La}$) for the individual gases will be in the same proportion to the rate for O_2 ($K'_{rO2} = K_{LaO2}$) as their diffusivity is to the diffusivity of O_2. Of the two gases they considered, only NH_3 has a $H_c < 0.55$ (= 0.011 at 20°C), so the value for K'_{rNH3} had to be determined independently of the values for K'_{rO2}, by calibration. For CO_2, $H_c = 0.95$ at 20°C (Katehis et al., 1998) and accordingly they defined K_{LaCO2} in terms of K_{LaO2}. However, since the compound oxygen was not included in their model, in effect only K_{LaCO2} was determined by calibration against measured data.

Sötemann et al. (2005a) integrated the biological processes of IWA Activated Sludge Model No. 1 into the two phase (aqueous-gas) mixed weak acid/base chemistry model of Musvoto et al. (2000a) allowing the reactor pH to become a model predicted parameter. Four gases were considered, viz. O_2, N_2, CO_2 and NH_3. For CO_2 and NH_3, the formulations of Musvoto et al. and van Rensberg et al. above were accepted. However, since gas production was of interest, for CO_2 they substituted $K'_{rCO2} \bullet K'_{HCO2} \bullet p_{CO2}$ for $K'_{fCO2} \bullet [CO_2(g)]$ (Table 3, Sötemann et al., 2005a). This allows the $CO_2(g)$ concentration to vary without influencing the rate of CO_2 gas exchange, of importance in their implementation of the model in Aquasim (Reichert, 1998), where for simplicity the gas compounds were considered part of the bulk liquid. This approach for CO_2 was adopted for N_2 gas also. For O_2, the more conventional approach for aeration transfer to the bulk liquid was followed (Process P11 in Table 3, Sötemann et al., 2005a). In their application, because equilibrium between the aqueous and gas (atmosphere) phases is not reached during aeration in the aerobic reactor, the expulsion rates of the four gases were important for the simulation results and so values for K'_r ($= K_{La}$) for the four gases had to be determined. For the K_{La} values for the gases, they followed the approach of Musvoto et al. (2000a) above. The K_{La} for CO_2 and N_2 were linked to the K_{La} for O_2 through the diffusivities. The K_{LaO2} was calibrated to reflect the CO_2 supersaturation observed on samples from the aerobic reactor of full-scale plants (~20%), and cross-checked against the model determined dissolved O_2 concentration. For K'_{rNH3} ($= K_{LaNH3}$), this was calibrated independently. However, because negligibly little NH_3 actually strips out of the aqueous phase with aeration in the usual pH range of 6.5 to 8 for activated sludge systems, the actual NH_3 stripping rate, and hence the value for K'_{rNH3}, was of little consequence (provided it is not excessively large) and in fact the process itself could have been omitted from the integrated model without loss in accuracy.

In the application here of integrating the biological processes of AD into the two phase (aqueous-gas) mixed weak acid/base chemistry model of Musvoto et al. (2000a), four gases also need to be considered, i.e. CO_2, CH_4, H_2 and NH_3. Of these four, only CO_2 needs to be modelled with both expulsion and dissolution processes, because this gas is significantly soluble. Hence, both dissolved and gaseous CO_2 compounds are included (compounds C3 and P1, Table 2) and the process scheme of Sötemann et al. (2005a) above was followed. CH_4 is very insoluble and not utilised in the biological or chemical processes, so its dissolved (aqueous) phase is bypassed and only a gas phase CH_4 compound is included (compound P4, Table 2). It is therefore assumed that the acetoclastic and hydrogenotrophic methanogenesis processes (D7 and D9) produce CH_4 gas directly and no CH_4 expulsion and dissolution processes need to be included in the model. Although H_2 also is very insoluble, it is utilised at an interspecies level in the hydrogenotrophic methanogenesis process (D9) and so it cannot be transferred instantaneously to the gas phase. H_2 is therefore modelled as a dissolved compound (D3, Table 2), but because it is utilised so rapidly and at an inter-organism species level, it's residual concentration is extremely small; from a gas production perspective, it can be

ignored. Hence, expulsion and dissolution processes for H_2 are not included in the model. NH_3 is readily soluble and its production from organically bound N in the sewage sludge is one of the processes governing the pH in the digester. It can diffuse from the dissolved (aqueous) to the gas phases and so a process for expulsion of NH_3 is included in the model. However, because the rate and quantity of NH_3 expulsion into the gas phase are so slow and low respectively with respect to the total gas production of the digester, in particular in the digester pH range 6.8 to 8, the gas phase is assumed to maintain a negligible NH_3 partial pressure. An NH_3 dissolution process is therefore not included in the model, only an expulsion process (in agreement with Musvoto et al., 2000a, Van Rensburg et al., 2003 and Sötemann et al., 2005a). The expulsion and dissolution processes for CO_2 and the expulsion process for NH_3 are shown in the Petersen matrix of the AD model (processes P6 - P8, Table 2). Thus, only the K_r' ($=K_{La}$) values for these two gases need to be considered. However, because transient conditions are not being modelled in this particular application, but only the final steady state, the expulsion rates of the gases are not important provided the simulation run times are long enough to reach steady state. From the above it is clear that the gas phase partial pressure required in the rate formulations for CO_2 gas exchange need be calculated only from the CO_2 and CH_4 gas concentrations.

Influent sewage sludge characterisation

In terms of the structure of the UCTADM1 above, in addition to requiring as input the influent concentrations of the various inorganic compounds (e.g. total inorganic carbon, C_T, speciated into H_2CO_3*, HCO_3^- and CO_3^{2-} for the relevant pH), various sewage sludge organic compounds need to be specified. For UCTADM1, the sewage sludge characterisation into its constituent fractions is shown in Fig. 4; the characterisation structure adopted is near identical to that for sewage in activated sludge modelling (ASM2, Henze et al., 1995). For undigested pristine sewage sludges, the two particulate fractions (biodegradable and unbiodegradable) can be expected to dominate to the extent that the other fractions can be neglected (this is evident from a mass balance around the primary settling tank for primary sludges, and simulation of activated sludge systems for waste activated sludges). However, primary sewage sludges are seldom in the pristine state, having undergone hydrolysis and acidogenesis within the primary settling tank (e.g. Barnard, 1984 measured SCFA concentrations in primary settling tank underflows in the range 1 700 to 2 700 mg/ℓ at various treatment plants in South Africa), and in transport and storage for laboratory investigations. The SCFA thus produced (and equal concentrations of non-SCFA soluble COD, Lilley et al., 1990) have a significant influence on the predicted pH in simulating anaerobic digesters, since uptake and utilisation of dissociated SCFA generates significant alkalinity (Sötemann et al., 2005b). Furthermore, the SCFAs influence the hydrolysis rate constants in model calibration Ristow et al. (2004a,b). Thus, quantifying and specifying the influent sludge organic fractions are essential both in model calibration and simulation. Of the sewage sludge fractions (Fig. 4), the unbiodegradable and biodegradable particulate (S_{upi} and S_{bpi}) and the two readily biodegradable fractions (S_{bsai} and S_{bsfi}) are of importance - the unbiodegradable soluble organics (S_{usi}) usually are present in such low concentrations that they can be neglected. For S_{bsai}, two SCFA types are recognised in the model, acetic and propionic, and hence these form two subfractions of the S_{bsai}.

The characterisation structure is based on COD units, which are widely applied to quantify wastes. Since the kinetic model is based on mole units, conversion between the COD and mole units would be needed to generate the input for the model. For the two readily biodegradable fractions, the S_{bsai} usually are measured directly, while in terms of the model presented here the S_{bsfi} is "idealised" glucose so that conversion of these to mole units is relatively simple. For the particulate fractions, the conversion to mole units requires that the stoichiometric formulation for these sewage sludge fractions be specified, i.e. X, Y, Z and A in $C_XH_YO_ZN_A$. This is discussed in more detail below.

Model calibration

From the above model development, the integrated two phase (aqueous-gas) chemical (C), physical (P) biological (B) processes AD model comprises (Table 2):

- the 16 forward and reverse chemical equilibrium dissociation (CED) processes (C1-C6, C9-C18) and their 13 associated compounds (C1-C2, C4-C14) – Table 1 in Musvoto et al. (1997);
- the two forward and reverse CED processes for propionic acid (C47-C48) and their two associated compounds (C28-C29),
- the three physical gas exchange processes of dissolution of CO_2 (P6) and its associated compound CO_2 gas (P1) and expulsion of CO_2 (P7) and NH_3 (P8) and,
- the 10 biological processes for AD (D1-D10) and their 8 associated compounds (P4 and D1-D7). The model was implemented in the computer programme Aquasim (Reichert, 1998).

Omitted from this AD model are the five mineral precipitation processes (P1/C19 – Musvoto et al., 1997 and P2/C42-P5/C45 – Musvoto et al., 2000a), because mineral precipitation is not included in this two phase AD model. Also omitted are the 22 chemical iron pairing (CIP) processes (C20-C41) and their 13 associated compounds (C15-C27), because these processes are important mainly for multiple mineral precipitation modelling, which will be included in the next phase of the AD and wastewater treatment plant model development.

In implementation of the model in Aquasim, since initial simulations were of steady state anaerobic digesters, the gas compounds were accepted to remain part of the bulk liquid and to leave the digester with the effluent flow. This is possible because at steady state the gas composition does not change. For dynamic simulations, the gas composition may change significantly and this may influence the dissolved species bulk liquid concentrations through the gas exchange processes, and hence a separate gas stream may need to be included, see later.

Kinetics and stoichiometric constants

The kinetic constants required for the C and P processes part of the model are the equilibrium constants (pK) of the six weak acid/base systems, Henry's law constant for CO_2 ($K'_{H,CO2}$), and the apparent reverse dissociation and expulsion rate constants (K'_r) respectively for these processes. The equilibrium constants (pK) and Henry's law constant for CO_2 ($K'_{H,CO2}$), and their temperature sensitivity equations were obtained from the literature (see Table 2c of Musvoto et al., 1997 – 1940s database). The pK value for propionic acid (pK_{Pr}) was accepted to be the same as for acetic acid, and is given by $pK_{Pr} = 1170.5/T_k - 3.165 + 0.0134T_k$, where T_k = temperature in Kelvin. The weak acid/base apparent reverse dissociation rate constants (K'_r) were

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TABLE 6
Experimental results for Izzett et al. (1992) 14 ℓ flow though mesophilic (37°C) anaerobic digesters operated from 20 to 7 d retention time on primary sewage sludge

Retention time (d)	20	15	12	10	7
Feed rate (ℓ/d)	0.7	0.93	1.17	1.4	2
Feed COD (mgCOD/ℓ)	42 595	42 367	39 222	40 721	43 286
Feed VFA (mgCOD/ℓ as HAc)	2 249	1 824	2 872	1 961	1 871
Feed TKN (mgN/ℓ)	1 171	1 075	1 028	1 100	1 105
Feed FSA (mgN/ℓ)	244	221	235	203	196
Feed VSS (mgVSS/ℓ)	25 690	25 863	24 727	25 768	25 971
Feed H_2CO_3* Alk (mg/ℓ as $CaCO_3$)	56	82	90	81	80
Feed pH	5.28	5.42	5.2	5.34	5.34
Effluent COD (mgCOD/ℓ)	19 005	19 969	18 678	20 521	23 637
Effluent VFA (mgCOD/ℓ as HAc)	23	27	28	28	50
Effluent TKN (mgN/ℓ)	1 157	976	992	1 039	1 041
Effluent FSA (mgN/ℓ)	511	404	430	404	511
Effluent H_2CO_3* Alk (mg/ℓ as $CaCO_3$)	2 066	1 994	2 072	1 951	1 882
Effluent pH	7.15	7.14	7.2	7.11	7.12
Gas production (ℓ/d at 20°C)	11.053	13.958	16.696	20.07	27.932
Gas composition (% methane)	63.3	63.6	63.3	62.1	63.2
COD balance (%)	107.3	106.9	109.1	108.6	108.4
N balances (%)	98.8	90.8	96.5	94.5	94.2
Model COD and N balances at all retention times 100.0053% and 99.999% respectively					

set at very high values to ensure that aqueous chemical equilibrium conditions are established very rapidly at every time step (< 2 sec), e.g. ammonia $K'_{rN} = 10^{12}$ /d, see Table 2a in Musvoto et al. (1997). The weak acid/base apparent forward (K'_f) dissociation rate constants are linked to the apparent reverse rate constants (K'_r) and the equilibrium constants (pK) appropriately adjusted for ionic strength effects, e.g. $K'_{fC1} = K'_{rC1}\ 10^{-pKC1}/\ f_m^{\ 2}$, where f_m is the mono-valent ion activity coefficient (Loewenthal et al., 1989), see Table 2a, Musvoto et al. (1997). For the expulsion rate constants of the CO_2 and NH_3 gases modelled ($K'_r = K_{La}$), for CO_2 the K_{LaCO2} was assumed to have a high value (1000/d) since only the steady state was initially simulated, while for NH_3 the K'_{rNH3} was accepted to have a low value (1/d). As noted above, the value for K'_{rNH3} does not influence the simulations provided it is not too high, since little NH_3 is lost at the pH < 7.5.

In the BD processes part of the model, required are the kinetic and stoichiometric constants (Y, μ_{max}, K_S and b) for the four AD organism groups (Table 5). In the literature there is considerable variation and hence uncertainty in these values. Accepting this uncertainty, values for these constants were taken from Sam-Soon et al. (1991), who obtained their values from a survey of the literature. Where specific weak acid/base species are included in the rate formulation (e.g. acetoclastic methanogenesis), the rate constants (e.g. Monod half saturation coefficients) had to be appropriately adjusted to take into account weak acid/base speciation. This was done via the relevant pK values and pH. In application, the maximum specific growth rate of the acetoclastic methanogens ($\mu_{max,AM}$ in Eq. 12) was increased from the range of 0.3 - 0.5/d used by Sam-Soon et al. (1991) to 4.39/d, to reproduce the observation of low HAc/Ac^- residual concentrations; due to the low HAc/Ac^- concentrations, decreasing the intuitively more satisfying half saturation constant ($K_{S,AM}$ in Eq. 12) as alternative caused instability in solution procedures. This aspect requires further investigation.

This left two parts of the AD model that required calibration against experimental data, viz, (i) the kinetic constants for the various hydrolysis rate expressions, e.g. maximum specific hydrolysis rate ($k_{max,HYD}$) and half saturation coefficient ($K_{S,HYD}$) in Eq. 8d, and selection of the most appropriate kinetic formulation, and (ii) the sewage sludge CHON composition, i.e. the X, Y, Z and A values in $C_XH_YO_ZN_A$. Additionally, in model application the sewage sludge constituent fractions and the input concentrations of the various compounds would need to be quantified. Values for all these parameters were obtained interactively through analysis of and model application to the experimental data set of Izzett et al. (1992), as described below.

Experimental anaerobic digester systems

In any calibration and validation exercise, the measured parameters must conform to the same mass balance and continuity principles as in the model, and hence must be sufficient to be able to calculate the material mass balances and the mass balances must be as close as possible to 100%. The data of Izzett et al. (1992) appeared to conform reasonably well to these criteria. They conducted a series of experiments aimed at identifying the effects of thermophyllic heat pre-treatment on the anaerobic digestibility of a mixture of primary and humus sewage sludges. In this investigation four laboratory scale anaerobic digesters were operated at a controlled temperature of 37°C, two of which were fed heat pre-treated (70°C for 24 h) sludge while the other two were fed untreated sludge. The digesters were run in parallel, and the retention times were progressively reduced to observe possible differences in digestibility (fraction unbiodegradable and rate of hydrolysis) between the heat pre-treated and untreated sludges. The digester fed untreated sludge was operated for a period of 211 d, during which time the retention time was reduced from 20 to 15, then 12, 10 and finally 7 d after the system had run at steady state for two to three retention times at each retention time. The data collected from this AD system (influent and effluent COD, VSS, TSS, TKN, FSA, SCFA, pH, $H_2CO_3^*$ alkalinity and gas production and CO_2 composition) at a particular retention time were averaged over the final two to

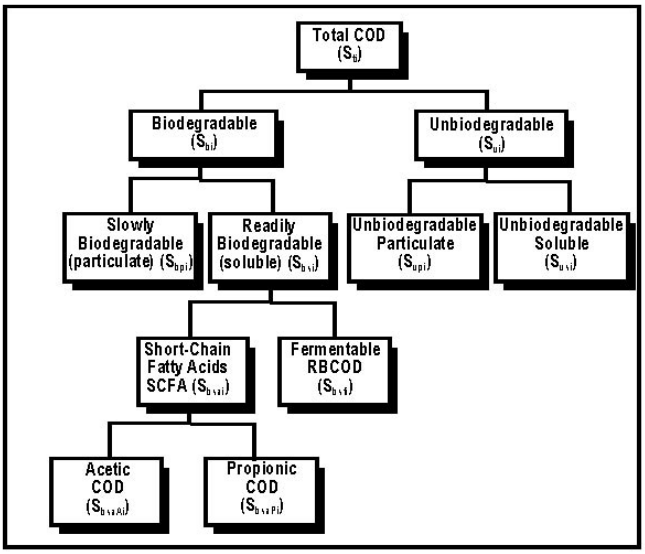

Figure 4
Schematic showing characterisation of the influent sewage sludge organics, required as input to the model; the acetic and propionic require speciation for the influent pH

three steady state retention times (Table 6). The averages were used to check the N and COD mass balances. The N and COD balances obtained at the 20, 15, 12, 10 and 7 d retention times were 91 to 99% and 107 to 109% respectively (Table 6), indicating that the measured parameters conformed closely to the mass balance requirement. The measured averages therefore could be accepted to represent the behavioural characteristics of the digester under stable operating conditions at the different retention times.

As input to the various simulations and calculations below, the influent inorganic and organic constituent fractions need to be specified. A number of these were available from direct measurements, or could be derived directly. For the inorganic concentrations, the inorganic carbon and nitrogen weak acid/base species are required. The total inorganic nitrogen (free and saline ammonia, FSA, Table 6) was measured directly and the total inorganic carbon (C_T) could be calculated from the measured influent H_2CO_3* alkalinity and pH (Loewenthal et al., 1986). From the influent total species concentrations, pH, temperature and relevant pK values adjusted for ionic strength effects, the influent inorganic carbon and nitrogen weak acid/base species concentrations could be calculated, as required for the simulations.

For the organic concentrations (Fig. 4), the total COD (S_{ti}) and SCFA (S_{bsai}) concentrations were available from direct measurement (Table 6). For the simulations, all S_{bsai} were accepted to be HAc/Ac^- and this weak acid/base was speciated from the influent total species concentration, pH, temperature and relevant pK value adjusted for ionic strength effects (Sötemann et al., 2005b). Further, from the experimental work of Lilley et al. (1990) and Ristow et al. (2004a), the non-SCFA fermentable biodegradable soluble COD concentration (S_{bsfi}) was accepted to be equal to the S_{bsai} concentration. The unbiodegradable soluble COD (S_{usi}) was accepted to be so low as to be negligible. This left two COD fractions to be quantified, the unbiodegradable and biodegradable particulates (S_{upi} and S_{bpi}). In the calculations and simulations below, the S_{upi} was determined, and hence S_{bpi} was calculated by difference.

Thus, the Izzett et al. (1992) data set was used to calibrate three parts of the model:

- hydrolysis process kinetic formulation and associated rate constants,
- sewage sludge CHON composition, and
- the unbiodegradable particulate fraction of the sewage sludge.

The three parts were determined interactively and iteratively through calculation and simulation of the experimental systems.

Sewage sludge stoichiometric formula

In the model, the biodegradable sewage sludge is hydrolysed to the intermediary compound "glucose" (Fig. 2). Since the stoichiometry of the subsequent products for complete anaerobic oxidation of the intermediate "glucose" is well established and essentially fixed (see above), the stoichiometric transformation of the sewage sludge to the intermediate "glucose" is crucial to predict the observed digester effluent and gas compositions. This is directly influenced by the CHON stoichiometric composition for the sewage sludge, Eq. 7. Furthermore, the carbonate weak acid/base species play an important role in fixing digester pH, $H_2CO_3^*$ alkalinity, CO_2 and CH_4 gas produced, and it is therefore necessary to establish the correct C content of the influent sewage sludge to correctly predict these parameters also.

As a starting point, the sewage sludge composition was assumed to be the same as the generally accepted stoichiometric formula for activated sludge: $C_5H_7O_2N$ (WRC, 1984). However, $C_5H_7O_2N$ could not correctly predict the digester output (pH, gas flow and composition) as measured by Izzett et al. (1992) and therefore needed to be changed. Accordingly an improved estimate was derived from the measurements made on the influent.

Since influent TKN and FSA measurements were available (Table 6), the organic nitrogen (OrgN) in the feed was calculated for the different retention times. The result was expressed as a ratio of the measured COD and remained fairly constant during the investigation, ranging between 0.0201 and 0.0220 gN/gCOD for the different retention times. VSS measurements on the influent were also available (Table 6). Recognising that the VSS represents particulate organics, the equivalent particulate COD was determined as (total COD - 2·SCFA COD, i.e. S_{ti} - 2·S_{bsai}). The particulate COD/VSS ratio at each retention time was calculated, and ranged from 1.36 to 1.52 gCOD/gVSS. Additionally the organic N/VSS ratios were calculated and ranged from 0.032 to 0.036 gN/gVSS. From these ratios and accepting the H:O ratio in $C_XH_YO_ZN_A$ as 7:2 (from $C_5H_7O_2N$ above), X and A could be calculated for each retention time, from:

$$\frac{COD}{orgN} = \frac{(Y + 4X - 2Z - 3A)\cdot MW_{O2}}{4\cdot A\cdot MW_N} \quad (15)$$

$$\frac{COD}{VSS} = \frac{(Y + 4X - 2Z - 3A)\cdot MW_{O2}}{4(MW_C\cdot X + MW_H\cdot Y + MW_O\cdot Z + MW_N\cdot A)} \quad (16)$$

$$\frac{orgN}{VSS} = \frac{A\cdot MW_N}{(MW_C\cdot X + MW_H\cdot Y + MW_O\cdot Z + MW_N\cdot A)} \quad (17)$$

where:

MW_X = molecular weight of compound X

In Eqs. 15 to 17 above, accepting Y = 7 and Z = 2, from the different pairings of equations (Eqs. 15 and 17, and Eqs. 15 and 16) two sets of (X; A) data pairs could be calculated for each retention time. The (X; A) pairs at the different retention times were all averaged, to give X = 3.4 and A = 0.192, giving a

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stoichiometric formulation for the sewage sludge of $C_{3.4}H_7O_2N_{0.192}$. These calculations did not require *a priori* information on the hydrolysis kinetics and S_{upi} and hence this formulation formed the starting point for the simulations, which were used to refine the stoichiometry (in conjunction with the hydrolysis kinetics and S_{upi}).

In the simulations the parameters that were targeted for improved estimation of the sewage sludge formulation were the gas flow and composition, which requires a carbon (C) balance over the digester. Izzett et al. (1992) did not measure the C content of the sewage sludge, so the influent C was calculated from an assumed 100% C balance over the digester (Fig. 3), through combined use of measured and predicted C output values. This was reasonable because the COD balances were good (107 to 109%). Essentially, the C content of the influent sewage sludge appears in the outputs, as gaseous CO_2 and CH_4, dissolved inorganic carbon weak acid/base species and effluent soluble and particulate organic C, the particulate organic C being made up of biomass, S_{up} and undegraded S_{bp}.

By tracking all the measured C in CO_2 (gaseous and dissolved) and CH_4 and the simulated organic C exiting the digester at different retention times and ensuring that the predicted and measured effluent CODs corresponded, the C content of the influent could be equated to the C exiting the digester. Subtracting the influent inorganic C (calculated from the measured influent H_2CO_3* and pH) gave the influent organic C. This was expressed as an influent organic C/COD ratio for the different retention times. Like the OrgN/COD ratio, the organic C/COD ratios also varied in a narrow band for the different retention times. The average organic C/COD ratio was therefore used to calculate the C content (X) in the sewage sludge feed. Taking due consideration that the influent OrgN/COD ratio must also remain at the measured value, a sewage sludge composition formula of $C_{3.5}H_7O_2N_{0.196}$ was determined, very close to the stoichiometry calculated above from the available influent measurements. This formulation was accepted for all subsequent calculations on and simulations of the Izzett et al. (1992) data. In the simulations, to derive the organic C/COD ratio the hydrolysis kinetics and S_{upi} needed to be correctly specified, and hence the requirement for interactive calculations and simulations.

To check how the model sewage sludge composition compares with real sludges, primary sludge from two different full-scale wastewater treatment plants (WWTP) around Cape Town (South Africa) were analysed for VSS, TSS, COD and their organic C, H, N and phosphorus (P) contents. From the measured data, the CHON composition of the primary sludge was calculated (P was omitted because it was not measured by Izzett et al., 1992). The average measured composition was $C_{3.65}H_7O_{1.97}N_{0.19}$. The model C, H, O, N content and molar mass of primary sludge are 95.9%, 100%, 98.5%, 94.5% and 98.7% of the measured values. This provides powerful validation of the UCTADM1 model.

Estimating the unbiodegradable fraction of sewage sludge and hydrolysis kinetics and constants

Before an even remotely reasonable correspondence could be obtained between model predicted and measured effluent parameters and gas composition and production, the fraction of unbiodegradable particulate COD of the sewage sludge ($f_{PSup} = S_{upi}/S_{ti}$) and the hydrolysis rate kinetics and constants needed to be determined. These were determined interactively between mass balance based calculations and simulations on the Izzett et al. data set. Initially, a value for the f_{PSup} was estimated and then the various kinetic formulations evaluated, and thereafter the estimate for f_{PSup} improved. In the mass balance based calculations below, COD units are used. The calculated values for the various parameters can be readily converted to the mole units required in the model, see below.

For the Izzett et al. data set, the influent sewage sludge is characterised by (Fig. 4):

$$S_{ti} = S_{bpi} + S_{bsfi} + S_{bsai} + S_{usi} + S_{upi} \quad \text{(mgCOD/ℓ)} \qquad (18)$$

In Eq. 18 as noted above, S_{ti} and S_{bsai} were directly available from measurement (Table 6); S_{usi} could be accepted to be negligible, and S_{bsfi} could be accepted to be equal to S_{bsai}. This left two unknowns, S_{bpi} and S_{upi}. Letting $S_{upi} = f_{PSup} \cdot S_{ti}$, then S_{bpi} could be found by difference and hence f_{PSup} was the only unknown.

For the effluent:

$$S_{te} = S_{bpe} + S_{bsfe} + S_{bsae} + S_{use} + S_{upe} + biomass \quad \text{(mgCOD/ℓ)} \qquad (19)$$

In Eq. 19, S_{te} and S_{bsae} were available from direct measurement and it could be accepted that $S_{bsfe} = S_{bsae}$ (the values are very low due to stable digester operation and hence do not influence the analysis significantly). Accepting negligible generation of unbiodegradable material in the anaerobic digester, then $S_{use} = S_{usi} = 0$ and $S_{upe} = S_{upi}$. With regard to the biomass, under stable digester operation three organism groups are generated, acidogens (Z_{AD}), acetoclastic methanogens (Z_{AM}) and hydrogenotrophic methanogens (Z_{HM}). Of these, the mass of Z_{HM} developed is very much smaller than that of Z_{AD} and Z_{AM}, and accordingly can be neglected in an initial steady state analysis. Thus Eq. 19 reduces to:

$$S_{te} = S_{bpe} + S_{bsfe} + S_{bsae} + S_{use} + S_{upe} + Z_{AD} + Z_{AM} \quad \text{(mgCOD/ℓ)} \qquad (20)$$

Developing mass balances around the digester (Ristow et al., 2004a,b) and recognising from Table 2 that in the death of biomass the released organics add to the sewage sludge, for biodegradable particulate COD (S_{bp}):

$$V \cdot S_{bp} = Q_i \cdot S_{bpi} \cdot dt - Q_e \cdot S_{bpe} \cdot dt - r^*_{HYD} \cdot V \cdot dt + (b_{AD} \cdot Z_{AD} + b_{AM} \cdot Z_{AM}) \cdot V \cdot dt \quad \text{(mgCOD/ℓ)} \qquad (21)$$

where:

r^*_{HYD} = volumetric hydrolysis rate, COD units (mgCOD/ℓ·d)
V_d = digester volume (ℓ)
$Q_i = Q_e$ = influent and effluent flow rate respectively (ℓ/d)

At steady state, solving for r_{HYD}:

$$r^*_{HYD} = \frac{1}{R_h}(S_{bpi} - S_{bpe}) + b_{AD} \cdot Z_{AD} + b_{AM} \cdot Z_{AM} \quad \text{(mgCOD/ℓ·d)} \qquad (22)$$

where:

R_h = V_d/Q_i = hydraulic retention time (d)

Similarly for S_{bsf} and S_{bsa} with r_{AD} and r_{AM} as the volumetric rates in COD units of acidogenesis and acetoclastic methanogenesis respectively:

$$r_{AD} = \frac{1}{R_h}(S_{bsfi} - S_{bsfe}) + r^*_{HYD} \quad \text{(mgCOD/ℓ·d)} \qquad (23)$$

$$r_{AM} = \frac{1}{R_h}(S_{bsai} - S_{bsae}) + f_{Sbsa/Sbsf} \cdot r_{AD} \quad \text{(mgCOD/ℓ·d)} \qquad (24)$$

where:

$f_{Sbsa/Sbsf}$ = fraction of S_{bsf} appearing as S_{bsa} in the acidogenesis reaction (Table 4)
= 0.607 (mgCOD/mgCOD)

Developing similar mass balances for the biomass concentrations:

$$Z_{AM} = \frac{r^*_{AM} \cdot Y^*_{AM} \cdot R_h}{(1 + b_{AM} \cdot R_h)} \quad (\text{mgCOD}/\ell) \tag{26}$$

where:

Y^*_{AD} = acidogen yield in COD units (mg COD/mg COD)

Y^*_{AM} = acetoclastic methanogen yield in COD units (mg COD/mg COD)

Recognising that from Eq. 20:

$$S_{bpe} = S_{te} - S_{bsfe} - S_{bsae} - f_{PSup} \cdot S_{ti} - Z_{AD} - Z_{AM} \text{ (mg COD}/\ell) \tag{27}$$

In the set of equations above, f_{PSup}, S_{bpe}, Z_{AD} and Z_{AM} are the principal unknowns. If an estimate for f_{PSup} is available, then S_{bpe}, Z_{AD} and Z_{AM} can be calculated through iteration. However, f_{PSup} is not known for the Izzett et al. data set, and would need to be determined via some other technique, see later.

Determining hydrolysis rate constants

In the section above, for any selected f_{PSup}, the volumetric rate of hydrolysis (r^*_{HYD}) can be calculated, as well as Z_{AD}, Z_{AM} and S_{bpe}, all in COD units. Converting these values to mole units:

$$r_{HYD} = r^*_{HYD} \Big/ \left(\frac{COD}{mol} \right)_{S_{bp}} \quad (\text{mol } S_{bp}/\ell \cdot \text{d}) \tag{28}$$

$$[S_{bpe}] = S_{bpe} \Big/ \left(\frac{COD}{mol} \right)_{S_{bp}} \quad (\text{mol } S_{bp}/\ell) \tag{29}$$

$$[Z] = Z \Big/ \left(\frac{COD}{mol} \right)_{Z} \quad (\text{mol } Z/\ell) \tag{30}$$

where:

$\left(\frac{COD}{mol} \right)_{S_{bp}}$ = COD/mol ratio for S_{bp}

= 131.3 gCOD/mol for $C_{3.5}H_7O_2N_{0.196}$

$\left(\frac{COD}{mol} \right)_{Z}$ = COD/mol ratio for biomass

= 160 gCOD/mol for $C_5H_7O_2N$

[ ] = mole concentration

Equating this r_{HYD} with the first order and first order specific kinetic expressions for the hydrolysis (Eqs. 8a and 8b respectively), and solving for K_H and K_{Hspec} yields:

$$K_h = r_{HYD}/[S_{bpe}] \quad (/\text{d}) \tag{31}$$

$$K_H = r_{HYD}/([S_{bpe}][Z_{AD}]) \quad (\ell/\text{mol } Z_{AD} \cdot \text{d}) \tag{32}$$

where as indicated by [ ], S_{bpe} and Z_{AD} are expressed in mole units.

Thus, from Eqs. 31 and 32 above, values for K_h and K_H could be determined, provided f_{PSup} was known.

Similarly, for the Monod (Eq. 8c) and surface mediated reaction (saturation, Contois, Eq. 8d) kinetics:

$$r_{HYD} = \left[\frac{\mu_{max,HYD} \, [S_{bp}]}{K_{SM,HYD} + [S_{bp}]} \right] [Z_{AD}] \tag{33}$$

$$r_{HYD} = \left[\frac{k_{max,HYD} \, \dfrac{[S_{bp}]}{[Z_{AD}]}}{K_{SS,HYD} + \dfrac{[S_{bp}]}{[Z_{AD}]}} \right] [Z_{AD}] \tag{34}$$

In each of Eqs. 33 and 34 above, the values for the two constants needed to be determined, namely $\mu_{max,HYD}$ and $K_{SM,HYD}$ and $k_{max,HYD}$ and $K_{SS,HYD}$ respectively. To determine these constants, the equations were linearised by three different methods, i.e. (i) Lineweaver-Burke, (ii) inversion and (iii) Eadie-Hofstee (Lehninger, 1977). For the Monod kinetics for example, these yielded respectively:

(i) $$\frac{[Z_{AD}]}{r_{HYD}} = \frac{K_{SM,HYD}}{\mu_{max,HYD}} \cdot \frac{1}{[S_{bpe}]} + \frac{1}{\mu_{max,HYD}} \tag{35a}$$

(ii) $$\frac{[S_{bpe}]}{r_{HYD}} = \frac{K_{SM,HYD}}{\mu_{max,HYD}} + [S_{bpe}] \cdot \frac{1}{\mu_{max,HYD}} \tag{35b}$$

(iii) $$\frac{r_{HYD}}{[Z_{AD}]} = -K_{SM,HYD} \cdot \frac{r_{HYD}}{[S_{bpe}] \cdot [Z_{AD}]} + \mu_{max,HYD} \tag{35c}$$

Linear regression was fitted to the Izzett et al. experimental data plotted according to the three linearisation methods, for example see Figs. 5a, b and c respectively for Monod kinetics. From the slopes and y-intercepts of the fitted lines, the appropriate pair of kinetic constants was determined. Again these calculations required that the value for f_{PSup} was known.

Determining the sewage sludge unbiodegradable particulate fraction (f_{PSup})

In all the calculations above, a value for f_{PSup} needed to be known. However, this value was not directly available from the Izzett et al. data set. In the calculations, for each value of f_{PSup} selected, a different set of kinetic constants was obtained for the different kinetic formulations.

Working on the principle that the most appropriate set of kinetic constants would be the one that provides the greatest consistency between predicted and measured values for all retention times of the Izzett et al. data set, techniques were devised to identify these constants and the corresponding f_{PSup} value. For the first order and first order specific kinetic formulations, the value for f_{PSup} was varied and the coefficient of variation (standard deviation/average) calculated for the relevant K values for the four retention times, for each f_{Psup} value. The coefficients of variations were then plotted against f_{PSup}, see Fig. 6. From Fig. 6, the coefficients of variations for first order and first order specific kinetics both exhibit minima; for the first order kinetics this is at $f_{PSup} = 0.34$, and for the first order specific kinetics at $f_{PSup} = 0.32$. In effect these values of f_{PSup} are the ones that give the least variation in the relevant kinetic rate constants across the four retention times. Since the Izzett et al. systems were operated on the same source sewage sludge, these values would provide the most suitable estimate for f_{PSup} and the kinetic constants. Furthermore, these values for f_{PSup} are very similar to that determined by O'Rourke (1968) of 0.36, and that expected (0.32 or 0.36) from a mass balance around the primary settling tank with typical South African raw and settled wastewater characteristics, i.e. raw ($f_{S,upR}$) and settled ($f_{S,upS}$) wastewater unbiodegradable particulate COD fractions of 0.15 and 0.04 and a COD removal (f_{PSR}) of 40% or 35% respectively in primary sedimentation (WRC, 1984), where (Sötemann et al., 2005a):

$$f_{PSup} = f_{S,upS} + (f_{S,upR} - f_{S,upS}) / f_{PSR} \tag{36}$$

Thus, accepting that for the first order kinetics $f_{PSup} = 0.34$, then $K_h = 0.381$ /d ± 0.0066, and for first order specific kinetics that $f_{PSup} = 0.32$, then $K_H = 40$ ℓ/mol Z_{AD}/d ± 2.0.

For the Monod and surface mediated reaction kinetics, in the three linearisation techniques, linear regression was used to fit a

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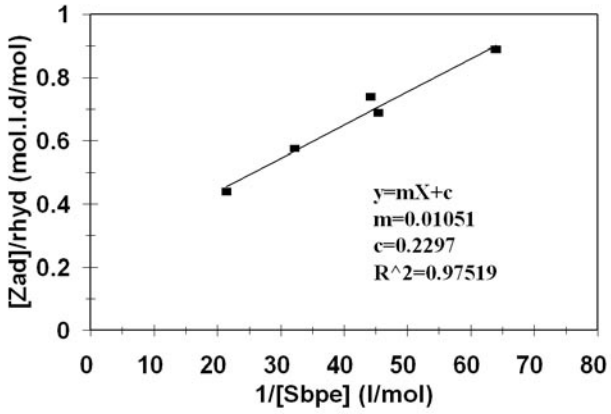

Figure 5a
Linearisation by inversion of Monod kinetics for hydrolysis of sewage sludge for the data of Izzet et al (1992) at retention times of 7, 10, 12, 15 and 20 d, with linear regression fit of straight line to data.

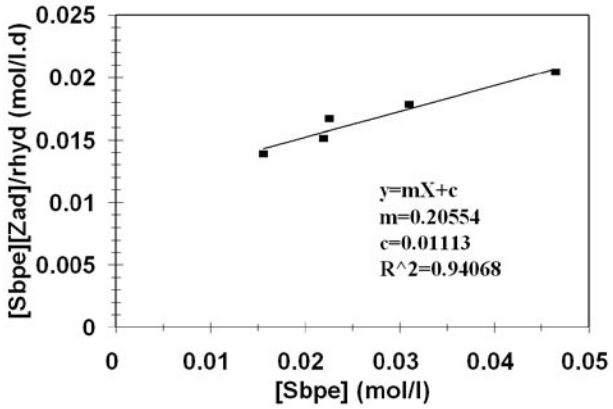

Figure 5b
Linearisation by inversion of Monod kinetics for hydrolysis of sewage sludge for the data of Izzet et al (1992) at retention times of 7, 10, 12, 15 and 20 d, with linear regression fit of straight line to data.

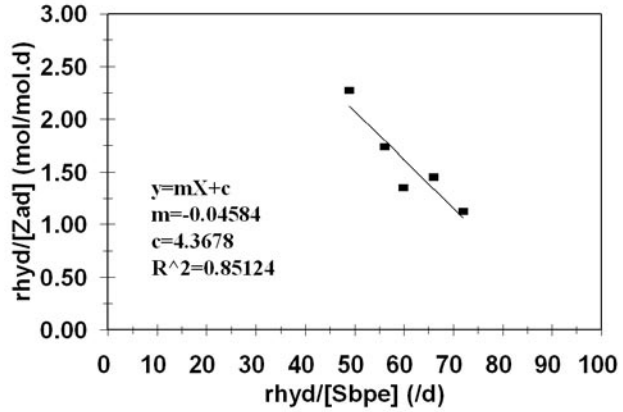

Figure 5c
Linearisation by Eadie-Hofstee of Monod kinetics for hydrolysis of sewage sludge for the data of Izzet et al (1992) at retention times of 7, 10, 12, 15 and 20 d, with linear regression fit of straight line to data.

straight line to the data, and the correlation coefficients (R^2) of these lines calculated, for example see Figs. 5a, b and c for linearisation of the Monod kinetics. Thus, for each selected value of f_{PSup} three correlation coefficients were obtained for each of

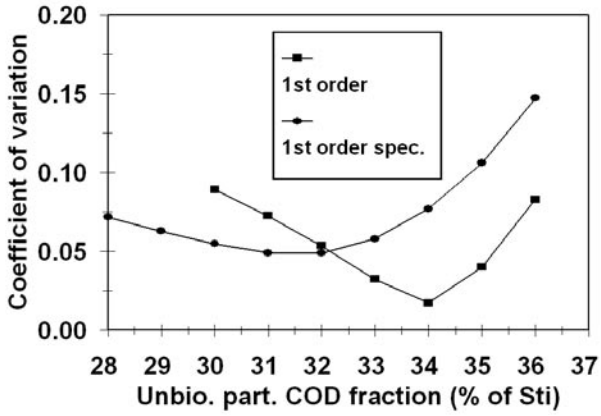

Figure 6
Coefficient of variation in the kinetic constants for 1st order and 1st order specific kinetics for sewage sludge hydrolysis, for the data of Izzet et al. (1992) at retention times of 7, 10, 12, 15 and 20 d.

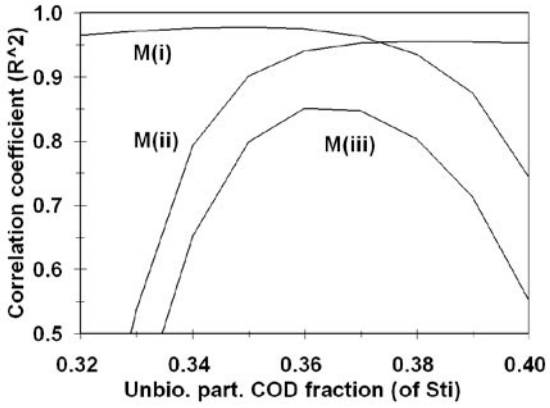

Figure 7
Correlation coefficients versus unbiodegradable particulate COD fraction for linear fits to Monod hydrolysis kinetics, for the data of Izzet et al. (1992) at retention times of 7, 10, 12, 15 and 20 d: M(i) Lineweaver-Burke, M(ii) inversion, M(iii) Eadie-Hofstee linearisations (see Fig. 5a to c).

Monod and surface mediated reaction kinetics. These correlation coefficients were plotted against f_{PSup}, see Figs. 7 and 8 for Monod and surface mediated reaction kinetics respectively. Both sets of R^2 values exhibit maximum values at $f_{PSup} = 0.36$, and hence this value was selected for these kinetics. Averaging the values for the three linearisations gives $\mu_{max,HYD} = 4.529$ mol S_{bp}/(mol Z_{AD}·d) and $K_{SM,HYD} = 0.0486$ mol S_{bp}/ℓ for Monod kinetics and $k_{max,HYD} = 6.797$ mol S_{bp}/(mol Z_{AD}·d) and $K_{SS,HYD} = 10.829$ mol S_{bp}/mol Z_{AD} for surface mediated reaction kinetics. To confirm the values determined with this method, the experimental data and predicted lines were plotted on the Monod type plot for both Monod kinetics (Fig. 9) and surface saturation kinetics (Fig. 10); in both cases a close fit to the data is obtained.

Selection of hydrolysis kinetics

In the section above, the data set of Izzett et al. was used to calibrate the constants for the four variations in hydrolysis kinetics, first order (Eq. 8a), first order specific (Eq. 8b), Monod (Eq. 8c) and surface mediated reaction or Contois (Eq. 8d). In this exercise, measures of variability were derived for the various kinetic expressions, namely coefficient of variation for the first two formulations and correlation coefficients (R^2) for the second two.

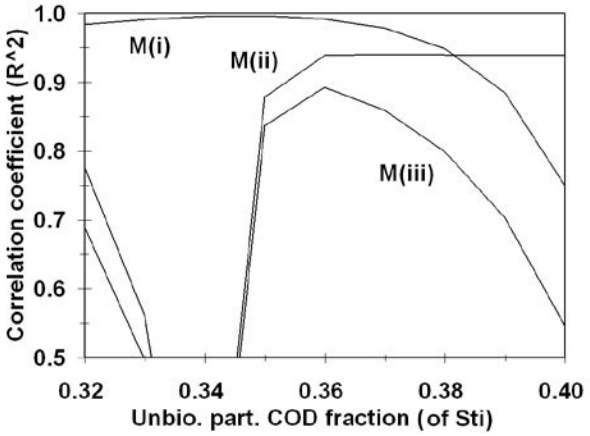

Figure 8

Correlation coefficients versus unbiodegradable particulate COD fraction for linear fits to surface mediated reaction hydrolysis kinetics, for the data of Izzet et al. (1992) at retention times of 7, 10, 12, 15 and 20 d: M(i) Lineweaver-Burke, M(ii) inversion, M(iii) Eadie-Hofstee linearisations.

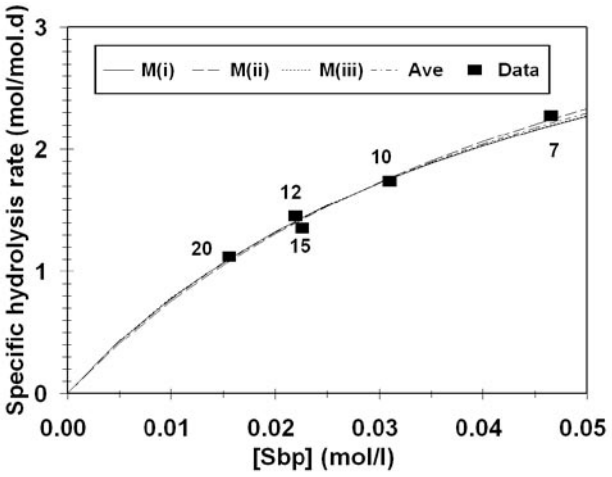

Figure 9

Monod specific hydrolysis rate versus biodegradable particulate organics (S_{bp}, mole/ℓ) for the Izzet et al. (1992) data at 7, 10, 12, 15 and 20 d retention time: M(i) Lineweaver-Burke, M(ii) inversion, M(iii) Eadie-Hofstee linearisations, see Fig. 5 .

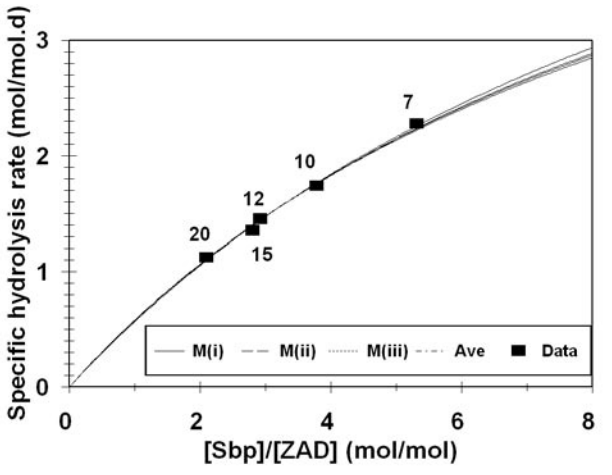

Figure 10

Surface mediated reaction specific hydrolysis rate versus biodegradable particulate organics (S_{bp}, mole/ℓ) to acidogen biomass (Z_{AD}, mole/ℓ) ratio for the Izzet et al. (1992) data at 7, 10, 12, 15 and 20 d retention time: M(i) Lineweaver-Burke, M(ii) inversion, M(iii) Eadie-Hofstee linearisations, see Fig. 5.

Comparing the coefficients of variation (Fig. 6), the minimum value for the first order kinetics is smaller than that for the first order specific, which would suggest that the former describes this data set marginally better. Comparing the R^2 values (Figs. 7 and 8), the values for surface mediated reaction kinetics are higher than those for Monod kinetics, also suggesting that the former kinetics describes the data set marginally better. With regard to first order versus surface mediated reaction kinetics, the data set cannot provide guidance as to which is superior, i.e. both kinetic formulations with the appropriate constants provide equally acceptable descriptions of the hydrolysis process for the Izzett et al. data set. However, since this process is mediated by the acidogens, the surface mediated reaction kinetics which includes this organism group intuitively would appear more reasonable. Furthermore, this kinetic formulation has been applied with considerable success in activated sludge system models (e.g. ASM1, Henze et al., 1987), in which the organisms act on the same biodegradable particulate substrate. Accordingly, the surface mediated reaction kinetics were accepted for incorporation in UCTADM1.

Refinement of values for sewage sludge composition, and model validation

Accepting the surface mediated reaction kinetics for hydrolysis and the estimates for the various constants (f_{PSup}, $k_{max,HYD}$ and $K_{SS,HYD}$) as determined above, the averages of the Izzett et al. measured influent parameters were set as input to AD model, with the influent weak acid/bases (NH_3/NH_4^+; HAc/Ac^-; H_2CO_3*/HCO_3^-/CO_3^{2-}; phosphorus not included as measurements not available). The model predictions for the effluent parameters and gas streams compositions and flows were compared with the corresponding measured averages at the different retention times. Only one part of the model required refinement (sewage sludge CHON composition) and this was then adjusted iteratively until the best correspondence between predicted and measured results at all retention times was obtained, to give $C_{3.5}H_7O_2N_{0.196}$; because the model is internally consistent and fixed by the kinetic and stoichiometric equations and determined constants, the only way a different effluent pH or gas composition can be predicted by the model is by changing the influent composition of the feed sludge. As noted above, independent validation was obtained by comparing the determined primary sludge composition with measured values. The model predicted parameters are compared with the corresponding measured values for all retention times in Fig. 11 a to f. The predicted COD removal (Fig. 11a) and gas composition (Fig. 11c) correspond very well to those measured. The gas production (Fig. 11b) is under predicted, because the model is based on 100% COD balance and the experimental data COD balances range from 107 to 109% (Table 6) - model calibration was on COD removal and hence the COD over recovery manifests in the gas production. The predicted effluent free and saline ammonia (FSA) concentration is generally higher than that measured, because the model is based on 100% N mass balance and the experimental mass balances were 91 to 99% (Table 6). By decreasing the N content of the influent organics (A in $C_XH_YO_ZN_A$) by a small amount (5% to 0.186), the predicted effluent FSA could be made to closely match the measured values, but this would cause the influent organic N concentration to be in error. The effluent H_2CO_3* alkalinity is over predicted, and this prediction can be improved by decreasing the N content of the organics or including some of the influent SCFA as propionic. However, both these would cause the predicted pH to decrease causing it to deviate from the

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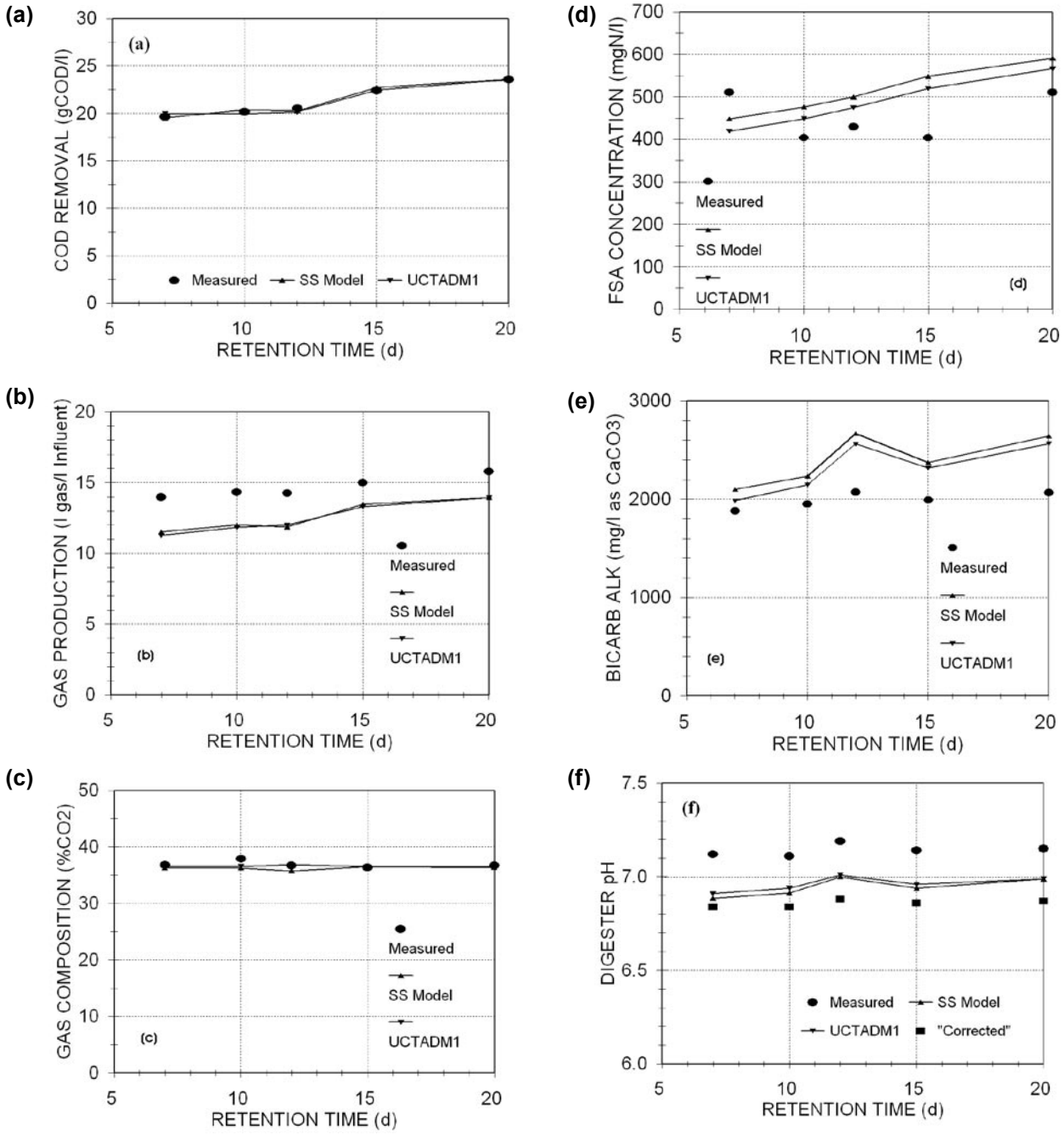

Figure 11

Comparison between kinetic simulation model (UCTADM1) predicted (lines) and measured (points) (a) COD removal, (b) gas production, (c) gas composition, (d) effluent free and saline ammonia (FSA), (e) H2CO3 alkalinity, and (f) digester pH versus retention time for the Izzett et al. (1992) data set; also shown are predictions with the steady state anaerobic digestion model of Sötemann et al. (2005b).*

measured value. Since insufficient experimental data are available to resolve this, these changes were not implemented. The experimentally measured pH, H_2CO_3* alkalinity and p_{CO2} show inconsistency in that these are not in equilibrium. Accepting the gas composition and H_2CO_3* alkalinity as the most reliable measurements (CO_2 loss on sampling would influence pH but not H_2CO_3* alkalinity, Loewenthal et al., 1991), the equilibrium "corrected" pH was calculated. Both experimentally measured and "corrected pH are shown in Fig. 11f together with the predicted pH values; the predicted and "corrected" pH values correspond closely. Overall, accepting the margin for error in the experimental measurements, good correlation between measured and predicted parameters was obtained. More extensive simulations with the model of a wider range of experimental systems is required for further model validation.

Modelling digester failure

The model applications above are all to stable anaerobic digesters operating at steady state. Under such conditions the rate limiting process is the hydrolysis, so that the other processes are essentially stoichiometric. This precluded assessment of the ability of the model to predict dynamic variations (except for hydrolysis). Very little quantitative information is available in the literature

TABLE 7
Inhibition constants for the different organism groups in anaerobic digestion

Organism group	Process	Compound	Symbol	Value	Units
Acetoclastic methanogens	D7	Hydrogen ion	$K_{I,AM}$	1.15×10^{-6}	mol/ℓ
Hydrogenotrophic methanogens	D9	Hydrogen ion	$K_{I,HM}$	530×10^{-6}	mol/ℓ
Acetogens	D5	Hydrogen gas	$K_{I,AC}$	0.45×10^{-6}	mol/ℓ

on the dynamics of anaerobic digestion. Accordingly, a theoretical simulation exercise was undertaken to evaluate dynamics, namely anaerobic digester failure. Acetoclastic methanogens are probably the most sensitive organisms in anaerobic digesters (Gujer and Zehnder, 1983) and so are strongly influenced by their surrounding environment. It is commonly accepted that failure of anaerobic digesters usually starts with the inhibition of acetoclastic methanogens. This can happen by an inhibitor or toxin in the influent, a shock load on the digester and/or a sudden drop in temperature because the acetoclastic methanogens (e.g. *Methanothrix soehngenii)* have been reported to show extreme temperature sensitivity (Zehnder et al., 1980). Any of these factors will slow down or inhibit the growth rate of the acetoclastic methanogens, resulting in an increase in acetic acid concentration in the digester. This increase causes a decrease in pH. Both acetoclastic methanogens and hydrogenotrophic methanogens (e.g. *Methanobrevibacter arboriphilus*) are pH sensitive, the latter also showing some sensitivity to temperature changes. Thus, the drop in pH will slow down their rates of growth, resulting in a further increase in acetic acid and an increase in hydrogen partial pressure p_{H2}. The increase in p_{H2} affects the acidogenesis process as described above (Eqs 9 and 10) and instead of producing only acetic acid, propionic acid also is produced. The increase in p_{H2} also slows the acetogenesis process (Eq. 11) so that the propionic acid concentration increases, causing a further decrease in pH. Clearly, anaerobic digestion is a poised system and even a small disturbance in one of the methanogenic processes causes irreversible system collapse. Such a collapse, called digester souring, is characterised by increases in acetic and propionic acid concentrations and hydrogen partial pressure and decreases in pH and gas production. The digester pH should not drop below 6.6 to maintain methanogenesis processes uninhibited by pH (Moosbrugger et al., 1993). The AD kinetic model was extended to include the above failure condition.

Inhibition of acetoclastic methanogens (Process 7)

These organisms are inhibited by the hydrogen ion activity (pH). To include this, the inhibition term commonly used with Monod kinetics of $(1+ I/K_I)$, where I is the aqueous inhibitor compound concentration and K_I the concentration at which the growth rate is half the normal rate (Batstone et al., 2002), was introduced into the growth rate equation (Eq. 12) i.e.:

$$K_{I,A}\, r_{Z_{AM}} = \frac{\mu_{max,AM}\,[HAc]}{\left(K_{S,AM} + [HAc]\right)\left(1 + \frac{[H^+]}{K_{I,AM}}\right)}\,[Z_{AM}] \qquad (37)$$

where:

$K_{I,AM}$ = Inhibition constant i.e. the hydrogen ion concentration at which the growth of acetoclastic methanogens is half the normal rate (mol/ℓ)

$[H^+]$ = Hydrogen ion concentration (mol/ℓ) from which $pH = -\log (H^+) = -\log f_m\, [H^+]$

Inhibition of hydrogenotrophic methanogens (Process 9)

Hydrogenotrophic methanogens function to keep the hydrogen partial pressure p_{H2} low, and like the acetoclastic methanogens, they are also neutrophiles and are inhibited at pH values below 6.6 (Gujer and Zehnder, 1983, Zehnder and Wuhrmann, 1977). Hence, an inhibition term was also introduced into the growth rate equation for this organism group (Eq. 13) i.e.:

$$r_{Z_{HM}} = \frac{\mu_{max,HM}\,[H_2]}{\left(K_{S,HM} + [H_2]\right)\left(1 + \frac{[H^+]}{K_{I,HM}}\right)}\,[Z_{HM}] \qquad (38)$$

Inhibition of acetogens (Process 5)

Due to the thermodynamics of the acetogenic process, the growth of acetogens decreases when the hydrogen partial pressure p_{H2} increases. This reduces the rate of propionic acid conversion to acetic acid and hydrogen. This reduction in growth rate at elevated p_{H2} has already been included in the acetogen growth process (Eq. 11).

Gas expulsion from aqueous to head space gas phases

In the implementation above of the kinetic model in Aquasim, the exchange of gases between the aqueous and gas (head-space) phases was not specifically modelled; the dissolved and non-dissolved gases were accepted to be part of the bulk liquid and hence flow out of the digester with the effluent, which is equivalent to a zero volume head-space. For steady state conditions this is acceptable, because the molar gas composition remains constant with time. Under digester failure conditions, the molar composition of the gas phase may not remain constant with time and hence have an influence on the dissolved gas concentrations. To ensure a more realistic AD system under failure conditions, a head-space compartment was added to the model in Aquasim, with a diffusive link to the reactor aqueous phase. The dissolved gaseous compounds CO_2 (as H_2CO_3*), CH_4 and H_2 diffuse from the aqueous phase to the gas phase in the head-space, in accordance with the usual diffusion gas exchange equations (Batstone et al., 2002), i.e. the gas exchange equations are applied across the diffusive link. In such an implementation, due cognisance must be taken of the different forms of the Henry's law constant and its dimensions. In Aquasim, the diffusive link is modelled as:

$$r_{gas} = K_{La\,gas}\,(K_{cgas}\,C_{hsgas} - C_{disgas}) \quad \text{mol gas/d} \qquad (39)$$

where:

r_{gas} = Rate of gas diffusion across head-space - bioreactor link

$K_{LA\,gas}$ = Specific gas mass transfer rate (/d)

K_{cgas} = Constant for the phase change from liquid to gas

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= K_{Hgas} or $1/K_{Hgas}$ depending on the form of the Henry's law constant

K_{Hgas} = ***Dimensionless*** Henry's law constant for the gas

C_{disgas} = Dissolved (aqueous) gas concentration in reactor liquid (mol/ℓ)

C_{hsgas} = Concentration of gas in the headspace (mol/ℓ)

p_{gas} = Partial pressure of the gas

= C_{hsgas} x RT_k

R = Universal gas constant = 8.206 x 10^{-2} (ℓ.atm)/(mol.K)

T_k = Temperature in Kelvin = (T in °C +273).

In modelling this gas exchange ammonia was omitted, because with its high pK value (9.1), negligibly little diffuses into the gas phase for pH < 8. The partial pressure of the three gases were calculated from the head-space gas concentrations (C_{hsgas}) using Dalton's law of partial pressures ($p_{gas} = [C_{hsgas}]$ RT) and the total gas pressure in head-space (P_{tot}) is sum of the partial pressures. The vent gas flow rate from the head-space (q_{gas}) was calculated from a proportional control loop with respect to atmospheric pressure (P_{atm}), which was accepted to be 101.3 kPa, viz.

$$q_{gas} = K_p \frac{(P_{tot} - P_{atm})}{P_{atm}} V_h \quad \ell/d \qquad (40)$$

where:

K_p = Gas vent rate constant (/d)

V_h = Volume of head space (1 ℓ for Izzett et al. digesters)

One constant in Eq. 39 has an important influence on the dynamics of the head-space gas concentrations, i.e. the specific gas mass transfer rate ($K_{La\ gas}$). If this rate is very rapid, then the head-space concentrations respond very quickly to the dissolved gas concentrations. The actual rate would be situation specific, depending on the mixing regime in the anaerobic digester, and would be faster with gas recirculation mixing than with mechanical mixing. Since no guidance in the literature could be found for this value, a fast rate of 1 000/d was selected for all $K_{La\ gas}$ so that the head-space gas concentrations rapidly respond to the dissolved gas concentrations. To provide a sense of the magnitude of this value, Musvoto et al. (2000a) observed K_{La} values between 200 and 600/d for CO_2 stripping in their anaerobic digester liquor aeration batch tests. The values for this constant requires further investigation.

Simulating digester failure

With the model set up as described, digester failure was simulated by halving the maximum specific growth rate of the acetoclastic methanogens ($\mu_{max,AM}$) for three days (72 h) in the middle of a 60 d simulation. The anaerobic digester at 15 d retention time in Table 6 was simulated for sufficient time to ensure steady state - very low effluent SCFA concentrations and hydrogen partial pressure were obtained and the pH was about 6.9. Failure was then artificially induced by temporarily halving the $\mu_{max,AM}$ value for the period of 3 d, and thereafter restoring it to its original value.

Immediately after halving $\mu_{max,AM}$, the acetic acid concentration increased sharply to reach a maximum of 0.14 mol/ℓ (8 400 mgHAc/ℓ) after 15 h. This increase caused the pH to decrease from 6.9 to 4.5 in 4 h. The reduction in pH caused the acetoclastic methanogen growth rate to reduce further, contributing to the sharp increase in acetic acid concentration and the hydrogenotrophic methanogen growth rate to reduce causing the hydrogen concentration to increase to a maximum of 0.00012 mol/ℓ (0.24 mgH_2/ℓ) after 22 h. The increased H_2 concentration raised the p_{H2} which caused the acidogens to produce also propionic acid, which increased from a very low concentration at around 5 h to a maximum concentration of 0.15 mol/ℓ (11 100 mgHPr/ℓ) at 55 h. Immediately after halving $\mu_{max,AM}$ of the acetoclastic methanogens, their concentration decreased sharply to reach 10% of its initial value after 15 h. The hydrogenotrophic methanogen organism concentration also decreased rapidly after about 4h to less than 10% of its initial value after 40 h. Concomitantly with the decrease in methanogen biomass concentrations, the CO_2 and CH_4 gas production rates decreased rapidly, reaching 10% of their original rates at 20 and 28 h respectively. Restoring the $\mu_{max,AM}$ of the acetoclastic methanogens to its original rate after 72 h had no affect on the results indicating that the failure was irreversible. Also, simulating this digester failure situation with and without the head-space gas dynamics made negligibly little difference to the results.

This simulation of AD failure by halving temporarily the acetoclastic methanogen growth rate indicates that the AD model correctly reflects the qualitatively observed digester failure behaviour and even a short (3 d) inhibition of these species causes irreversible failure (pH<5.5) within 4 h. The % decrease in acetoclastic methanogen growth rate from which the digester can recover without intervention was not determined. Because the conceptual AD model (Fig. 2) is similar to that developed for UASB digesters (Sam-Soon et al., 1991), the simulation model shows the same progression to failure as the lower bed volume of an upflow anaerobic sludge bed (UASB) digester, except that in the UASB system, collapse of the methanogens does not take place because the pH is maintained above 6.6 in the high SCFA concentration region (Moosbrugger et al., 1993). From the UASB digester behaviour and practical experience, anaerobic digestion failure due to a reduction in methanogen activity can be averted if the pH can be maintained above 6.6. This may require dosing lime which needs to be carefully controlled to avoid calcium carbonate precipitation (Capri and Marais, 1974). Digester failure and recovery is a dynamic modelling problem and will be examined in further research.

Conclusion

An integrated two phase (aqueous-gas) mixed weak acid/base chemistry and biological processes anaerobic digester kinetic model for sewage sludge is presented. The salient features of this model are:

(1) As an alternative to characterising the sewage sludge feed into carbohydrates, proteins and lipids, as is done in IWA ADM1 (Batstone et al., 2002), it is characterised in terms of total COD, its particulate unbiodegradable COD fraction (f_{PSup}), the short chain fatty acid (SCFA) COD and the CHON content of the particulate organics, i.e. X, Y, Z and A in $C_XH_YO_ZN_A$. This approach characterises the sludge in terms of measurable parameters and allows COD, C and N mass balances to be set up over the anaerobic digestion system. 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.

(2) The COD, C and N mass balances and continuity basis of the model fixes quantitatively, via the interrelated chemi-

cal, physical and biological processes, the relationship between all the compounds of the system so that for a given biodegradation 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 (and aqueous) characteristics. All the kinetic and stoichiometric constants in the model, except those for hydrolysis, were obtained from the literature so that model calibration reduced to determining the unbiodegradable particulate COD fraction of the sewage sludge (f_{PSup}), the hydrolysis kinetics formulation and associated constants and the sewage sludge CHON composition, i.e. the X, Y, Z and A values in $C_XH_YO_ZN_A$.

(3) Interactively with determining the hydrolysis kinetics ((4) below), the unbiodegradable particulate fraction of the sewage sludge was estimated at 0.32 to 0.36 for the sewage sludge fed to the mesophilic anaerobic digesters of Izzett et al. (1992) ranging over 7 to 20 d retention time, depending on the type of hydrolysis kinetics selected. These values are very close to the value of 0.36 determined by O'Rourke (1968) and the values estimated from a COD mass balance around the primary settling tank from typical raw and settled wastewater characteristics (0.32 to 0.36 for COD removals of 40 to 35%).

(4) Various formulations for the hydrolysis rate of sewage sludge particulate biodegradable organics were evaluated, see below. Surface mediated reaction (Contois) kinetics similar to that used by Dold et al. (1980) and IWA Activated Sludge Model 1 (Henze et al., 1987) for slowly biodegradable organics in activated sludge systems, were selected. Once calibrated against the Izzett et al. (1992) data, this formulation showed the required sensitivity of gas production and unfiltered effluent COD concentration to variation in retention time, without changing the constants in the hydrolysis rate equation.

(5) From the influent COD, organic N and VSS measurements of Izzett et al., the stoichiometric formulation of the influent sewage sludge was estimated to be $C_{3.4}H_7O_2N_{0.192}$. With the sludge biodegradability and hydrolysis process rate defined, to match the anaerobic digester performance data of Izzett et al. (1992) ranging over 7 to 20 d retention time, (i.e. effluent COD, TKN, FSA, SCFA, H_2CO_3* Alk, pH, gaseous CO_2 and CH_4 production and partial pressures), the sewage sludge composition was refined to $C_{3.5}H_7O_2N_{0.196}$ to conform to the COD, C and N mass balances of the data. This formulation was confirmed with primary sludge CHON composition tests, the average of which was $C_{3.65}H_7O_{1.97}N_{0.19}$. The model predicted CHON content and molar mass of the PS was therefore 95.9%, 100%, 98.5%, 94.5% and 98.7% of the measured values. This provides persuasive validation of the UCTADM1 model.

(6) Validation of the AD model under steady state conditions validates only its stoichiometry and the system rate limiting process, which is hydrolysis. However, the model, which includes the influence of high hydrogen partial pressure on the acidogenesis and acetogenesis processes, showed the expected sensitivity to a digester upset initiated by temporary inhibition of the acetoclastic methanogens, which is the usual cause in practise. The model demonstrated that even a brief inhibition of this organism group causes an irreversible failure of the digester (pH < 6.6).

The proposed surface mediated reaction (or Contois kinetic) hydrolysis rate equation reproduced the observed change in biodegradable particulate COD acidified versus retention time with the same kinetic constants. Based on the Izzett et al. anaerobic digester data, a Monod type hydrolysis rate equation also showed consistency of constants over 7 to 20 d retention time, but simple first order and first order specific hydrolysis rate equations yielded different rate constants at different retention times. However, by changing the unbiodegradable particulate COD fraction of the sewage sludge (f_{PSup}) the fit of both the first order and first order specific hydrolysis rate equations to the experimental data of Izzett et al. (1992) could be significantly improved (with concomitant deterioration in the fit with Contois and Monod kinetics). Hence, the Izzet et al. anaerobic digester data set is too limited to make a definitive conclusion as to which is the best equation to model the hydrolysis process, and what the best value for f_{PSup} is. Intuitively and based on its widespread application in activated sludge systems acting on the same biodegradable particulates, the surface mediated reaction (Contois) kinetics has been selected for hydrolysis. Experimental work to *inter alia* refine the modelling of the hydrolysis process is currently being conducted on mesophilic methanogenic and sulphidogenic anaerobic digester systems (Ristow et al., 2004a,b,c).

The characterisation of sewage sludge in terms of its CHON(P) contents appears a sound approach. While testing primary sludges for the UCTADM1 model validation, a range of other sewage sludges were also tested, such as waste activated, anaerobic digested and mixtures of primary and waste activated. From the tests done to date, it seems that the CHON contents of sludges are consistent and grouped approximately in conformity with type. It appears likely, therefore, that typical CHON(P) contents of the different sludges may be selected, and that the standard characterisation tests such as COD, TKN and VSS, are sufficiently discerning and accurate for modelling AD of sewage sludges. Measurement of sewage sludge composition is continuing and its effect on digester pH and gas composition will be evaluated when more information has been collected.

The successful integration in a kinetic way of the two phase mixed weak acid/base chemistry and biological processes of AD has provided a sound basis for further model development. Still to be included in the AD model are mineral precipitation and the P content of sewage sludges. This will extend the model to digestion of biological excess P removal waste activated sludges and provide a direct and quantitative link between feed sludge composition and mineral precipitation problems in digesters.

The integrated physical, chemical and biological processes kinetic modelling approach, applied in this series of papers to biological N removal activated sludge systems and anaerobic digesters, has opened the way to develop a kinetic simulation model for the entire wastewater treatment plant on a materials mass balance and continuity basis. The plant would comprise selected unit operations such as primary settling, biological N and/or P removal activated sludge and anaerobic or aerobic digestion of waste sludges. With such a model, the impact of wastewater characteristics and type and upstream unit operations performance on downstream unit operations, and the recycling of liquors from downstream unit operations to upstream unit operations, can be assessed for improved and more economical design and operation.

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