Biological sulphate reduction with primary sewage sludge in an upflow anaerobic sludge bed reactor – Part 6: Development of a kinetic model for BSR

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Abstract

A 2-phase (aqueous-gas) kinetic model for biological sulphate reduction (BSR) using primary sewage sludge (PSS) as carbon source is presented. The methanogenic anaerobic digestion (AD) model of Sötemann et al. (2005) is extended by adding the biological, chemical and physical processes associated with BSR, i.e. propionic acid degrading sulphate-reducing bacteria (SRB), acetoclastic SRB and hydrogenotrophic SRB, the aqueous weak acid/base chemistry processes of the sulphate and sulphide systems and an aqueous-gas sulphide exchange process. The model is validated with experimental data from 2 upflow anaerobic sludge bed (UASB) reactors fed various PSS COD/SO_4^{2-} ratios under constant flow and load conditions at 35°C and 20°C. The kinetic model results, including the reactor pH (within 0.1 pH unit) compare well with the experimental results and with those calculated from a steady-state BSR model. The kinetic model confirms that: (1) at ambient temperature (20°C), the hydrolysis rate is significantly reduced compared with that at 35°C, which requires a longer sludge age (larger bed volume) in the UASB reactor; (2) the hydrolysis rate of the PSS biodegradable particulate organics (BPO) is the same under methanogenic and sulphidogenic conditions; (3) the PSS BPO are carbon deficient for BSR in that more electrons are donated than carbon supplied for the required alkalinity increase, with the result that the sulphide system supplies the alkalinity deficit; and (4) due to (3) there is zero CO_2 gas generation and in effect the sulphide system establishes the reactor pH. This observation allows the carbon content of the utilised organics to be determined from the H_2CO_3* alkalinity increase in the reactor, which can be simply measured by titration methods.

Keywords: biological sulphate reduction, primary sewage sludge, upflow anaerobic sludge bed reactor, dynamic model, kinetics, stoichiometry, mixed weak acid/base chemistry

Nomenclature

a	molar nitrogen composition of organics in $C_xH_yO_zN_a$
AB	acetogenic bacteria
AD	anaerobic digestion
Alk H_2S	alkalinity with respect to the H_2S reference species excluding the water species
b_j	endogenous respiration rate, where j refers to the different SRB#
BPO	biodegradable particulate organics
BSR	biological sulphate reduction
C	carbon
COD	chemical oxygen demand
$f_{PS'up}$	unbiodegradable fraction of PSS with respect to total COD (S_{ti})
FRBCOD	fermentable readily biodegradable (soluble) COD
FRBO	fermentable readily biodegradable (soluble) organics
FSA	free and saline ammonia
H_2CO_3* alk	alkalinity with respect to the H_2CO_3 reference species including the water species
HAc	acetic acid
HRT	hydraulic retention time
k	molar carbon composition of BSR biomass in $C_kH_lO_mN_n$
K_{H2S}	Henry's law constant for sulphide
$K_{I,j}$	sulphide inhibition kinetic constant for SRB species j#
$K_{N,j}$	switching function sulphate concentration for SRB species j#
$K_{S,j}$	Monod half saturation coefficient for SRB species j#
K'_f, K'_r	forward and reverse aqueous dissociation constants adjusted for ionic strength affects; additional subscripts HSO4, H2S refer to aqueous H_2SO_4 and H_2S dissociations
K'_f, K'_r	forward and reverse gas exchange constants; additional subscript H2Sg refer to H_2S gas exchange
l	molar hydrogen composition of BSR biomass in $C_kH_lO_mN_n$
m	molar oxygen composition of BSR biomass in $C_kH_lO_mN_n$
M	experimentally measured
MA	methanogenic archae
n	molar nitrogen composition of BSR biomass in $C_kH_lO_mN_n$
OLR	organic loading rate
P	theoretically predicted
PBR	packed bed reactor
p_{H2S}	partial pressure of H_2S gas
pK'_{S1}, pK'_{S2}	1st and 2nd dissociation constant for the sulphide weak acid base system corrected for ionic strength effects

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Received 10 August 2009; accepted 15 February 2010.

PSS	primary sewage sludge
Q_i	influent flow
Q_w	waste flow
R1	UASB Reactor 1
R2	UASB Reactor 2
r_j	endogenous mass loss rate for SRB species j[#]
R_h	hydraulic retention time
R_s	sludge age
Sim	simulation
S_j	substrate concentration for the SRB species j[#]
S_{bp}	biodegradable particulate COD concentration
S_{bsa}	acetic acid COD concentration
S_{bsf}	fermentable biodegradable soluble COD concentration
S_{bsp}	propionic acid COD concentration
SRB	sulphate reducing bacteria
SS	steady state
S_T	total sulphide species concentration
S_{up}	unbiodegradable particulate COD concentration
T	temperature in °C
TOC	total organic carbon
Total Alk	sum of weak acid/base subsystem alkalinities
UASB	upflow anaerobic sludge bed reactor
UCTADM1	University of Cape Town Anaerobic Digester Model No. 1
UCTADM1-BSR	University of Cape Town Anaerobic Digester Model No. 1 including biological sulphate reduction
UPO	unbiodegradable particulate organics
USO	unbiodegradable soluble organics
V_d	volume of digester (equivalent to bed volume, V_b)
VFA	volatile fatty acids
VSS	volatile suspended solids
x	molar carbon composition of organics in $C_xH_yO_zN_a$
y	molar hydrogen composition of organics in $C_xH_yO_zN_a$
$Y^{\#}$	specific yield coefficient (metabolic)
$Y'^{\#}$	specific yield coefficient (anabolic)
z	molar oxygen composition of organics in $C_xH_yO_zN_a$
$Z^{\#}$	biomass concentration mgCOD/ℓ
γ_B	electron-donating capacity of BSR biomass
γ_S	electron-donating capacity of biodegradable organics
μ_j	specific growth rate, where j refers to the different AD organisms[#]
$\mu_{j,max}^{\#}$	maximum specific growth rate
[#]	*Additional subscripts PS, AS and HS refer to propionate degrading, acetoclastic and hydrogenotrophic SRB respectively*

Introduction

The core unit process in the BioSURE® system is biological sulphate reduction (BSR) with primary sewage sludge (PSS). To assist in and optimise the design, operation of and research into this unit process, mathematical models are very useful process evaluation tools. Mathematical models provide quantitative descriptions of the treatment system of interest that allow prediction of the system response and performance.

The kinetic model of Sötemann et al. (2005) for methanogenic anaerobic digestion (AD) of PSS (UCTADM1) appeared most suitable to extend to include BSR and was therefore selected as a basis for the development of the kinetic model for BSR with PSS as substrate. To extend UCTADM1 to incorporate BSR, the kinetics and stoichiometry for the biological, chemical and physical processes of BSR in 2 phases (aqueous-gas) were developed. Integration of BSR into UCTADM1 was commenced by Van Wageningen et al. (2006) and Van Wageningen (2007) to model the flow through methanogenic and BSR digesters of Ristow et al. (2005). This paper reviews this kinetic model for BSR (called the UCTADM1-BSR) using PSS as energy source, and presents its application to the upflow anaerobic sludge bed (UASB) BSR reactors of Poinapen et al. (2009a; b). The kinetic model is revised and the necessary corrections and adjustments made – some of the changes involved:

- Replacing the unstable linear hydrogen sulphide inhibition function to a more stable one
- Including a temperature function to simulate the effect of temperature on PSS hydrolysis/acidification and BSR processes. After revision, the model is verified, calibrated and validated by modelling the 2 UASB BSR systems (R1 at 35°C and R2 at 20°C) operated by Poinapen et al. (2009a; b) and the simulated results compared with those measured and calculated with the steady-state BSR model (Poinapen and Ekama, 2010).

Development of the kinetic model for BSR (UCTADM1-BSR)

The development of the kinetic model for BSR and its integration into UCTADM1 was conducted in 3 parts.

Part 1: The acidogenic process

In the AD of complex organics such as PSS, the hydrolysis/solubilisation process is usually the rate-limiting step. This bioprocess takes place first, followed by acidification, mediated by the acidogenic organism group. The products of these processes are volatile fatty acids (VFA), hydrogen (H_2) and CO_2, which then enter either the methanogenic or sulphidogenic (BSR) bioprocesses, which operate in competition (Fig. 1). Ristow et al. (2005) found that the hydrolysis/acidogenesis kinetics

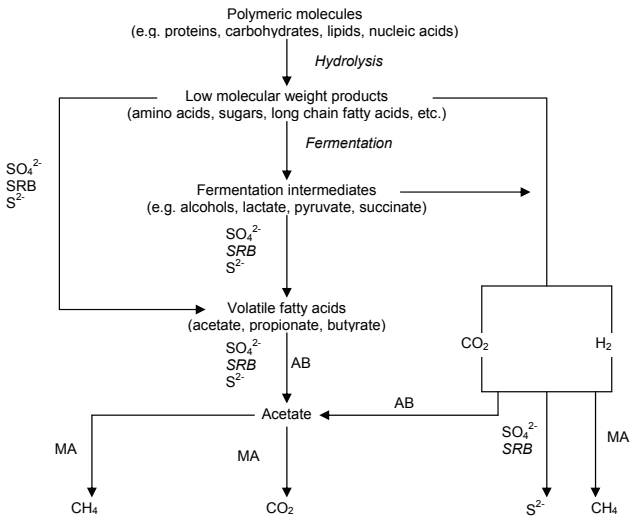

Figure 1

Pathways for the anaerobic degradation of organic matter (Gibson, 1990), showing potential interactions between methanogenic and sulphidogenic microorganisms (SRB = sulphate-reducing bacteria; MA = methanogenic archae; AB = acetogenic bacteria)

Available on website http://www.wrc.org.za
ISSN 0378-4738 (Print) = Water SA Vol. 36 No. 3 April 2010
ISSN 1816-7950 (On-line) = Water SA Vol. 36 No. 3 April 2010

and rate are the same under methanogenic and sulphidogenic conditions. Therefore, only the BSR processes on the products of the hydrolysis/acidogenesis process need to be included in the model because the hydrolysis/acidogenesis process precedes both methanogenesis and sulphidogenesis. However, the sulphide end-product of BSR is inhibitory to the methanogens and sulphidogens, so this inhibition needs to be included in the dynamic model for BSR.

Part 2: Development of BSR biological processes

The approach of Kalyuzhnyi et al. (1998) formed the basis for the biological processes part of the kinetic model for BSR. These researchers identified 9 trophic groups of microorganisms that convert substrates into products in an anaerobic reaction sequence. These bacterial groups are:

1. Fermentative bacteria (Sugars → Acetate)
2. Butyrate-degrading acetogenic bacteria (Butyrate → Acetate)
3. Butyrate-degrading SRB (Butyrate → Acetate & H_2S)
4. Propionate-degrading acetogenic bacteria (Propionate → Acetate)
5. Propionate-degrading SRB (Propionate → Acetate & H_2S)
6. Acetoclastic methanogenic archae (Acetate → Methane & CO_2)
7. Acetoclastic SRB (Acetate → H_2S & CO_2)
8. Hydrogenotrophic methanogenic archae (H_2 & CO_2 → Methane)
9. Hydrogenotrophic SRB (H_2 → H_2S)

Of these 9 microorganism groups, only 3 SRB (5, 7 and 9) groups are of particular interest when integrating BSR with the methanogenic UCTADM1 model. This model already explicitly incorporates microorganism groups 1 (acidogens), 4 (acetogens), 6 (acetoclastic methanogens) and 8 (hydrogenotrophic methanogens). The butyrate-degrading acetogenic (2) and SRB (3) bacterial groups were not included in the model, as butyrate is not usually present in significant concentrations in sewage sludge digestion systems. However, if required these trophic groups and their respective processes can be incorporated. Thus, the process stoichiometry and kinetics for only the 3 SRB groups (5, 7 and 9) are considered for both the organism growth and endogenous decay.

Part 3: Development of aqueous chemistry and physical processes

The biological processes consume and produce significant acid/base species, e.g. VFA, sulphide and bicarbonate (dissolved CO_2). The weak acid/base chemistry of these species (subsystems) needs to be incorporated in the model. The consumption and production of acid/base species influences the pH established in the digester, which in turn can influence the biologically-mediated processes. Hence, pH needs to be incorporated directly into the model as a model-predicted parameter, and its interaction with the biological processes modelled.

The weak acid/base systems already in UCTADM1 are water, acetate, propionate, carbonate, ammonium and phosphate. Weak acid/base systems associated with BSR are sulphide and sulphate and need to be added to the model.

Some of the AD (methanogenic and sulphidogenic) end-products are gases so their 2-phase (aqueous-gas) equilibrium processes need to be included (the third solid phase is not included at this stage). The carbon dioxide and ammonia gas exchange processes are already included in UCTADM1. Due to its low solubility, methane is produced directly to the gas phase. Hydrogen remains dissolved in the aqueous phase and is consumed by the hydrogenotrophic methanogens directly from the aqueous phase. So, the only gas to be added for BSR is sulphide. Sulphide is a highly soluble gas so usually very little (<1%) exits the digester in the gas phase. This was also observed experimentally (Poinapen et al., 2009a; b). In contrast, methane is very insoluble at low pressures (~atmospheric) so usually very little exits the digester in the dissolved phase.

In their steady-state BSR model, Poinapen and Ekama (2010) show that organics with COD/TOC ratio > 2.67, which includes PSS and VFA, are carbon deficient for BSR. These organics can donate more electrons than supply carbon for the alkalinity (HCO_3^-) required. This results in zero CO_2 gas production, and the alkalinity deficit is supplied by the sulphide system. Accordingly, this affects the relative HS^-/H_2S concentrations, so in effect the sulphide system establishes the sulphidogenic digester pH, not the inorganic carbon system as in methanogenic digesters (Poinapen and Ekama, 2010).

The development of these 3 parts is described in more detail in the following sections. The end result essentially will be a 2-phase biological, chemical and physical process model for the AD of PSS, with competitive methanogenesis and sulphidogenesis.

Stoichiometry of the BSR growth and endogenous processes

BSR growth processes

The procedure of Sötemann et al. (2005) for UCTADM1 was followed where the stoichiometry for the growth bioprocesses was determined by adding the catabolic and anabolic stoichiometry, linked via the yield coefficient of each SRB group. The development of this growth process stoichiometry for each of the 3 SRB groups is described below. UCTADM1 has embedded in it a biomass composition of $C_5H_7O_2N_1$ and the development of the stoichiometry of both the growth and endogenous respiration processes of the organisms was based and programmed on this biomass composition. When calibrating their steady-state BSR model against the UASB system data, Poinapen and Ekama (2010) found the biomass composition to be approximately $C_5H_7O_2N_{0.55}$, which is the same as the UCTADM1 biomass composition, except for the N content. Because the BSR biomass production is very low (Table 6), small differences in biomass composition have a negligible influence on the predicted results. Therefore, it was not necessary to change the stoichiometric equations in the dynamic model to conform to a biomass composition of $C_5H_7O_2N_{0.55}$ and the dynamic model is expected to give results that are closely similar to those of the steady-state model.

The derivation of the stoichiometric equations for growth of BSR biomass of composition $C_5H_7O_2N_1$ is demonstrated below for the acetogens only. The stoichiometry of the other BSR organisms follows the same procedure.

Acetogenic sulphidogenesis (by propionate degrading SRB)

The reaction sequence for the substrate utilisation of propionate by the propionate degrading SRB (Z_{PS}) is reported by Kalyuzhnyi et al. (1998) to be:

$$C_2H_5COOH + \frac{3}{4}\,SO_4^{2-} + \frac{3}{2}\,H^+ \rightarrow CH_3COOH + \frac{3}{4}H_2S + CO_2 + H_2O \quad (1)$$

The anabolic growth process of Z_{PS} was accepted to be identical to that of the methanogenic acetogenic biomass group in the UCTADM1 model because both species use propionate as substrate (Sötemann et al., 2005). This anabolic growth process producing biomass of composition $C_5H_7O_2N_1$ is:

$$3C_2H_5COOH + CO_2 + 2NH_4^+ \rightarrow 2C_5H_7O_2N_1 + 4H_2O + H_2 + 2H^+ \quad (2)$$

Multiplying Eq. (2) by the anabolic organism yield (Y'_{PS}), dividing it by 2 to form 1 mol of biomass, and adding the associated catabolism Eq. (1) gives:

$$(1 + \frac{3}{2}\,Y'_{PS})\,C_2H_5COOH + \frac{3}{4}\,SO_4^{2-} + \frac{Y'_{PS}}{2}CO_2 + Y'_{PS}NH_4^+ + \frac{3}{2}\,H^+ \rightarrow \quad (3)$$
$$Y'_{PS}\,C_5H_7O_2N_1 + CH_3COOH + \frac{3}{4}\,H_2S + CO_2 + \frac{Y'_{PS}}{2}H_2 + Y'_{PS}\,H^+ + (1 + 2\,Y'_{PS})H_2O$$

Dividing Eq. (3) by Y'_{PS} for 1 mol of acetogen biomass formation yields:

$$\frac{\left(1+\frac{3}{2}Y'_{PS}\right)}{Y'_{PS}}C_2H_5COOH + \frac{3}{4Y'_{PS}}SO_4^{2-} + NH_4^+ \rightarrow C_5H_7O_2N_1 + \frac{1}{Y'_{PS}}\,CH_3COOH + \quad (4)$$
$$\frac{3}{4Y'_{PS}}\,H_2S + \left(\frac{1}{Y'_{PS}} - \frac{1}{2}\right)\,CO_2 + \frac{1}{2}H_2 + \left(1 - \frac{3}{2Y'_{PS}}\right)\,H^+ + \frac{1+2Y'_{PS}}{Y'_{PS}}H_2O$$

The stoichiometry, in terms of the anabolic organism yield Y'_{PS} for the growth process of the propionate-degrading SRB, is taken directly from Eq. (4) and is listed in Table 1.

To represent the ratio of biomass formed per unit total substrate (in this case propionate) utilised, the anabolic yield (Y'_{PS}) is changed to the metabolic (anabolic + catabolic) yield (Y_{PS}) which is the usual way of expressing yield. The metabolic yield (Y_{PS}) is obtained from Eq. (4).

From the stoichiometry (Table 1):

1 mol biomass (160 gCOD) is grown from $\frac{1+\frac{3}{2}Y'_{PS}}{Y'_{PS}}$ moles propionate. Expressing the metabolic (or true) yield Y_{PS} (mol/mol) in terms of Y'_{PS} gives:

$$Y_{PS} = \frac{Y'_{PS}}{\left(1+\frac{3}{2}Y'_{PS}\right)} \quad (5)$$

Changing Eq. (5) to make Y'_{PS} its subject:

$$Y'_{PS} = \frac{Y_{PS}}{\left(1-\frac{3}{2}Y_{PS}\right)} \quad (6)$$

Rewriting the stoichiometric terms in Table 1 by substituting Eq. (6) for Y'_{PS} and accepting that $CO_2 + H_2O \rightarrow H_2CO_3^*$ gives the stoichiometry for propionate-utilising SRB in terms of the true (metabolic) organism yield as shown in Table 2.

Acetoclastic sulphidogenesis (by acetoclastic SRB) and hydrogenotrophic sulphidogenesis (by hydrogenotrophic SRB)

The same method described above for the propionate-degrading SRB was used for developing the stoichiometry for the growth of the acetoclastic SRB (Z_{AS}) and the hydrogenotrophic SRB (Z_{HS}), based on the reaction sequence for the catabolic and anabolic substrate utilisation taken from Kalyuzhnyi et al. (1998).

BSR Endogenous processes

The organism death/decay for the SRB groups was assumed to be the same as that for the methanogenic microorganism groups in the UCTADM1 model, and therefore the same approach was followed in the BSR model.

With endogenous mass loss, the biomass dies and releases its biodegradable organics (accepted to be all particulate) to the bulk liquid, adding to the biodegradable particulate organics (BPO) from the influent. Because the yield and endogenous mass loss rates of SRB biomass are very low, it was accepted that generation of unbiodegradable endogenous residue is negligible and so was neglected. Endogenous mass loss transforms the biomass BPO to the same composition as the influent BPO while conserving COD. An influent BPO composition of $C_{3.35}H_7O_{1.45}N_{0.45}$ was measured in this investigation (Poinapen and Ekama, 2010) which is slightly different to that measured by Sötemann et al. (2005), i.e. $C_{3.5}H_7O_{2.0}N_{0.196}$. Because this endogenous transformation may need to be done with different biomass and PSS BPO compositions, the transformation stoichiometry is developed in general for biomass of composition $C_kH_lO_mN_n$ and an influent BPO composition of $C_xH_yO_zN_a$, i.e.

$$C_kH_lO_mN_n + \boldsymbol{A'}\,H_2O \rightarrow \boldsymbol{B}\,C_xH_yO_zN_a + \boldsymbol{C'}\,CO_2 + \boldsymbol{D}\,NH_3 \quad (7)$$

Re-writing the equation recognising that $CO_2 + H_2O \rightarrow H_2CO_3^*$ gives:

Table 1
Stoichiometry for propionate degrading SRB in terms of the anabolic organism yield (Y'_{PS})

HPr mol	SO_4^{2-} mol	CO_2 mol	NH_4^+ mol	Z_{PS} mol	HAc Mol	H_2S mol	H_2 mol	H^+ mol	H_2O mol
$-\left(\frac{1+\frac{3}{2}Y'_{PS}}{Y'_{PS}}\right)$	$-\left(\frac{3}{4Y'_{PS}}\right)$	$\left(\frac{1}{Y'_{PS}}-\frac{1}{2}\right)$	-1	1	$\frac{1}{Y'_{PS}}$	$\frac{3}{4Y'_{PS}}$	$\frac{1}{2}$	$\left(1-\frac{3}{2Y'_{PS}}\right)$	$\frac{1+2Y'_{PS}}{Y'_{PS}}$

Table 2
Stoichiometry for growth of propionate degrading SRB in terms of Y_{PS}

HPr mol	SO_4^{2-} mol	$H_2CO_3^*$ mol	NH_4^+ mol	Z_{PS} mol	HAc mol	H_2S mol	H_2 mol	H^+ mol	H_2O Mol
$-\left(\frac{1}{Y_{PS}}\right)$	$-\left(\frac{3}{4Y_{PS}}-\frac{9}{8}\right)$	$\frac{1}{Y_{PS}}-2$	-1	1	$\frac{1}{Y_{PS}}-\frac{3}{2}$	$\frac{3}{4Y_{PS}}-\frac{9}{8}$	$\frac{1}{2}$	$\frac{13}{4}-\frac{3}{2Y_{PS}}$	$\frac{5}{2}$

Available on website http://www.wrc.org.za
ISSN 0378-4738 (Print) = Water SA Vol. 36 No. 3 April 2010
ISSN 1816-7950 (On-line) = Water SA Vol. 36 No. 3 April 2010

Table 3

Stoichiometry of endogenous mass loss for all SRB organism groups (Z_j) with a BPO composition of $C_kH_lO_mN_n$ generating a BPO organic with a composition of $C_xH_yO_zN_a$

NH_3 mol	H_2CO_3* mol	S_{bp} mol	H_2O mol	Z_j mol
$\frac{n(4x+y-2z)+a(2m-4k-l)}{(4x+y-2z-3a)}$	$\frac{k(y-2z-3a)+x(2m+3n-l)}{(4x+y-2z-3a)}$	$\frac{(4k+l-2m-3n)}{(4x+y-2z-3a)}$	$\frac{k(3y-2z-9a)+l(z-3x)+m(2x+3a-y)+n(9x-3z)}{(4x+y-2z-3a)}$	-1

$$C_kH_lO_mN_n + \boldsymbol{A}\,H_2O \rightarrow \boldsymbol{B}\,C_xH_yO_zN_a + \boldsymbol{C}\,H_2CO_3^* + \boldsymbol{D}\,NH_3 \quad (8)$$

where:

A = $[k(3y-2z-9a)+l(z-3x)+m(2x+3a-y)+n(9x-3z)]$ / $[4x+y-2z-3a]$

= $[k(3y-2z-9a)+l(z-3x)+m(2x+3a-y)+n(9x-3z)]/\gamma_S$

B = $[4k+l-2m-3n] / [4x+y-2z-3a] = \gamma_B/\gamma_S$

C = $[k(y-2z-3a)+x(2m+3n-l)] / [4x+y-2z-3a]$

= $[k(y-2z-3a)+x(2m+3n-l)]/\gamma_S$

D = $[n(4x+y-2z)+a(2m-4k-l)] / [4x+y-2z-3a]$

= $[n(4x+y-2z)+a(2m-4k-l)]/\gamma_S$

The generalised stoichiometry equation for endogenous decay of all organism groups expressed in Eq. (8) is listed in Table 3.

From the compositions of the biomass ($C_5H_7O_2N_1$) and influent BPO organics ($C_{3.35}H_7O_{1.45}N_{0.45}$), the stoichiometry of the endogenous mass loss process simplifies to Eq. (9) which is summarised in Table 4.

$$C_5H_7O_2N_1 + \mathbf{2.360}H_2O \rightarrow \mathbf{1.237}C_{3.35}H_7O_{1.45}N_{0.45} + \mathbf{0.855}H_2CO_3^* + \mathbf{0.449}NH_3 \quad (9)$$

Table 4

Stoichiometry for endogenous mass loss of SRB organism groups (Z_j) of composition $C_5H_7O_2N_1$ to BPO of composition $C_{3.35}H_7O_{1.45}N_{0.45}$

Z_j mol	H_2CO_3* mol	H_2O mol	NH_3 mol	S_{bp}	
				g COD	mol
-1	0.855	2.360	0.449	129.2	1.237

The biomass COD/VSS ratio is 1.412 mgCOD/mgVSS and 1 mol biomass has a COD of 160 gCOD. Therefore, 160 g biomass COD has a VSS of 113.1 gVSS which produces 160 gVSS or 1.237 mol BPO with a COD/VSS ratio of 1.682 mgCOD/mgVSS.

Kinetics of the BSR growth and endogenous processes

Growth kinetic rates

The approach adopted for the kinetic rate equations for the growth of SRB was taken from Kalyuzhnyi et al. (1998) as follows:

- The bacterial growth of each SRB group was modelled using the Monod kinetic equation in terms of the relevant substrates, with concomitant inhibition by undissociated H_2S and pH.
- The undissociated H_2S inhibition was formulated as first-order for all SRB bacterial groups.

Accordingly, the generalised specific growth rate (μ_j) equation for SRB wasdescribed by Kalyuzhnyi et al. (1998) as:

$$\mu_j = \mu_{max,\,j}\frac{[S_j]F(pH)}{K_{Sj}+[S_j]}\left[1-\left(\frac{[H_2S]_f}{K_{I,j}}\right)\right]\left(\frac{[SO_4^{2-}]}{K_N+[SO_4^{2-}]}\right) \quad (10)$$

where

S_i is the substrate concentration for SRB organism i, the middle term is the undissociated H_2S inhibition equation with $K_{I,j}$ being the inhibition constant by undissociated H_2S for the bacterial group j, and the last term is the sulphate switching function when $[SO_4^{2-}]$ is low.

The H_2S inhibition term $\left[1-\left(\frac{[H_2S]_f}{K_{I,j}}\right)\right]$ in Eq. (10) represents a 100% inhibition in SRB growth should $[H_2S]_f = K_I$. However, this equation is found to be unstable and reversed when $[H_2S]$ is greater than the $K_{I,j}$ value. When $[H_2S] > K_{I,j}$, the inhibition term becomes negative and the model simulation results become unstable with a see-saw effect. This inhibition term therefore was replaced by a more stable one which approaches zero more gradually, i.e.

$$\exp\left[-\left(\frac{[H_2S]_f}{0.60056K_{I,j}}\right)^2\right] \quad (11)$$

This term has an exponential behaviour and can never become negative. The factor 0.60056 was found by matching the linear (or first-order) inhibition term of Kalyuzhnyi et al. (1998) at the 50% inhibition point using the same value of K_I. For example, if K_I = 206 mgS/ℓ, and $[H_2S]_f$ = 103 mgS/ℓ, then the $\left[1-\left(\frac{[H_2S]_f}{K_{I,j}}\right)\right]$ term and Eq. (11) must give the same 50% inhibition. If instead of Eq. (11), a Monod type inhibition term is used, i.e. $\left[\left(\frac{K_{I,j}}{K_{I,j}+[H_2S]_f}\right)\right]$ the K_I value will be 206/2 = 103 mgS/ℓ to give 50% inhibition at $[H_2S]_f$ = 103 mgS/ℓ. Figure 2 illustrates the fraction uninhibited with $[H_2S]$ for the 3 inhibition terms. Also plotted is the fraction inhibition versus $[H_2S]$ concentration for the exponential inhibition term (Eq. (11)).

Should pH inhibition be required, it can be added to the UCTADM1-BSR model. In integrating BSR with ADM1, Fedorovich et al. (2003) used the following pH inhibition function in ADM1:

$$IpH = \frac{1+2x10^{0.5(pK_1-pK_2)}}{1+10^{(pH-pK_2)}+10^{(pH-pK_1)}} \quad (12)$$

However, this pH inhibition was omitted from the UCTADM1-BSR model due to the uncertainty of its behaviour.

From the above, and omitting pH inhibition, the general form of the SRB growth rate equation is:

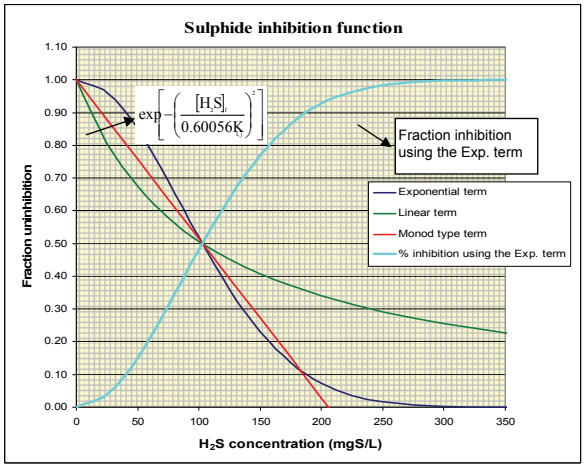

Figure 2
Fraction uninhibited versus H_2S concentration for 3 inhibition terms

$$\mu_j = \mu_{max,\,j}\frac{[S_i]}{K_{Sj}+[S_i]}\exp\left[-\left(\frac{[H_2S]_f}{0.60056K_{I,j}}\right)^2\right]\left(\frac{[SO_4^{2-}]}{K_N+[SO_4^{2-}]}\right) \quad (13)$$

When incorporating BSR into the UCTADM1 model, the H_2S inhibition term was also added to the existing kinetic rate equations for acidogenic, acetogenic and methanogenic bacterial groups. This was done by following the approach of Kalyuzhnyi et al. (1998) where:

$$\mu_j = \mu_{max,\,j}\frac{[S_i]}{K_{Sj}+[S_i]}\exp\left[-\left(\frac{[H_2S]_f}{0.60056K_{I,j}}\right)^2\right] \quad (14)$$

In the literature, it is reported that the sensitivity of SRB to hydrogen sulphide toxicity depends on the bacterial species (Maillacheruvu and Parkin, 1996; O'Flaherty et al., 1998). Maillacheruvu and Parkin (1996) investigated the effect of H_2S on propionate-oxidising, acetate-oxidising and hydrogenotrophic SRB and reported that acetotrophic SRB in particular were highly sensitive to H_2S. Likewise, Yamaguchi et al. (1999) reported that acetate utilisers were more susceptible to H_2S inhibition than hydrogen utilisers. In the UCTADM1-BSR model, the K_I values of 185 mgS/ℓ and 550 mgS/ℓ for the propionate-degrading and the hydrogenotrophic SRB, respectively, were taken directly from Kalyuzhnyi et al. (1998) while that of acetotrophic SRB was refined during model calibration.

Endogenous mass loss kinetic rates

Kalyuzhnyi et al. (1998) and Sötemann et al. (2005) formulated the endogenous mass loss with first-order kinetics. Therefore, this approach is also used for the 3 SRB groups considered here. Accordingly, the general equation for the rate (i) of endogenous mass loss of SRB group at concentration Z_j is:

$$r_j = b_j[Z_j] \quad (15)$$

where

b_j = specific endogenous mass loss rate constant for the 3 SRB groups.

Matrix representation of the biological kinetic model for BSR

The complete bioprocesses stoichiometric and kinetic model for SRB represented in the Petersen matrix format is shown in Table 5. The matrix includes both the growth and endogenous decay processes for all 3 SRB groups, namely, the propionate-degrading SRB ($Z_{PS,}$ growth process S1 and endogenous mass loss process S2), acetotrophic SRB ($Z_{AS,}$ growth process S3 and endogenous mass loss process S4) and hydrogenotrophic SRB ($Z_{HS,}$ growth process S5 and endogenous mass loss process S6).

Values for the stoichiometric and kinetic constants

Van Wageningen (2007) used values for the stoichiometric and kinetic constants for the SRB from Kalyuzhnyi et al. (1998), who obtained these values from model fitting the data of Omil et al. (1996). These values are also employed here (Table 6).

The constants in Table 6 are expressed in terms of gram units. Since UCTADM1, and therefore also the kinetic model for BSR (Table 5), expresses concentrations as mole units, the constants were converted to the appropriate mole units. This was done by accepting a biomass composition of $C_5H_7O_2N_1$ and substrates (acetic acid, propionic acid and hydrogen) as per their known chemical composition (Table 7). In addition, because the kinetic rates are expressed in terms of total species concentrations in the literature sources, the half-saturation constants needed to be converted to express them in terms of the undissociated weak acid/base species, because this is the form in which they are utilised by the SRB. This was done in model application by multiplying the appropriate half-saturation constant by the undissociated species to total species concentration ratio (Van Wageningen, 2007), which in effect decreased the half-saturation concentrations by the undissociated species to total species concentration ratio. With this approach, the relative concentrations may change as the pH changes, which was considered more appropriate. In the neutral pH 6 to 8 range, the undissociated species concentrations are very low. Depending on the half-saturation concentrations, this results in very low growth rates for the SRB. In this model application, this did not lead to run-time problems because the precursor hydrolysis/acidogenesis process is very slow. In applications requiring high growth rates on VFA at neutral pH, utilising the undissociated species of the VFAs can lead to run-time problems (Van Zyl et al., 2008).

Inclusion of the aqueous chemical and physical processes

In the BSR processes described above, weak acid/base species are both produced and consumed. These species, together with their associated weak acid/base chemistry, need to be included in the kinetic model. In addition, the compound H_2CO_3*, which is both produced and consumed, and the compound H_2S produced, have physical gas exchange processes with the gas phase which require inclusion in the model.

The aqueous chemistry processes were extracted from Musvoto et al. (1997), for the ammonia, carbonate, phosphate, acetate and water subsystems; from Sötemann et al. (2005) for the propionate subsystem; and from Tables 8 and 9 below for the sulphate and sulphide subsystems. In addition, the physical gas exchange processes for CO_2 and NH_3 were taken from Sötemann et al. (2005), whereas the H_2S gas exchange processes were taken from Table 10. Following the approach of Sötemann et al. (2005), methane is included as a gas phase compound, that is, it is generated directly as a gas because it is very insoluble and is not utilised in any of the processes.

Available on website http://www.wrc.org.za
ISSN 0378-4738 (Print) = Water SA Vol. 36 No. 3 April 2010
ISSN 1816-7950 (On-line) = Water SA Vol. 36 No. 3 April 2010

Available on website http://www.wrc.org.za
ISSN 0378-4738 (Print) = Water SA Vol. 36 No. 3 April 2010
ISSN 1816-7950 (On-line) = Water SA Vol. 36 No. 3 April 2010

Table 5
Petersen matrix representation of the bioprocess kinetic model for sulphate-reducing bacteria (SRB) only. The stoichiometry and kinetics for the acidogens and the mixed weak acid/base chemistry processes are the same as in UCTADM1 (Sötemann et al., 2005) and so are not repeated here. The columns (compounds) labelled C31, C32, S1, S2 and S3 and rows (processes) labelled S1 to S6 are added to include BSR in UCTADM1.

	Number→	C1/B10	C2	C3	C7	C13	D4	D3	C31	C32	D1	S1	S2	S3		↓Process Rate
No.	**Process↓ Compound→**	**NH_4^+**	**NH_3 dis.**	**H_2CO_3***	**H^+**	**HAc**	**HPr**	**H_2 dissolved**	**SO_4^{2-}**	**H_2S**	**S_{bp}**	**Z_{PS}**	**Z_{AS}**	**Z_{HS}**	**H_2O[c]**	
S1	Growth of propionate-degrading SRB	-1		$\left(\frac{1}{Y_{PS}}-2\right)$	$\left(\frac{13}{4}-\frac{3}{2Y_{PS}}\right)$	$\left(\frac{1}{Y_{PS}}-\frac{3}{2}\right)$	$-\left(\frac{1}{Y_{PS}}\right)$	$\frac{1}{2}$	$-\left(\frac{3}{4Y_{PS}}-\frac{9}{8}\right)$	$\left(\frac{3}{4Y_{PS}}-\frac{9}{8}\right)$		1			$\frac{5}{2}$	$\frac{\mu_{max}[H\,Pr]}{K_S+[H\,Pr]}\left[\exp\left\{-\left(\frac{[H_2S]_f}{0.60056K_{I,j}}\right)^2\right\}\right]\left[\frac{[SO_4^{2-}]}{K_N+[SO_4^{2-}]}\right]Z_{PS}$
S2	Endogenous decay of propionate-degrading SRB		0.449[b]	0.855[b]							129.2[b]	-1			2.36	$b_{PS}[Z_{PS}]$
S3	Growth of acetotrophic SRB	-1		$\frac{(2-5Y_{AS})}{Y_{AS}}$	$1-\frac{(2-5Y_{AS})}{Y_{AS}}$	$-\left(\frac{1}{Y_{AS}}\right)$			$-\frac{\left(1-\frac{5}{2}\right)Y_{AS}}{Y_{AS}}$	$\frac{\left(1-\frac{5}{2}\right)Y_{AS}}{Y_{AS}}$			1		3	$\frac{\mu_{max}[HAc]}{K_S+[HAc]}\left[\exp\left\{-\left(\frac{[H_2S]_f}{0.60056K_{I,j}}\right)^2\right\}\right]\left[\frac{[SO_4^{2-}]}{K_N+[SO_4^{2-}]}\right]Z_{AS}$
S4	Endogenous decay of acetotrophic SRB		0.449[b]	0.855[b]							129.2[b]		-1		2.36	$b_{AS}[Z_{AS}]$
S5	Growth of hydrogenotrophic SRB	-1		-5	$\left(6-\frac{1}{2Y_{HS}}\right)$			$-\left(\frac{1}{Y_{HS}}\right)$	$-\left(\frac{1}{4Y_{HS}}-\frac{5}{2}\right)$	$\left(\frac{1}{4Y_{HS}}-\frac{5}{2}\right)$				1	$\frac{1}{Y_{HS}}+3$	$\frac{\mu_{max}[H_2]}{K_S+[H_2]}\left[\exp\left\{-\left(\frac{[H_2S]_f}{0.60056K_{I,j}}\right)^2\right\}\right]\left[\frac{[SO_4^{2-}]}{K_N+[SO_4^{2-}]}\right]Z_{HS}$
S6	Endogenous decay of hydrogenotrophic SRB		0.449[b]	0.855[b]							129.2[b]			-1	2.36	$b_{HS}[Z_{HS}]$
		mol/ℓ	**mol/ℓ**	**mol/ℓ**	**mol/ℓ**	**mol/ℓ**	**mol/ℓ**	**mol/ℓ**	**mol/ℓ**	**mol/ℓ**	**gCOD/ℓ[a]**	**mol/ℓ**			**mol/ℓ**	

[a] *See Table 4 for units in mol/ℓ*
[b] *This is the COD for the biodegradable particulate (S_{bp}) substrate with formulation $C_{3.35}H_7O_{1.45}N_{0.45}$; see Table 3 for the generalised formulation for $S_{bp} = C_xH_yO_zN_a$*
Z_j = SRB j concentration; Y = true (metabolic) organism yield; b = specific mass loss rate; rate symbols defined in Eq. (10).
Subscripts PS, AS and HS = propionate-degrading, acetoclastic and hydrogenotrophic SRB, respectively.
Compound- and process-numbering system follows Sötemann et al. (2005).
[c] *H_2O is usually not included in the Petersen matrix but is shown here for completeness and mass balances checks on H and O.*

Table 6
Values for SRB stoichiometric and kinetic constants used in the BSR kinetic model (from Kalyuzhnyi et al., 1998)

	μ_{max} /d	K_S[1] gCOD/ℓ	K_N[1] gSO_4^{2-}/ℓ	K_I[1] gS/ℓ	Y[1] gVSS/gCOD	b /d
Propionate-degrading SRB	0.583	0.295	0.0074	0.185	0.027	0.0185
Acetotrophic SRB	0.612	0.024	0.0192	0.164	0.033	0.0275
Hydrogenotrophic SRB	2.8	7E-05	0.0192	0.550	0.050	0.0600

[1] *Constants in mgCOD/ℓ converted to mol/ℓ in UCTADM1-BSR to ensure consistency (Table 7)*

Table 7
Corrected values used in UCTADM1-BSR for the appropriate half saturation constants

Organism Group	*M*		*K_s*		*K_n*		*Y*		*b*	
	Kalyuzhnyi et al. (1998)	UCTADM1 (Sötemann et al., 2005)	Kalyuzhnyi et al. (1998)	UCTADM1 (Sötemann et al., 2005)	Kalyuzhnyi et al. (1998)	UCTADM1 (Sötemann et al., 2005)	Kalyuzhnyi et al. (1998)	UCTADM1 (Sötemann et al., 2005)	Kalyuzhnyi et al. (1998)	UCTADM1 (Sötemann et al., 2005)
Comparison	mol(org)/ mol(subs)/d	mol(org)/ mol(subs)/d	mol(subs)/ℓ	mol(subs)/ℓ	molSO$_4$/ℓ	molSO$_4$/ℓ	mol(org)/ mol(subs)	mol(org)/ mol(subs)	mol(org)/ mol(org)/d	mol(org)/ mol(org)/d
Acidogens	4.000	0.80	7.676E-05	7.810E-04	N/A	N/A	0.10964	0.1074	0.0900	0.041
Acetogens	0.160	1.15	2.203E-03	8.900E-05	N/A	N/A	0.01586	0.0278	0.0140	0.015
Propionate degrading SRB	0.583	*	2.631E-03	*	7.703E-05	*	0.02676	*	0.0185	*
Acetoclastic methanogens	0.264	4.39	1.873E-03	1.300E-05	N/A	N/A	0.01218	0.0157	0.0200	0.037
Acetotrophic SRB	0.612	*	3.747E-04	*	1.999E-04	*	0.01869	*	0.0275	*
Hydrogenotrophic methanogens	1.000	1.20	7.500E-06	1.560E-04	N/A	N/A	0.00212	0.0040	0.0400	0.010
Hydrogenotrophic SRB	2.800	*	4.375E-06	*	1.999E-04	*	0.00707	*	0.0600	*

**Organism not included in UCTADM1. Constants for SRB used in UCTADM1-BSR are taken from Kalyuzhnyi et al. (1998). Org = Organism; Subs = Substrate*

Table 8
Petersen matrix representation of the HSO_4^- acid / base dissociation processes

Number→		C7	C30	C31	
Compound→		H^+	HSO_4^-	SO_4^{2-}	
↓No	↓Process				↓Process rates
C48	Forward dissociation HSO_4^-	+1	-1	+1	$K^*_{fHSO4}[HSO_4^-]$
C49	Reverse dissociation HSO_4^-	-1	+1	-1	$K^*_{rHSO4}[SO_4^{2-}][H^+]$
		mol/ℓ	mol/ℓ	mol/ℓ	

Table 9
Petersen matrix representation of the H_2S weak acid / base dissociation processes

Number→		C7	C32	C33	
Compound→		H^+	H_2S	HS^-	
↓No	↓Process				↓Process rates
C50	Forward dissociation H_2S	+1	-1	+1	$K^*_{fH2S}[H_2S]$
C51	Reverse dissociation H_2S	-1	+1	-1	$K^*_{rH2S}[HS^-][H^+]$
		mol/ℓ	mol/ℓ	mol/ℓ	

Table 10
Petersen matrix representation of the H_2S exchange physical processes

Number→		C32	C33	
Compound→		H_2S	H_2S(g)	
↓No	↓Process	Dissolved	Gas	↓Process rates
P12	Dissolution of H_2S gas	+1	-1	$K^*_{rH2Sg}(p_{H2S})(K_{H2S})$
P13	Expulsion of H_2S gas	-1	+1	$K^*_{rH2Sg}[H_2S]$
		mol/ℓ	mol/ℓ	

In the model, the gas compounds were accepted to remain part of the bulk liquid and exit the digester with the effluent flow. This is acceptable because at steady state the gas composition does not change. However, for dynamic simulations, the gas composition of the headspace may change with time and can influence the dissolved species bulk liquid concentrations through the gas exchange processes. In this case, a separate gas stream needs to be implemented following the processes set out in Batstone et al. (2002) and Sötemann et al. (2005).

Integrating the aqueous chemistry, physical and biological processes with UCTADM1

The biological processes (stoichiometric and kinetics), aqueous chemistry and physical processes relevant to BSR were integrated with the existing methanogenic UCTADM1 model in Aquasim (Reichert, 1998). This resulted in an integrated kinetic model for both BSR and methanogenesis in competition for the volatile fatty acids (VFA) and H_2 substrates. Should BSR be required as the only biological process consuming the VFA and H_2 substrates, the methanogenic processes can be switched off in the model application. This will result in a 'stand-alone' integrated 2-phase chemical, physical and biological process model for BSR with PSS as energy source. In a real BSR system, sulphidogenesis outcompetes methanogenesis resulting in an exclusively BSR system, which was the case for the 2 UASB BSR systems (R1 at 35°C and R2 at 20°C) of Poinapen et al. (2009a; b), simulated with UCTADM1-BSR.

Available on website http://www.wrc.org.za
ISSN 0378-4738 (Print) = Water SA Vol. 36 No. 3 April 2010
ISSN 1816-7950 (On-line) = Water SA Vol. 36 No. 3 April 2010

UCTADM1-BSR model application and validation

Systems simulated and influent characteristics

After calibration, the UCTADM1-BSR model was validated by applying it to simulate the 2 UASB BSR systems Poinapen et al. (2009a; b), viz:

- R1 at 1 500 mgSO_4^{2-}/ℓ at 35°C with PSS COD/SO_4^{2-} ratio of 1.25 (Poinapen et al., 2009a – Part 1).
- R1 at 1 800 mgSO_4^{2-}/ℓ at 35°C with PSS COD/SO_4^{2-} ratio of 1.44 and no $NaHCO_3$ dosed to feed (Poinapen et al., 2009b).
- R2 at 1 500 mgSO_4^{2-}/ℓ at 20°C with PSS COD/SO_4^{2-} ratio of 1.75 and no $NaHCO_3$ dosed to feed (Poinapen et al., 2009b).

Table 11 lists the average measured (or calculated from measured results) influent characteristics of the 3 UASB BSR systems, and these values were used as inputs to the UCTADM1-BSR model. The COD units were converted to mole units with the relevant stoichiometric compositions of the organics, namely:

- Influent biodegradable particulate organics (BPO, S_{bp}) – stoichiometric composition of $C_xH_yO_zN_a$ where *x*, *y*, z and *a* are determined from measured values (Poinapen and Ekama, 2010)
- Fermentable biodegradable soluble organics (FRBO, S_{bsf}) – represented by glucose ($C_6H_{12}0_6$)
- Biodegradable soluble acetic and propionic acids (S_{bsa}, S_{bsp}) – known stoichiometric compositions ($C_2H_4O_2$ and $C_3H_6O_2$ for associated and $C_2H_3O_2^-$ and $C_3H_5O_2^-$ for dissociated species respectively)
- Unbiodegradable soluble and particulate organics (USO, S_{us} and UPO, S_{up}) – not converted since these are not degraded and utilised in the system and hence appear in the effluent (only S_{us}) and the waste (both S_{us} and S_{up}) flows respectively.

As mentioned earlier, the UASB reactor is simulated as a completely mixed digester because of the effect of the sludge recycle line which continuously mixed the top sludge with the bottom sludge.

Comparisons of the UCTADM1-BSR kinetic model predictions with experimentally measured and steady-state model data

The simulated results were compared with the experimental measured values and the steady-state model results. These comparisons are listed in Table 12.

It can be seen that there is a very good correlation between the experimental measured data and the simulated results from both the steady-state (SS) and the UCTADM1-BSR (kinetic) models.

The difference on one or two effluent concentrations may appear significant but the absolute difference is very small when compared with the removal concentrations (e.g. the effluent sulphate concentration as compared with the sulphate removal concentration). Moreover, some of the differences (though not significant) possibly come from imperfect mass balances – with the models all the mass balances (COD, S and N) are 100% while with the experimental data they are between 95 and 105%.

The gaseous CO_2 production in the UCTADM1-BSR is zero as anticipated from the steady-state stoichiometry of BSR, where the PSS ($C_{3.35}H_7O_{1.45}N_{0.45}$) is carbon deficient (Poinapen and Ekama, 2010).

Another interesting outcome from the good UCTADM1-BSR model predictions is the successful integration and calibration of the sulphide inhibition term and the temperature dependency equation (in the case of R2 at 20°C). The $K_{I\text{-}as}$ value for the acetoclastic SRB was found to be 206 mgS/ℓ for a 94% growth inhibition by the undissociated H_2S using the exponential inhibition term $\exp[-([H_2S]_i/0.60056K_{I,j})^2]$. The θ value for the temperature dependency equation was 1.114 in the UCTADM1-BSR model, representing a 30% decrease in the PSS biodegradable organics hydrolysed when the temperature is decreased from 35°C to 20°C.

Conclusion

An integrated 2-phase (aqueous-gas) mixed weak acid/base chemistry and biological processes simulation model for

Table 11
Average measured/determined influent concentrations used as input to the UCTADM1-BSR model to simulate the three UASB BSR systems

Input/Influent parameters	Units	R1 at 35°C Fed 1500 mgSO_4^{2-}/ℓ	R1 at 35°C Fed 1800 mgSO_4^{2-}/ℓ	R2 at 20°C Fed 1500 mgSO_4^{2-}/ℓ
Total COD	mgCOD/ℓ	1880	2584	2596
[a]Unbiodegradable particulate COD	mgCOD/ℓ	677	930	935
Total soluble COD	mgCOD/ℓ	236	337	339
VFA COD	mgCOD/ℓ	126	164	169
Unbiodegradable soluble COD	mgCOD/ℓ	6	7	8
Biodegradable particulate COD	mgCOD/ℓ	967	1317	1322
Sulphate	mgSO_4^{2-}/ℓ	1500	1800	1500
Free and saline ammonia (FSA)	mgN//ℓ	10.0	9.2	9.6
pH	-	7.2	5.99	5.94
H2CO3* alkalinity	mg/ℓ $CaCO_3$	456	22	23
[b]Volume of reactor bed/digester (V_r)	ℓ	7.2	7.4	7.6
Feed flow rate (Qi)	ℓ/d	13.8	10.1	9.2
Hydraulic retention time (HRT)	h	13.7	18.5	20.4
Sludge age (Rs)	d	18	21	24
Waste flow rate (Qw)	ℓ/d	0.40	0.35	0.32

[a] Based on an unbiodegradable particulate COD fraction of primary sludge ($f_{PS'up}$) of 0.36.
[b] Reactor bed volume includes waste volume.

Table 12
Comparison of experimentally measured (M) effluent values with the steady state (SS) BSR and the UCTADM1-BSR kinetic (Sim) model prediction

Comparison of experimentally measured (Meas) effluent concentrations with those predicted by the steady state (SSM) and UCTADM1-BSR dynamic kinetic (DM) models.	Units	R1 at 35°C Fed 1500 mgSO_4^{2-}/ℓ			R1 at 35°C Fed 1800 mgSO_4^{2-}/ℓ			R2 at 20°C Fed 1500 mgSO_4^{2-}/ℓ		
		Meas	SSM	DM	Meas	SSM	DM	Meas	SSM	DM
Effluent sulphate	mgSO_4^{2-}/ℓ	149	149	136	146	145	115	101	104	103
Sulphate removal	mgSO_4^{2-}/ℓ	1351	1351	1364	1654	1355	1685	1399	1396	1397
Organic COD removal	mgCOD/ℓ	1624	1632	1757	2153	2242	2264	23098	2444	2410
Effluent total soluble COD	mgCOD/ℓ	761[a]	761[b]	1031	1234[b]	1234	1442	951	951[b]	1116
Effluent organic soluble COD	mgCOD/ℓ	141	141[b]	123	229[b]	229	320	96	96[b]	186
Effluent HS^-/H_2S	mgS/ℓ	209/101[a]	277/173	336/120	318/184	339/213	409/153	261/166	280/185	321/145
Reactor pH	-	7.15	7.05	7.19	7.08	7.04	7.17	7.21	7.20	7.26
Effluent H_2CO_3* alk + H_2S alk	mg/ℓ as $CaCO_3$	1938[a]	2063	2039	1855	1974	1982	1558	1672	1668
Effluent H_2CO_3* alk	mg/ℓ as $CaCO_3$	1611[a]	1627	1516	1358	1441	1343	1144	1234	1166
Effluent VFA	mgHAc/ℓ	48	48[b]	22	72[b]	72	82	62	62[b]	42
Effluent FSA	mgN/ℓ	32	50	57	46	60	76	38	48	57
H_2S exiting as gas	mgS/ℓ influent	0	0	0	0	0	0	0	0	0
CO_2 exiting as gas	mol/ℓ	0	0	0	0	0	0	0	0	0

[a] H_2S measurement problem during first 280 days of UASB R1 operation – system total alkalinity unaffected by loss of H_2S while H_2CO_3 alk and Alk H_2S are affected (Poinapen et al., 2009c).*

[b] The steady state model for BSR is based on substrate utilization, hence the effluent soluble organics concentrations are given by the measured values.

competitive methanogenic and sulphidogenic anaerobic digestion with PSS as energy source for BSR (UCTADM1-BSR) was developed by Van Wageningen et al. (2006). This model was reviewed and modified to simulate the lab-scale UASB BSR systems. The kinetic model predictions (restricted to steady-state conditions) conform favourably to the experimental measurements and the SS model results and therefore provide support for the successful development, calibration and validation of the kinetic simulation model.

This model allows for 5 organic types (USO, UPO, BPO, FRBO, VFA) with different compositions in the influent feed. This characterisation structure conforms to the characterisation of municipal wastewater developed for activated sludge system models. Should a kinetic model with only BSR biological processes consuming the VFA and H_2 substrates generated from PSS hydrolysis and acidification be required, the methanogenic processes can be switched off in the UCTADM1-BSR model. Moreover, although UCTADM1-BSR has been developed purposely for the situation where PSS serves as the feed substrate, it offers a much broader application. For instance, should the feed be a particulate substrate (e.g. a mixture of PSS and compost, compost alone or a mixture of PSS and waste activated sludge), only the feed substrate composition and kinetic constants for hydrolysis would require modification. For soluble organics (e.g. acetate or a mixture of VFA), they would be used directly as input to the model as they serve as intermediates in the processes already included in the model.

Acknowledgements

This research was financially supported by the Water Research Commission, the National Research Foundation and the University of Cape Town and is published with their permission.

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