# Biological sulphate reduction with primary sewage sludge in an upflow anaerobic sludge bed reactor – Part 5: Steady-state model

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## Abstract

This paper describes the development of a steady-state anaerobic digestion model for biological sulphate reduction using primary sewage sludge (PSS) as substrate. The model comprises: a chemical oxygen demand (COD) based hydrolysis kinetics part in which the PSS biodegradable COD and sulphate removals are calculated for given hydraulic and sludge retention times; a C, H, O, N, P, S, COD and charge mass balance stoichiometry part in which the alkalinity generated (from both the $HCO_3^-$ and $HS^-$) is determined from the COD and sulphate removals; and an inorganic carbon ($CO_2$) and sulphide mixed weak acid/base chemistry part in which the digester pH is calculated from the $HCO_3^-$ and $HS^-$ species formed. From the stoichiometry, it was found that the PSS is carbon limited in that it does not generate sufficient $HCO_3^-$ alkalinity for the sulphate reduction, i.e., its COD/C ratio is too high which accounts for the observed zero gas ($CO_2$) generation. The $H_2S/HS^-$ system provides the alkalinity shortfall and establishes the system pH. Once developed and calibrated, the model results were compared with experimental data from 2 laboratory-scale upflow anaerobic sludge bed reactors (operated at 35°C and 20°C respectively) fed PSS and sulphate. The predicted COD and sulphate removals, alkalinity and digester pH correspond very well to the measured data. The model assists in identifying design and operation parameters sensitive to the system and provides a basis for developing an integrated biological, chemical and physical process dynamic model.

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

## Nomenclature

| | |
|---|---|
| *a* | molar nitrogen composition of organics in $C_xH_yO_zN_aP_b$ |
| AD | anaerobic digestion |
| Alk $H_2S$ | alkalinity with respect to the $H_2S$ reference species excluding the water species |
| AMD | acid mine drainage |
| *b* | molar phosphorus composition of organics in $C_xH_yO_zN_aP_b$ |
| $b_{AD}$ | endogenous respiration rate of acidogens |
| BPO | biodegradable particulate organics |
| BRT | bed retention time |
| BSO | biodegradable soluble organics |
| BSR | biological sulphate reduction |
| COD | chemical oxygen demand |
| *E* | flux of acidogen and endogenous mass wasted per day as a fraction of the flux of hydrolysable biodegradable organics utilised per day |
| EDC | electron donating capacity |
| *f* | proportion $H_2PO_4^-$ in phosphate ($H_2PO_4^- + HPO_4^{2-}$) weak acid base species |
| $f_{AD}$ | unbiodegradable fraction of acidogen biomass |
| FBR | fluidised bed reactor |
| $f_c$ | mass carbon to mass (VSS) ratio |
| $f_{cv}$ | mass COD to mass (VSS) ratio |
| $f_h$ | mass hydrogen to mass (VSS) ratio |
| $f_n$ | mass OrgN to mass VSS ratio |
| $f_o$ | mass oxygen to mass (VSS) ratio |
| $f_p$ | mass OrgP to mass VSS ratio |
| $f_{PS'up}$ | 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 |
| ISS | inorganic suspended solids |
| *k* | molar carbon composition of acidogen biomass in $C_kH_lO_mN_nP_p$ |
| $K_I$ | sulphide inhibition kinetic constant |
| $K_M$ | Monod maximum specific hydrolysis rate for saturation kinetics |
| $K_{MT}$ | Monod maximum specific hydrolysis rate for saturation kinetics at T°C |
| $K_{M20}$ | Monod maximum specific hydrolysis rate for saturation kinetics at 20°C |
| $K_S$ | Monod half saturation coefficient for hydrolysis for saturation kinetics |
| $K_{ST}$ | Monod half saturation coefficient for hydrolysis for saturation kinetics at T°C |
| $K_{S20}$ | Monod half saturation coefficient for hydrolysis for saturation kinetics at 20°C |
| *l* | molar hydrogen composition of acidogen biomass in $C_kH_lO_mN_nP_p$ |
| *m* | molar oxygen composition of acidogen biomass in $C_kH_lO_mN_nP_p$ |

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| | |
|---|---|
| M | experimentally measured |
| $M_B$ | molar mass of acidogen biomass |
| $M_S$ | molar mass of biodegradable organics |
| $n$ | molar nitrogen composition of acidogen biomass in $C_kH_lO_mN_nP_p$ |
| OLR | organic loading rate |
| OP | ortho-phosphate |
| P | theoretically predicted |
| $p$ | molar phosphorus composition of acidogen biomass in $C_kH_lO_mN_nP_p$ |
| PBR | packed bed reactor |
| $pK'_{S1}$ | 1st dissociation constant for the sulphide weak acid base system corrected for ionic strength effects |
| PSS | primary sewage sludge |
| $Q_e$ | effluent flow |
| $Q_i$ | influent flow |
| $Q_r$ | recycle flow |
| $Q_w$ | waste flow |
| R1 | UASB Reactor 1 |
| R2 | UASB Reactor 2 |
| RBCOD | readily biodegradable COD ($S_{bsi}$) |
| $r_h$ | volumetric hydrolysis rate – gCOD/(ℓ.d) |
| $R_h$ | hydraulic retention time |
| $R_s$ | sludge age |
| $S_{bp}$ | biodegradable particulate COD concentration |
| $S_{bpi}$ | biodegradable particulate COD concentration in influent |
| $S_{bsi}$ | biodegradable soluble COD concentration in influent |
| $S_{bsai}$ | VFA (all assumed acetic acid) COD concentration in influent |
| $S_{bsfi}$ | fermentable biodegradable soluble COD concentration in influent |
| SBR | sequencing batch reactor |
| SLR | sludge loading rate |
| SRB | sulphate reducing bacteria |
| SRT | solids retention time |
| SS | steady state |
| SSD | sample standard deviation |
| $S_T$ | total sulphide species concentration |
| $S_{ti}$ | total COD concentration in influent |
| $S_{up}$ | unbiodegradable particulate COD concentration |
| $S_{upi}$ | unbiodegradable particulate COD concentration in influent |
| $S_{usi}$ | unbiodegradable soluble COD concentration in influent |
| $S_{bpi}$ | biodegradable particulate COD concentration in influent |
| $T$ | temperature in °C |
| TKN | total Kjeldahl nitrogen |
| TOC | total organic carbon |
| Total alk | sum of weak acid/base subsystem alkalinities |
| TSS | total suspended solids (VSS+ISS) |
| 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 |
| USCOD | unbiodegradable soluble COD |
| USO | unbiodegradable soluble organics |
| $V_d$ | volume of digester (equivalent to bed volume, $V_b$) |
| VFA | volatile fatty acids |
| VSS | volatile suspended solids |
| $V_{up}$ | hydraulic upflow velocity in UASB reactor |
| WS | waste sludge |
| WWTP | wastewater treatment plant |
| $x$ | molar carbon composition of organics in $C_xH_yO_zN_aP_b$ |
| $y$ | molar hydrogen composition of organics in $C_xH_yO_zN_aP_b$ |
| $Y_{AD}$ | specific yield coefficient of acidogens |
| $z$ | molar oxygen composition of organics in $C_xH_yO_zN_aP_b$ |
| $Z_{BAD}$ | acidogen biomass concentration mgCOD/ℓ |
| $Z_{EAD}$ | acidogen endogenous mass concentration mgCOD/ℓ |
| $\gamma_B$ | electron donating capacity of acidogen biomass |
| $\gamma_S$ | electron donating capacity of biodegradable organics |
| $\theta$ | Arhenius temperature sensitivity coefficient for $K_M$ |

## Introduction

Biological sulphate reduction (BSR) is an attractive treatment process in the remediation of sulphate-rich waters such as acid mine drainage (AMD). Conventionally, organic substrates such as molasses, ethanol, acetate or lactate have been used as electron donor and organic carbon source for BSR. However, these organics are relatively expensive, making AMD remediation via BSR costly. Since the economics of BSR are governed by the cost of the carbon source, the BioSURE® technology was developed, in which BSR is achieved using primary sewage sludge (PSS) as carbon source and electron donor (Rose et al., 2002). The core unit process in the BioSURE® system is BSR with PSS. To assist in, and optimise, the design, operation of, and research into this unit process, mathematical models (both steady-state and dynamic) represent very useful process evaluation tools. Mathematical models provide quantitative descriptions of the treatment system of interest that allow predictions of the system response and performance to be made. Based on the predictions, design and operation criteria can be identified to optimise the system performance. The model predictions can be evaluated and as such make it possible to test hypotheses of the system behaviour, such as biological processes and their response to system constraints, in a consistent and integrated fashion. In this paper, a steady-state (SS) anaerobic digestion model for BSR using PSS as energy source is developed and calibrated. The SS BSR model results are compared with experimental data from the 2 laboratory-scale UASB reactors, R1 at 35°C (when fed 1 500 and 1 800 $mgSO_4^{2-}/ℓ$) and R2 at 20°C (fed 1 500 $mgSO_4^{2-}/ℓ$) (Poinapen et al., 2009).

## Importance of steady-state models

Steady-state models are comparatively simple kinetic and stoichiometric models based on constant flows and loads as inputs to determine the system design parameters. They are based on the slowest process kinetic rate governing the overall behaviour of the system and relate this process to the system design and operating parameters. These design and operating parameters, such as reactor volume, recycle ratios and retention time, can be estimated in a relatively simple and quick way with explicit equations from the system performance criteria, for instance, effluent quality. Usually, steady-state models constitute the initial step to estimate the design and operating parameters of a system. These parameters then serve as input to the more complex kinetic dynamic simulation models to explore the time-varying behaviour of the system and refine the design and operating parameters. A dynamic model for BSR in a UASB reactor fed PSS is developed in the last paper of this 6-part series (Poinapen and Ekama, 2010).

## Characterisation of PSS

In conformity with mass balance and continuity principles, the effluent parameters (COD (all constituents), TKN, FSA, VFA, $H_2CO_3$* alk, Alk $H_2S$, $H_2S/HS^-$ and pH) are defined by the influent PSS and $SO_4^{2-}$ constituents transformed in the system. Thus, in the development of the steady-state (SS) model for BSR, the PSS is fully characterised based on the COD (total and unbiodegradable particulate fraction, $f_{PS'up}$), short chain (volatile) fatty acids (VFA) COD, TKN and FSA and the PSS CHON composition of the particulate solids, i.e. *x*, *y*, *z* and *a* in $C_xH_yO_zN_a$. This approach is similar to that used by Sötemann et al. (2005a) and characterises the PSS in terms of the measurable parameters used in calculating the COD, C, H, O, N, S and charge mass balances.

## Anaerobic digestion steady-state model for methanogenesis

Sötemann et al. (2005a) developed a SS model for anaerobic digestion (AD) of PSS under methanogenic conditions. This model consists of 3 sequential parts, namely:

- A COD-based kinetic part in which the influent COD concentration hydrolysed, VFA COD utilised, methane gas COD generated, biomass COD produced and COD concentrations of the effluent are determined for a given sludge age
- A $C_xH_yO_zN$, charge and COD mass balance based stoichiometry part in which the gas composition (or partial pressure of $CO_2$), ammonia released and alkalinity generated are calculated from the VFA and PSS COD concentration hydrolysed (and utilised) and its *x*, *y*, *z* and *a* composition in $C_xH_yO_zN_a$ of the biodegradable organics
- An inorganic carbon system weak/acid-base chemistry part in which the pH of the digester is obtained from the partial pressure of $CO_2$ and $HCO_3^-$ (or $H_2CO_3^*$alkalinity) generated

Based on the above, a steady-state model for BSR of sulphate-rich waters using a generic biodegradable organic $C_xH_yO_zN_aP_b$ as carbon source was developed. This SS BSR model will be useful to:

- Estimate product generation from influent organic C, H, O, N and P composition and establish whether or not a particular organic type is C-deficient, i.e. generates insufficient inorganic C to supply the alkalinity ($HCO_3^-$) required for the $SO_4^{2-}$ reduction
- Estimate reactor volume and retention time for a required substrate COD loading and sulphate removal rate
- Estimate product concentrations (such as hydrogen sulphide) and their sensitivity to system performance
- Provide a basis for cross-checking BSR kinetic dynamic simulation model results

In the development of the SS model using PSS as organic, it is assumed that the slowest biological process, i.e. hydrolysis/acidogenesis, generates directly the BSR end-products, which are $H_2S$, $HS^-$, $HCO_3^-$, $CO_2$, $NH_4^+$ and biomass. Thus, the SS BSR model includes the same 3 parts as the methanogenesis SS AD model of Sötemann et al. (2005a), namely:

COD-based kinetics of the hydrolysis/acidogenesis process (as for Sötemann et al. (2005a) because Ristow et al. (2005) found that this also applies to BSR)

C,H,O,N,P,S, charge and COD mass balance based stoichiometric conversion of the reactants from the 1st part and utilisation of VFA to BSR end-products

Effect of the end-products on the digester pH by applying mixed weak acid/base chemistry of the inorganic carbon ($CO_2$) and sulphide systems. For PSS, the ortho-phosphate and, under normal operating conditions, the VFA (acetic acid) weak acid-base systems are low enough to have a negligible effect on digester pH.

## Steady-state AD model for BSR

With the modified UASB configuration operated in this research, the sludge recycle line from the top to the bottom of the reactor bed ensured that the biomass was fairly evenly distributed along the bed axis. This biomass recycle line offered 2 advantages – it initiated BSR at the bottom of the bed thus maximising the system performance, and it allowed the UASB reactor bed to be modelled as a completely mixed digester. This avoids the necessity of evaluating uncertain and complex granular sludge dynamics, along the reactor bed height in UASB reactors, caused by dispersion, sedimentation and convection.

### Hydrolysis of primary sewage sludge

Consider a UASB reactor of bed volume $V_b$ (ℓ) and influent flow rate $Q_i$ (ℓ/d). The UASB reactor configuration has the benefit of uncoupling the solid and liquid (hydraulic) retention times compared with a flow-through digester. For this reason, the fundamental design parameter, sludge age, ($R_s$ in days) is considered in this case (Fig. 1).

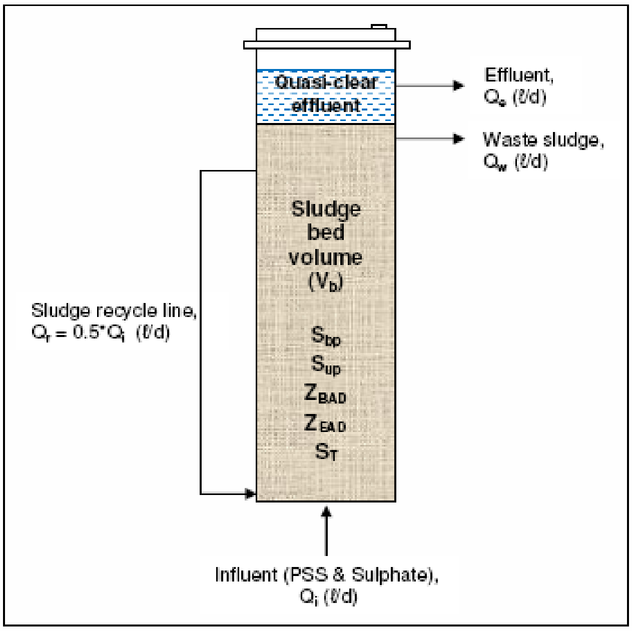

***Figure 1***
*Schematic diagram of the UASB reactor used in this research*

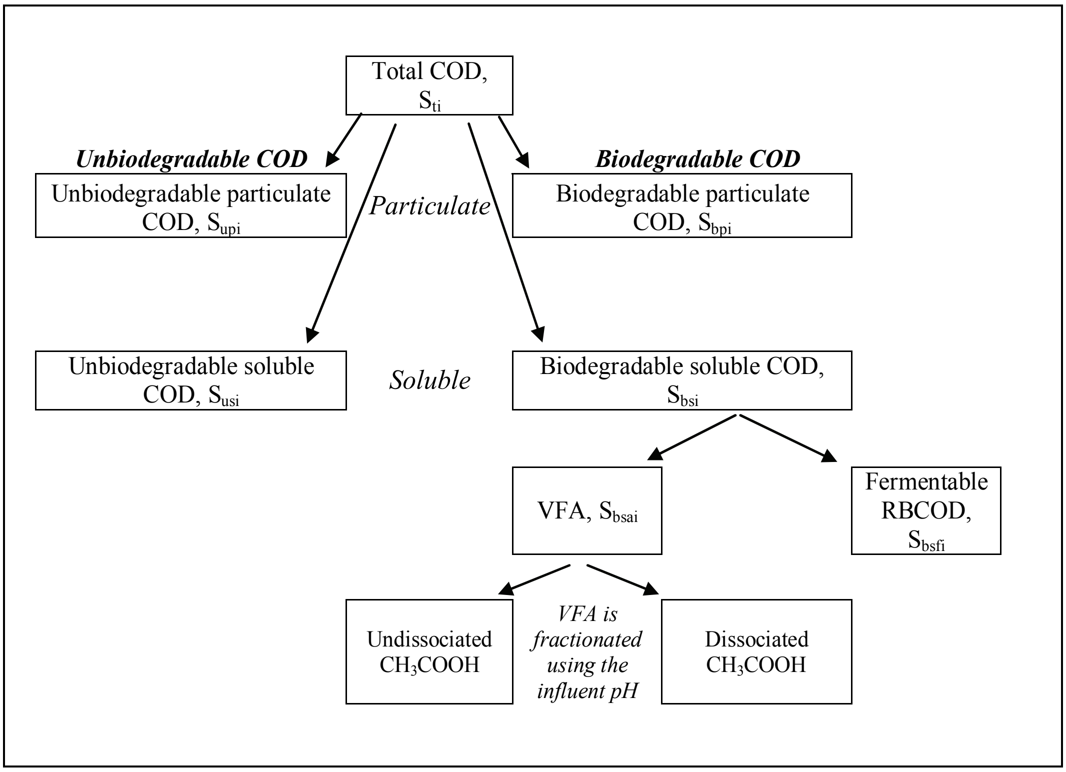

***Figure 2***
*Influent primary sewage sludge COD fractionation for the steady-state anaerobic digestion model for biological sulphate reduction*

The influent PSS COD is characterised in terms of measurable parameters (Fig. 2). The influent parameters are as follows:

- Total influent PSS COD, $S_{ti}$ (mgCOD/ℓ)
- Total soluble COD (membrane filtered), $S_{bsi} + S_{usi}$ (mgCOD/ℓ)
- Volatile fatty acids (VFA), $S_{bsai}$ (mgHAc/ℓ, then converted to mgCOD/ℓ), with the 5 point titration method of Moosbrugger et al. (1992)

With a known (or assumed) value of the unbiodegradable particulate fraction ($f_{PS'up}$) of the influent total PSS COD ($S_{ti}$), the biodegradable particulate COD ($S_{bpi}$) concentration in the influent is defined. The unbiodegradable soluble COD ($S_{usi}$) concentration forms part of the total soluble COD. Since the $S_{usi}$ concentration is very low in relation to the $S_{bsi}$, it can be given an approximate value based on previous research. Usually $S_{usi}$ is about 50 to 75 mgCOD/ℓ in PSS. With the above, the influent PSS COD can be fully characterised (Fig. 2). Knowing $S_{usi}$ and $S_{bsai}$, the fermentable readily biodegradable soluble COD (FRBCOD, $S_{bsfi}$) concentration can be quantified. The $S_{bsfi}$ also undergoes the same hydrolysis/acidogenesis processes as the $S_{bpi}$ and both are converted to VFA and $H_2$ which then get utilised in BSR to generate hydrogen sulphide ($H_2S/HS^-$), bicarbonate ($HCO_3^-$), $NH_4^+$ and biomass.

In contrast, the influent VFA ($S_{bsai}$) is not included in the hydrolysis process but it does generate $H_2S/HS^-$ and $HCO_3^-$ with negligible (assumed zero) biomass production. So, $S_{bsai}$ is included in the stoichiometry part of the steady-state model. The zero sludge production for the utilisation of influent VFA is accepted in the SS model because the yield of acetoclastic sulphidogens is very low compared with that of the acidogens.

Ristow et al. (2005) concluded that the rate of PSS hydrolysis is the same under both methanogenic and sulphidogenic conditions. Since BSR does not affect the rate of PSS hydrolysis, the same hydrolysis kinetics (rate formulations and rate constants) for methanogenic AD can be applied to sulphidogenic AD conditions. As outlined by Sötemann et al. (2005a), the acidogens have the highest yield coefficient ($Y_{AD}$ = 0.089 gCOD biomass/gCOD organics hydrolysed) and constitute more than 77% of the total biomass formed in the AD of hydrolysable organics. By increasing the $Y_{AD}$ value from 0.089 to 0.113, the biomass formation of the other organism groups is taken into account. This adjustment in the $Y_{AD}$ value resulted in similar percentage COD removal predictions and so was also accepted for BSR. The SS model for BSR derived here also uses the COD to quantify the organics and biomass concentrations and the saturation equation for the hydrolysis/acidogenesis rate.

The steady-state anaerobic digester equations for the hydrolysis part of the SS BSR model applied to the UASB system (Fig. 1) were derived and are listed below.

- Hydrolysis rate equation – saturation (Contois) kinetics:

$$r_h\ [\mathrm{gCOD/(\ell.d)}] = \frac{K_{MT}\left(S_{bp}/Z_{BAD}\right)}{[K_{ST} + (S_{bp}/Z_{BAD})]} Z_{BAD} \qquad (1)$$

- Residual biodegradable organics concentration in reactor and waste flow:

$$S_{bp}(\mathrm{gCOD}/\ell) = \frac{S_{bpi}R_s/R_h}{\left\{1 + \frac{[Y_{AD}K_{MT} - (1/R_s + b_{AD})][1 + b_{AD}R_s(1 - Y_{AD}(1 - f_{AD}))]}{Y_{AD}K_{ST}(1/R_s + b_{AD})}\right\}} \qquad (2)$$

- Acidogen biomass concentration in reactor and waste flow:

$$Z_{BAD}(\mathrm{gCOD}/\ell) = \frac{Y_{AD}\left(S_{bpi}R_s/R_h - S_{bp}\right)}{[1 + b_{AD}R_s(1 - Y_{AD}(1 - f_{AD}))]} \qquad (3)$$

- Unbiodegradable organics concentration in reactor and waste flow,

$$S_{up} = S_{upi}R_s/R_h \qquad (4)$$

- The acidogen endogenous residue concentration:

$$Z_{EAD}(\text{gCOD}/\ell) = f_{AD} b_{AD} R_s Z_{BAD} \tag{5}$$

where

$K_{MT}$ = the saturation maximum specific hydrolysis rate constant at T°C
= 5.27 gCOD organics/(gCOD biomass·d) at 35°C
$K_{ST}$ = the half saturation coefficient at T°C
= 7.98 gCOD organics/gCOD biomass at 35°C
$Y_{AD}$ = pseudo acidogen yield coefficient = 0.113 gCOD biomass/gCOD organics hydrolysed
$S_{bpi}$, $S_{bp}$ = Influent and waste flow (bed) COD concentration to and from digester (gCOD/ℓ)
$b_{AD}$ = acidogen endogenous respiration rate
= 0.041 (/d)
$R_s$ = bed solids retention time or sludge age (d)
$R_h$ = hydraulic retention time in the bed volume (d)
$f_{AD}$ = endogenous residue of acidogens (assumed zero)

Equations (2) to (4) are the same as for flow-through AD systems except that the influent particulate COD concentrations ($S_{upi}$ and $S_{bpi}$) are multiplied by $R_s/R_h$ to take account of the bed solids retention effect.

From the hydrolysis kinetics, the COD concentration of the biodegradable particulate organics utilised in the BSR AD ($S_{bpi} R_s/R_h - S_{bp}$) is known. Following the hydrolysis process, the stoichiometry of BSR needs to be established taking into account the utilisation of the influent volatile fatty acids (VFA, undissociated and dissociated, and assumed to be all acetate) which also affect alkalinity generation and hence digester pH.

## Stoichiometry of BSR

By following the generalised procedure of McCarty (1975), the general stoichiometry of BSR with a biodegradable organic compound of composition $C_xH_yO_zN_aP_b$ and generating sludge mass of composition $C_kH_lO_mN_nP_p$ and $CO_2$ gas (i.e. C sufficiency) is given by:

$$\begin{aligned}
&C_xH_yO_zN_aP_b + \frac{\gamma_S}{8}(1-E)SO_4^{2-} + \left(2x-z+a+b(2+f)-E\frac{\gamma_S}{\gamma_B}(2k-m+n+p(2+f)) - \frac{2\gamma_S}{8}(1-E)\right)H_2O \Rightarrow \\
&+\frac{\gamma_S}{8}(1-E)\,H_2S + \left(E\frac{\gamma_S}{\gamma_B}\right)C_kH_lO_mN_nP_p + \left(a-nE\frac{\gamma_S}{\gamma_B}\right)NH_4^+ + f\left(b-pE\frac{\gamma_S}{\gamma_B}\right)H_2PO_4^- + (1-f)\left(b-pE\frac{\gamma_S}{\gamma_B}\right)HPO_4^{2-} \\
&+\left(x-a+b(2-f)-E\frac{\gamma_S}{\gamma_B}(k-n+p(2-f))-\frac{2\gamma_S}{8}(1-E)\right)CO_2 + \left(a-b(2-f)-E\frac{\gamma_S}{\gamma_B}(n-p(2-f))+\frac{2\gamma_S}{8}(1-E)\right)HCO_3^-
\end{aligned} \tag{6}$$

where

$\gamma_S$ = 4x + y - 2z - 3a +5b
= EDC per mole biodegradable organics $C_xH_yO_zN_aP_b$ (7a)
$\gamma_B$ = 4k + l - 2m - 3n+5p = EDC per mole biomass $C_kH_lO_mN_nP_p$ (7b)
EDC = electron donating capacity
$M_S$ = molar mass of organics
12x+y+16z+14a+31b g/mol (7c)
$M_B$ = molar mass of biomass
12k+l+16m+14n+31p g/mol (7d)
$f$ = fraction $H_2PO_4^-$ of the OP species formed (OP= $H_2PO_4^-$ + $HPO_4^{2-}$)
$E$ = the mass of COD exiting the digester as active ($Z_{BAD}$) and endogenous ($Z_{EAD}$) sludge mass per day as a fraction of the mass of biodegradable organics (COD) utilised in the digester per day at steady state (note the unbiodegradable sludge mass is not included because it does not originate from the influent biodegradable organics), i.e. from the COD-based kinetic model:

$$\begin{aligned}
E &= V_d(Z_{BAD} + Z_{EAD})/[R_s(Q_iS_{bpi} - Q_wS_{bp})] \\
&= Y_{AD}(1+f_{AD}b_{AD}R_s)/[1+ b_{AD}R_s(1- Y_{AD}\{1-f_{AD}\})]
\end{aligned} \tag{8}$$

(sludge COD produced/COD utilised)

where

$Z_{BAD}$, $Z_{EAD}$ = COD concentration of the anaerobic biomass and endogenous residue respectively (gCOD/ℓ).
$V_d$ = volume of the digester (ℓ)
= UASB Sludge bed volume (ℓ)
$Q_i$ = influent flow to digester (ℓ/d)
$Q_w$ = bed waste flow from the digester (ℓ/d)

From $\gamma_S$ and $\gamma_B$, the COD of the biodegradable organics and sludge mass (accepting the live biomass and endogenous residue have the same composition) is $8\gamma_S$ and $8\gamma_B$ gCOD/mol respectively. Also, from Ekama (2009), with known values of the COD/VSS ($f_{cv}$), TOC/VSS ($f_c$), OrgN/VSS ($f_n$) and OrgP/VSS ($f_p$) ratios, the elemental composition of the biodegradable organics ($x$, $y$, $z$, $a$ and $b$) can be calculated from Eq. (9), which also applies to the biomass ($k$, $l$, $m$, $n$ and $p$). Accepting $y$ = 7, then:

$$y = 7 \tag{9a}$$

$$z = y/2[(1-f_{cv}/8-8f_c/12-17f_n/14-26f_p/31)/(1+f_{cv}-44f_c/12+10f_n/14-71f_p/31)] \tag{9b}$$

$$x = f_c/12[(y+16z)/(1-f_c-f_n-f_p)] \tag{9c}$$

$$a = f_n/14[(y+16z)/(1-f_c-f_n-f_p)] \tag{9d}$$

$$b = f_p/31[(y+16z)/(1-f_c-f_n-f_p)] \tag{9e}$$

$$f_c = 12x/M_S\,;\ f_h = 1y/M_S\,;\ f_o = 16z/M_S\,;\ f_n = 14a/M_S\,;\ f_p = 31b/M_S\,;\ f_{cv} = 8\,\gamma_S/M_S \tag{9e}$$

where $f_c$, $f_h$, $f_o$, $f_n$, $f_p$ and $f_{cv}$ are the mass fractions of C, H, O, N, P and COD of the organics respectively (9)

Alternatively, if the composition of the biodegradable influent organics ($x$, $y$, $z$, $a$, $b$) and biomass ($k$, $l$, $m$, $n$, $p$) are known, the COD/VSS ($f_{cv}$), TOC/VSS ($f_c$), OrgN/VSS ($f_n$) and OrgP/VSS ($f_p$) ratios of the influent organics and biomass can be calculated from Eq. (10).

$$\begin{aligned}
f_{cv} &= 8[4x+y-2z-3a+5b]/[12x+y+16z+14a+31b]; \\
f_c &= [12x]/[12x+y+16z+14a+31b]; \\
f_n &= [14a]/[12x+y+16z+14a+31b]; \\
f_p &= [31b]/[12x+y+16z+14a+31b]; \\
f_o &= 16/18(1-1/8f_{cv}-8/12f_c-17/14f_n-26/31f_p); \\
f_h &= 2/18(1+f_{cv}-44/12f_c+10/14f_n-71/31f_p)\,; \\
f_{cv} &= 8(4/12f_c+1/1f_h-2/16f_o-3/14f_n+5/31f_p)\,; \\
z &= y/16\,f_o/f_h
\end{aligned} \tag{10}$$

The influent VFA is assumed to be acetate. The split between the undissociated and dissociated acetate (HAc and $Ac^-$ respectively) species is governed by the influent pH and, since the influent pH was always greater than 5.9, almost all the influent VFA was in the dissociated ($Ac^-$) form.

Equation (6) holds also for acetate, both associated (HAc) and undissociated ($Ac^-$) provided the correct composition $x$(=2), $y$(=4 for HAc, =3 $Ac^-$), $z$(=2) and charge (=0 for HAc, =-1 for $Ac^-$) are inserted. Because the yield of sulphidogens is very low, $E = 0$ when applying Eq. (6) to acetate, which yields:

$$CH_3COOH + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \text{ (no biomass but } HCO_3^- \text{ alkalinity generation)} \qquad (11a)$$

$$CH_3COO^- + SO_4^{2-} \rightarrow HS^- + 2HCO_3^- \text{ (no biomass but } HCO_3^- \text{ and } HS^- \text{ alkalinity generation)} \qquad (11b)$$

From Eqs (11a) and (11b) it can be seen that the influent VFA (both undissociated and dissociated) concentration is important for establishing the digester pH because its utilisation makes a significant contribution to the alkalinity generated.

Equation (6) is valid for organics that generate sufficient $CO_2$ for the required alkalinity increase. This will be the case if the $CO_2$ term in Eq. (6) is positive, i.e.

$$x-a+2b(2-f) - E\gamma_S/\gamma_B[k-n+p(2-f)] - 2(1-E)\,\gamma_S/8 > 0$$

Accepting zero biomass production ($E$=0) and negligible organic P content ($b$=0), substituting $4x+y-2z-3a+5b$ for $\gamma_S$ yields $2z>y+a$. So organics with a composition that conforms to $2z>y+a$ are carbon sufficient. Most organics do not conform to this, e.g. the amino acids, alcohols, all of the fatty acids except formic and acetic acids, and PSS. The mono-, di- and polysaccharides and acetic acid conform exactly, i.e. $2z=y$ for $a$=0, but with biomass growth ($E$>0) they also become carbon deficient. The COD/C ratio of these organics is 2.67, so organics with a COD/C ratio>2.67 are C deficient for BSR in the sense that they can donate more electrons for BSR than supply $CO_2$ for the alkalinity increase.

So for most organics, the gaseous $CO_2$ term in Eq. (6) is negative. In this event the sulphide system produces the alkalinity shortfall in the form of $HS^-$. Re-arranging Eq. (6) for C deficiency ($HS^-$ and zero gaseous $CO_2$ production) yields:

$$\begin{aligned}
&C_xH_yO_zN_aP_b + \frac{\gamma_S}{8}(1-E)SO_4^{2-} + \left(3x-z+4b-E\frac{\gamma_S}{\gamma_B}(3k-m+4p) - \frac{4\gamma_S}{8}(1-E)\right)H_2O \Rightarrow \\
&+\left(E\frac{\gamma_S}{\gamma_B}\right)C_kH_lO_mN_nP_p + \left(a-nE\frac{\gamma_S}{\gamma_B}\right)NH_4^+ + f\left(b-pE\frac{\gamma_S}{\gamma_B}\right)H_2PO_4^- + (1-f)\left(b-pE\frac{\gamma_S}{\gamma_B}\right)HPO_4^{2-} + \left(x-kE\frac{\gamma_S}{\gamma_B}\right)HCO_3^- \\
&+\left(x-a+b(2-f)-E\frac{\gamma_S}{\gamma_B}(k-n+p(2-f)) - \frac{\gamma_S}{8}(1-E)\right)H_2S + \left(a-x-b(2-f)+E\frac{\gamma_S}{\gamma_B}(k-n+p(2-f)) + \frac{2\gamma_S}{8}(1-E)\right)HS^- \qquad (12)
\end{aligned}$$

The PSS (which contained negligible P, $f_p$<0.015 gP/gVSS) with its determined composition from this investigation (see below) of $C_{3.35}H_7O_{1.45}N_{0.45}$ is C deficient, so Eq. (12) instead of Eq. (6) applies in this SS BSR model development.

## Mixed weak acid/base chemistry

Once the BSR products are known from the stoichiometry above, the digester pH is predicted using the mixed weak acid/base chemistry. For C deficient systems and low P content PSS, in effect the $H_2S/HS^-$ system with a $pK'_{S1}$ value near 7 establishes the reactor pH because a gaseous $CO_2$ phase is absent, namely:

$$[H^+] = K_{s1}[H_2S]/[HS^-] \qquad (13a)$$

$$pH = -\log(K'_{s1}[H_2S]/[HS^-]) = pK'_{s1} + \log[HS^-] - \log[H_2S] \qquad (13b)$$

where

$K_{s1}$ = first dissociation constant ($H_2S/HS^-$) of the sulphide system (13c)

$pK_{s1}$ = $-\log(K_{S1}) = 7.05$ at 25°C (Lide, 2001)

$pK'_{s1}$ = $pK_{s1}$ adjusted for ionic strength (TDS~4000 mg/ℓ) and temperature = 6.833 at 35°C and 7.014 at 20°C.

The validity of Eq. (13b) to approximate the reactor pH can be shown from the principles of mixed weak acid-base systems (Loewenthal et al., 1989; 1991). For a mixed weak acid/ base system comprising the inorganic carbon, acetic acid, ammonia, phosphate and sulphide systems in water, the total alkalinity with respect to the most protonated species is defined as:

$$\begin{aligned}
\text{Total alk} &= \text{Alk } H_2CO_3^* + \text{Alk HAc} + \text{Alk } H_2S + \text{Alk } NH_4^+ + \text{Alk } H_3PO_4 + \text{Alk } H_2O \\
&= [HCO_3^-] + 2[CO_3^{2-}] + [Ac^-] + [HS^-] + [NH_3] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] + [OH^-] - [H^+] \qquad (14a)
\end{aligned}$$

In Eq. (14a), the nomenclature of Loewenthal et al.(1989) is adopted, i.e. Alk as a prefix refers to the alkalinity with respect to the named reference species **without** the water (+$[OH^-]$ -$[H^+]$) terms, i.e. the alkalinity of only the named weak acid-base system by itself. Alk as a suffix refers to the alkalinity with respect to the named reference species **including** the water terms. For example, $H_2CO_3^*$ alk = Alk $H_2CO_3^*$ + $[OH^-]$ - $[H^+]$.

Assuming the acetic acid is completely utilised so its concentration is too low to affect pH and noting that in the pH range 6.5 to 8, $[CO_3^{2-}]$, $[NH_3]$, $[PO_4^{3-}]$, $[OH^-]$ and $[H^+]$ are negligible compared with $[HCO_3^-]$, $[HS^-]$, $[H_2PO_4^-]$ and $[HPO_4^{2-}]$, the Total alkalinity reduces to:

$$\text{Total alk} = [HCO_3^-] + [HS^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] \qquad (14b)$$

With 6 weak acid-base systems (inorganic carbon, acetic acid, ammonia, phosphate, sulphide and water), 6 parameters need to be known to define all the system species including the pH. From the stoichiometry (Eq. (12)), these 6 knowns are the $[HCO_3^-]$, the Total alk (Eq. (14b)), the total sulphide and OP species concentrations ($S_T = [HS^-] + [H_2S]$, $P_T = [H_2PO_4^-] + [HPO_4^{2-}]$), the acetic acid concentration (assumed zero) and the ammonia concentration (not required in Eq. (14b) – completely protonated between pH 6.5 and 8). Accepting that for PSS the organic P content is very low ($b$≈0), so that the alkalinity generated by the phosphate system is very low in relation to the inorganic carbon alkalinity, the Total alk reduces to:

$$\text{Total alk} = [HCO_3^-] + [HS^-] \qquad (14c)$$

For the sulphide system, from equilibrium chemistry it can be shown that:

$$S_T = [H_2S] + [HS^-] = [HS^-]\,(1+10^{pK'_{s1}-\text{pH}}) \qquad (15)$$

Hence Total alk = $[HCO_3^-] + [HS^-] = [HCO_3^-] + ([H_2S]+[HS^-])/(1+10^{pK'_{s1}-\text{pH}})$ from which Eq. (13b) can be obtained.

For the experimental system fed carbon deficient organics, the 6 parameters which are required to be known are the same 6 parameters as mentioned above, except that the $[HCO_3^-]$ concentration is exchanged for the pH. The reactor *in situ* pH, total sulphide ($S_T$), OP ($P_T$) and ammonia ($N_T$) concentrations are direct measurements; the sulphide is measured with the

COD test (Poinapen et al., 2009b). The $H_2CO_3$* Alk and VFA concentrations are measured with the 5-point titration method of Moosbrugger et al. (1992) using the 4 direct measurements as input.

Interestingly, the Total alk generated is governed only by the composition of the biodegradable organics utilised and the type of bioprocess, e.g. methanogenesis or sulphidogenesis. With methanogenesis, the Total alk generated is a consequence of the difference between the protons taken up or released in the breakdown of the biodegradable organics and the production of biomass. When organic N is present in the biodegradable organics in significant concentrations, effectively in the non-ionised $NH_3$ form, the released $NH_3$ takes up a proton from the aqueous phase to form $NH_4^+$. The $H^+$ is supplied by the dissolved $CO_2$ ($H_2CO_3$*) to form $HCO_3^-$, viz. $H_2CO_3^* + NH_3 \rightarrow NH_4^+ + HCO_3^-$. The Total alk increases because the released $NH_3$ is not reference species for the ammonia system. The $CO_2$ produced by the breakdown of the biodegradable organics that cannot be 'held' in the digester in this way escapes as gas with the methane (which is governed by the COD of the biodegradable organics) and sets the partial pressure of the gas phase. Similarly, when dissociated acetic acid ($Ac^-$) is utilised, a $H^+$ is taken up, viz. $H_2CO_3^* + Ac^- \rightarrow HAc + HCO_3^-$. So the N content of the biodegradable organics and the influent acetic acid concentration and pH, fix the Total alkalinity (≈$[HCO_3^-]$) generated in the digester and partial pressure of the gas phase and hence the pH in the digester. When organic P is present in the biodegradable organics in significant concentrations, effectively in the non-ionised $H_3PO_4$ form, the released $H_3PO_4$ releases protons to the aqueous phase to form $H_2PO_4^-$ and $HPO_4^{2-}$. The released protons ($H^+$) react with $HCO_3^-$ to form dissolved $CO_2$ and water, viz. $HCO_3^- + H^+ \rightarrow H_2CO_3^* \rightarrow H_2O + CO_2$. This decreases the dissolved $CO_2$ that can be 'held' in the digester with the result that more $CO_2$ escapes as gas. This decreases the Alk $H_2CO_3$* ($HCO_3^-$) and increases the $CO_2$ partial pressure of the gas phase, **but the Total alk (= $[HCO_3^-] + [H_2PO_4^-] + 2[HPO_4^{2-}]$) remains constant**. The reason the Total alk remains constant is because the phosphate species released by the organics are reference species ($H_3PO_4$) for the phosphate system. Although the Total alk remains constant, the species making up the Total alk are not the same and now include phosphate system species, so the pH in the digester is now governed by both the inorganic carbon and phosphate systems.

The above also applies to sulphidogenic systems but, additionally, protons are taken up by the sulphate reduction, i.e. in effect $H_2SO_4$ is utilised. This increases the Total alkalinity by so much that not even all of the $CO_2$ produced by the breakdown of the biodegradable (carbon deficient) organics and 'held' in the aqueous phase, is sufficient to supply it. The alkalinity deficit therefore has to be supplied by the other weak acid/base systems to meet the Total alkalinity required. The phosphate system in effect makes more of the $CO_2$ available to form $HCO_3^-$ and the difference between the Total alkalinity required and the sum of the Alk $H_2CO_3$* (= $[HCO_3^-]$) and Alk $H_3PO_4$ (=$[H_2PO_4^-] + 2[HPO_4^{2-}]$) produced has to be supplied by the sulphide system as Alk $H_2S$ (= $[HS^-]$) from $H_2S \rightarrow H^+ + HS^-$. So the Total alkalinity generated is governed only by the composition of the biodegradable organics utilised and the type of bioprocess.

## Steady-state BSR model validation

Figure 3 illustrates the characterisation of the different components of the influent (PSS) and bed waste sludge (WS) and the determination of their respective elemental compositions from the mass fraction ratios ($f_{cv}, f_c, f_n; f_p$ was accepted as zero). The circled notes 1 to 4 marked in Fig. 3 are described below.

### Characterisation of primary sewage sludge (PSS)

***(Unbiodegradable particulate COD fraction (Fig. 3; Note 1):*** In this study, the unbiodegradable particulate fraction ($f_{PS'up}$) of the PSS was set at 0.36. Ristow et al. (2005) and Sötemann et al. (2005a) conducted studies on methanogenic and sulphidogenic anaerobic digestion of PSS at different retention times (sludge ages) between 5 and 60 d and so were able to determine the $f_{PS'up}$ value of PSS. They found that the $f_{PS'up}$ of different batches of PSS collected from the same wastewater treatment plant (WWTP, Athlone, Cape,

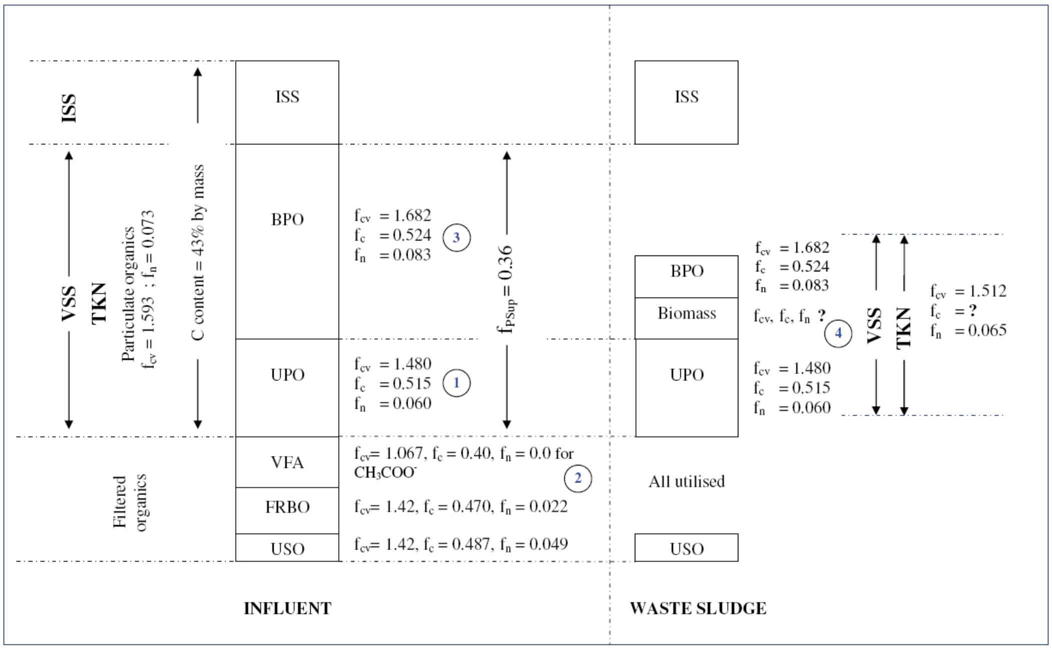

***Figure 3***
*Characterisation of primary sewage sludge (influent) and waste sludge in the development of the steady state model (Notes 1 to 4 are described in the text)*

South Africa) varied from 0.34 to 0.36. The PSS used in this study was obtained from the same WWTP. Because running UASB systems at different sludge ages to determine the $f_{PS'up}$ was beyond the scope of this investigation, the $f_{PS'up}$ value from previous studies was accepted. Accordingly, an $f_{PS'up}$ value of 0.36 was used in the steady-state (SS) BSR model developed in this study.

### *Dissolved organic compounds (USO, FRBO, VFA) (Fig. 3; Note 2):*

The concentration of the unbiodegradable soluble organics (USO) of the PSS was assumed to be 75 mgCOD/ℓ, which is very low with respect to the total PSS COD (~ 50 000 mgCOD/ℓ). The volatile fatty acids (VFA) (and $H_2CO_3$* Alk) concentration was measured using the 5-pH point titration method (Moosbrugger et al., 1992) and the unit mgHAc/ℓ converted to mgCOD/ℓ by multiplying by 64/60. The concentration of the total soluble organic comprising the USO, VFA and fermentable readily-biodegradable organics (FRBO) was measured in the COD test. Thus, by difference the FRBO concentration was calculated. The compositions of the USO and FRBO were determined using $f_{cv}$, $f_c$ and $f_n$ ratios of 1.42, 0.487, 0.049 and 1.42, 0.470, 0.022, respectively, taken from Brink and Ekama (2008), who obtained these $f_c$ and $f_n$ from wastewater characterisation tests using an assumed $f_{cv}$ = 1.42 for both the USO and FRBO fractions. The actual VFA composition ($C_2H_4O_2$ for HAc and $C_2H_3O_2^-$ for $Ac^-$) was used.

### *Biodegradable particulate organics (BPO) composition (Fig. 3; Note 3):*

To determine the composition of the biodegradable particulate organics $C_xH_yO_zN_a$ of the PSS, 4 measurements are required, COD, TKN, VSS and total organic carbon (TOC), because there are 4 unknowns, namely $x$, $y$, $z$ and $a$. The COD, TKN and VSS (and TSS) of the PSS particulate organics (comprising both unbiodegradable (UPO) and biodegradable (BPO) particulate organics were determined with the COD, TKN and VSS/TSS tests, whereas the TOC was obtained from elemental analysis of dried PSS (TSS). The TOC of the influent PSS was found to be ~43% of the total suspended (dried) solids (TSS). From this, the TOC/VSS ratio ($f_c$) of the PSS particulate organics (PO=BPO+UPO) was calculated.

With the accepted $f_{PS'up}$ = 0.36, the UPO concentration was calculated and its composition, i.e. $x$, $y$, $z$ and $a$ in $C_xH_yO_zN_a$, was determined from $f_{cv}$, $f_c$ and $f_n$ values of 1.480, 0.515 and 0.0597, respectively, taken from Wentzel et al. (2006), which conforms to the composition of these organics used in Activated Sludge Model No.1 (ASM1, Henze et al., 1987). A composition of $C_{4.26}H_7O_{2.2}N_{0.42}$ was obtained for UPO. By fractionating the particulate COD concentrations of the PSS using the UPO $f_{cv}$, $f_c$ and $f_n$ values of 1.480, 0.515 and 0.0597, respectively, the biodegradable particulate organics (BPO) of the PSS was found by mass difference between the PO (UPO + BPO) and unbiodegradable (UPO) and $f_{cv}$, $f_c$ and $f_n$ values of 1.682, 0.524, 0.083, respectively, were obtained for the BPO. Accordingly, from these values, the composition of the BPO calculated from Eq. (9) was found to be $C_{3.35}H_7O_{1.45}N_{0.45}$.

## **Characterisation of waste sludge (WS)**

### *WS concentration and composition (Fig. 3; Note 4)*

To characterise the waste sludge (WS), the same principle as above was applied except that the WS comprised: $S_{upi}$ (or UPO) with known concentration (Eq. (4)) and the same composition as the influent UPO; residual biodegradable organics (BPO or $S_{bp}$) with concentration calculated from the hydrolysis kinetic model (Eq. (2)) and with the same composition as the influent BPO ($S_{bpi}$); and biomass with concentration also calculated from the hydrolysis kinetic model (Eq. (3) but with an unknown composition (endogenous residue concentration was assumed zero, $f_{AD}$ = 0). The kinetic model saturation rate values were taken from Sötemann et al. (2005a) with $K_M$ (the maximum specific hydrolysis rate constant) = 5.27 gCOD organics/(gCOD biomass.d) and $K_S$ (the half saturation coefficient) = 7.98 gCOD organics/gCOD biomass, both at T = 35°C. The FRBO and VFA concentrations combined were very low (< 0.8%) with respect to that of the total WS and were thus considered to have all been utilised and therefore zero in the waste sludge.

To determine the biomass composition, 4 measurements are again required (COD, TKN, VSS and TOC). However, in using the TOC value determined from elemental analysis of the WS, it was found that the biomass composition was far out of the normal range obtained from previous studies, in that the oxygen composition ($m$) in the biomass formulation of $C_kH_lO_mN_n$ was < 1.2. This value was considered too low and so the results from the elemental analysis of the waste sludge were not used to determine the biomass composition. Instead, the composition of the biomass was obtained from the measured WS COD/VSS and TKN/VSS ratios and an assumed value for $m$ = 2 in the biomass composition. This assumption makes a small difference to the overall WS composition because the biomass is only a small proportion (<8%) of the total. Adding the concentrations of all the three above waste sludge constituents (residual $S_{bp}$, $S_{upi}$ and biomass) gives the total particulate COD concentration of the waste sludge (and reactor sludge bed). The calculated waste total particulate COD concentration was found to be very close to the measured value; this was expected because the biomass concentration is a very small part (<10%) and indicates the selected hydrolysis kinetic constants and unbiodegradable particulate COD fraction apply to the UASB systems.

Knowing the COD concentrations of the $S_{upi}$ and residual $S_{bp}$ in the WS, their VSS concentrations were calculated from their $f_{cv}$ values of 1.48 and 1.682, respectively, (as determined for the influent). The only $f_{cv}$ ratio still missing and required to obtain the overall (combined) $f_{cv}$ of the total particulate organics in the WS is that of the biomass. For instance, in the case of R1 at 1 500 $mgSO_4^{2-}$/ℓ, the measured waste total particulate COD/VSS ($f_{cv}$) and TKN/VSS ($f_n$) ratios were 1.512 and 0.065 respectively. To match these measured values, the $f_{cv}$ of the biomass was found by iteration so that the combined $f_{cv}$ and $f_n$ equalled to the 1.52 and 0.065 measured. This yielded a biomass $f_{cv}$ of 1.599. Now, from this $f_{cv}$ of 1.599, the $k$ and $n$ values for $l$=7 and $m$=2 in the $C_kH_lO_mN_n$ biomass composition were also determined by iteration and were found to be 5 and 0.55, respectively, giving a biomass composition of $C_5H_7O_2N_{0.55}$, identical to the $C_5H_7O_2N_1$ accepted by Sötemann et al. (2005b) in the UCTADM1 model, except for the N content. This biomass composition gives a TKN/VSS ($f_n$) ratio of 0.072 mgN/mgVSS, compared with 0.124 mgN/mgVSS for $C_5H_7O_2N_1$. A different biomass N content is expected because Sötemann et al. (2005b) assumed the $C_5H_7O_2N_1$ composition from the commonly accepted value for activated sludge. From the residual $S_{bp}$, $S_{upi}$ and biomass individual COD concentrations in the WS, and their respective $f_n$ ratios, the combined $f_n$ ratio of the WS was calculated and found to be 0.063 mgN/mgVSS, very close to the measured value of 0.065 mgN/mgVSS as expected and therefore the $C_5H_7O_2N_{0.55}$ was accepted here. The same principle was applied for UASB R1 fed 1 800 $mgSO_4^{2-}$/ℓ and

UASB R2 (20°C) fed 1 500 mg$SO_4^{2-}$/ℓ. It was found that using the biomass composition of $C_5H_7O_2N_{0.55}$ and biomass $f_{cv}$ ratio of 1.599, the calculated waste sludge $f_{cv}$ and $f_n$ closely matched the measured waste sludge $f_{cv}$ and $f_n$ values of both systems.

As stated above, the saturation (Contois) hydrolysis rate equation and its associated kinetic constants were used in the hydrolysis kinetic part of the steady-state BSR model (and in the dynamic simulation model, UCTADM1-BSR, Poinapen and Ekama, 2010). At 35°C, the saturation maximum specific hydrolysis rate $K_M$ = 5.27 gCOD organics/(gCOD biomass·d) and the half saturation coefficient $K_S$ = 7.98 gCOD organics/gCOD biomass. For UASB reactor R2 operated at 20°C, both $K_M$ and $K_S$ were adjusted for temperature dependency in the steady-state model application. The temperature function $\frac{K_2}{K_1} = \theta^{(T_2 - T_1)}$ was used where $K_1$ and $K_2$ are here the maximum specific hydrolysis rate constants at $T_1$ = 35°C and $T_2$ = 20°C, respectively, and $\theta$ = 1.133. $K_{M20}$ was found to be 0.808 gCOD organics/(gCOD biomass·d) and $K_S$= 1.223 gCOD organics/gCOD biomass.

## SS BSR model application

Once developed and calibrated, the SS BSR model was validated by applying it to the UASB systems operated in this study. Table 1 compares the SS BSR predicted results with the experimental data from the 2 laboratory-scale UASB reactors. Overall the SS model predictions correspond well with the measured data for all 3 systems. The COD removal is lower for the measured data because the UASB effluent contains some particulate COD (since the effluent is not 100% soluble COD) while in the steady-state model this is assumed to be zero. The predicted digester pH values for R1 (1 800 mg$SO_4^{2-}$/ℓ) and R2 correspond very well to the measured values, while for R1 (at 1 500 mg$SO_4^{2-}$/ℓ) it is 0.1 pH unit lower. Though not significant, this pH difference may be ascribed to either minor experimental error in pH measurements or to the composition of the primary sludge. The composition of the influent biodegradable particulate organics (BPO) $C_xH_yO_zN_a$ is calculated from the influent PSS characterisation using the stoichiometric equations and is found to be $C_{3.35}H_7O_{1.45}N_{0.45}$ which differs slightly from that found by Sötemann et al. (2005a) for the primary and humus sludge mixture of Izzett and Ekama (1992), i.e. $C_{3.5}H_7O_2N_{0.196}$ and their own tests on pure PSS, i.e. $C_{3.65}H_7O_{1.97}N_{0.190}$. In fact, with C-deficient substrates for BSR, as PSS is, it is possible to calculate the C released from the utilised biodegradable organics from the C content of the $HCO_3^-$ concentration, which is known from the $H_2CO_3$* alkalinity, because no $CO_2$ gas is generated by the system (Eq. (12) and the C in the biomass generated is small. For R1 (1 500 mg$SO_4^{2-}$/ℓ), R1 (1 800 mg$SO_4^{2-}$/ℓ) and R2, the C released in the utilisation

**Table 1**
**Comparison of experimentally measured (M) values with SS BSR model predictions (P)**

| **Parameter** | **R1 (35°C)** (1 500 mg$SO_4^{2-}$/ℓ) | | **R1 (35°C)** (1 800 mg$SO_4^{2-}$/ℓ) | | **R2 (20°C)**[4] (1 500 mg$SO_4^{2-}$/ℓ) | |
|---|---|---|---|---|---|---|
| Influent total COD (mgCOD/ℓ) | 1 880 | | 2 584 | | 2 596 | |
| Influent unbiodegradable particulate COD[1] ($f_{PS'up}$ = 0.36) (mgCOD/ℓ) | 677 | | 930 | | 935 | |
| Influent VFA (mgCOD/ℓ) | 126 | | 164 | | 169 | |
| Influent fermentable readily biodegradable COD (mgCOD/ℓ) | 104 | | 108 | | 155 | |
| Influent slowly biodegradable COD (mgCOD/ℓ) | 967 | | 1 374 | | 1 330 | |
| Influent unbiodegradable soluble (mgCOD/ℓ) | 6 | | 8 | | 8 | |
| Influent TKN/FSA (mgN/ℓ) | 82/6 | | 109/10 | | 113/11 | |
| Reactor bed/liquid volume ratio | 6.7/7.8 | | 7.1/7.8 | | 7.4/7.8 | |
| Influent flow rate, $Q_i$ (ℓ/d) | 13.8 | | 10.1 | | 9.2 | |
| Sludge age, $R_s$ (d), HRT (d) | 18, 0.57 | | 21, 0.77 | | 24, 0.85 | |
| E (sludge COD produced/COD utilised) | 0.0680 | | 0.0641 | | 0.0602 | |
| | **M** | **P** | **M** | **P** | **M** | **P** |
| COD removal (mgCOD/ℓ) | 1 691 | 1 638 | 2 153 | 2 199 | 2 309 | 2 301 |
| Sulphate removal (mg $SO_4^{2-}$/ℓ) | 1 351 | 1 326 | 1 654 | 1 637 | 1 399 | 1 387 |
| Effluent alkalinity ($H_2CO_3$* alk + Alk $H_2S$) (mg/ℓ as $CaCO_3$) | 1 938 | 2 049 | 1 855 | 1 981 | 1 552 | 1 688 |
| Effluent $H_2CO_3$* alk (mg/ℓ as $CaCO_3$) | 1 611 | 1 599 | 1 359 | 1 453 | 1 144 | 1 249 |
| Effluent $H_2S$ (mgS/ℓ)[2] | 101[3] | 173 | 184 | 210 | 166 | 181 |
| Effluent $HS^-$ (mgS/ℓ)[2] | 209[3] | 269 | 318 | 336 | 261 | 281 |
| Effluent TKN (mgN/ℓ) | 52 | 51 | 58 | 60 | 63 | 73 |
| FSA | 32 | 46 | 46 | 55 | 38 | 47 |
| Mass balances (%) - COD | 88.7[3] | 100 | 96.5 | 100 | 96.1 | 100 |
| - S | 68.7[3] | 100 | 95.8 | 100 | 95.9 | 100 |
| - N | 97.1 | 100 | 97.3 | 100 | 104.5 | 100 |
| - C | 98.5 | 100 | 94.0 | 100 | 91.6 | 100 |
| Effluent pH | 7.15 | 7.05 | 7.08 | 7.04 | 7.21 | 7.20 |

**1**: *$f_{cv}$, $f_c$, $f_n$ of unbiodegradable particulate organics (UPO) in the influent PSS and waste sludge = 1.480, 0.515, 0.0597, respectively.*

**2**: *Effluent $H_2S/HS^-$ determined via filtered COD test before and after ZnS precipitation.*

**3.** *Loss of $H_2S$ in analytical procedures particularly during vacuum filtration. Speciation of $HS^-/H_2S$ is based on pH 7.6 and total sulphide 310 mgS/ℓ after vacuum filtration. Procedure was corrected by vacuum filtering at pH≥10 which fixed the S-balance to approximately 100%.*

**4**. *$K_M$ and $K_S$ were adjusted for temperature. $K_{M20}$=0.808 and $K_{S20}$=1.223 with $\Theta$=1.133.*

of BPO, VFA and FRBO was 283, 349 and 300 mgC/ℓ, respectively, and the C in the $H_2CO_3$ Alk measured was 279, 326 and 275 mgC/ℓ respectively. This validates the C content of the biodegradable organics and established the C balance over the 3 systems, i.e. 98.5%, 94.0% and 91.6%. In addition, the good correlation between the measured and steady-state results suggests that the assumption of a completely mixed digester for the UASB reactor bed is valid and reasonable. This was made possible because of the introduction of the sludge recycle line from the top to the bottom of the reactor.

## Conclusions

A steady-state AD model for BSR using PSS as carbon source and electron donor has been developed. The model comprises 3 sequential parts: a COD-based hydrolysis kinetics part, a C,H,O,N,P,S, COD and charge mass balanced stoichiometry part and a mixed weak acid/base chemistry part. The hydrolysis kinetics of PSS were taken from Ristow et al. (2005) and Sötemann et al. (2005a) since they concluded that this is the same for both sulphidogenic and methanogenic systems. From the stoichiometry, it was found that the PSS is carbon limited in that it does not generate sufficient $HCO_3^-$ alkalinity for the sulphate reduction, i.e. its COD/C ratio is too high (>2.67), which accounts for the observed zero gas ($CO_2$) generation. As a result, the $H_2S/HS^-$ system provides the alkalinity shortfall, establishes the system pH and allows the C released in the utilisation of the biodegradable organics to be accounted for in the C of the $H_2CO_3$* alkalinity ($HCO_3^-$) generated. Once developed and calibrated, the model results were compared with experimental data from 2 laboratory-scale UASB reactors (operated at 35°C and 20°C, respectively) fed PSS and sulphate. The model-predicted results, including pH, correlate very well with the experimental results. This provides support for:

- The PSS hydrolysis rate determined by Ristow et al. (2005) and Sötemann et al. (2005a)
- The developed BSR stoichiometry which gives considerable insight into the inter-relationships between the biological processes and weak acid/base chemistry systems
- The method of characterising the organics via the $f_{cv}$, $f_c$, $f_n$ and $f_p$ ratios for sulphidogenic and methanogenic AD systems.

The SS BSR model also provides a basis for crosschecking the results of an integrated 2-phase (aqueous-gas) mixed weak acid/base chemistry and biological processes simulation model for BSR which is presented in the last paper of this series (Poinapen and Ekama, 2010).

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## References

BRINK IC and EKAMA GA (2008) Measurement of composition of organic constituents of municipal wastewater for plant wide modelling. Research Report No. W131, Department of Civil Engineering, University of Cape Town.

EKAMA GA (2009) Using bioprocess stoichiometry to build a plant wide mass balanced based steady state WWTP model. *Water Res.* **43** (8) 2010-2120.

HENZE M, GRADY CPL (Jnr), GUJER W, MARAIS GvR and MATSUO T (1987) *Activated Sludge Model No. 1.* IWA Scientific and Technical Report No. 1. IWA, London.

IZZETT HB and EKAMA GA (1992) The effect of thermophilic heat treatment on the anaerobic digestibility of primary sludge. Research Report No. W76, Department of Civil Engineering, University of Cape Town. LIDE D (2001) *CRC Handbook of Chemistry and Physics* ($82^{nd}$ edn.). CRC Press, Boca Raton, FL.

LOEWENTHAL RE, EKAMA GA and MARAIS GVR (1989) Mixed weak acid/base systems – Part 1: Mixture characterisation. *Water SA* **15** (1) 3-24.

LOEWENTHAL RE, WENTZEL MC, EKAMA GA and MARAIS GVR (1991) Mixed weak acid/base systems – Part II: Dosing estimation, aqueous phase. *Water SA* **17** (2) 107-122.

McCARTY PL (1975) Stoichiometry of biological reactions. *Prog. Water Tech*. **7** (1) 157-172.

MOOSBRUGGER RE, WENTZEL MC, EKAMA GA and MARAIS GvR (1992) Simple Titration Procedures to Determine $H_2CO_3$* Alkalinity and Short Chain Fatty Acid Concentrations in Aqueous Solutions Containing Known Concentrations of Ammonium, Phosphate and Sulphide Weak Acids/Bases. WRC Report No. TT 57/92. Water Research Commission, Pretoria, South Africa.

POINAPEN J, EKAMA GA and WENTZEL MC (2009) Biological sulphate reduction with primary sewage sludge in an upflow anaerobic sludge bed reactor – Part 3: Performance at 20°C and 35°C. *Water SA* **35** (5) 543-552.

POINAPEN J and EKAMA GA (2010) Biological sulphate reduction with primary sewage sludge in an upflow anaerobic sludge bed reactor – Part 6: Dynamic Model. *Water SA* **36** (3) 203-214.

RISTOW NE, SÖTEMANN SW, LOEWENTHAL RE, WENTZEL MC and EKAMA GA (2005) Hydrolysis of Primary Sewage Sludge under Methanogenic, Acidogenic and Sulphate Reducing Conditions. WRC Report No. 1216/1/05. Water Research Commission, Pretoria, South Africa.

ROSE PD, CORBETT CJ, WHITTINGTON-JONES K and HART OO (2002) The Rhodes BioSURE® Process Part 1: Biodesalination of Mine Drainage Wastewaters, WRC Report No. TT 195/02. Water Research Commission, Pretoria, South Africa..

SÖTEMANN SW, RISTOW NE, WENTZEL MC and EKAMA GA (2005a) A steady state model for anaerobic digestion of sewage sludges. *Water SA* **31** (4) 511-527.

SÖTEMANN SW, VAN RENSBURG P, RISTOW NE, WENTZEL MC, LOEWENTHAL RE and EKAMA GA (2005b) Integrated chemical, physical and biological processes modelling – Part 2: anaerobic digestion of sewage sludges. *Water SA* **31** (4) 545-568.

WENTZEL MC, EKAMA GA and SÖTEMANN SW (2006) Mass balance-based plant-wide wastewater treatment plant models – Part 1: Biodegradability of wastewater organics under anaerobic conditions. *Water SA* **32** (3) 269-276.