Using bioprocess stoichiometry to build a plant-wide mass balance based steady-state WWTP model

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ABSTRACT

Steady-state models are useful for design of wastewater treatment plants (WWTPs) because they allow reactor sizes and interconnecting flows to be simply determined from explicit equations in terms of unit operation performance criteria. Once the overall WWTP scheme is established and the main system defining parameters of the individual unit operations estimated, dynamic models can be applied to the connected unit operations to refine their design and evaluate their performance under dynamic flow and load conditions. To model anaerobic digestion (AD) within plant-wide WWTP models, not only COD and nitrogen (N) but also carbon (C) fluxes entering the AD need to be defined. Current plant-wide models, like benchmark simulation model No 2 (BSM2), impose a C flux at the AD influent. In this paper, the COD and N mass balance steady-state models of activated sludge (AS) organics degradation, nitrification and denitrification (ND) and anaerobic (AD) and aerobic (AerD) digestion of wastewater sludge are extended and linked with bioprocess transformation stoichiometry to form C, H, O, N, chemical oxygen demand (COD) and charge mass balance based models so that also C (and H and O) can be tracked through the whole WWTP. By assigning a stoichiometric composition (x, y, z and a in $C_xH_yO_zN_a$) to each of the five main influent wastewater organic fractions and ammonia, these, and the products generated from them via the biological processes, are tracked through the WWTP. The model is applied to two theoretical case study WWTPs treating the same raw wastewater (WW) to the same final sludge residual biodegradable COD. It is demonstrated that much useful information can be generated with the relatively simple steady-state models to aid WWTP layout design and track the different products exiting the WWTP via the solid, liquid and gas streams, such as aerobic versus anaerobic digestion of waste activated sludge, N loads in recycle streams, methane production for energy recovery and green

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house gas (CO_2, CH_4) generation. To reduce trial and error usage of WWTP simulation software, it is recommended that they are extended to include pre-processors based on mass balance steady-state models to assist with WWTP layout design, unit operation selection, reactor sizing, option evaluation and comparison and wastewater characterization before dynamic simulation.

1. Introduction

Recently research attention has been devoted to linking dynamic models for activated sludge (AS) and anaerobic digestion (AD) to develop plant-wide wastewater treatment plant (WWTP) models (Jeppsson et al., 2006). In such models, the outputs of one unit operation become inputs to the next down stream one. However, the output compounds (components) of the source model, e.g. Activated Sludge Model No1 (ASM1, Henze et al., 1987), are not compatible with the input compounds of the destination model, e.g. Anaerobic Digestion Model No. 1 (ADM1, Batstone et al., 2002) (Volcke et al., 2006). Two basic approaches have been proposed to resolve this: (i) develop mass balance based compound transformation interfaces which map one set of compounds (outputs) onto another set of compounds (inputs)—the continuity based interface method or CBIM approach (Volcke et al., 2006), (ii) define all the compounds required in the entire WWTP and model the changes in these through each unit operation—the "super-model approach" of Jones and Takács (2004) and Seco et al. (2004), both cited in Grau et al. (2007); and (iii) the approach of Grau et al. (2007), which is a combination of the CBIM and super-model approaches. All three approaches require the definition of the composition of the state-variables (compounds) in either relative molar composition x, y, z, a and b values in $C_xH_yO_zN_aP_b$ as per Sötemann et al. (2005a) or as elemental mass fractions (g C, H, O, N and P/g compound) as per Volcke et al. (2006) because AD influent carbon fluxes are required to predict its gas production and composition. The organics composition in these forms require elemental data, in particular carbon data, which are not commonly measured at WWTPs, with the result that case studies used to describe the modelling approaches (e.g. Jeppsson et al., 2006; Volcke et al., 2006; Zaher et al., 2007) have used assumed compositions for the different organics.

Irrespective of the approach, plant-wide dynamic models are large, complex and require significant modelling skills, experience and understanding to master and use effectively. Dynamic models comprise differential equations of many bioprocesses that require numerical integration for solution and so demand much input information because each of the bioprocesses has several kinetic constants that need to be defined (Fig. 1). In contrast, in steady-state models, many of the bioprocesses are assumed to reach completion, e.g. utilization of influent biodegradable organics, which reduce these bioprocesses to ones of stoichiometry only, while other bioprocesses which do not reach completion, are either simplified, such as ordinary heterotrophic organism (OHO) death regeneration to endogenous respiration, or retained because they are the slowest and so govern the sizing of the system,

such as nitrification for the activated sludge system. The steady-state models therefore have the advantage that they demand much less input information. Also, their equations, which link system design parameters (such as sludge age) to system performance (such as effluent quality), are algebraic and so give explicit solutions. This makes steady-state models very useful for determining WWTP size for specified capacity (design) or WWTP capacity for specified size (operation).

Dynamic models are not compatible with design and operation because they require all the influent characteristics, reactor sizes, inter-connecting flows and the initial reactor concentrations to be quantitatively defined before simulation. In contrast, the explicit equations linking influent characteristics to unit operation performance of steady-state models allow (i) reactor sizes and interconnecting flows to be directly calculated from influent characteristics (design) or (ii) reactor concentrations and influent characteristics to be calculated from known reactor volumes and system performance (operation). Because steady-state models use the same bioprocesses as dynamic models, but in much simpler ways, their solutions closely match dynamic model outputs (Sötemann et al., 2005a, 2006). Steady-state models therefore can enhance, simplify and increase the reliable use of dynamic models if they are incorporated as pre-processors to generate the required input information for the dynamic models. Steady-state models of WWTP unit operations are therefore a very useful complement to the dynamic simulation ones (Fig. 1).

With steady-state models one can (i) estimate reasonably simply and quickly the principal system design and operating parameters, such as sludge age, reactor volume, unaerated (anaerobic and/or anoxic) mass fractions, recycle ratios and oxygen requirement, aerobic or anaerobic digester retention time and gas production from system performance criteria specified for the design, such as effluent and sludge quality, (ii) estimate reactor concentrations and influent characteristics from existing plant data, (iii) investigate the sensitivity of the system performance to parameters that most affect the system, i.e. the influent characteristics unbiodegradable particulate organic (UPO) fraction, maximum specific growth rate of nitrifiers (μ_{A20}) and readily biodegradable soluble organics (BSO) fraction and design and operation parameters, i.e. sludge age, (iv) estimate product stream concentrations for design of down- (or up-) stream unit operations of the WWTP and (v) very importantly, provide a basis for cross-checking dynamic model output results. In fact, all the preparatory work recommended by the IWA Good Modelling Practice Task Group (Gillot et al., 2008) for applying dynamic models to existing WWTPs does not require dynamic models and can be done with steady-state models such as checking water (flow), COD, N and total phosphorus (TP) balances and estimating the

Nomenclature

a	nitrogen content of organics, mol N/mol
b	phosphorus content of organics, mol P/mol
b_A	ANO endogenous respiration rate; additional subscript T and 20 denotes rate at T and 20 °C, /d
b_{AD}	anaerobic (acidogen) biomass endogenous respiration rate, /d
b_H	OHO endogenous respiration rate; additional subscript T and 20 denotes rate at T and 20 °C, /d
d	day
E	fraction of influent biodegradable organics COD utilized/d harvested as sludge mass, COD/d
f_{AD}	Anaerobic (acidogen) biomass unbiodegradable fraction, –
$f_{Sb's}$	fraction of influent biodegradable COD that is soluble , g COD/g COD
f_c	Carbon content of organics, g C/g
f_{cv}	COD content of organics, g COD/g
f_{EA}	autotrophic nitrifier unbiodegradable fraction, –
f_{EH}	OHO unbiodegradable fraction, –
f_H	Hydrogen content of organics, g H/g
f_N	Nitrogen content of organics, g N/g
$f_{Nb'a}$	fraction of influent TKN that is ammonia, g N/g N
$f_{N'us}$	fraction of influent TKN that is unbiodegradable and soluble, g N/g N
f_O	Oxygen content of organics, g O/g
f_P	Phosphorus content of organics, g P/g
$f_{PN'up}$	unbiodegradable particulate TKN fraction of primary sludge, g COD/g COD
$f_{PS'up}$	unbiodegradable particulate COD fraction of primary sludge, g COD/g COD
$f_{S'up}$	fraction of influent COD that is unbiodegradable and particulate, g COD/g COD
$f_{S'us}$	fraction of influent COD that is unbiodegradable and soluble, g COD/g COD
K_m	Monod maximum particulate biodegradable substrate hydrolysis rate in AD, g COD/g COD/d
K_n	Monod half saturation concentration for ANOs; additional subscript T and 20 denotes rate at T and 20 °C, mg N/l
K_s	Monod half saturation concentration for particulate biodegradable substrate hydrolysis rate in AD, g COD/l
K_1	Specific denitrification rate by OHO utilizing BSO in the primary anoxic reactor; additional subscript T and 20 denotes rate at T and 20 °C, mg NO$_3$-N/mg OHOVSS/d
K_2	Specific denitrification rate by OHO utilizing BPO in the primary anoxic reactor; additional subscript T and 20 denotes rate at T and 20 °C, mg NO$_3$-N/mg OHOVSS/d
K_3	Specific denitrification rates by OHO utilizing BPO in the secondary anoxic reactor; additional subscript T and 20 denotes rate at T and 20 °C, mg NO$_3$-N/mg OHOVSS/d
k	carbon content of sludge mass, mol C/mol
l	hydrogen content of sludge mass, mol H/mol
m	oxygen content of sludge mass, mol O/mol
M_B	molar mass of biomass, g/mol
M_S	molar mass of organics, g/mol
n	nitrogen content of sludge mass, mol N/mol
N_{ae}	effluent ammonia concentration, mg N/l
N_{ai}	influent ammonia concentration, mg N/l
N_{obpi}	influent biodegradable particulate organic N concentration, mg N/l
N_{obsi}	influent biodegradable soluble organic N concentration, mg N/l
N_{oupi}	influent unbiodegradable particulate organic N concentration, mg N/l
N_{ousi}	influent unbiodegradable soluble organic N concentration, mg N/l
N_{ti}	influent TKN concentration, mg N/l
p	phosphorus content of sludge mass, mol P/mol
Q_i	influent flow, l/d
R_s	sludge age, d
S_{be}	effluent biodegradable COD concentration, mg COD/l
S_{bi}	influent biodegradable COD concentration, mg COD/l
S_{bpi}	influent biodegradable particulate COD concentration, mg COD/l
S_{bsi}	influent biodegradable soluble COD concentration, mg COD/l
S_{upi}	influent unbiodegradable particulate COD concentration, mg COD/l
S_{usi}	influent unbiodegradable soluble COD concentration, mg COD/l
V_d	volume of digester, l
V_r	volume of activated sludge reactor, l
x	carbon content of organics, mol C/mol
X_{BA}	autotrophic nitrifier organism (ANO) concentration, mg COD/l
X_{BAD}	anaerobic (acidogen) active biomass concentration, mg COD/l
X_{BH}	ordinary heterotrophic organism (OHO) concentration, mg COD/l
X_{EA}	ANO endogenous residue concentration, mg COD/l
X_{EAD}	anaerobic (acidogen) endogenous residue concentration, mg COD/l
X_{EH}	OHO endogenous residue concentration, mg COD/l
y	hydrogen content of organics, mol H/mol
Y_A	ANO yield coefficient, mg COD/mg COD
Y_{AD}	anaerobic (acidogen) biomass yield coefficient, mg COD/mg COD
Y_H	OHO yield coefficient, mg COD/mg COD
z	oxygen content of organics, mol O/mol
α^C	carbon content of organics, g C/g
α^{COD}	COD content of organics, g COD/g
α^H	hydrogen content of organics, g H/g
α^N	nitrogen content of organics, g N/g
α^O	oxygen content of organics, g O/g
α^P	phosphorus content of organics, g P/g
γ_B	electron donating capacity of biomass with respect to CO_2, H_2O and ammonia (i.e. COD), e-eq/mol

γ_S	electron donating capacity of organics with respect to CO_2, H_2O and ammonia (i.e. COD), e-eq/mol	μ_{A20}	maximum specific growth rate of ANOs; additional subscript T and 20 denotes rate at T and 20 °C, /d

influent wastewater characteristics, in particular the influent unbiodegradable particulate organic (UPO) fraction, to match sludge production and oxygen demand. For design, once the overall WWTP scheme is established and the main system defining parameters of the individual unit operations are estimated, and for operation, once the major sources of plant data error have been eliminated, dynamic models can be applied to the connected unit operations to refine their design and evaluate their performance under dynamic flow and load conditions. Accordingly, not only dynamic simulation but also steady-state WWTP models need to be developed.

While steady-state models require similar process knowledge as dynamic models, the level of detail required is significantly different. Being more accessible (can be programmed into spreadsheets), steady-state models make explicit the calculation steps, and hence knowledge gaps. In fact, if the basics cannot be managed with the "hand" calculation steady-state models, it is best not to use dynamic models. If dynamic models are used to cover gaps in knowledge and understanding (which they often are), a range of knobs, switches and buttons (like kinetic constants) will be twiddled that can lead to serious error (like me with a flight simulator, where I have at least 10 times as many take-offs as landings!). Dynamic models always demand more information than available and prompt more questions than can be answered. So they drive users too quickly to try and answer questions at too a low level of detail and supply information that is often irrelevant when determining size for design or capacity for operation. The main problem of using dynamic models in WWTP simulation is to keep the main problem the main problem. Inexperienced users of dynamic models too quickly get their attention diverted away from the main problem. Steady-state models help keep in focus the high level

decisions and the main drivers for WWTP size in design or capacity in operation (Henze et al., 2008, p. 81).

For both steady-state and dynamic plant-wide models, Wentzel et al. (2006), Ekama et al. (2006a,b) and Sötemann et al. (2006) took the view that if one is going to impose carbon fluxes at the AD influent to model it within a WWTP (as is done in the BSM2 plant-wide model and the CBIM approach to link ASM1 and ADM1), one may as well impose the carbon fluxes in the WWTP influent and track the carbon (and H, O, N, P, COD and charge) through all the unit operations of the WWTP including the AD. However, to do this requires C, H, O, N, (and P), COD and charge mass balanced stoichiometry for all the bioprocesses in the WWTP, not only the AD.

Current steady-state models of WWTP unit operations (except AD) are based on COD, N and P mass balances and exclude C, H and O mass balances. In this paper, to complement the dynamic plant-wide modelling software, the existing COD and N mass balanced kinetic steady-state AS and AerD ND models (WRC, 1984; Henze et al., 2008) are extended with elemental mass balance stoichiometry like the steady-state AD model. The steady-state model for AD comprises three parts (Fig. 2): (i) A COD based kinetic part which links the biodegradable organics (COD) concentration removed and methane (COD) production to the digester sludge age, (ii) a stoichiometry part which transforms the biodegradable COD removed and its C, H, O and N composition (reactant) to AD biomass, gaseous CO_2, ammonia, methane and dissolved CO_2 (HCO_3^- ≈ alkalinity) (products) and (iii) an inorganic carbon weak acid/base chemistry part from which the digester pH is calculated from the partial pressure of CO_2 and alkalinity generated (Sötemann et al., 2005a). To develop the stoichiometric parts for the other WWTP unit operations, the same approach, which is essentially a C, H, O, N, P and charge
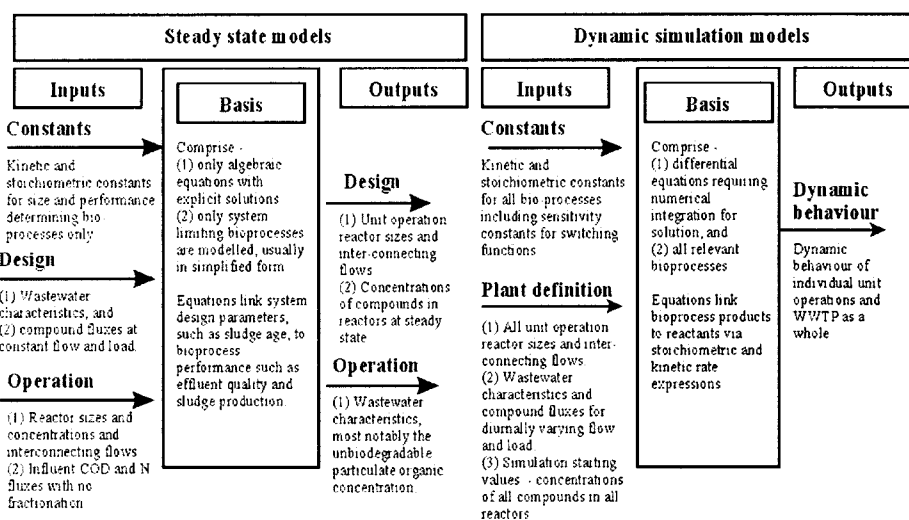

Fig. 1 – Inputs, basis and outputs of steady-state (left) and dynamic models (right) showing that steady-state models can conveniently and accurately generate the input for dynamic simulation software.
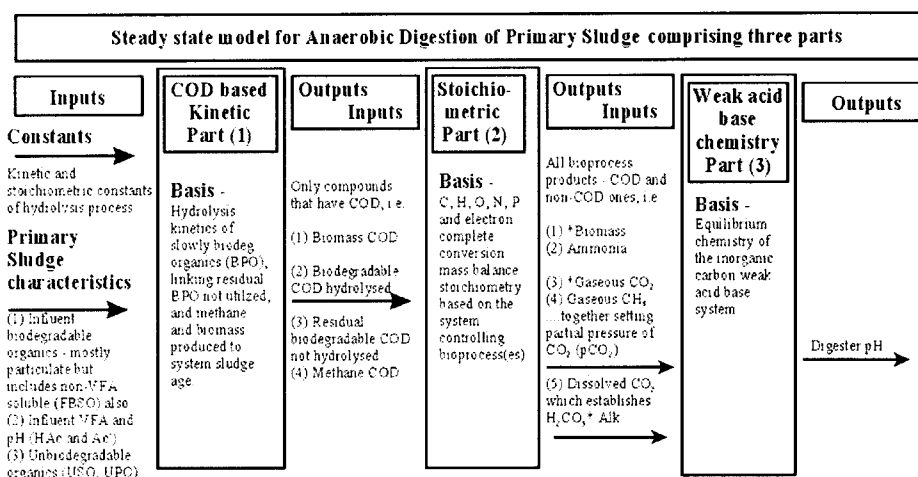
Fig. 2 – Steady-state model for anaerobic digestion of primary sludge showing its three constituent parts: A COD mass balanced kinetic part (Part 1), from which is calculated the biodegradable COD hydrolysed and utilized, an element and electron mass balance stoichiometric part (Part 2), from which all the bioprocess products are calculated, including the non-COD ones from the biodegradable COD utilized, and a weak acid based chemistry part (Part 3), from which the digester pH is calculated from the products of the stoichiometric part.

balance, will be applied to activated sludge (AS) and aerobic digestion (AerD) of waste activated sludge (WAS), both with nitrification and denitrification (ND). For the aerobic and anoxic–aerobic systems, the weak acid base chemistry part (Part 3) cannot be used to calculate the reactor pH because the partial pressure of CO_2 in the liquid phase is not in equilibrium with the head-space (atmosphere)—it is usually supersaturated by an unknown amount (Sötemann et al., 2005b). However, it can used to calculate the alkalinity change and so establish whether or not chemical dosing is required to keep the alkalinity above 40 mg/l as $CaCO_3$ which usually keeps the pH above 7 (WRC, 1984).

By assigning a stoichiometric composition, either with x, y, z, a and b values in $C_xH_yO_zN_aP_b$ or with f_C, f_H, f_O, f_N, f_P, f_{cv} mass fractions (g element/g compound) to each of the five main influent wastewater organic fractions, i.e. (i) influent volatile fatty acids (VFA, assumed to be acetic acid), (ii) fermentable readily biodegradable soluble organics (F-BSO), (iii) unbiodegradable soluble organics (USO), (iv) slowly biodegradable particulate organics (BPO) and (v) unbiodegradable particulate organics (UPO), the influent free and saline ammonia (FSA) and the activated sludge (AS) and anaerobic digester (AD) biomass, these, and the products generated from them via the biological processes, are tracked through the WWTP. This approach is feasible because Ekama et al. (2006b) showed that the influent and endogenously generated unbiodegradable particulate organics, as defined by aerobic (AS) conditions are also unbiodegradable under anaerobic (AD) conditions. This simplifies the steady-state and dynamic models (and has been assumed to be true in the plant-wide models developed to

date, Jeppsson et al., 2006; Volcke et al., 2006), because it allows calculation of the unbiodegradable particulate fraction of (i) the primary sludge (PS) from the wastewater character-istics of the raw and settled wastewater and compound mass balances around the primary settling tank (PST) and (ii) of the waste activated sludge (WAS) from the ordinary heterotrophic organism (OHO) active fraction.

2. Stoichiometry of WWTP biological processes

2.1. Stoichiometry of anaerobic digestion

The stoichiometry of AD derived by Sötemann et al. (2005a) was based on a defined biomass composition of $CH_{1.4}O_{0.4}N_{0.2}$ ($C_5H_7O_2N$). Accepting instead a variable biomass composition, i.e. $C_kH_lO_mN_n$ and adding P, this stoichiometry becomes,

$$C_xH_yO_zN_aP_b + \left(2x - z + a + 3b - E\frac{\gamma_S}{\gamma_B}(2k - m + n + 3p)\right.$$
$$\left. - \frac{2\,\gamma_S}{8}(1 - E)\right) H_2O \Rightarrow \left(x - a + b - E\frac{\gamma_S}{\gamma_B}(k - n + p)\right.$$
$$\left. - \frac{(1 - E)D_S}{8}\right) CO_2 + \left(\frac{\gamma_S}{8}(1 - E)\right) CH_4 + \left(E\frac{\gamma_S}{\gamma_B}\right) C_kH_lO_mN_nP_p$$
$$+ \left(a - nE\frac{\gamma_S}{\gamma_B}\right)NH_4^+ + \left(b - pE\frac{\gamma_S}{\gamma_B}\right)H_2PO_4^-$$
$$+ \left(a - b - E\frac{\gamma_S}{\gamma_B}(n - p)\right)HCO_3^- \tag{1}$$

where

$\gamma_S = 4x + y - 2z - 3a + 5b$ = electrons per mole biodegradable organics $C_xH_yO_zN_aP_b$ with respect to CO_2, H_2O and ammonia (i.e. COD)

$$\tag{2a}$$

$\gamma_B = 4k + l - 2m - 3n + 5p$ = electrons per mole biomass $C_kH_lO_mN_nP_p$ with respect to CO_2, H_2O and ammonia (i.e. COD)   (2b)

M_S = molar mass of organics $12x + y + 16z + 14a$
$\qquad + 31b$ g/mol   (2c)

M_B = molar mass of biomass $12k + l + 16m + 14n$
$\qquad + 31p$ g/mol   (2d)

$f_C = 12x/M_S$; $f_H = 1y/M_S$; $f_O = 16z/M_S$; $f_N = 14a/M_S$;
$f_P = 31b/M_S$; $f_{cv} = 8\gamma_S/M_S$ (2e)

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.

E = mass of COD exiting the AD as active and endogenous sludge mass per day as a fraction of the mass of biodegradable organics (COD) utilized in the digester per day at steady-state (note the unbiodegradable sludge mass from the influent is not included because it is not a product from the utilization of influent biodegradable organics), i.e.

$$E = \frac{V_d (X_{BAD} + X_{EAD})}{Q_i (S_{bi} - S_{be})R_s}$$

$$= \frac{Y_{AD} (1 + f_{AD} b_{AD} R_s)}{[1 + b_{AD} R_s (1 - Y_{AD}\{1 - f_{AD}\})]} \text{(sludge produced/COD utilized)}$$

(3)

where

X_{BAD}, X_{EAD} = COD concentration of the AD biomass and endogenous residue, respectively (mg COD/l)
V_d, Q_i, R_s = AD volume (l), influent flow (l/d) and sludge age (d)
S_{bi}, S_{be} = AD influent and effluent biodegradable COD concentration (mg COD/l)
Y_{AD} = yield coefficient of AD biomass (mg COD biomass/mg COD utilized)
b_{AD}, f_{AD} = endogenous respiration rate (/d) and unbiodegradable fraction of AD biomass.

The second part of Eq. (3) where E is given in terms of Y_{AD}, b_{AD}, f_{AD} and R_s is obtained from the COD based kinetic part (1) of the steady-state AD model (see Sötemann et al., 2005a).

Equation (1) was derived from the bioenergetics of organism growth where the electrons (e^-) and protons (H^+) donated by the organic compound are used in (i) anabolism to form new biomass and (ii) catabolism to generate the energy required to transform the organics to biomass (McCarty, 1975). The e^- (and H^+) donated by organics of a general composition of $C_xH_yO_zN_aP_b$, is given by,

$C_xH_yO_zN_aP_b + (2x - z + a + 3b)H_2O \Rightarrow (x - a + b)\,CO_2$
$\qquad + a\,NH_4^+ + b\,H_2PO_4^- + (a - b)\,HCO_3^- + \gamma_S[H^+ + e^-]$ (4)
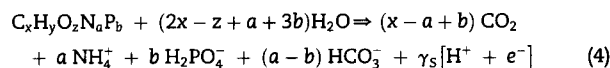
The formation of biomass (anabolism) of general composition $C_kH_lO_mN_nP_p$ from the basic building blocks of the e^- and H^+

donated by the organics, CO_2, ammonia (NH_4^+) and phosphorus ($H_2PO_4^-$) is given by,

$(k - n + p)\,CO_2 + n\,NH_4^+ + p\,H_2PO_4^- + (n - p)HCO_3^-$
$\qquad + \gamma_B[H^+ + e^-] \Rightarrow C_kH_lO_mN_nP_p + (2k - m + n + 3p)H_2O$ (5)
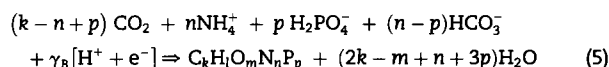
Under anaerobic conditions, the electrons used catabolically to generate energy for the anabolic process are passed to the terminal electron acceptor CO_2, which is given by

$8\,[H^+ + e^-] + CO_2 \Rightarrow CH_4 + 2H_2O$ (6)
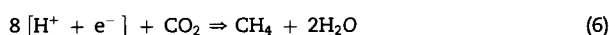
The e^- and H^+ donated by the organics (Eq. (4)) must be equal to the e^- and H^+ captured in biomass (Eq. (5)) and passed to the electron acceptor (Eq. (6)). If E is the fraction of the e^- and H^+ donated by the organics conserved as sludge mass, then Eq. (4) + $E\gamma_S/\gamma_B \times$ Eq. (5) + $(1 - E)\gamma_S/8 \times$ Eq. (6) = 0, which yields Eq. (1) above after grouping like terms and placing reactants on the left and products on the right. Equation (1) is therefore a COD, C, H, O, N, P and charge mass balanced stoichiometric equation for the methanogenic AD process. By following this procedure, the stoichiometry can be formulated for any bioprocess for which the electron donors and acceptors are known, e.g. those developed by Poinapen et al. in press for biological sulphate reduction using sewage sludge and by Lu et al. in press for autotrophic denitrification using reduced S compounds.

From γ_S and γ_B, the COD of the biodegradable organics and sludge mass (accepting the biomass and endogenous residue have the same composition) is $8\gamma_S$ and $8\gamma_B$ g COD/mol, respectively. Also, if the values are known of the COD/VSS (f_{cv}, g COD/g VSS), TOC/VSS (f_C, g C/g VSS), Org N/VSS (f_N, g N/g VSS) and Org P/VSS (f_P, g P/g VSS) ratios of the biodegradable organic compounds (which are the same as the α^{COD}, α^C, α^N and α^P mass fractions of Volcke et al., 2006), then the molar composition of the biodegradable organics $(x, y, z, a$ and $b)$ can be calculated from Eq. (7a)–(7j), i.e.:

If say

$y = 7$, (any value can be chosen)   (7a)

then

$$z = \frac{y}{2}\left(\frac{1 - \frac{1}{8}f_{cv} - \frac{8}{12}f_C - \frac{17}{14}f_N - \frac{26}{31}f_P}{1 + f_{cv} - \frac{44}{12}f_C + \frac{10}{14}f_N - \frac{71}{31}f_P}\right);$$ (7b)

$$x = \frac{f_C}{12}\left(\frac{y + 16z}{1 - f_C - f_N - f_P}\right);$$ (7c)

$$a = \frac{f_N}{14}\left(\frac{y + 16z}{1 - f_C - f_N - f_P}\right);$$ (7d)

$$b = \frac{f_P}{31}\left(\frac{y + 16z}{1 - f_C - f_N - f_P}\right);$$ (7e)

Table 1 – Composition of various organics compounds from data measured on methanogenic and sulphidogenic anaerobic digesters.

Reference	Data source	Sludge type	Organic type	Unbio Frac	COD/g VSS	g C/g VSS	g H/g VSS	g O/g VSS	g N/g VSS	mg N/g COD	x	y	z	a	Notes
McCarty (1975)	Theoretical	Activated sludge	Biomass		1.416	0.531	0.062	0.283	0.124	87.6	1.00	1.40	0.40	0.20	Commonly accepted composition for WAS. Used when linking ASM1 and ADM1 models (Volcke et al., 2006; Jeppsson et al., 2006)
			End residue – UPO	–											
Dold et al. (1980)	Used in ASMs 1&2	Activated sludge	Biomass		1.48	0.515	0.074	0.311	0.10	67.6	1.00	1.717	0.453	0.166	Used in ASM 1 and 2 dynamic models
			End residue UPO												
McCarty (1975)	Theoretical	Specific organics	Starch	0.46	1.185	0.444	0.062	0.494	0.0	0.0	1.00	1.671	0.833	0.0	A mixture of 46% starch ($C_6H_{10}O_5$) + 37% lipids [$H(CH_2)_nCOOH$] and 17% proteins ($C_{16}H_{24}O_5N_4$) produces $CH_{1.741}O_{0.502}N_{0.050}$, which is close to PS BPO of Poinapen et al. in press
			Lipids	0.37	2.875	0.750	0.125	0.125	0.0	0.031	1.00	2.000	0.125	0.0	
			Proteins	0.17	1.500	0.545	0.068	0.228	0.159	106.0	1.00	1.501	0.313	0.250	
			Mix	Mix	1.633	0.534	0.077	0.358	0.031	19.0	1.00	1.741	0.313	0.050	
Sötemann et al. (2005a)	Izzett and Ekama, 1992	Primary and humus	UPO+BPO	0.36											Determined C content of BPO from C balance over ADs. Calculated UPO by difference between PS (UPO+BPO) data below and BPO
	Meth ADs		BPO		1.568	0.502	0.084	0.382	0.033	21.0	1.00	2.000	0.571	0.056	
			UPO		1.69	0.54	0.081	0.352	0.027	16.0	1.00	1.800	0.488	0.043	
Sötemann et al. (2005a)	Own data	Primary sludge	UPO+BPO	?	1.609	0.515	0.08	0.371	0.03	19.3	1.00	1.918	0.540	0.052	From COD, VSS, TSS and Org N (TKN-FSA) and C, H and N elemental analysis of PS from 2 WWTPs
	Meth ADs														
Wentzel et al. (2006)	Moen et al. (2001)	Primary sludge	UPO+BPO	0.35	1.617	0.502									TKN and FSA concs not reported. C content of BPO from difference between influent and effluent concs and gas measurements
	Meth ADs		BPO		1.321										
			UPO		2.167										
Ekama et al. (2006)	van Haandel et al., 1998b	Waste	WAS	0.25 to 0.79	1.50		0.064	0.293	0.099	65.8	1.00	1.411	0.403	0.156	No elemental analysis. Assumed z = 2
		Activated Sludge	Biomass		1.55	0.544	0.059	0.269	0.102	66.0	1.00	1.235	0.353	0.153	
			ER+UPO			0.570				68.5					
Ekama et al. (2006)	Own data	Waste	WAS	0.637	1.482	0.491	0.081	0.358	0.070	47.2	1.00	1.993	0.547	0.123	60 d retention time—all BPO utilized. C, H and N elemental analysis on influent and effluent solids
		Activated Sludge	Biomass		1.444	0.491	0.078	0.353	0.078	54.0	1.00	1.896	0.540	0.136	
			ER+UPO		1.552	0.512	0.080	0.345	0.063	40.6	1.00	1.880	0.540	0.106	
Wentzel et al. (2006)	Ristow et al. (2004)	Primary sludge	UPO+BPO	0.334	1.400	0.491	0.069	0.411	0.029	21.0	1.00	1.683	0.627	0.050	UPO from C, H and N elemental analysis, BPO from gas and alkalinity measurements
	Meth ADs		BPO		1.533	0.456	0.098	0.416	0.030	19.6	1.00	2.583	0.690	0.055	
			UPO		1.194	0.456	0.060	0.457	0.027	22.6	1.00	1.584	0.751	0.050	
Takács and Vanrolleghem (2006)	Own estimates	Waste-water organics	USO & UPO		1.551	0.553	0.058	0.388	0.0	0.0	1.00	1.258	0.526	0.00	Estimates from specific organic types and literature values
			BSO & BPO		1.907	0.594	0.081	0.325	0.0	0.0	1.00	1.630	0.412	0.00	
			Biomass		1.416	0.531	0.081	0.283	0.124	87.6	1.00	1.400	0.400	0.20	

Table 1 (continued)

Reference	Data source	Sludge type	Organic type	Unbio Frac	g COD/g VSS	g C/g VSS	g H/g VSS	g O/g VSS	g N/g VSS	mg N/g COD	x	y	z	a	Notes
van Wageningen Ristow et al. (2004) BSR ADs	Primary sludge	BPO	0.334	1.469	0.505	0.071	0.393	0.031	21.1	1.00	1.687	0.583	0.053	With zero gas production, C content of BPO from $H_2CO_3^*$ alkalinity
		BPO	0.334	1.390	0.490	0.068	0.412	0.030	21.6	1.00	1.679	0.631	0.053	
		BPO	0.334	1.263	0.468	0.063	0.438	0.030	23.8	1.00	1.624	0.703	0.056	
		BPO	0.334	1.665	0.468	0.072	0.400	0.027	18.4	1.00	1.724	0.596	0.048	
		BPO (ave)	0.334	1.397	0.491	0.069	0.410	0.030	21.5	1.00	1.679	0.626	0.053	
Poinapen et al. (in press)	Own data	Primary sludge	UPO+BPO	0.36	1.593	0.430	0.119	0.378	0.073	45.8	1.00	3.313	0.660	0.145	C content from elemental analysis and C balance with $H_2CO_3^*$ alkalinity. Determined composition from difference between influent and effluent COD, VSS and Org N
	BSR ADs		BPO		1.480	0.515	0.072	0.357	0.060	40.5	1.00	1.694	0.524	0.101	
			UPO		1.682	0.524	0.091	0.302	0.083	49.3	1.00	2.086	0.432	0.136	
			AD biomass		1.600	0.562	0.066	0.300	0.072	45.0	1.00	1.400	0.400	0.110	

Elemental ratio for O (f_O, α^O) and H (f_H, α^H) are not required because COD replaces one and mass balance ($f_C + f_H + f_O + f_N + f_P = 1$) the other.

$$z = \frac{y}{16}\frac{f_O}{f_H};\qquad(7f)$$

$$f_O = \frac{16}{18}\left(1 - \frac{1}{8}f_{cv} - \frac{8}{12}f_C - \frac{17}{14}f_N - \frac{26}{31}f_P\right);\qquad(7g)$$

$$f_H = \frac{2}{18}\left(1 + f_{cv} - \frac{44}{12}f_C + \frac{10}{14}f_N - \frac{71}{31}f_P\right);\qquad(7h)$$

$$f_{cv} = 8\left(\frac{4}{12}f_C + \frac{1}{1}f_H - \frac{2}{16}f_O - \frac{3}{14}f_N + \frac{5}{31}f_P\right);\qquad(7i)$$

$$f_C + f_H + f_O + f_N + f_P = 1\qquad(7j)$$

Equation (7a)–(7j) applies also to the biomass so if f_{cv}, f_C, f_N and f_P ratios are known for the biomass, and $l = 7$ (say), then the well known $C_5H_7O_2N$ example composition for activated sludge first published by Porges et al. (1956) will be obtained from $f_{cv} = 1.416$ g COD/g VSS, $f_C = 0.515$ g C/g VSS, $f_N = 0.124$ g N/g VSS and $f_P = 0.0$ g P/g VSS. In Eq. (7a)–(7j), the molar composition values (x, y, z, a, b) are expressed with respect to the H content of the organics. If for example, y (or l) is selected to be 7, then the C, O, N and P molar composition values (x, z, a, b) will be with respect to the organic containing 7 mol H. The element that forms the basis for expressing the molar composition can be easily changed. If, for example, C is selected and the C content (x) is assumed to be 1 mol (as is accepted in this paper), then the molar compositions of the organics is $CH_{y/x}O_{z/x}N_{a/x}P_{b/x}$, where ($x, y, z, a, b$) are given by Eq. (7a)–(7j). Also, for a unit molar mass (1 g), the molar composition can be written $C_{f_C/12}H_{f_H/1}O_{f_O/16}N_{f_N/14}P_{f_P/31}$, where f_C, f_H, f_O, f_N and f_P are the composition mass fractions.

In the steady-state AD model of Sötemann et al. (2005a), the influent VFA is assumed to be acetate. Equation 1 holds also for acetate, both associated (HAc) and undissociated (Ac^-) provided the correct composition $x(=2)$, $y(=4$ for HAc, $=3$ Ac^-), $z(=2)$, $a = b = 0$, and charge ($=0$ for HAc, $=-1$ for Ac^-) are inserted. Because the yield of methanogens on acetate is very low in relation to the acidogens, E is accepted to be zero when applying Eq. (1) to acetate, which yields,

$$CH_3COOH \Rightarrow CH_4$$
$$+ CO_2 \text{ (Neither biomass nor Alkalinity generation)}\qquad(8a)$$

$$CH_3COO^- + H_2O \Rightarrow CH_4$$
$$+ HCO_3^- \text{ (No biomass but Alkalinity generation)}\qquad(8b)$$
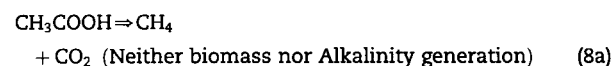
From Eq. (8b) it can be seen that the influent dissociated VFA concentration is an important compound for establishing the digester pH because its utilization makes a significant contribution to the alkalinity generated—the other is the N composition of the influent biodegradable organics (a in Eq. (1)). Because the P content of the biodegradable organics in primary sludge is very low ($f_P < 0.01$ mg P/mg VSS), P release in PS AD is low with the result that the alkalinity contribution by the phosphate system is very low (Eq. (1)). This is not the case with AD of P rich waste activated sludge (WAS) from BEPR systems (Pitman, 1999), which will be considered in a future paper.

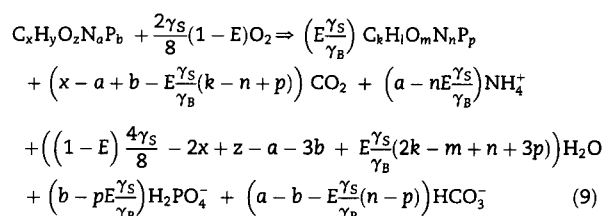| Table 2 – COD/TOC and COD/mass ratios of some simple soluble organic compounds.							
Organic compound	Formula	COD/TOC ratio			COD/mass ratio		
		n	3	12	n	3	12
Carbohydrates	$C_n(H_2O)_n$	2.67 for all n	2.67	2.67	1.067 for all n	1.067	1.067
Sugars	$C_n(H_2O)_{n-1}$	2.67 for all n	2.67	2.67	$16n/(15n-9)$	1.33	1.123
Carboxylic acids[a]	$CH_3(CH_2)_nCOOH$	$4(3n+4)/[3(n+2)]$	3.47	3.81	$8(3n+4)/(7n+30)$	2.04	2.81
Primary amines	$CH_3(CH_2)_n NH_2$	4 for all n	4.0	4.0	$48(n+1)/(14n+31)$	2.63	3.14
Amino acids	$H(CH_2)_nC_2H_4O_2N$	$4(n+1)/(n+2) < 4$	3.20	3.71	$48(n+1)/(14n+75)$	1.64	2.57
Alcohols	$H(CH_2)_nOH$	4 for all n	4.0	4.0	$24n/(7n+9)$	2.40	3.09

a Unsaturated fats have slightly lower COD/TOC ratio because for every double C bond (C = C), there are 2 Hs fewer.

2.2. Stoichiometry of aerobic activated sludge

Applying the same e^- and H^+ balance outlined above but changing the electron acceptor to oxygen to conform to aerobic conditions, the stoichiometry of the aerobic activated sludge (AS) process was derived, viz.

$$C_xH_yO_zN_aP_b + \frac{2\gamma_S}{8}(1-E)O_2 \Rightarrow \left(E\frac{\gamma_S}{\gamma_B}\right) C_kH_lO_mN_nP_p$$
$$+ \left(x - a + b - E\frac{\gamma_S}{\gamma_B}(k-n+p)\right)CO_2 + \left(a - nE\frac{\gamma_S}{\gamma_B}\right)NH_4^+$$
$$+ \left(\left(1-E\right)\frac{4\gamma_S}{8} - 2x + z - a - 3b + E\frac{\gamma_S}{\gamma_B}(2k - m + n + 3p)\right)H_2O$$
$$+ \left(b - pE\frac{\gamma_S}{\gamma_B}\right)H_2PO_4^- + \left(a - b - E\frac{\gamma_S}{\gamma_B}(n-p)\right)HCO_3^- \qquad (9)$$

where

E = the mass of COD exiting the AS reactor as active and endogenous sludge per day as a fraction of the mass of biodegradable organics (COD) utilized in the reactor per day at steady-state (note the unbiodegradable sludge mass from the influent is not included because it is not a product from the utilization of influent biodegradable organics), i.e.

$$E = \frac{V_r (X_{BH} + X_{EH})}{Q_i (S_{bi} - S_{be})R_s} = \frac{Y_H (1 + f_{EH} b_H R_s)}{(1 + b_H R_s)} \qquad (10)$$

where

X_{BH}, X_{EH} = COD concentration of the AS biomass (OHO) and endogenous residue, respectively (mg COD/l)

V_r, Q_i, R_s = AS volume (l), influent flow (l/d) and sludge age (d)
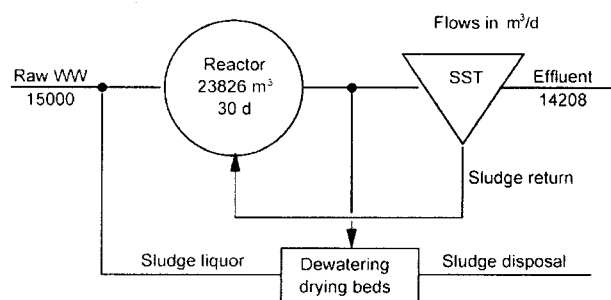
Fig. 3 – The first theoretical case study WWTP comprising raw wastewater (WW) treatment in a long sludge age (30 d) AS system (extended aeration).

S_{bi}, S_{be} = AS influent and effluent biodegradable COD concentration (COD/l)

Y_H = yield coefficient of AS biomass (mg COD biomass/mg COD utilized).

b_H, f_{EH} = endogenous respiration rate (/d) and unbiodegradable fraction of AS biomass

The second part of Eq. (10) where E is given in terms of Y_H, b_H, f_{EH} and R_s is obtained from the COD based kinetic part (1) of the steady-state AS model (Marais and Ekama, 1976; WRC, 1984; Henze et al., 2008).

The γ_S, γ_B, M_S and M_B of the biodegradable organics and sludge mass are given by Eq. (2a)–(2e) above. From γ_S and γ_B, the COD of the biodegradable organics and sludge mass (assuming the live biomass and endogenous residue have the same composition) is $8\gamma_S$ and $8\gamma_B$ g COD/mol, respectively. Also, from known values of the COD/VSS (f_{cv}), TOC/VSS (f_C), Org N/VSS (f_N) and Org P/VSS (f_P) ratios, the composition of the biodegradable organics (x, y, z, a and b) and biomass (k, l, m, n and p) can be calculated from Eq. (7a)–(7j).

2.3. Stoichiometry of autotrophic nitrification

Again by considering the electron donor and electron acceptor of autotrophic nitrification, the stoichiometry of this aerobic process was derived, i.e.

$$\frac{14pE}{8\gamma_B}H_2PO_4^- + \frac{14kE}{8\gamma_B}CO_2 + NH_4^+ + 14\left\{\frac{1}{7} - \frac{E}{4}\left(\frac{n}{\gamma_B} + \frac{1}{8}\right)\right\}O_2$$
$$\Rightarrow \left(\frac{14E}{8\gamma_B}\right)C_kH_lO_mN_nP_p + 14\left(\frac{1}{14} - \frac{nE}{8\gamma_B}\right)NO_3^-$$
$$+ 14\left(\frac{1}{7} - \frac{E}{8\gamma_B}(n+p)\right)H^+$$
$$+ 14\left(\frac{1}{14} + \frac{E}{8\gamma_B}(2k - m - n + 4p) - \frac{E}{16}\right)H_2O \qquad (11)$$

where E = mass of COD exiting the AS reactor as autotrophic nitrifier organism (ANO) biomass and endogenous residue per day as a fraction of the mass of ammonia oxidized in the reactor per day at steady-state (net yield of autotrophic biomass and endogenous residue), i.e.

$$E = \frac{V_r (X_{BA} + X_{EA})}{Q_i (N_{ai} - N_{ae})R_s}$$
$$= \frac{Y_A (1 + f_{EA} b_A R_s)}{(1 + b_A R_s)} \text{ mg COD sludge mass/mg NH}_4\text{-N nitrified}$$

$$(12a)$$

Table 3 – Raw and settled wastewater and primary sludge characteristics calculated from a mass balance around the primary settling tank (PST) for raw and settled wastewater unbiodegradable particulate COD fractions ($f_{S'up}$) of 0.15 and 0.04 and raw wastewater soluble unbiodegradable and biodegradable COD fractions ($f_{S'us}$ and $f_{Sb's}$) of 0.07 and 0.25, respectively.

Parameter	Raw WW	Settled WW	Primary sludge	Units
Flow	15000	14925	75	m³/d
Total COD (S_{ti})	750	450	60450	mg COD/l
Unbiodegradable particulate COD (S_{upi})	112	18	18818	mg COD/l
Unbiodegradable soluble COD (S_{usi})[d]	53	53	53	mg COD/l
Biodegradable particulate COD (S_{bpi})	439	233	41433	mg COD/l
Biodegradable soluble COD (S_{bsi})[d]	146	146	146	mg COD/l
Unbiodegradable COD fraction of PS ($f_{PS'up}$)	–	–	0.312[a]	
Total TKN (N_{ti})	60.0	51.1	1831	mg N/l
Free and saline ammonia (N_{ai})	45.0	45.0	45.0	mg N/l
Unbiodegradable particulate Org N (N_{oupi})[b]	7.6	1.2	1281	mg N/l
Unbiodegradable soluble Org N (N_{ousi})[c]	1.8	1.8	1.8	mg N/l
Biodegradable particulate Org N (N_{obpi})[d]	3.9	1.4	501	mg N/l
Biodegradable soluble Org N (N_{obsi})[d]	1.7	1.7	1.7	mg N/l
Unbiodegradable TKN fraction of PS ($f_{PN'up}$)			0.719	
Total suspended solids (TSS)	301	78.7	44459	mg TSS/l
Volatile suspended solids (VSS)	253	69.2	36829	mg VSS/l
Inorganic suspended solids (ISS)	48	9.5	7650	mg ISS/l

a Obtained from a strict mass balance—the simplified Eq. (1) in Wentzel et al. (2006) yields 0.315.

b Calculated from a TKN/VSS ratio (f_N) = 0.10 mg N/mg VSS and COD/VSS (f_{cv}) = 1.48 mg COD/mg VSS for the influent unbiodegradable particulate organics.

c Based on a raw wastewater FSA/TKN ratio and unbiodegradable soluble TKN fraction of ($f_{Nb'a}$ and $f_{N'us}$) of 0.75 and 0.03, respectively.

d Based on 0.45 μm membrane filtered COD and TKN concentrations of 199 mg COD/l and 3.5 mg N/l, and accepting that 0.45 μm membrane filtrate concentrations are soluble.

where

X_{BA}, X_{EA} = COD concentration of the ANOs and their endogenous residue, respectively, (mg COD/l)

V_r, Q_i, R_s = AS volume (l), influent flow (l/d) and sludge age (d)

N_{ai}, N_{ae} = AS influent and effluent ammonia concentrations (mg N/l)

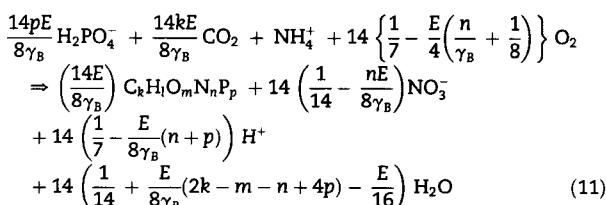Y_A = yield coefficient of ANO biomass (mg COD biomass/mg COD utilized)

b_A, f_{EA} = endogenous respiration rate (/d) and unbiodegradable fraction of ANOs

Because both the yield (Y_A) and endogenous respiration rate (b_A) for ANOs are very low (e.g. 0.15 mg COD/mg N and 0.04/d, WRC, 1984; ASM1—Henze et al., 1987), it is reasonable to accept that endogenous residue generation is negligible (f_{EA} = 0), which yields for Eq. (12a),

$$E = \frac{Y_A}{(1 + b_A R_s)} \text{ mg COD biomass produced/mg NH}_4^+\text{-N nitrified}$$

(12b)

If the unbiodegradable fraction of the ANOs (f_{EA}) is 0.20 (same as for OHOs), then from Eq. (12a) at 10 d sludge age, E is 0.116 instead of 0.107 with f_{EA} = 0.0. This is only 8% higher. At 30 d sludge age, E is 0.0845 with f_{EA} = 0.20 instead of 0.0682 with f_{EA} = 0.0, i.e. 24% higher but both are lower than at 10 d sludge age. Because ANOs make up less than 3% of the VSS mass in the reactor, accepting endogenous residue generation by ANOs as zero makes less than 0.5% difference to the VSS mass and less than 0.1% difference to the predicted nitrate concentration (Eq. (11)).

The γ_B and M_B of the biomass are given by Eq. (2a)–(2e) above and as before, the second part of Eq. (12a) where E is given in terms of Y_A, b_A, f_{EA} and R_s is obtained from the COD and N based kinetic part (1) of the steady-state nitrification model for the AS system (WRC, 1984; Henze et al., 2008). From Eq. (11), it can be seen that the mass of oxygen required per mass of ammonia as N nitrified (mg O_2/mg NH$_4^+$-N) is given by

$$32\left[\frac{1}{7} - \frac{E}{4}\left(\frac{n}{\gamma_B} + \frac{1}{8}\right)\right],$$

which gives 4.36 at R_s = 0 (highest net yield, E = Y_A) and 4.57 at R_s = ∞ (zero net yield, E = 0) and 4.42 to 4.47 for sludge ages between 10 and 30 days.

2.4. Stoichiometry of heterotrophic dissimilative denitrification

The stoichiometry of anoxic denitrification was derived by selecting the electron acceptor and bioprocess reaction products that conform to anoxic conditions, viz.

$$C_xH_yO_zN_aP_b + \frac{\gamma_S}{5}(1-E)NO_3^- \Rightarrow \left(E\frac{\gamma_S}{\gamma_B}\right)C_kH_lO_mN_nP_p$$

$$+ \left(x - a + b - E\frac{\gamma_S}{\gamma_B}(k - n + p) - \frac{\gamma_S}{5}(1-E)\right)CO_2$$

$$+ \frac{\gamma_S}{10}(1-E)N_2 + \left((1-E)\frac{2\gamma_S}{5} - 2x + z - a - 3b\right.$$

$$\left. + E\frac{\gamma_S}{\gamma_B}(2k - m + n + 3p)\right)H_2O + \left(a - nE\frac{\gamma_S}{\gamma_B}\right)NH_4^+$$

$$+ \left(b - pE\frac{\gamma_S}{\gamma_B}\right)H_2PO_4^- + \left(a - b - E\frac{\gamma_S}{\gamma_B}(n - p) + \frac{\gamma_S}{5}(1-E)\right)HCO_3^- \quad (13)$$

Table 4 – Raw and settled wastewater and primary sludge fractionation and COD, N, C and VSS concentrations.

Raw wastewater

SOLBL

	FSA	VFA	F-BSO	USO	Total
COD	0	36	110	53	199
N	45	0	1.7	1.8	48.5
C	0	13.5	36.5	18	68

PARTIC

	BPO	UPO	Total
COD (mg COD/l)	439	112	551
VSS (mg VSS/l)	276	76	352
N (mg N/l)	3.9	7.6	11.5
C (mg C/l)	141	39.2	180

TOTAL

	FSA	VFA	BO[a]	UO	Total
COD	0	36	549	165	750
N	45	0	5.6	9.4	60
C	0	13.5	177.5	57	248

Settled wastewater

SOLBL

	FSA	VFA	F-BSO	USO	Total
COD	0	36	110	53	199
N	45	0	1.7	1.8	48.5
C	0	13.5	36.5	18	68

PARTIC

	BPO	UPO	Total
COD	233	18	251
VSS	157	12	169
N	1.3	1.2	2.5
C	75.7	6.3	82

TOTAL

	FSA	VFA	BO[a]	UO	Total
COD	0	36	343	71	450
N	45	0	3.0	3.0	51.0
C	0	13.5	112.5	24.3	150

Primary sludge

SOLBL

	FSA	VFA	F-BSO	USO	Total
COD	0	36	110	53	199
N	45	0	1.7	1.8	48.5
C	0	13.5	36.5	18	68

PARTIC

	BPO	UPO	Total
COD	41299	18915	60214
VSS	24017	12781	36798
N	506.0	1278.0	1784.0
C	13099	6583	19682

TOTAL

	FSA	VFA	BO[a]	UO	Total
COD	0	36	41409	18968	60413
N	45	0	507.7	1279.8	1832.5
C	0	13.5	13135	6601	19750

a Biodegradable organics excluding VFA.

where E is given by Eq. (10) from the aerobic stoichiometry above and γ_S, γ_B, M_S and M_B by Eq. (2a)–(2e).

2.5. Stoichiometry of aerobic and anoxic–aerobic digestion of waste activated sludge (WAS)

By considering the reactants and products of the endogenous utilization of AS biomass organics under aerobic conditions, the stoichiometry of the aerobic digestion (AerD) of WAS is,

$$C_kH_lO_mN_nP_p + (1-E)\frac{2\,\gamma_B}{8}O_2 \Rightarrow E\,C_kH_lO_mN_nP_p$$
$$+ (1-E)(k-n+p)CO_2 + \frac{(1-E)}{2}(l-5n-p)H_2O$$
$$+ n(1-E)NH_4^+ + p(1-E)H_2PO_4^- + (1-E)(n-p)HCO_3^-$$

(14)

where γ_B is given by Eq. (2b).

E = proportion of influent active biomass not degraded, i.e.

$$E = \frac{V_r\,(X_{BHe}+X_{EHe})}{Q_i\,(X_{BHi})R_s} = \frac{(1+f_{EH}\,b_H\,R_s)}{(1+b_H\,R_s)}$$

(15)

where

X_{BH}, X_{EH} = COD concentration of the AS biomass and endogenous residue, respectively, (mg COD/l); additional subscripts i and e denote influent and effluent, respectively
V_r, Q_i, R_s = Volume (l), influent flow (l/d) and sludge age (d) of the aerobic digester
b_H, f_{EH} = Endogenous respiration rate (/d) and unbiodegradable fraction of AS biomass

The second part of Eq. (15) where E is given in terms of b_H, f_{EH} and R_s is obtained from the COD based kinetic part (1) of the steady-state aerobic digestion model of WAS (Marais and Ekama, 1976; Ekama et al., 2006a).

The ammonia released in aerobic digestion is usually completely nitrified to nitrate, for which Eq. (11) can be applied. Alternatively, assuming complete nitrification and zero ANO growth, Eq. (14) can be modified to become,

$$C_kH_lO_mN_nP_p + \frac{(1-E)}{4}(\gamma_B+8n)\,O_2 \Rightarrow EC_kH_lO_mN_nP_p$$
$$+ (1-E)\,k\,CO_2 + \frac{(1-E)}{2}(l-n-3p)H_2O + n(1-E)NO_3^-$$
$$+ p(1-E)H_2PO_4^- + (1-E)(n+p)H^+$$

(16)

Additionally, if the aerobic digester is intermittently aerated with a 3 h air on—3 h air off cycle, Warner et al. (1986) showed that complete nitrification still is achieved and also complete denitrification. In this event, and again assuming no generation of ANOs in the anoxic–aerobic digester, the stoichiometry of anoxic–aerobic digestion of WAS simplifies to

$$C_kH_lO_mN_nP_p + \frac{(1-E)}{4}(\gamma_B+3n)\,O_2 \Rightarrow EC_kH_lO_mN_nP_p$$
$$+ (1-E)\,k\,CO_2 + \frac{(1-E)}{2}(l-3p)H_2O + \frac{(1-E)}{2}\,n\,N_2$$
$$+ p(1-E)H_2PO_4^- + p(1-E)H^+$$

(17)

Like the mass balance based steady-state model for AD of sewage sludge of Sötemann et al. (2005a), the steady-state AS
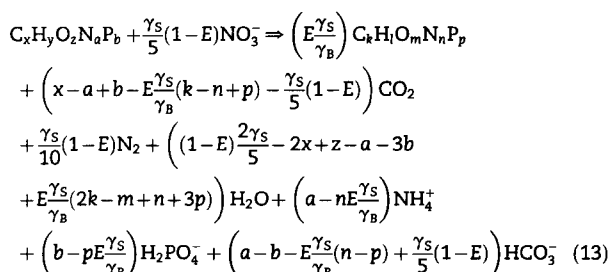
Table 5 – Raw wastewater (R), settled wastewater (S), primary sludge (PS) organic concentrations and compositions, and activated sludge (AS) and anaerobic digestion (AD) biomass compositions used in the two WWTP case study calculations.

	R, S, PS VFA	R, S, PS F-BSO	R, S, PS USO	Raw BPO	Settled BPO	PS BPO	Raw UPO	Settled UPO	PS UPO	AS Biomass	AD Biomass
COD conc (mg COD/l)	36	110.2	52.5	438.7	233.4	41299	112.5	18	18915	–	–
Org N conc (mg Org N/l)	0	1.73	1.80	3.9	1.3	506	7.6	1.2	1278	–	–
TOC conc (mg C/l)	13.5	36.5	18.0	140.8	75.7	13099	39.2	6.3	6583	–	–
VSS or conc. (mg/l)	33.7	77.6	37	276.0	156.7	24017	76	12.2	12781	–	–
COD/VSS (f_{cv}, a^{COD})	1.067	1.42	1.42	1.589	1.489	1.72	1.480	1.48	1.48	1.48	1.42
C/VSS ratio (f_c, a^9)	0.4	0.470	0.487	0.51	0.483	0.545	0.515	0.515	0.515	0.515	0.531
Org N/VSS ratio (f_N, a^N)	0.000	0.022	0.049	0.014	0.008	0.021	0.1	0.1	0.1	0.1	0.124
Carbon content (x)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Hydrogen content (y)	2.00	2.019	1.833	1.903	1.996	1.796	1.715	1.715	1.715	1.715	1.400
Oxygen content (z)	1.00	0.683	0.601	0.580	0.664	0.484	0.453	0.453	0.453	0.453	0.400
Nitrogen content (a)	0.000	0.041	0.086	0.023	0.015	0.033	0.166	0.166	0.166	0.166	0.200
g VSS/mol or g/mol	30	25.53	24.65	23.52	24.84	21.99	23.30	23.30	23.30	23.30	22.60

and aerobic digestion (AerD) models (including nitrification and denitrification), extended to include the stoichiometry derived above, now also comprise three parts: (i) A COD mass balanced based kinetic part (Part 1), which links the biodegradable organics (COD) concentration removed to the sludge production and oxygen demand via the system sludge age (these Parts 1 were developed previously, Marais and Ekama, 1976; WRC, 1984; Ekama et al., 2006a; Henze et al., 2008); (ii) a COD, C, H, O, N, (P) and charge balanced stoichiometry part (Part 2 developed above) which transforms the biodegradable COD removed and its C, H, O, N and P composition (reactants) to sludge mass, oxygen demand, gaseous CO_2, ammonia, nitrate, nitrogen gas, ortho-phosphate and dissolved CO_2 (HCO_3^- ≈ Alkalinity) (products); and (iii) an inorganic carbon (and phosphate if significant) weak acid/base chemistry part (Part 3), from which the alkalinity consumption can be calculated to determine whether or not chemical dosing is required to maintain the activated sludge (AS) and aerobic digester (AerD) reactors pH above 7. For AD systems (methanogenic and sulphidogenic), this Part 3 can be used to calculate the AD pH (Sötemann et al., 2005a; Poinapen et al., in press). For AS systems, pH calculation is not possible because the partial pressure of CO_2 (pCO_2) is not known - CO_2 is usually supersaturated by some unknown degree depending on aeration and mixing conditions in the AS reactor.

2.6. Some comments on the stoichiometry

The total (TOD) or theoretical (ThOD) oxygen demand is the electron donating capacity in terms of oxygen of all compounds that can donate electrons with respect to some assigned datum. For the COD, this datum is CO_2, H_2O and NH_4^+ and for the TOD, this datum is CO_2, H_2O and NO_3^-. Because the stoichiometric equations derived above are based on element and electron balances, the ThOD is conserved in all of them. In practical terms the ThOD (or TOD) is the COD (in which the reduced (Kjeldahl) nitrogen, or TKN, is not oxidized to nitrate) of the organics plus the oxygen demand of the TKN, i.e. TOD = COD + 4.57 × TKN mg TOD/l. There may be many other compounds in wastewater that can donate electrons, such as sulphide and nitrite, but these are not included in the stoichiometric equations derived in this paper. Therefore, if significant concentrations of sulphide, nitrite or other electron donating compounds are present, the measured COD must be corrected before input to the steady-state (and dynamic) models.

In order to maintain TOD mass balance, the autotrophic biomass (and it endogenous residue if this is not accepted to be zero) should be included with the influent OHO biomass (X_{BHi}) to the aerobic (and anaerobic) digester. If this is not done, then a TOD mass balance deficit of 2 to 4% will be obtained because a small fraction of the electron donating capacity of the TKN is captured in the ANO biomass, which will be lost if ignored. In steady-state and dynamic models it is important to check TOD mass balances in every unit operation—if this is done then mass balance deviations >0.1% from 100.0% are useful signals pointing to programming errors.

In Eqs. (14)–(17), the oxygen utilized can be used directly in TOD mass balances. Because Eq. (14) excludes

Table 6 – Kinetic rates, stoichiometric constants and unit operation design parameters used in the steady-state models.		
Description	Value	Units

1. Activated sludge (WRC, 1984; Henze et al., 2008, Chapter 4)

b_{H20}	OHO endogenous respiration rate: $b_{HT} = b_{H20} (1.029)^{(T-20)}$	0.24	/d
f_{EH}	OHO unbiodegradable fraction	0.2	–
Y_H	OHO yield coefficient	0.67	mg COD/mg COD
Q_i	Influent flow: Raw wastewater 15.0 Ml/d; Settled 14.925 Ml/d	15	Ml/d
R_s	Sludge age: Raw wastewater 30 d; Settled 8 d	30; 8	d
V_r	Volume of activated sludge reactor: Raw 23.83; Settled 3.52		Ml

Kinetic parameters for OHO growth not required because all biodegradable organics completely utilized

2. Nitrification (WRC, 1984; Henze et al., 2008, Chapter 5)

b_{A20}	ANO endogenous respiration rate: $b_{AT} = b_{A20} (1.029)^{(T-20)}$	0.04	/d
f_{EA}	ANO unbiodegradable fraction	0	–
K_{nT}	Half saturation concentration of ANOs: $K_{nT} = K_{n20} (1.123)^{(T-20)}$	1	mg N/l
Y_A	ANO yield coefficient	0.15	mg COD/mg N
μ_{A20}	Maximum specific growth rate of ANOs: $\mu_{AT} = \mu_{A20} (1.123)^{(T-20)}$	0.6	/d

Provided sludge age is longer than the minimum for nitrification, nitrate concentration generated per l influent is influent TKN (N_{ti}) minus unbiodegradable soluble Org N (N_{ousi}) + biodegradable organic N ($N_{obpi} + N_{obsi}$) minus N required for sludge production [$N_s = f_n(X_{BH} + X_{EH} + X_I)$/($Q_i R_s$) minus effluent ammonia concentration ($N_{ae} = [K_{nT}(b_{AT} + 1/R_s)]/[\mu_{AT} - (b_{AT} + 1/R_s)]$ (WRC, 1984; Henze et al., 2008)

3. Denitrification (WRC, 1984; Henze et al., 2008, Chapter 5)

K_{120}	Denitrification rate on BSO in primary anoxic reactor: $K_{1T} = K_{120} (1.20)^{(T-20)}$	0.72	mg NO$_3$-N /mg OHOVSS/d
K_{220}	Denitrification rate on BPO in primary anoxic reactor: $K_{2T} = K_{220} (1.08)^{(T-20)}$	0.1	mg NO$_3$-N/mg OHOVSS/d
K_{320}	Denitrification rate on BPO in secondary anoxic reactor: $K_{3T} = K_{320} (1.029)^{(T-20)}$	0.07	mg NO$_3$-N /mg OHOVSS/d

The concentration of nitrate denitrified is calculated with the procedure in WRC (1984) or Henze et al. (2008). The order in which the biodegradable organics are utilized for denitrification is VFA, F-BSO, BPO. The biodegradable organics not utilized for denitrification (Eq. (13)) are utilized with oxygen (Eq. (9)). Output for settled WW 8d sludge age NDAS system at 14 °C is given in Table 8.

4. Aerobic digestion of WAS (Ekama et al., 2006a)

The b_{H20}, f_{EH} and Y_H of the activated sludge model above apply. The aerobic digestion steady-state kinetic model is given by Marais and Ekama (1976) or Ekama et al. (2006a). Performance below for 14 °C

Q_i	Influent flow at 6.78% TSS to not exceed OUR of 100 mg O/(l.h)	26.0	m³/d
R_h	Retention time	19.1	d
V_d	Volume of aerobic digester	496	m³

5. Anaerobic digestion of PS (see Table 7) and WAS (Sötemann et al., 2005a)

Q_i	Influent flow	PS 75; WAS 25.1	m³/d
R_h	Retention time	PS 10; WAS 10	d
b_{AD}	Anaerobic (acidogen) biomass endogenous respiration rate	0.041	/d
f_{AD}	Anaerobic (acidogen) biomass unbiodegradable fraction	0	–
Y_{AD}	Anaerobic (acidogen) biomass yield coefficient	0.113	mg COD/mg COD
K_m	Monod maximum specific hydrolysis rate for primary sludge	3.34	g COD organics /g COD biomass/d
K_s	Monod half saturation concentration for primary sludge	3.76	g COD/l
K_m	Monod maximum specific hydrolysis rate for waste activated sludge	0.36	g COD organics /g COD biomass/d
K_s	Monod for half saturation concentration waste activated sludge	35	g COD/l
V_d	Volume of anaerobic digester	PS 750; WAS 251	m³

nitrification, the TOD balance is in effect a COD balance (i.e. ammonia is not oxidized). Hence the products of Eqs. (14) and (16) refer directly to the basis of the COD and TOD respectively. The TOD also balances over Eq. (17), but the ThOD of the N$_2$ gas product with respect to NO$_3^-$ must be taken into account when setting up the balance.
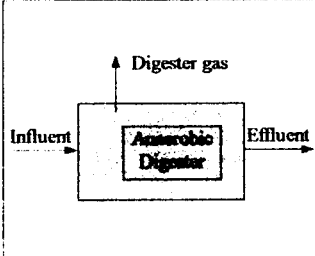
The above stoichiometry developed for the steady-state AS and AerD models apply also to the dynamic models, if these are programmed to include elemental balances. The only difference is the E value: For steady-state models, E is a net sludge production, which is a combination of the growth and endogenous processes; for dynamic models, E is disaggregated into the growth process (with its anabolic yield Y) and the endogenous respiration (or death) process,

which returns some of the components of the biomass to the bulk liquid according to Eq. (5) in reverse and the electrons and protons so generated transformed to biodegradable and unbiodegradable organics according to Eq. (4) in reverse.

3. Estimation of organic compositions

A list of biodegradable (BPO) and unbiodegradable particulate organic (UPO) compositions in wastewater determined in a number of investigations is given in Table 1. For reference and comparison, also given in Table 1 are the COD/VSS (f_{cv}), TOC/VSS (f_C) and Org N/VSS (f_N) ratios, with their corresponding x, y, z and a values in CH$_{y/x}$O$_{z/x}$N$_{a/x}$ for activated

Table 7 – Spreadsheet output for the PS anaerobic digester (see Fig. 4 for WWTP layout).

	Methane	532.7	kgCH4-C/d	CO2	342.8	kgCO2-C/d
	Methane	994.3	Nm3/d	CO2	639.9	Nm3/d
	Methane	2840.9	kgCOD/d	Gas pCO2	39.2	%
DesMan	Methane	62.7	% Influent COD			
Sludge Age (d)		10	AD Volume	750.0 m3		

Influent	Mass - kg	Concs - mg/l
MI/d	0.075	0.075
COD	4530.9	60412.6
TOD	5159.2	68790.0
C	1481.3	19750.0
H	218.5	2912.9
O	937.2	12495.4
TKN-N	137.4	1832.6
FSA-N	3.4	44.967
OrgN-N	134.1	1787.6
VSS	2759.8	36797.9
ISS	574.7	7663.2
TSS	3334.6	44461.0
Water use	454.9	6065.3

Influent → Anaerobic Digester → Effluent (Digester gas)

Effluent	Particulate Mass - kg	Particulate Conc - mg/l	Dissolved Mass - kg	Dissolved Conc - mg/l	Total Mass - kg
MI/d	0.075	0.075	0.075	0.075	0.075
COD	1675.1	22334.3	14.93	199.1	1690.0
TOD	2192.5	29233.0	125.84	1677.8	2318.3
C	583.0	7773.3	22.76	303.5	605.8
H	83.3	1111.2	8.11	108.2	91.5
O	352.3	4697.2	75.04	1000.5	427.3
TKN-N	113.2	1509.1	24.26	323.5	137.4
FSA-N	0.0	0.0	23.99	319.9	24.0
OrgN-N	113.2	1509.1	0.27	3.6	113.5
VSS	1131.8	15090.8	0.0	0.0	1131.8
ISS	574.7	7663.2	0.0	0.0	574.7
TSS	1706.5	22753.9	0.0	0.0	1706.5

Mass Balances	
COD	100.0 %
TOD	100.0 %
Carbon	100.0 %
Hydrogen	100.0 %
Oxygen	100.0 %
Nitrogen	100.0 %

sludge commonly given as example in the literature, viz. $CH_{1.40}O_{0.40}N_{0.20}$ ($C_5H_7O_2N$) and (ii) used in activated sludge dynamic models (ASM) 1 and 2, viz. $f_{cv} = 1.48$ g COD/g VSS, $f_C = 0.515$ g C/g VSS and $f_N = 0.10$ g N/g VSS ($CH_{1.715}O_{1.85}N_{0.68}$). In Anaerobic Digestion Model No. 1 (ADM1), complex influent organics like primary sludge (PS) is considered to be a mixture of starch, lipids and proteins so the f_{cv}, f_C and f_N ratios and compositions of starch, lipids and a common protein, as well as a mixture of these three representing PS, are also given in Table 1.

Table 8 – Spreadsheet output for the 8 d sludge age NDAS system treating settled wastewater at 14 °C (see Fig. 4).

					GAS OUT CO2	GAS OUT N2
DesMan		OXYGEN	Carbonace	2820.5 kgO/d		
SETTLED WW		DEMAND	Nitrificatior	2347.1 kgO/d	1190.9	328.1
WINTER	Temp oC	14	Total	5167.6 kgO/d	kgCO2-C/d	kgN2-N/d
Sludge Age (d)		8	Denitrificat	937.4 kgO/d	53.2	43.1 % of C,N In

Influent	
MI/d	14.925
kgCOD/d	6718.1
kgTOD/d	10201.1
kgC/d	2238.8
kgH/d	559.4
kgO/d	2037.5
kgN/d	761.9
kgFSA-N/d	671.1
kgOrgN-N	90.8
kgTKN-N/d	761.9
kgNO3-N/	0.0
kgVSS/d	2662.5
kgISS/d	141.9
kgTSS/d	2804.4

Influent → Biological reactor → Secondary settling → Effluent; Return sludge flow; Waste sludge

Effluent		
MI/d	14.485	97.1 %
kgCOD/d	760.4	11.3 %
kgTOD/d	1131.5	11.1 %
kgC/d	260.7	11.6 %
kgH/d	112.0	20.0 %
kgO/d	870.7	42.7 %
kgN/d	274.2	36.0 %
kgFSA-N/d	55.1	8.2 %
kgOrgN-N/	26.1	28.7 %
kgTKN-N/c	81.2	10.7 %
kgNO3-N/c	193.0	
kgVSS/d	0.0	0.0 %
kgISS/d	0.0	0.0 %
kgTSS/d	0.0	0.0 %
Water l/d	2994	

Mass Balances		
COD	100.9 %	Biomass of autotrophs
TOD	100.0 %	
Carbon	100.0 %	
Hydrogen	100.0 %	
Oxygen	100.0 %	
Nitrogen	100.0 %	

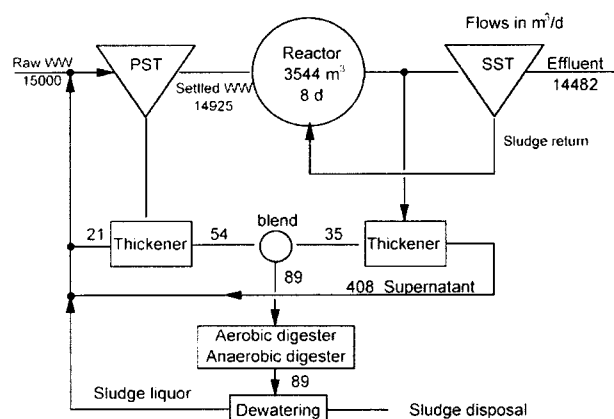| Waste Flo	Dissolved	Particulate	Total	
MI/d	0.440	0.440	0.440	2.9 %
kgCOD/d	23.1	2238.7	2261.8	33.7 %
kgTOD/d	34.3	2930.2	2964.6	29.1 %
kgC/d	7.9	779.2	787.1	35.2 %
kgH/d	3.4	111.4	114.8	20.5 %
kgO/d	26.4	470.8	497.3	24.4 %
kgN/d	8.3	151.3	159.6	20.9 %
kgFSA-N/d	1.7	0.0	1.7	0.2 %
kgOrgN-N/	0.8	151.3	152.1	16.9 %
kgTKN-N/c	2.5	151.3	153.7	17.1 %
kgNO3-N/c	5.9	0.0	5.9	0.7 %
kgVSS/d	0.0	1512.6	1512.6	
kgISS/d	0.0	288.0	288.0	203.0 %
kgTSS/d	0.0	1800.7	1800.7	64.2 %

Fig. 4 – The second theoretical case study WWTP comprising primary settling tanks (PST) and anaerobic digestion (AD) of primary sludge (PS), activated sludge (AS) treatment of settled WW at a short sludge age (8 d), flotation thickening of the waste activated sludge (WAS) and aerobic (AerD) or anaerobic (AD) digestion to stabilize the WAS to the same final residual biodegradable COD as the extended aeration WWTP (Fig. 3).

Table 1 shows there is considerable variation in the sewage sludge organic type compositions. Perhaps with modern total organic carbon and organic nitrogen analysers, which were not available for the investigations listed in Table 1, less variation can be obtained. The indirect methods employed in the investigations often lead to significant variability because it relies on several measurements, each of which is subject to error. The accuracy of the COD and elemental mass balances over the experimental systems also play a major role.
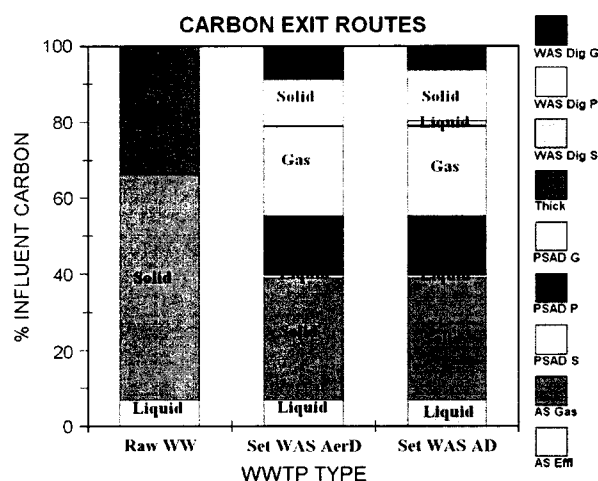
Fig. 5 – Carbon exit routes for 3 WWTP schemes at 14 °C: (1) Long sludge age (30 d) NDAS treating raw wastewater with direct discharge of waste activated sludge (WAS) to dewatering/drying beds (left bar), and short sludge age (8 d) NDAS treating settled wastewater with PSAD, flotation thickening of WAS with (2) anoxic–aerobic digestion of WAS (centre bar) or (3) AD of WAS (right bar) (In legend S = Soluble, P = Particulate, G = Gas).

An aspect not considered in the investigations listed in Table 1 is the composition of the dissolved organics, i.e. the unbiodegradable soluble organics (USO) and the fermentable biodegradable soluble organics (F-BSO). In AD of concentrated PS and WAS, these soluble organic fractions have little influence, unlike the influent VFA which has a significant influence on AD systems (Eq. (8a) and (8b)). For activated sludge systems, this is not the case because the F-BSO can be up to be 25% of the influent COD. So for plant-wide modelling, compositions for the F-BSO and USO need to be established for mass balance and completeness. For the different simple soluble organics listed in Table 2, the COD/TOC and COD/mass ratios were calculated and varied between 2.67 and 4.0 g COD/ g C and 1.07 and 3.1 g COD/g, respectively. Takács and Vanrolleghem (2006) used $C_{0.553/12}H_{0.058/1}O_{0.388/16}N_{0/14}$ and $C_{0.594/12}H_{0.081/1}O_{0.325/16}N_{0/14}$ for USO and BSO respectively, which have COD/C ratios of 2.80 and 3.2 and COD/mass ratios of 1.55 and 1.91 respectively (Table 1). Because most of the organics in wastewater are of carbohydrate/sugar type with a relatively small proportion of organics with high COD/TOC and COD/ mass ratios, an average COD/TOC ratio of 3.0 and COD/mass ratio 1.42 g COD/g were accepted for both F-BSO and USO. These ratios, together with the Org N/COD ratio from the wastewater characteristics, define the compositions of these two soluble organic types.

4. Using the stoichiometry in two plant-wide WWTP case studies

The two theoretical case study WWTPs comprise (1) raw wastewater (WW) treatment in a long sludge age (30 d) AS system (extended aeration, Fig. 3) and (2) primary settling tanks (PST) and anaerobic digestion (AD) of primary sludge (PS), activated sludge (AS) treatment of settled WW at a short sludge age (8 d), flotation thickening of the waste activated sludge (WAS) and aerobic (AerD) or anaerobic (AD) digestion to stabilize the WAS to the same final residual biodegradable COD as the extended aeration WWTP (Fig. 4). The raw and settled WW concentrations and characteristics are similar to those used by Sötemann et al. (2006) and Henze et al. (2008). The only difference is that the influent VSS (and hence TSS) concentrations in the raw and settled WWs were increased and Total Organic Carbon (TOC) concentrations added to obtain CHON compositions for the particulate organics close to those measured in PS AD (Table 1). Also TOC concentrations for F-BSO and USO organics were added to obtain COD/TOC and COD/mass ratios for these organics of 3.0 g COD/g C and 1.42 g COD/g (see above). The raw WW average dry weather flow (ADWF) was 15.0 Ml/d and the PST underflow is 0.5% of this ADWF (75 m³/d). The seasonal minimum and maximum WW temperatures are 14 and 22 °C.

From the WW characteristics and concentrations (Tables 3 and 4), the COD, C and N concentrations (P was assumed zero) of the five influent organic types were calculated from mass balances around the PST and are listed in Table 5, viz. influent VFA (assumed to be acetic acid), fermentable readily biodegradable soluble organics (F-BSO), unbiodegradable soluble organics (USO), slowly biodegradable particulate organics (BPO) and unbiodegradable particulate organics (UPO). The
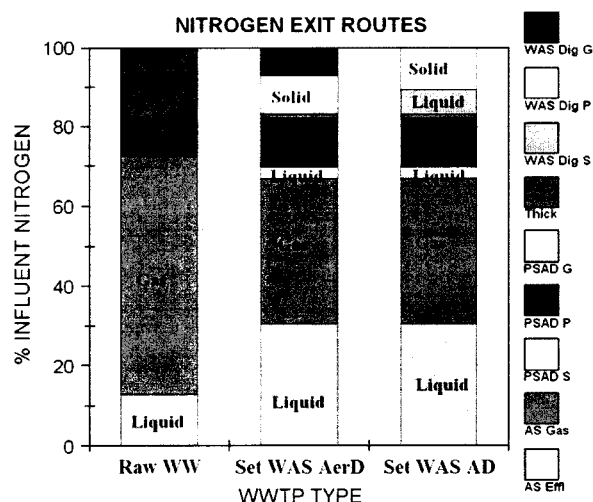
Fig. 6 – Nitrogen exit routes for 3 WWTP schemes at 14 °C: (1) Long sludge age (30 d) NDAS treating raw wastewater with direct discharge of waste activated sludge (WAS) to dewatering/drying beds (left bar), and short sludge age (8 d) NDAS treating settled wastewater with PSAD, flotation thickening of WAS with (2) anoxic–aerobic digestion of WAS (centre bar) or (3) AD of WAS (right bar) (In legend S = Soluble, P = Particulate, G = Gas).

Fig. 7 – C (a, top) and N (b, bottom) fluxes from the raw wastewater 30 d sludge age WWTP at 22 °C.

compositions of the various organic fractions (Table 5) were determined from the COD, TOC, Organic N and VSS (or compound) concentrations (Tables 3 and 4). For the USO and UPO, compositions of $CH_{1.833}O_{0.600}N_{0.166}$ and $CH_{1.717}O_{0.453}N_{0.166}$, respectively, were accepted, which were obtained from f_{cv}, f_C and f_N ratios of 1.42, 0.487 and 0.049 for USO and 1.48, 0.515 and 0.10 for UPO, respectively. The N content of the USO was obtained from the unbiodegradable soluble organic N concentration (TKN minus FSA). Because the USO and UPO were assumed to remain unchanged, these compositions apply to these organics in the raw and settled WWTPs in all the unit operations. The composition of the settleable and non-settleable UPO may be different in raw and settled WW but this level of detail was not considered in the absence of measured data. A VFA (acetic acid) fraction of the BSO of 0.25 was accepted making the influent VFA 36 mg COD/l and the F-BSO COD 110 mg COD/l. The f_{cv}, f_C and f_N ratios and composition (x, y, z, a) of the BPO in the raw, settled and primary sludge were calculated by difference of the total particulate and unbiodegradable particulate concentrations (VSS, COD, TOC, OrgN). Similarly, the composition (x, y, z, a) of the F-BSO in the raw and settled WWs were found from the difference between the total soluble and unbiodegradable soluble organics concentrations minus the VFA. The composition of the AS biomass, and the endogenous residue that it generates, was accepted to be $CH_{1.717}O_{0.453}N_{0.166}$ in conformity with the commonly accepted $f_{cv} = 1.48$, $f_C = 0.515$ and $f_N = 0.10$ ratios in ASM1 and 2 (Tables 1 and 4). Consequently, in this paper the three constituents of AS, i.e. OHO biomass, its endogenous residue and UPO, have the same composition. In Table 1, it can be seen that the composition of UPO differs
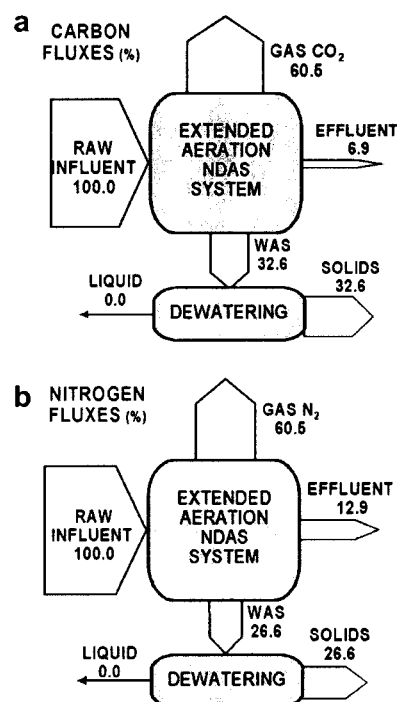
from that of OHOs, in particular with respect to their N content, but this difference was not considered in this paper. The composition of AD biomass was accepted to be $CH_{1.4}O_{0.4}N_{0.2}$ $(f_{cv} = 1.416$, $f_C = 0.531$ and $f_N = 0.124)$ and endogenous residue generation was assumed to be zero $(f_{AD} = 0)$. Because the yield of AD biomass is very low, its actual composition makes negligible difference to the AD product generation $(CO_2, CH_4, FSA, H_2CO_3^*$ Alk).

The kinetic Part 1 of the steady-state AD model of Söte-mann et al. (2005a) was applied to the design and performance determination of the PS and WAS AD, the kinetic Part 1 of the steady-state NDAS model of WRC (1984) or Henze et al. (2008) to the NDAS reactors and the kinetic Part 1 of the steady-state AerD model of Ekama et al. (2006a) for the aerobic digester. The kinetic and stoichiometric constants of these models and the design parameters of the different unit operations are listed in Table 6. An ANO maximum specific growth rate at 20 °C (μ_{A20}) of 0.60/d and a primary anoxic mass fraction of 0.40 were accepted for the modified Ludzack–Ettinger (MLE) NDAS systems. The outputs of the COD and N mass balance steady-state kinetic Part (1) of the models provided the concentration changes in biodegradable COD, ammonia and nitrate over the systems for input to the elemental balance stoichiometric Part (2) of the models (Fig. 2), i.e. for Eq. (1) for AD, Eq. (9) for aerobic AS, Eq. (11) for nitrification, Eq. (13) for denitrification and Eq. (17) for anoxic–aerobic digestion. For the AS system, kinetics constants for the growth process were not required because it was assumed that all the influent biodegradable organics are utilized. The WAS was thickened
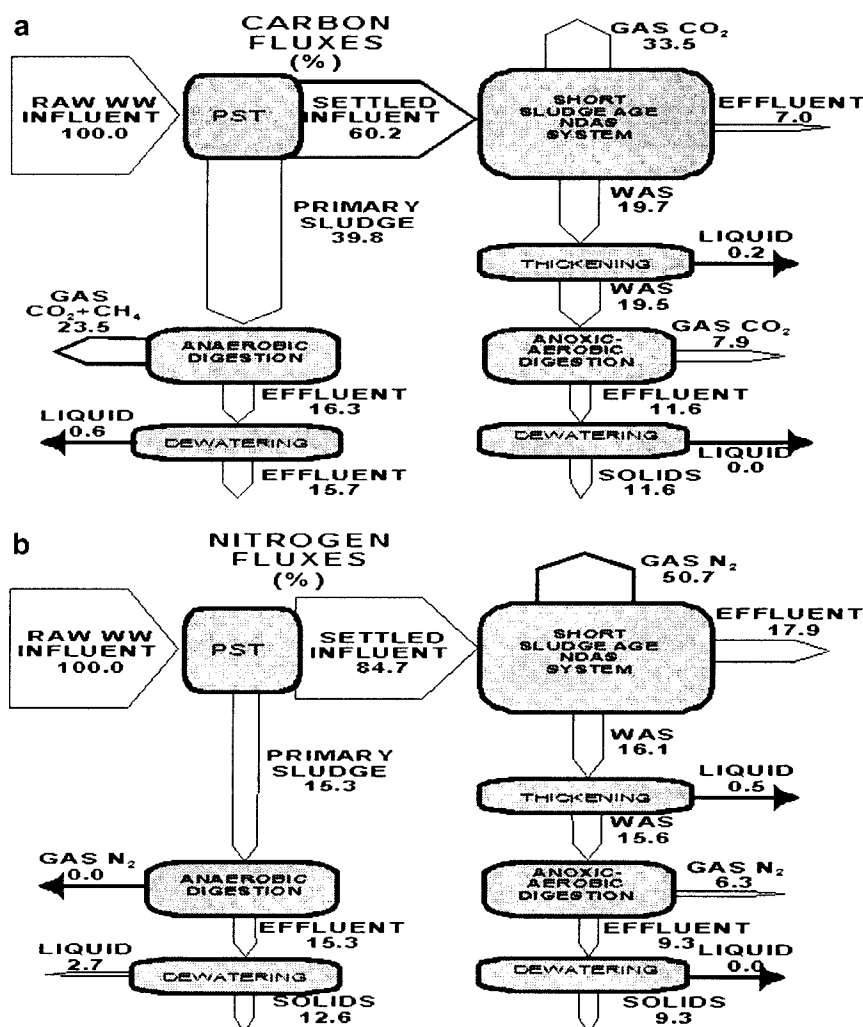
a

b
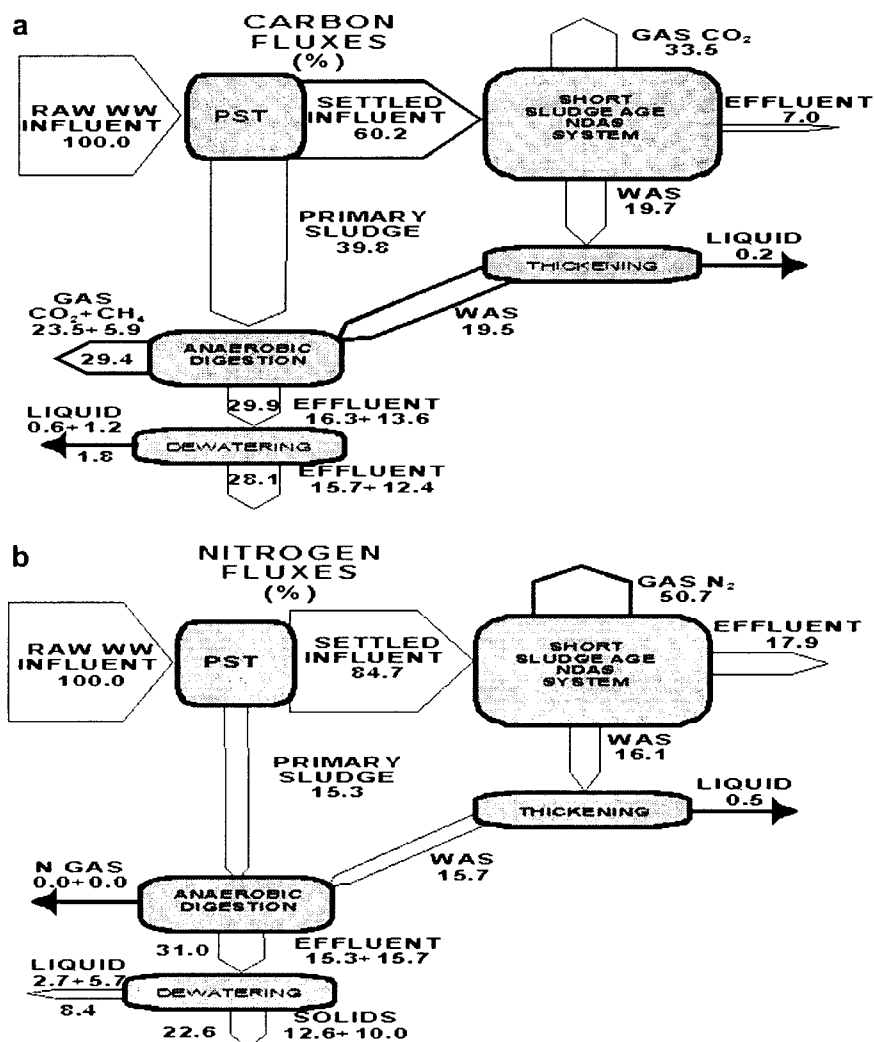

Fig. 8 – C (a, upper) and N (b, lower) fluxes from the short sludge age (8d) NDAS WWTP treating settled wastewater at 22 °C with AD of PS and aerobic digestion of WAS to the same residual biodegradable COD as the extended aeration (30 d) WWTP (Fig 3).

to 6.8% TSS (the upper limit to not exceed an oxygen utilization rate, OUR, of 100 mg O/(l.h)) before anoxic–aerobic digestion or AD. Complete ND of the WAS released N was accepted for the anoxic–aerobic digester (Warner et al., 1986). The kinetic parts of the NDAS, AD and AerD models and the stoichiometry of the degradation processes described above which take place in the different unit operations were programmed into a spreadsheet. The stoichiometry was applied to each organic (VFA, F-BSO, BPO, USO UPO, OHO biomass and endogenous residue) and inorganic (ISS, FSA, nitrate) compound entering a unit operation and added to obtain the overall behaviour in that unit operation reactor. As examples, the spreadsheet summary mass balance inputs and outputs for the PSAD and NDAS system treating settled wastewater at 14 °C are given in Tables 7 and 8.

Both Parts 1 (kinetic) and 2 (stoichiometric) parts of the steady-state model predict reactor outputs which have COD, such as VSS, oxygen demand and methane gas production and these matched within 2%. The C, H, O, N and TOD (which includes the electron donating capacity of the TKN) balances were 100.0% over each unit operation and over the WWTPs as a whole, which validated that the kinetic and stoichiometric parts of the models were developed and programmed correctly (Tables 7 and 8). However, in the COD balance (which excludes the electron donating capacity of the reduced N) over the WWTPs, the model outputs amount to slightly more than the model inputs, ~101% (Table 8). This is due to the inclusion of the ANO biomass in the mass balances—the ANOs synthesize biomass (which has COD) from CO_2, H_2O and NH_3, which have zero COD. The TOD mass balance is therefore

Fig. 9 – C (a, upper) and N (b, lower) fluxes from the short sludge age (8 d) NDAS WWTP treating settled wastewater at 22 °C with AD of PS and WAS to the same residual biodegradable COD as the extended aeration (30 d) WWTP (Fig 3).

preferable (and simpler) because it includes the electron donating capacity of the TKN.

The spreadsheet[1] is general and can accommodate realistic influent wastewater characteristics, organic compound compositions and unit operation design conditions. Because the TOC concentrations of the different influent organics are not well defined or regularly measured at this stage, these have to be estimated from the existing limited data set, e.g. those in Table 1.

4.1. Evaluation of WWTP output streams

For the particular wastewater characteristics and case study WWTPs (Figs. 3 and 4):

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[1] This spreadsheet (in Corel Quattro Pro) is not complete—currently P and PAOs are being added—and so is not generally available.

(1) For the raw WW extended aeration nitrification-denitrification activated sludge (NDAS) system at 14 °C, of the influent C flux, 6.9% exits via the effluent, 59.4% as gas (CO_2) and 33.7% in the waste sludge stream, of which 0.4% is in the dissolved form (Figs. 5 and 7a). Of the influent N flux, 12.8% exits via the effluent, 59.7% as gas (N_2) and 27.5% in the waste sludge stream, of which 0.7% is in the dissolved form (Figs. 6 and 7b). At 14 °C, a total of 2210 kg CO_2-C (59.4% of influent TOC) is generated. With the very low dissolved C and N content of the WAS, the supernatant from sludge thickening/drying beds can be recycled to the influent.

(2) For the settled wastewater short sludge age (8 d) NDAS system at 14 °C, of the influent C flux, 7.0% exits via the effluent and 32.0% as gas (CO_2) (Figs. 5 and 8a). Of the influent N flux, 30.5% exits via the effluent (ND not complete at the 8 d sludge age) and 36.5% as gas (N_2) (Figs. 6 and 8b).

(3) For the primary sludge anaerobic digester (PSAD), of the influent C flux, 0.6%, 15.7% and 23.5% (of which 61% is

methane) exits in soluble, particulate and gaseous forms, respectively (Figs. 5 and 8a); of the influent N flux, 2.7%, 12.6% and 0.0% exits the PSAD in soluble, particulate and gaseous forms, respectively (Figs. 6 and 8b).

(4) Of the influent C and N fluxes, 0.2% and 0.5% exits in the waste activated sludge (WAS) flotation thickener supernatant, which can be returned to the final reactor of the AS system because its quality is similar to that of the final effluent (Figs. 8 and 9).

(5) With anoxic–aerobic digestion of WAS (Fig. 8), 0.0%, 12.0% and 9.0% of the influent C flux exits in soluble, particulate and gaseous forms (Figs. 5 and 8a) and 0.0%, 9.7% and 7.2% of the influent N flux exits in soluble, particulate and gaseous forms (Fig. 6 and 8b). With anaerobic digestion (AD) of WAS (Fig. 9), 1.3% (mostly as dissolved CO_2), 13.2% and 6.5% of the influent C flux exits in soluble, particulate and gaseous forms (Figs. 5 and 9a) and 6.2%, 10.6% and 0.0% of the influent N flux exits in soluble, particulate and gaseous forms (Figs. 6 and 9b). Clearly, AD of WAS increases the N content of the AD dewatering liquor sharply due the much higher (4 times) N content of AS compared with PS. Therefore to keep the final (AS) effluent N low, N removal from PS and WAS AD dewatering liquor is important before return to the influent. Alternatively, anoxic–aerobic digestion of WAS could be considered, in which case (i) complete N removal of WAS digested N to N_2 gas is achieved in the anoxic–aerobic digester (Warner et al., 1986) and (ii) due to its low N content, side-stream N removal from PSAD dewatering liquor would not be required.

(6) For the settled wastewater short sludge age (8 d) NDAS system with anoxic–aerobic digestion of WAS at 14 °C, a total of 1868 kg CO_2-C (50.2% of influent TOC) and 533 kg CH_4-C (14.3%) is generated, total 2400 kg C (64.5%). With AD of WAS, a total of 1636 kg CO_2-C (44.0% of influent TOC) and 719 kg CH_4-C (19.3%) is generated, a total of 2355 kg C (63.3%). If all the CH_4 is combusted (beneficially or flared), the settled WWTP produces only 6% more CO_2 than the raw WWTP, due to the lower sludge production with AD, with the result that the WWTP type makes little difference to the % influent TOC converted to CO_2.

5. Conclusions

In this paper, the COD and N mass balance steady-state kinetic models of activated sludge (AS) organics degradation, nitrification and denitrification (ND) and anaerobic (AD) and aerobic (AerD) digestion of wastewater sludge are extended and linked with bioprocess transformation stoichiometry to form C, H, O, N, TOD and charge mass balance based models so that not only N (and P) but also C (and H and O) can be tracked through the whole WWTP. By assigning a stoichiometric composition (x, y, z and a in $C_xH_yO_zN_a$) to each of the five main influent wastewater organic fractions and ammonia, these, and the products generated from them via the biological processes, are tracked through the WWTP. The same stoichiometry also can be applied in the dynamic models for activated sludge and aerobic and anaerobic digestion, when programmed to include C, H, O, N and P

element balances. The principles on which the stoichiometry has been developed are general and can be applied to any bioprocess for which the electron donor(s) and acceptor(s) are known. It has been used very beneficially to develop steady-state and dynamic models for biological sulphate reduction with primary sludge as electron donor (Poinapen et al., in press) and autotrophic denitrification with reduced S compounds (Lu et al., in press).

It is demonstrated that with the extended steady-state models for the different WWTP unit operations, much useful information for design and operation can be generated, including WWTP layout design, input data generation for dynamic models, tracking the different products exiting the WWTP unit operations via the solid, liquid and gas streams, evaluating the consequences of aerobic or anaerobic digestion of PS and/or WAS, quantifying N loads in recycle streams, methane production for energy recovery and green house gas (CO_2, CH_4) generation.

This paper provides a basis for and demonstrates the benefits of including steady-state mass balances based kinetic and stoichiometric models in plant-wide WWTP dynamic simulation software for design and operation. It is recommended that WWTP simulation software be extended to include steady-state mass balance kinetic and stoichiometric models as pre-processors to assist with WWTP layout design, reactor sizing, option exploration and comparisons, wastewater characteristic estimation, recycle ratio determination, initial concentration calculation and simulation software output evaluation. The WWTP layout so developed then can get read seamlessly into the WWTP dynamic simulators to investigate individual unit operation performance and the WWTP as a whole, under dynamic flow and load conditions. This will lead to easier, more efficient and reliable use of WWTP simulators for design and operation.

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